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COMPARATIVE DISTRIBUTION COEFFICIENTS AND CATION-EXCHANGE BEHAVIOUR OF THE ALKALINE EARTH ELEMENTS WITH VARIOUS COMPLEXING AGENTS

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Summary—Equilibrium distribution coefficients are presented for the alkaline earth metals Be(II), Mg(II), Ca(II), Sr(II) and Ba(II) with the complexing agents acetate, formate, lactate, citrate, tartrate, α-hydroxyisobutyrate, malonate, malate, acetylacetonate, EDTA, EGTA and DCTA, and the AG50W-X8 cation-exchange resin. Coefficients in HCl, HNO_3, $HClO_4$ and NH_4Cl are included for the sake of completeness. The merits of the various complexing agents for the separation of adjacent element pairs are discussed and experimental elution curves are presented for selected separations. Separation factors for adjacent elements are calculated at eluting agent concentrations corresponding to a distribution coefficient of 10 for the less strongly absorbed element and are presented together with the eluting agent concentrations to form a basis for comparison.

SEPARATION factors for cation-exchange chromatography of the alkaline earth elements in aqueous hydrochloric or other non-complexing acids are rather small.[1–4] Many complexing agents such as acetate,[5,6] formate,[7] citrate,[8,9] lactate,[10] malonate,[2] α-hydroxyisobutyrate,[11,12] EDTA,[13] DCTA,[14,15] EGTA,[16] 2,6-pyridinedicarboxylate[17] and acetylacetonate therefore have been suggested for improved separation. In almost all cases the suggested methods seem to have been developed empirically by trying out a few eluting concentrations in a column procedure and settling for the best one. Distribution coefficient data from which the most favourable eluent concentration could be obtained directly, and which also would make possible an evaluation and comparison of the merits of the various eluting agents, do not seem to be available. Therefore, a systematic investigation of the cation-exchange distribution coefficients of the alkaline earth elements, Be, Mg, Ca, Sr and Ba, in various complexing solutions was carried out in this laboratory. Included were the following complexing agents: acetate, formate, lactate, citrate, tartrate, α-hydroxyisobutyrate, malonate, malate, acetylacetonate, EDTA, EGTA and DCTA. The results, their application, and discussion are presented in this paper. The malonate system has been investigated before,[2] but the coefficients are included for comparative purposes. Coefficients in hydrochloric, nitric and perchloric acids and ammonium chloride solutions are also given for the sake of completeness.

EXPERIMENTAL

Reagents

Chemicals of analytical-reagent grade purity were used throughout with the exception of malonic and DL-malic acid which were obtained as 99% pure reagents and were further purified by an ion-exchange method.[2]

The resin used was the AG50W-X8 sulphonated polystyrene marketed by Bio-Rad Laboratories, Richmond, California. Resin of 100–200-mesh particle size was used for equilibrium and of 200–400 mesh for column experiments.

Apparatus

Borosilicate glass tubes of 20 mm inner diameter with fused-in sintered glass plates of No. 2 porosity and a burette tap at the bottom, were used as columns.

A Perkin–Elmer 303 atomic absorption spectrometer was employed for determinations of low concentration of alkaline earth metals (elution curves).

Procedures

Distribution coefficients. Coefficients were determined by equilibrating for 24 hr in a mechanical shaking apparatus 2·718 g of dry AG50W-X8 resin in the ammonium form (equivalent to 2·500 g of resin in the hydrogen form) with 250 ml of a solution containing 1 mmole of the required element and the required concentration of the organic complexing agent as the ammonium salt. Only 0·1 mmole of magnesium(II) was used for equilibria with ammonium α-hydroxyisobutyrate because of its limited solubility with this reagent. The pH was kept at 7·0 throughout except for the equilibration of beryllium in ammonium chloride, acetate and formate where a pH of 5·0 was used to prevent hydroxide precipitation in the external solution, and the equilibration of all elements in acetylacetonate, where a pH of 9·0 was used. Coefficients in EDTA, EGTA and DCTA were determined at starting pH values ranging from 5 to 9 at intervals of 1·0, and at concentrations of 0·02M and 0·10M for EDTA and 0·02M for EGTA and DCTA. One series of coefficients was measured in the presence of 0·30M ammonium acetate as buffer, another series was measured in the absence of the buffer.

After equilibration the resin was separated from the aqueous phase by filtration and the pH of the filtrate was measured with a pH meter in the cases of EDTA, EGTA and DCTA. The amounts of the elements in the resin phase (after ashing) and in the water phase were determined by suitable analytical methods.[2] From the results the equilibrium distribution coefficients,

$$D = \frac{\text{amount of element in resin phase}}{\text{amount of element in water phase}} \times \frac{\text{ml of solution}}{\text{g of resin (dry weight in H}^+\text{ form)}}$$

were calculated. For EDTA, EGTA and DCTA, curves of D against pH after equilibration were plotted and the coefficients at the required pH values were read from these curves. The results are presented in Tables I and II. Coefficients in perchloric acid were also determined. Their values and those of the coefficients in hydrochloric and nitric acids, for 1 mmole of the element and 2·5 g of resin are included in the Tables. Coefficients for 2·5 mmole have been published before,[1, 19] but the coefficients for lower loading are included for the sake of completeness.

Separation factors. For comparison of the merits of the various eluting agents the values of the separation factors for element pairs at a distribution coefficient of 10 for the less strongly adsorbed element were obtained from plots of coefficients against eluent concentration or pH value (for EDTA, EGTA and DCTA). Table III presents a summary of these separation factors and the corresponding eluent concentration.

Elution curves. Satisfactory column kinetics are required in addition to a favourable separation factor to obtain a good chromatographic separation. The excellence of the separations possible for adjacent group IIA elements when working under near optimum conditions are demonstrated by some elution curves.

Figure 1 shows an elution curve for the 2 mmole of beryllium, 1 mmole of magnesium and 0·10N ammonium malate of pH 7·5 as eluting agent. The column had an inner diameter of 15 mm and contained 15 ml (5 g) of AG50W-X8 resin of 200–400-mesh particle size in the ammonium form. The flow rate was kept at 2·0 ± 0·2 ml/min.

Figure 2 shows an elution curve for the magnesium(II)–calcium(II) pair with a similar column, but 0·20M ammonium acetylacetonate of pH 9·0 as eluting agent; the same column and 2·0M ammonium acetylacetonate of pH 9·0 as eluting agent were used for the calcium(II)–strontium(II) pair as shown in Fig. 3. The eluting agent was prepared by neutralizing a mixture of acetylacetone and water with aqueous ammonia to a pH of 9, with vigorous stirring. The solution was left standing for 15–20 min before elution was started. When a 30-ml (10-g) column was used the calcium was eluted quantitatively with 300 ml of the eluting agent while no strontium appeared in the first 1000 ml of eluate when 1 mmole of each element was present.

Figures 4–6 show elution curves for the calcium(II)–strontium(II) pair with 0·70N ammonium α-hydroxyisobutyrate of pH 7·0, 0·20N ammonium citrate of pH 7·5, 0·10M EDTA of pH 5·0 containing 0·30M ammonium acetate, and 0·10M EDTA of pH 5·0 and 5·5 in the absence of ammonium acetate, as eluents. The columns contained 60 ml (20 g) of AG50W-X8 resin of 200–400-mesh

TABLE I.—DISTRIBUTION COEFFICIENTS

Eluent	Be	Mg	Ca	Sr	Ba
0·10*N* $HClO_4$	834	1340	2980	4510	$>10^4$
HNO_3	763	1180	2310	4350	6800
HCl	334	1320	4570	6500	$>10^4$
NH_4Cl	1530	816	2390	4300	13800
NH_4 acetate	1900	915	2060	3900	10900
NH_4 formate	1870	804	2060	3500	10000
NH_4 lactate	770	331	473	881	1320
NH_4 malate	3·5	311	502	1070	2815
NH_4 α-hydroxyisobutyrate	440	811	1360	4060	20000
NH_4 tartrate	38·6	476	52	952	2460
NH_4 acetylacetonate	5·7	48·0	12300	16600	$>10^4$
NH_4 malonate	7·8	205	910	1760	4500
NH_4 citrate	$<0·5$	27·9	48·0	172	565
0·20*N* $HClO_4$	283	418	871	1290	3370
HNO_3	244	393	719	1150	2330
HCl	158	387	1160	1590	4450
NH_4Cl	440	254	631	944	2480
NH_4 acetate	805	214	481	817	3460
NH_4 formate	140	219	475	774	2480
NH_4 lactate	79	100	142	283	498
NH_4 malate	1·8	86	118	284	766
NH_4 α-hydroxyisobutyrate	51	142	285	678	2280
NH_4 tartrate	5·6	124	30	226	503
NH_4 acetylacetonate	$<1·0$	8·0	2640	9900	$>10^4$
NH_4 malonate	5·1	49·3	290	460	990
NH_4 citrate	$<0·5$	7·8	10·8	43·3	144
0·50*N* $HClO_4$	65	98	198	268	645
HNO_3	63	93	150	196	309
HCl	51	88	188	278	746
NH_4Cl	106	51	124	170	379
NH_4 acetate	30·1	33·5	73	132	323
NH_4 formate	8·7	32·0	74	125	288
NH_4 lactate	2·1	13·2	23·5	61	123
NH_4 malate	1·0	11·7	15·2	42·3	114
NH_4 α-hydroxyisobutyrate	1·8	12·1	24·3	91	280
NH_4 tartrate	1·8	19·3	7·4	26·7	68
NH_4 acetylacetonate	$<1·0$	2·2	377	2500	$>10^4$
NH_4 malonate	3·3	6·1	33·7	71	160
NH_4 citrate	$<0·5$	1·5	2·5	7·6	22·2
1·00*N* HCl_4	18·7	26·9	60	88	173
HNO_3	16·1	24·6	38·1	43·1	88
HCl	14·4	21·8	43·8	73	168
NH_4Cl	29·2	15·2	39·2	52	116
NH_4 acetate	4·2	8·6	18·3	35·3	85
NH_4 formate	2·7	7·7	18·4	35·1	76
NH_4 lactate	$<1·0$	2·9	4·8	14·2	38·6
NH_4 malate	$<1·0$	3·7	3·0	9·4	26·7
NH_4 α-hydroxyisobutyrate	1·2	4·2	5·9	18·4	61
NH_4 tartrate	1·2	5·1	2·1	5·8	14·3
NH_4 acetylacetonate	$<1·0$	1·2	115	1170	$>10^4$
NH_4 malonate	$<1·0$	3·2	7·3	17·3	40·5
NH_4 citrate	$<0·5$	0·7	0·7	2·0	5·6

TABLE I. (*Contd.*)

Eluent	Be	Mg	Ca	Sr	Ba
2·00*N* $HClO_4$	4·7	8·5	18·9	25·2	53
HNO_3	8·5	9·7	10·5	11·2	13·1
HCl	5·4	6·4	13·2	19·2	38·9
NH_4Cl	8·9	5·7	12·5	17·9	37·1
NH_4 acetate	2·3	2·5	4·5	9·4	22·7
NH_4 formate	1·5	2·7	4·8	8·5	19·9
NH_4 lactate	<1·0	1·6	2·2	3·3	10·3
NH_4 malate	<1·0	1·7	0·9	1·7	6·9
NH_4 α-hydroxyisobutyrate	<1·0	1·7	2·5	6·3	17·9
NH_4 tartrate	<1·0	1·8	0·9	2·1	2·9
NH_4 acetylacetonate	<1·0	1·0	78	838	6800
NH_4 malonate	<1·0	1·6	1·8	3·8	13·3
NH_4 citrate	<0·5	0·4	0·2	0·6	1·7
3·00*N* $HClO_4$	2·2	4·2	11·0	14·4	27·3
HNO_3	4·5	5·8	4·8	6·2	4·7
HCl	3·3	4·3	7·1	10·6	20·0
NH_4Cl	7·5	3·4	7·7	10·0	19·5
NH_4 acetate	1·6	1·4	2·5	4·7	11·4
NH_4 formate	1·0	1·9	3·2	4·4	9·6
NH_4 lactate	<1·0	1·4	1·4	2·0	5·8
NH_4 α-hydroxyisobutyrate	<1·0	1·0	1·7	3·6	10·6
NH_4 tartrate	<1·0	1·3	0·8	1·2	1·5
NH_4 acetylacetonate					
NH_4 malonate	<1·0	0·8	0·9	2·0	11·1
NH_4 citrate	<0·5	0·2	<0·2	0·3	0·9
4·00*N* $HClO_4$	1·7	2·9	7·9	10·9	20·2
HNO_3	2·8	4·1	2·8	4·7	3·2
HCl	2·4	3·0	5·8	7·6	12·4
NH_4Cl	6·4	2·2	5·2	7·5	13·5
NH_4 acetate	1·1	1·1	2·0	3·9	7·1
NH_4 formate	<1·0	1·7	3·0	3·7	5·9
NH_4 lactate	<1·0	1·3	1·2	1·7	4·8
NH_4 α-hydroxyisobutyrate	<1·0	<1·0	1·4	2·7	7·5
NH_4 tartrate	<1·0	1·0	0·5	0·9	1·1
NH_4 malonate	<1·0	0·5	0·6	1·3	9·7
NH_4 citrate	<0·5	<0·2	<0·2	0·2	0·6

TABLE II.—DISTRIBUTION COEFFICIENTS WITH 0·02*M* COMPLEXONES CONTAINING 0·30*M* NH_4 ACETATE

Eluting agent	pH	Mg(II)	Ca(II)	Sr(II)	Ba(II)
EDTA	4·5	101 (2250)	33·1 (128)	396 (8300)	1210 ($>10^4$)
	5·0	53 (401)	3·9 (26·8)	292 (1220)	784 (10^4)
	6·0	3·1 (15·3)	0·2 (2·1)	16·3 (54)	104 (535)
	7·0	0·8 (1·2)	<0·2 (<0·2)	2·4 (5·7)	7·5 (33·5)
	8·0	<0·5 (<0·5)	<0·2 (<0·2)	0·8 (1·1)	1·2 (3·7)
	9·0	<0·5 (0·5)	<0·2 (<0·2)	<0·5 (<0·5)	0·5 (1·0)
DCTA	4·5	42·5 (958)	19·4 (305)	394 (10^4)	865 ($>10^4$)
	5·0	8·3 (130)	2·6 (36·5)	274 (3400)	504 (6500)
	6·0	0·5 (2·7)	<0·2 (2·1)	37·8 (183)	202 (1460)
	7·0	<0·5 (<0·5)	<0·2 (<0·2)	5·6 (8·2)	65 (356)
	8·0	<0·5 (<0·5)	<0·2 (<0·2)	0·9 (<0·5)	13·6 (80)
	9·0	<0·5 (<0·5)	<0·2 (<0·2)	<0·5 (<0·5)	1·9 (18·4)

TABLE II. (*Contd.*)

EGTA	4·5	91 (765)	60 (1540)	161 (2980)	740 (4500)
	5·0	88 (765)	32·6 (865)	157 (2830)	715 (3700)
	6·0	75 (665)	1·6 (19·8)	87 (1590)	345 (1820)
	7·0	48·0 (322)	<0·2 (4·5)	5·9 (50)	28 (69)
	8·0	11·4 (67)	<0·2 (1·9)	<0·5 (4·1)	2·8 (5·0)
	9·0	2·6 (12·0)	<0·2 (1·3)	<0·5 (<1·0)	<1·0 (<1·0)
EDTA	4·5	(120)	(9·8)	(26·7)	(1030)
(0·10*M*)	5·0	(20·4)	(2·7)	(70)	(315)
	6·0	(1·2)	(<0·5)	(3·9)	(30·5)
	7·0	(<0·5)	(<0·5)	(<0·5)	(2·4)
	8·0	(<0·5)	(<0·5)	(<0·5)	(<0·5)
	9·0	(<0·5)	(<0·5)	(<0·5)	(<0·5)

Coefficients in brackets were determined in absence of NH$_4$ acetate (0·133*M* acetate present in the case of EGTA).

particle size in the ammonium form and had an inner diameter of 22 mm. The flow-rate was kept at 3·0 ± 0·3 ml/min, and 1 mmole of each element was used.

Figures 7 and 8 present elution curves for the strontium(II)–barium(II) pair with 0·020*M* DCTA of pH 7·0 containing 0·30*M* ammonium acetate and with 1·20*N* α-hydroxyisobutyrate of pH 7·0, respectively. Resin, column dimensions and flow-rate were the same as those for Figs. 4–6. No

TABLE III.—SEPARATION FACTORS

Eluting agent	Mg/Be Conc., *N*	Mg/Be Factor	Ca/Mg Conc., *N*	Ca/Mg Factor	Sr/Ca Conc., *N*	Sr/Ca Factor	Ba/Sr Conc., *N*	Ba/Sr Factor
Acetylacetonate	0·08	>10	0·18	~320	~2·0*	~15*	—	—
Citrate	0·06	~50	0·18	1·3	0·20	4·3	0·44	2·9
α-hydroxyisobutyrate	0·30	4·0	0·55	1·9	0·74	3·8	1·40	3·2
Lactate	0·33	3·1	0·53	2·0	0·72	3·0	1·17	2·8
Malate	0·07	~100	0·54	1·3	0·60	2·9	0·97	2·8
Malonate	0·08	~30	0·45	4·3	0·87	2·4	1·27	2·7
Formate	0·48	3·4	0·87	2·4	1·33	1·9	1·82	2·3
Acetate	0·67	1·9	0·92	2·2	1·34	2·0	1·92	2·5
Tartrate	0·15	28	0·41	0·40	0·41	3·7	0·75	2·7
NH$_4$Cl	1·85	0·6	1·32	2·4	2·32	1·4	3·00	2·0
HCl	1·25	1·4	1·50	2·1	2·55	1·4	3·00	1·9
HClO$_4$	1·32	1·6	1·75	2·1	3·10	1·3	4·20	1·9
HNO$_3$	1·33	1·5	1·85	1·1	2·03	1·1	2·10	1·2

Eluting agent	Ca/Mg pH	Ca/Mg Factor	Sr/Ca pH	Sr/Ca Factor	Ba/Sr pH	Ba/Sr Factor
0·02*M* EDTA + B	4·77	1/7·4	4·77	34	6·21	5·5
0·02*M* EDTA	5·43	1/11	5·43	28	6·68	7·1
0·10*M* EDTA	4·48	1/12	4·48	27	5·65	6·8
0·02*M* DCTA	5·33	1/3·6	5·33	148	6·92	38
0·02*M* DCTA + B	4·65	1/2·8	4·65	34	6·72	9·1
0·02*M* EGTA	6·36	1/54	6·36	66	7·59	1·2
0·02*M* EGTA + B	5·40	1/8·2	5·40	15	6·85	4·3

* From elution curves.
B = buffer of 0·30*M* NH$_4$ acetate.

barium appeared in the first 1000 ml of eluate on elution with 0·020*M* DCTA, but the strontium peak was very wide for larger amounts of strontium. When the DCTA concentration was increased to 0·10*M* and the pH was decreased to 6·0 or 6·5, the separation factor α_{Sr}^{Ba} decreased considerably and a slight overlapping of the barium and strontium occurred when 1 mmole of each element was present in a column run.

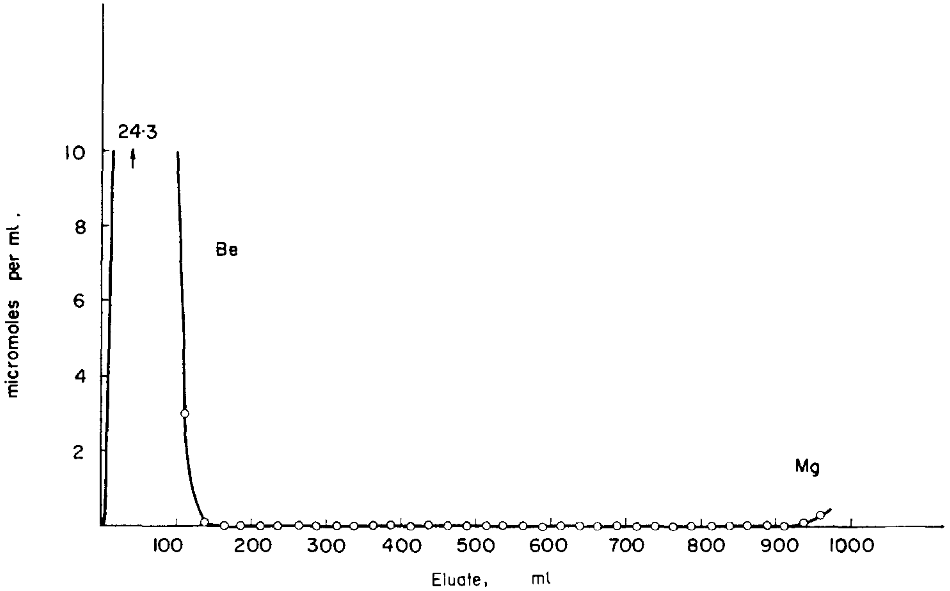

FIG. 1.—Elution curve for Be(II)-Mg(II) with 0·10*N* NH_4 malate of pH 7·0. Column, 15 ml of AG50W-X8 resin, 200–400-mesh, NH_4^+-form. Diameter 15 mm. Flow-rate 2·0 ± 0·2 ml/min.

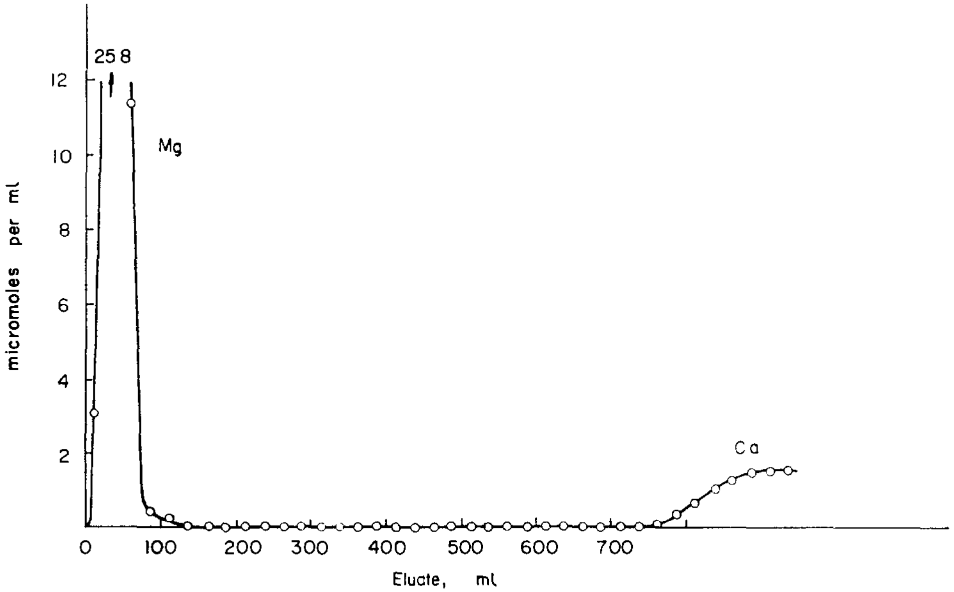

FIG. 2.—Elution curve for Mg(II)-Ca(II) with 0·20*M* NH_4 acetylacetonate of pH 9·0. Column, 15 ml of AG50W-X8 resin, 200–400-mesh, NH_4^+-form. Diameter 15 mm. Flow-rate 2·0 ± 0·2 ml/min.

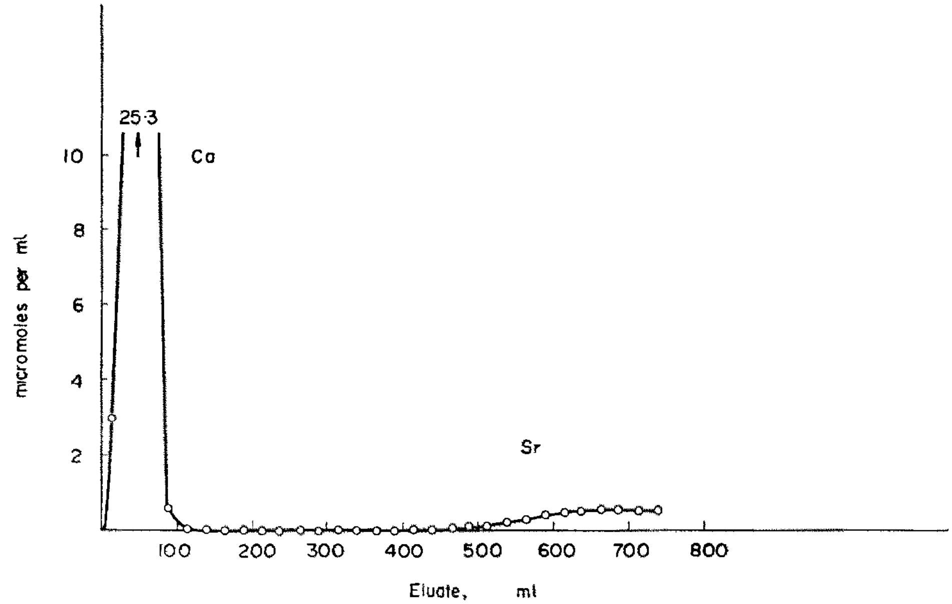

FIG. 3.—Elution curve for Ca(II)-Sr(II) with 2·0M NH_4 acetylacetonate of pH 9·0. Column, 15 ml of AG50W-X8 resin, 200–400-mesh NH_4^+-form. Diameter 15 mm. Flow-rate 2·0 ± 0·2 ml/min.

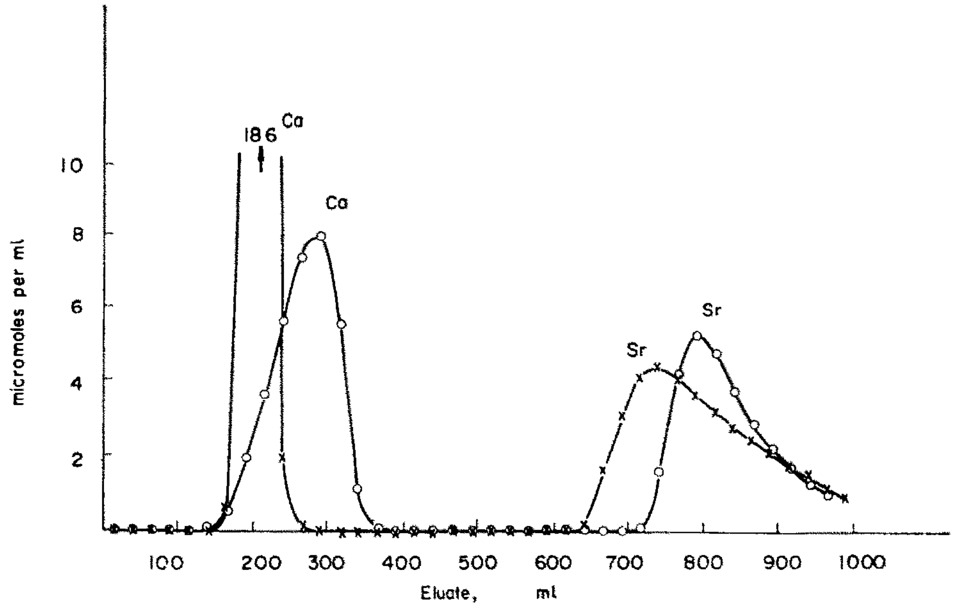

FIG. 4.—Elution curves for Ca(II)-Sr(II) with
×—×—× 0·70N NH_4 α-hydroxyisobutyrate of pH 7·0.
⊙—⊙—⊙ 0·20N NH_4 citrate of pH 7·5.
Column, 60 ml of AG50W-X8 resin, 200–400-mesh, NH_4^+-form. Diameter 21 mm. Flow-rate 3·0 ± 0·3 ml/min.

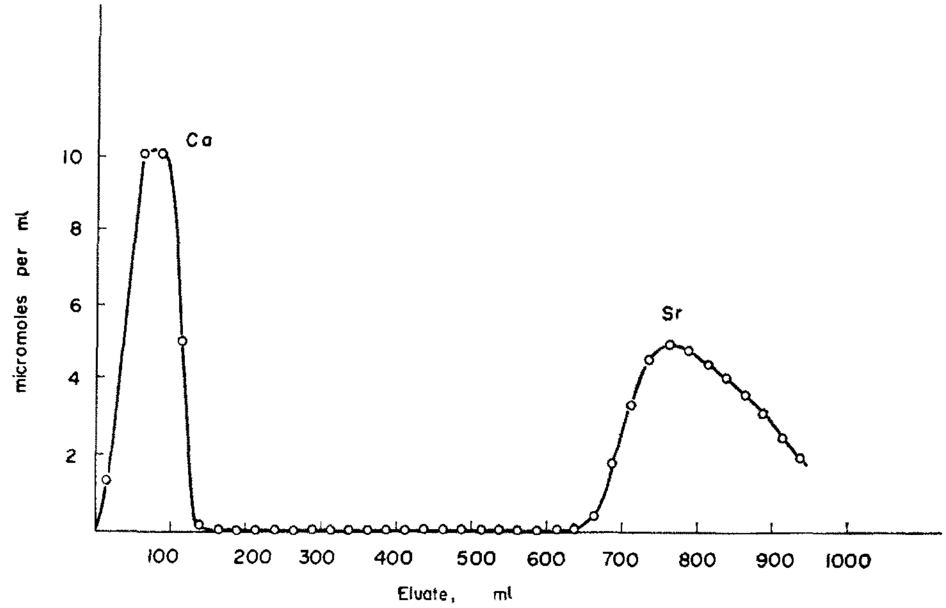

Fig. 5.—Elution curve for Ca(II)-Sr(II) with 0·10*M* EDTA of pH 5·0 containing 0·30*M* NH_4 acetate.
Column, 60 ml of AG50W-X8 resin, 200–400-mesh, NH_4^+-form. Diameter 22 mm. Flow-rate 3·0 ± 0·3 ml/min.

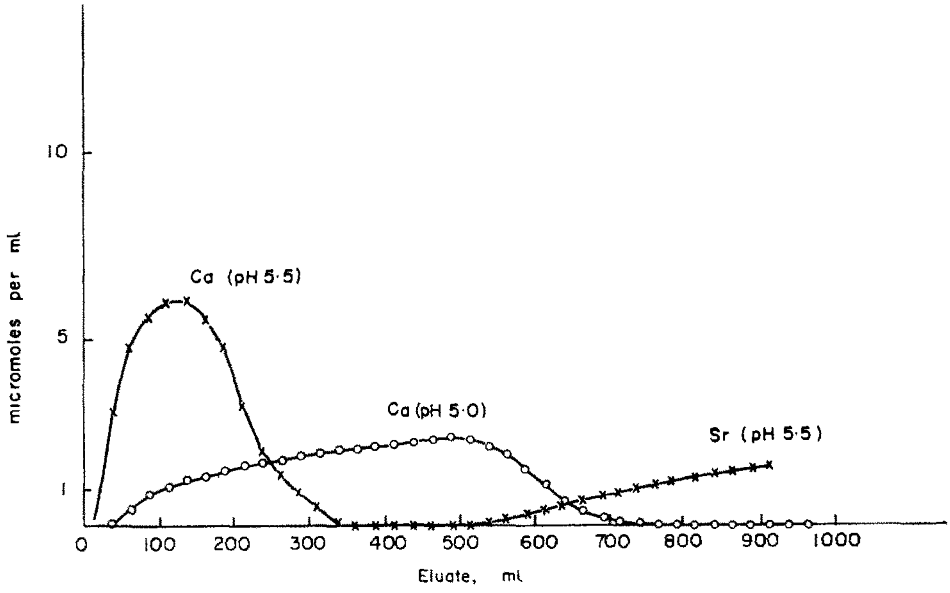

Fig. 6.—Elution curves for Ca(II)-Sr(II) with 0·10*M* EDTA of pH 5·0 and 5·5. Column, 60 ml of AG50W-X8 resin, 200–400-mesh, NH_4^+-form. Diameter 22 mm. Flow-rate 3·0 ± 0·3 ml/min.

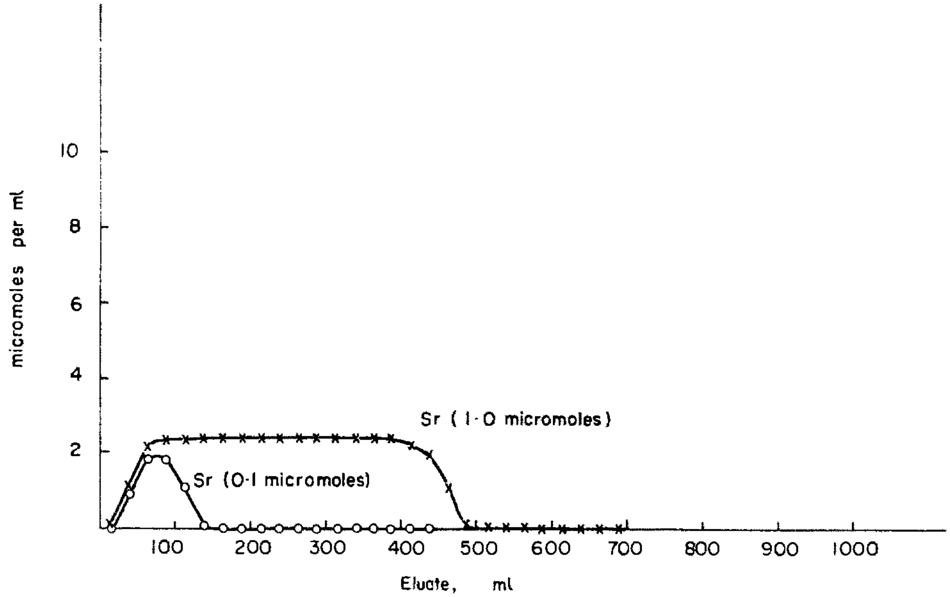

Fig. 7.—Elution curves for Sr(II)-Ba(II) with 0·020M DCTA of pH 7·0 containing 0·30M NH_4 acetate. Column, 60 ml of AG50W-X8 resin, 200–400-mesh, NH_4^+-form. Diameter 21 mm. Flow-rate 3·0 ± 0·3 ml/min. No Ba(II) detectable in first 1000 ml.

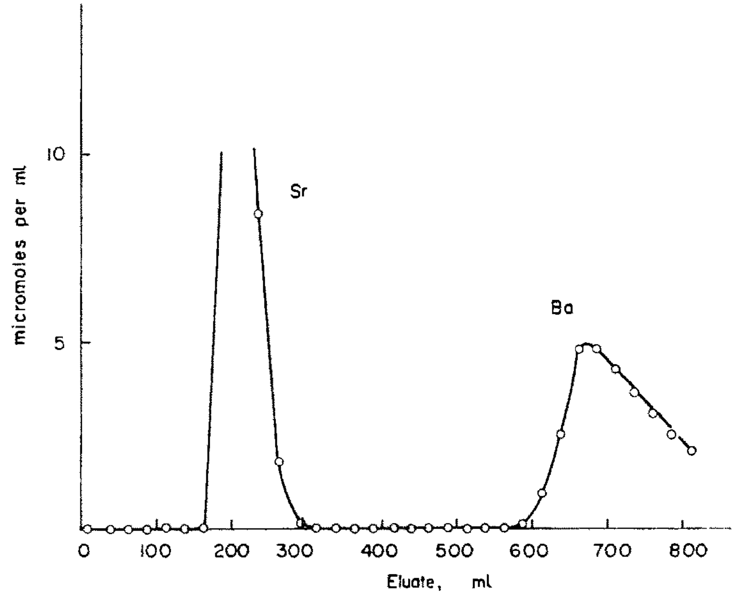

Fig. 8.—Elution curve for Sr(II)-Ba(II) with 1·20N NH_4 α-hydroxyisobutyrate of pH 7·0.
Column, 60 ml of AG50W-X8 resin, 200–400-mesh, NH_4^+-form. Diameter 21 mm. Flow-rate 3·0 ± 0·3 ml/min.

DISCUSSION

The analytical errors for the coefficients presented are about ±1% or better in the range of values from 20 to 100 and are greater for higher or lower values. This does not apply to the coefficients in EDTA, EGTA, DCTA and acetylacetonate. These coefficients are strongly pH-dependent with the first three reagents and therefore less accurate because of uncertain pH-values (not better than ±0·03 pH), while coefficients in acetylacetonate depend on the history of the eluting agent and are very much less reproducible than those in acetate, malonate *etc.* The values given can be considered only as approximate. Furthermore, calcium, strontium and barium are eluted with acetylacetonate at much lower eluent concentration than predicted by the distribution coefficient. Apparently the reagent undergoes a slow reaction in ammoniacal aqueous solution which changes its ion-exchange properties, and no correlation between coefficients and elution curves can be obtained.

Be(II)–Mg(II). The largest separation factor ($\alpha_{Be}{}^{Mg} \sim 90$) and excellent separations are obtained with 0·10*N* ammonium malate of pH 7·0 as eluting agent (Fig. 1). This seems to be the largest separation factor known for this pair. The 0·10*N* ammonium citrate and malonate of pH 7·0 and 0·20*N* ammonium tartrate of pH 7·0 also give a large separation factor and good separations. The 0·20*N* ammonium malonate containing 0·1*N* malonic acid is a good eluting agent for practical purposes. Beryllium(II) is eluted with a small volume of eluting agent, the separation factor is still reasonably large ($\alpha_{Be}{}^{Mg} \sim 10$) and the reagent can be destroyed very easily.[2] The 0·10*M* ammonium acetylacetonate of pH 9 also gives a large separation factor, but actual separations are less satisfactory, because magnesium appears in the eluate sooner than predicted by the distribution coefficients.

Ca(II)–Mg(II). The most effective separation of this pair is obtained with 0·20*M* ammonium acetylacetonate of pH 9, with the very large separation factor of $\alpha_{Mg}{}^{Ca} \sim 200$ (Fig. 2). A good separation is also obtained by using 0·40 or 0·45*N* ammonium malonate as eluting agent.[2] The separation factor is not very large ($\alpha_{Mg}{}^{Ca} = 4{\cdot}3$), but exchange kinetics are good and the reagent can be destroyed easily. The 0·10*M* EGTA of pH 6·0 containing 0·3*M* sodium acetate–acetic acid buffer also gives a large separation factor, but calcium is eluted first. The separation factor with EGTA is considerably reduced by the presence of ammonium acetate (Table III) as has been observed by Povondra and Přibil[16] previously. A fairly good separation is also obtained with 0·10*M* EDTA of pH 4·5 containing 0·20*M* sodium acetate–acetic acid buffer, but with DCTA separation is not satisfactory. With both eluents calcium is again eluted first. Lactate,[10] formate,[7] acetate,[5,6] α-hydroxyisobutyrate[11,12] and ammonium chloride have separation factors not much different from those with aqueous hydrochloric acid and therefore do not present any advantage over this reagent. More attractive for practical purposes than any of the reagents above seems to be 3·00*M* hydrochloric acid containing 60% of ethanol.[3] The separation factor is still reasonably large $\alpha_{Mg}{}^{Ca} \sim 6$ (~ 8 for small amounts), separations are excellent, and the eluting agent can be removed most easily.

Sr(II)–Ca(II). The 0·10*M* DCTA of pH 4·7 containing 0·30*M* ammonium acetate provides the best separation of strontium from calcium (Fig. 5), and 0·10*M* EDTA under similar conditions is almost as good, with about 5 fraction volumes less between the peaks when a 60-ml resin column and 1 mmole of each element are used. At pH 5·0 the calcium peaks are even sharper for both reagents, while strontium is still retained strongly enough for an excellent separation. While batch separation factors are as high as, or higher in the absence of ammonium acetate buffer than in its presence, actual column separations are considerably improved by the presence of the buffer (Figs. 5 and 6). An even more effective separation is obtained with 2·0*M* ammonium acetylacetonate of pH 9·0 as eluent ($\alpha_{Ca}{}^{Sr} \sim 15$ according to column work), and 1-mmole amounts can easily be separated even on a 15-ml (5-g) resin column (Fig. 3), but the removal of the reagent is much more troublesome than that of EDTA. The 0·10*M* EGTA of pH 5·8 containing 0·30*M* ammonium acetate also provides an excellent separation of calcium and strontium. Citrate ($\alpha_{Ca}{}^{Sr} = 4{\cdot}3$) and α-hydroxyisobutyrate ($\alpha_{Ca}{}^{Sr} = 3{\cdot}8$), both of pH 7, have somewhat lower separation factors than the above reagents, but they still provide very good separations, as shown in Fig. 4. It is remarkable that despite a lower separation factor the α-hydroxyisobutyrate separation is as good as the separation with citrate. The somewhat sharper elution peak of calcium with α-hydroxyisobutyrate seems to indicate that this reagent has better column kinetics which make up for the larger separation factor with citrate. Citrate nevertheless is quite attractive because good separation can be obtained at low eluting agent concentration (0·20*N*). This facilitates removal of the eluting agent. After addition of hydrochloric acid to reduce the pH to below 3, the eluate can be passed directly onto a small second cation-exchange column in the hydrogen-ion form which will absorb the calcium while the citrate passes through. Figure 4 seems to contradict the work of Milton and Grummit[8] who came to the conclusion that cation-exchange in citrate is unsatisfactory for the separation of calcium from strontium. The reason for this is that their elutions were carried out with 5% citrate of pH 5. Our own investigations showed that distribution coefficients are considerably higher and separation factors distinctly lower at pH 5 than at pH 7. This is caused by the dissociation of the second and third hydrogen ions of citric acid between pH 5 and pH 7. Apparently complexes of Ca with L^{3-} are somewhat more stable than complexes with HL^{2-} (L^{3-} = citrate).[20] From pH 7 to 9 distribution coefficients and separation factors remain practically constant. Ammonium lactate and malate are less effective eluting agents than α-hydroxyisobutyrate, but are still quite satisfactory, while even malonate is superior to acetate and formate, which again are better than hydrochloric acid. Tsubota[21] has suggested 1*M* ammonium formate containing 50% of acetone and 1*M* ammonium acetate containing 50% of methanol as eluting agents for the improved separation of calcium from strontium. The separation factor has values of about 5–6, but the elution curves do not show much improvement as compared with the aqueous reagents, apparently because the increased separation factors are accompanied by less favourable column kinetics caused by the partly organic solvent. Separations appear to be less effective than those with citrate or α-hydroxyisobutyrate.

Ba(II)–*Sr*(II). The highest separation factor for this pair is obtained in 0·02*M* DCTA of pH 7·0 containing 0·30*M* ammonium acetate. Unfortunately the separation factor decreases with increasing concentration of DCTA and decreasing pH values. Separations with 0·10*M* DCTA are therefore not satisfactory. For this reason 1·20*N* ammonium α-hydroxyisobutyrate of pH 7·0 (Fig. 8) is preferred for the separation of large amounts of strontium from small amounts of barium, but DCTA has definite advantages for the separation of small amounts of strontium from large amounts of barium. Reasonable separations can also be obtained with 1·0*N* ammonium lactate, 0·85*N* ammonium malate or 1·1*M* ammonium malonate of pH 7·0 or with 0·10*M*

EDTA of pH 6·0 in the presence of 0·30*M* ammonium acetate. More attractive than any of these eluting agents for practical purposes is 3·0*N* hydrochloric acid containing 20% of ethanol.[4]

Zusammenfassung—Die Gleichgewichts-Verteilungskoeffizienten der Erdalkalimetalle Be(II), Mg(II), Ca(II), Sr(II) und Ba(II) zwischen den Komplexbildnern Acetat, Formiat, Lactat, Citrat, Tartrat, α-Hydroxyisobutyrat, Malonat, Malat, Acetylacetonat, EDTA, EGTA sowie DCTA und dem Kationenaustauschharz AG50W-X8 werden angegeben. Der Vollständigkeit halber werden die Koeffizienten in HCl, HNO_3, $HClO_4$ und NH_4Cl beigefügt. Die Vorteile der verschiedenen Komplexbildner zur Trennung von Paaren benachbarter Elemente werden diskutiert und experimentelle Elutionskurven ausgewählter Trennungen wiedergegeben. Trennfaktoren für benachbarte Elemente werden berechnet für Konzentrationen des Elutionsmittels, die einem Verteilungskoeffizienten von 10 für das schwächer adsorbierte Element entsprechen. Sie werden zusammen mit den Konzentrationen an Elutionsmittel als Vergleichsbasis angegeben.

Résumé—On présente les coefficients de partage à l'équilibre pour les métaux alcalins-terreux Be(II), Mg(II), Ca(II), Sr(II) et Ba(II) avec les agents complexants acétate, formiate, lactate, citrate, tartrate, α-hydroxyisobutyrate, malonate, malate, acétylacétonate, EDTA, EGTA et DCTA, et la résine échangeuse de cations AG 50W-X8. On inclut les coefficients en HCl, HNO_3, $HClO_4$ et NH_4Cl pour être complet. On discute des mérites des divers agents complexants pour la séparation de paires d'éléments adjacents et présente des courbes d'élution expérimentales pour des séparations choisies. On calcule les facteurs de séparation pour les éléments adjacents à des concentrations d'agent éluant correspondant à un coefficient de partage de 10 pour l'élément le moins fortement absorbé, et les présente en même temps que les concentrations d'agent éluant pour former une base de comparaison.

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ANALYTICAL APPLICATIONS OF TERNARY COMPLEXES—VIII*

AN IMPROVED REAGENT SYSTEM FOR THE SPECTROPHOTOMETRIC DETERMINATION OF ALUMINIUM

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Summary—Aluminium ions form a ternary complex with Catechol Violet (CV) and cetyltrimethylammonium bromide (CTAB) in which an Al^{3+}:CV:CTAB ratio of 1:2:5 is observed. The sensitivity of the binary complex between aluminium and Catechol Violet $\varepsilon_{615nm} = 1\cdot50 \times 10^3$ l. mole^{-1} . mm^{-1} is enhanced on ternary complex formation to $\varepsilon_{670nm} = 5\cdot30 \times 10^3$ l. mole^{-1} . mm^{-1}. The colour is formed instantaneously, stabilizes within 20 min, and may be used for the detection of aluminium in the range 0·27–54 pm in the presence of EDTA which prevents the interference of most ions. A benzoate extraction procedure for aluminium is used to prevent interference from hundredfold amounts of Cr(VI), Fe(II), Fe(III), Hg(II), Sb(III), Ti(IV) and acetate, but Be, Cr(III), rare earths, V(V), Zr and tartrate must be absent, as must high concentrations of phosphate and fluoride ions.

Catechol Violet was proposed as a reagent for the absorptiometric determination of aluminium by Anton[1] in 1960. Subsequently, Tanaka and Yamayoshi[2] reported extremely high sensitivities with the same reagent for tin and aluminium (molar absorptivity for Al = $6\cdot8 \times 10^3$ l.mole^{-1}.mm^{-1}). In common with other workers[3,4] we have been unable to obtain such high values for tin in this laboratory[5] and have only been able to approach the sensitivity for aluminium by ternary complex formation.

During our studies on the sensitizing effect of cetyltrimethylammonium bromide (CTAB) on the reaction of Catechol Violet with various metal ions,[3,6,7] it was established that the addition of CTAB to the binary aluminium–Catechol Violet complex produced a marked bathochromic shift in wavelength of absorption from 615 to 670 nm. In addition, the molar absorptivity increased from $1\cdot50 \times 10^3$ to $5\cdot30 \times 10^3$ l.mole^{-1}.mm^{-1}. This communication describes the spectrophotometric determination of aluminium by means of this ternary complex, which is of comparable or greater sensitivity than methods previously described utilizing Chromazurol,[8–10] Eriochrome Cyanine,[11] Aluminon[12,13] or 8-hydroxyquinoline.[12–15] We have found this colour reaction to be more reproducible and less prone to variations in reagent composition than the binary complex.

EXPERIMENTAL

Reagents

All are of analytical grade unless stated otherwise.
Benzoic acid (*GPR*), *5% solution in ethyl acetate.*
Ammonium benzoate, 10% *aqueous solution.*
Ammonium acetate, 50% *aqueous solution.*
1,10-Phenanthroline, 2% *aqueous solution.*
Hydroxylammonium chloride, 10% *aqueous solution.*
Ascorbic acid, 5% *aqueous solution.* Prepared fresh every 2 days.

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* Part VII—Talanta, 1968, **15**, 1359.

EDTA, ca. 0·1*M*. Dissolve 7·5 g of EDTA (GPR free acid) in *ca.* 200 ml of water by addition of the minimum volume of conc. ammonia solution. Adjust the pH to 9·5 and dilute to 250 ml with distilled water.

Buffer, pH 10·2. Dilute 50 ml of conc. ammonia solution to 350 ml with distilled water and adjust the pH to 10·2 with conc. hydrochloric acid. Dilute to 400 ml with distilled water.

Aluminium solution. Dissolve 0·2267 g of ammonium alum [$NH_4Al(SO_4)_2.12H_2O$] in 500 ml of distilled water. (More dilute solutions may be prepared from this stock solution.) Store in polythene or glassware treated with a silicone water-repellent such as "Repelcote" (Hopkin and Williams).

Reagent solution. Catechol Violet 2 × $10^{-4}M$ and CTAB 2 × 10^{-3} *M*. Dissolve 0·1546 g of Catechol Violet in 500 ml of distilled water, add 1·458 g of CTAB and stir to dissolve until there is no turbidity (the solution may need gentle warming). Dilute to 2 l. with distilled water.

Procedure

To prepare the calibration curve transfer by pipette 1–10 ml portions of $10^{-4}M$ aluminium solution into 100-ml volumetric flasks. Add 25 ml of the reagent solution, 5 ml of 5% ascorbic acid solution and 5 ml of the pH 10·2 buffer solution. After 20 min, add 5 ml of 0·1*M* EDTA, make up to volume and measure the absorbance at 670 nm against a reagent blank. The curve is a straight line passing through the origin.

Proceed similarly for test samples, but modify the procedure as follows for both test samples and calibration if interfering species are present. Transfer an appropriate aliquot (1–10 ml) of the *ca.* $10^{-4}M$ aluminium test solution into a 100-ml separating-funnel. Add 2 ml of 50% ammonium acetate solution, 2 ml of 2% 1,10-phenanthroline solution, 1 ml of 10% hydroxylammonium chloride solution and 5 ml of 10% ammonium benzoate solution. If necessary, adjust the pH to 7·5–9. Add 10 ml of 5% benzoic acid solution in ethyl acetate and shake vigorously. Separate and discard the lower (aqueous) layer and back-extract the organic phase with two 10-ml portions of 1*M* hydrochloric acid. Combine these extracts in a 100-ml flask containing 25 ml of the reagent solution and 5 ml of ascorbic acid. Add conc. ammonia solution dropwise until the colour of the solution changes from orange to green. Then add 5 ml of the pH 10·2 buffer solution and, after 20 min, 5 ml of 0·1*M* EDTA solution, make up to volume and measure the absorbance at 670 nm against a reagent blank. The coloured complex tends to adhere strongly to glassware so it is necessary to wash all vessels which have come into contact with it, concentrated hydrochloric acid being used for this purpose; this procedure must also be used for cleaning the cuvettes between each measurement.

RESULTS AND DISCUSSION

Spectral characteristics

The absorption spectra of the reagent solution (Catechol Violet and CTAB) and the ternary complex with aluminium at pH 10·2 are shown in Fig. 1. Included, for comparison, are the spectra of Catechol Violet and the binary complex obtained with aluminium at the same pH value. The ternary complex shows a pronounced absorption at *ca.* 670 nm whereas the binary aluminium complex gives a less well-defined absorption (compared with the reagent alone) with a peak at 615 nm. The absorption of Catechol Violet at 615 nm is reduced appreciably by the addition of CTAB.

Optimum conditions for colour development

The optimum pH for complex formation was found to lie in the range 9·7–10·2 (Fig. 2). Values of pH greater than about 10·5 could not be achieved without very rapid oxidation of the mixed reagent solution. Oxidation of Catechol Violet was in fact found to occur in alkaline solutions at pH values less than 10·5 unless an antioxidant such as ascorbate or hydroxylammonium chloride was present. These were ineffective above pH 10·5.

Maximum colour formation was found to occur with slightly greater than a 2-fold molar excess of Catechol Violet and a 5-fold molar excess of CTAB over aluminium. A greater molar excess of Catechol Violet than about 2-fold produced a slightly

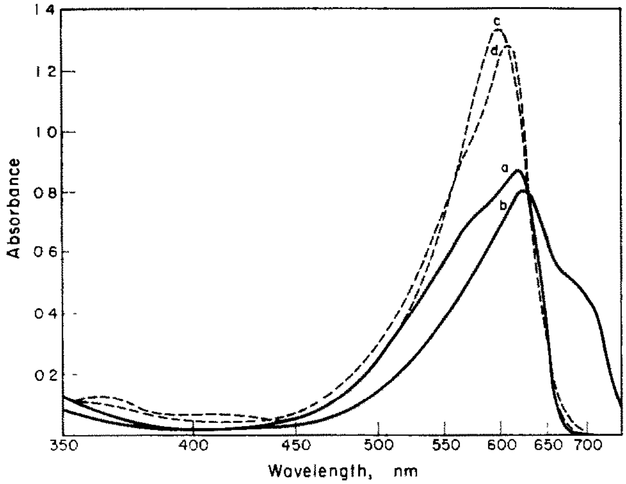

FIG. 1.—Absorption spectra.
(*a*) 5 ml of $10^{-3}M$ Catechol Violet and 5 ml of $10^{-2}M$ CTAB diluted to 100 ml with distilled water; (*b*) as (*a*) plus 1 ml of $10^{-3}M$ aluminium; (*c*) 5 ml of $10^{-3}M$ Catechol Violet diluted to 100 ml with distilled water; (*d*) as (*c*) plus 1 ml of $10^{-3}M$ aluminium. All solutions adjusted to pH 10·2.

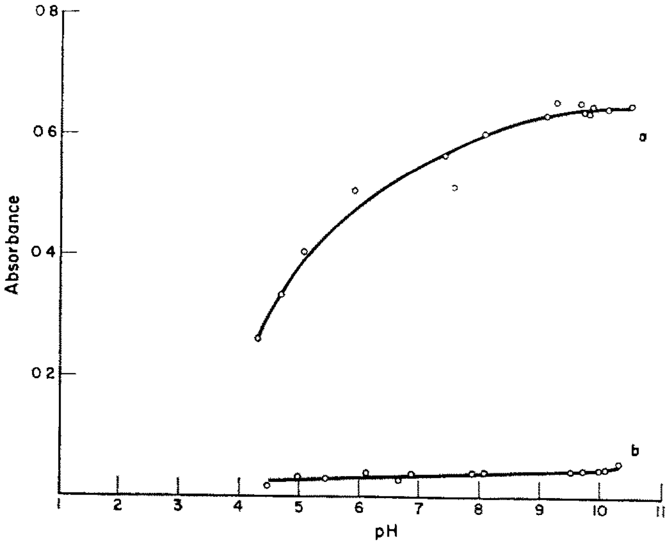

FIG. 2.—Optimum pH for colour formation.
(*a*) 5 ml of $10^{-3}M$ Catechol Violet, 5 ml of $10^{-2}M$ CTAB and 1 ml of $10^{-3}M$ aluminium solution diluted to 100 ml with distilled water. (*b*) as (*a*) but with no aluminium.

diminished sensitivity. It was, however, found necessary to use a 25–50-fold molar excess of CTAB over aluminium in order to stabilize the colour and prevent a rapid decrease in absorbance owing to precipitation of the complex. This necessitated special treatment of the mixed reagent solution to secure the maximum colour formation and prevent the reagent solution from precipitating. When the temperature of the mixed reagent solution fell below *ca.* 20° for any length of time, the reagent solution deposited a flocculent precipitate of CTAB. This deposition could be postponed almost indefinitely by constant low-speed stirring or reversed by warming the solution to *ca.* 30°.

When these precautions were not observed and the mixed reagent solution was allowed to become even faintly turbid, the blank absorbance value increased without a corresponding increase in the complex absorbance. This behaviour prevented an absolute value being ascribed to the molar absorptivity of the complex, although a series of solutions prepared at the same time from the same mixed reagent solution obeyed Beer's Law.

Colour development in alkaline solution was found to be instantaneous but this was followed immediately by a rapid decrease for some 20 min. After this time, the rate of decrease in absorbance was found to have slowed so that there was only a further 15% decrease over the next 24 hr. Measurement of a series of solutions allowed to age for 20 min was found to give consistent absorbance values. The decrease in absorbance in the first 20 min was measured as 30% of the initial absorbance value; this decrease could not be prevented.

With the optimum conditions described above, a linear calibration curve was obtained for the direct method over the range 0·27–54 ppm aluminium, the effective molar absorptivity being $5{\cdot}30 \times 10^3$ $\text{l.mole}^{-1}.\text{mm}^{-1}$ (±4%). The solvent extraction procedure which was subsequently developed to avoid certain interferences was found to give a linear calibration curve over the range 2·7–27 ppm aluminium, the molar absorptivity coefficient remaining the same.

Nature of complex

The Catechol Violet: aluminium ratio was determined by the method of continuous variation to be 2:1. No other complexes were observed. Potentiometric titrations indicated the formation of the $\text{Al(Catechol Violet)}_2\text{(CTAB)}_5$ complex. Figure 3 shows a possible form of it, which is supported by the observed partial extraction of a blue species into chloroform. This extract was not studied further because it was not found possible to separate completely the emulsion formed when CTAB-containing solutions were shaken with chloroform. The ternary complex is insoluble in water. Salts of the cetyltrimethylammonium ion with bulky anions such as perchlorate or iodide are also insoluble.[3]

In the light of these observations and the known requirement for the presence of micelles for complex formation,[6,7] it is postulated that the complex formed with aluminium is present as finely dispersed particles protected within the CTAB micelles in solution. This is supported by the observed initial rapid drop in absorbance of the complex, corresponding to aggregation of these particles.

The bathochromic shift is thought to be due to further deprotonation of the hydroxyl groups on the dye molecule with formation of the ion shown in Fig. 3. Potentiometric titrations indicated the release of eight equivalents of protons per equivalent of ternary complex which is in agreement with the results obtained by Malát and Zelinka.[16] It also demonstrated that the nature of the cationic surfactant plays at most a minor role in the colour change, in that when cetylpyridinium bromide was substituted for CTAB, the absorption spectra obtained for the respective ternary complexes were nearly identical. Thus, the colour change is not thought to be a charge-transfer phenomenon. Further support is lent to this view by the formation of

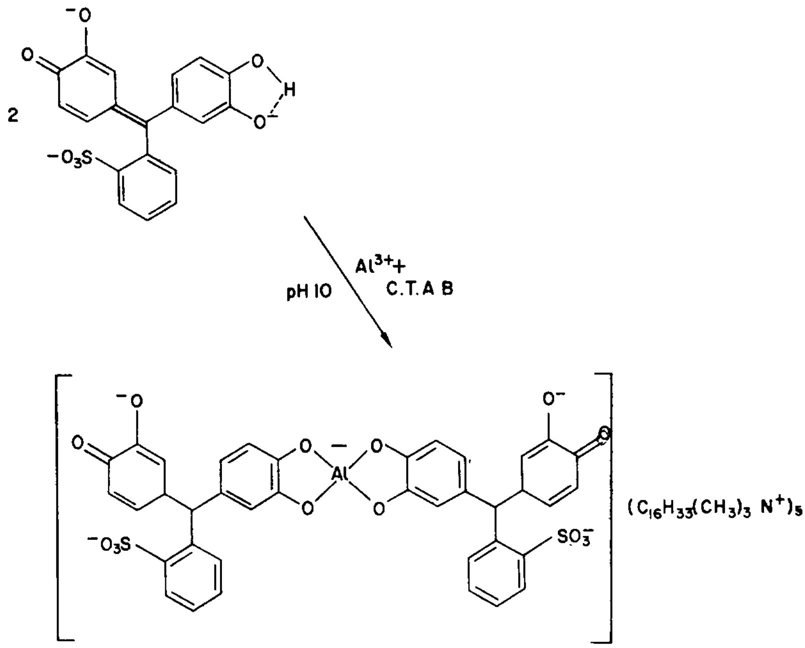

FIG. 3.—Formation of complex.

a ternary molybdenum(VI)/carminic acid/CTAB complex together with a bathochromic shift and increased absorbance. The binary molybdenum(VI)/carminic acid complex possesses a number of hydroxyl groups which would be expected to deprotonate readily.

A notable physical property of the ternary complex with aluminium was its adsorbability onto the walls of glass vessels, even after treatment with a silicone water-repellent. An adhering film was found to build up slowly and continuously over a period of days until the original solution became noticeably decolorized. The film could be removed by washing with acetone or concentrated hydrochloric acid which destroys the complex. Washing with water had little effect.

Interferences

A number of possible interfering species likely to be present in a sample for analysis were investigated. No interference was found from the alkalis, boron (as borate), molybdenum(VI), selenium(IV), fluoride or phosphate when present in concentrations less than $10^{-3}M$ (*i.e.*, less than about 100-fold molar excess over aluminium). The addition of EDTA after formation of the ternary aluminium complex (*i.e.*, after adjustment of pH to 10·2) prevented interference from a 100-fold molar excess over aluminium of magnesium, cobalt, nickel, zinc, copper(II), cadmium and lead. EDTA added *before* complex formation was also found to interfere.

The solvent extraction procedure developed was able to prevent interference from 100-fold molar excesses of iron(II), iron(III), chromium(VI), mercury(II), titanium (IV), antimony(III) and acetate. Interference was, however, still observed from zirconium, vanadate, beryllium, the rare earth elements, chromium(III) and tartrate. High concentrations of phosphate, ascorbate and fluoride (1000-fold molar excess over aluminium) interfered by reducing the extraction efficiency. Ascorbate does not interfere with the formation of the ternary complex when it is subsequently added as a protective agent.

Solvent extraction of aluminium with benzoate

The solvent extraction procedure used for the separation of aluminium as its benzoate is based on the procedure described by Morrison and Freiser.[17] It was found necessary to modify the procedure by using 5% benzoic acid in ethyl acetate in order to increase the recovery of aluminium from 75% to 100%. The addition of ammonium rather than sodium benzoate to the aqueous solution was effective in reducing the absorbance of the blank. It was found to be beneficial to form the extractable complex in an acid solution *ca.* pH 4 since the efficiency of extraction was improved, probably because of the formation of a basic benzoate at higher pH values. The presence of the ascorbic and tartaric acids in the extraction medium decreased the extraction efficiency by competing for the aluminium ions.

The anomalous interference of chromium(III) arose from the complete obscuration of the phase boundary by the bulky precipitate formed at the interface. Chromium(VI), reduced to chromium(III) *in situ* by the hydroxylamine, yielded less precipitate and although the phase boundary was still indistinct its precise location was rendered possible by the red colour imparted to the solution in the presence of iron by the tris-1,10-phenanthrolinium iron(II) ion. When iron was absent an addition of iron was made to chromium containing solutions to render the phase boundary visible.

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Zusammenfassung—Aluminiumionen bilden einen ternären Komplex mit Catechinviolett (CV) und Cetyltrimethylammoniumbromid (CTAB), in dem das Verhältnis Al^{3+}:CV:CTAB = 1:2:5 beobachtet wird. Die Empfindlichkeit des binären Komplexes zwischen Aluminium und Catechinviolett $\varepsilon_{615nm} = 1{,}50 \,.\, 10^3$ l. mol^{-1} mm^{-1} wird durch Bildung des ternnären Komplexes auf $\varepsilon_{670nm} = 5{,}3 \,.\, 10^3$ l. mol^{-1} mm^{-1} gesteigert. Die Farbe bildet sich augenblicklich stabilisiert sich in 20 min und kann zur Bestimmung von Aluminium im Bereich 0,27–54 ppm verwendet werden. Zur Vermeidung von Störungen durch die meisten Ionen gibt man EDTA zu. Um Störung durch hundertfache Mengen Cr(VI), Fe(II), Fe(III), Hg(II), Sb(III), Ti(IV) und Acetat zu vermeiden, wird Aluminium mit Benzoat extrahiert. Be, Cr(III), seltene Erden, V(V), Zr und Tartrat dürfen nicht anwesend sein ebenso hohe Konzentrationen von Phosphat- und Fluoridionen.

Résumé—Les ions aluminium forment un complexe ternaire avec le Violet de Catéchol (CV) et le bromure de cétyltriméthylammonium (CTAB) dans lequel on observe un rapport Al^{3+}:CV:CTAB de 1:2:5. La sensibilité du complexe binaire entre l'aluminium et le Violet de Catechol, $\varepsilon_{615nm} = 1{,}50 \times 10^3$ l. $mole^{-1}$. mm^{-1} est exaltée par formation du complexe ternaire à $\varepsilon_{670nm} = 5{,}30 \times 10^3$ l. $mole^{-1}$. mm^{-1}. La coloration se forme instantanément, se stabilise en 20 min, et peut être utilisée pour la détection de l'aluminium dans le domaine 0,27–54 ppm en la présence d'EDTA qui évite l'interférence de la plupart des ions. On utilise une technique d'extraction au benzoate pour l'aluminium pour éviter l'interférence de quantités cent fois plus élevées de Cr(VI), Fe(II), Fe(III), Hg(II), Sb(III), Ti(IV) et acétate, mais Be, Cr(III), les terres rares, V(V), Zr et tartrate doivent être absents, ainsi que des concentrations élevées d'ions phosphate et fluorure.

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THE PERFORMANCE-CHARACTERISTICS OF ANALYTICAL METHODS—I

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Summary—The ever-increasing volume of analytical literature makes it important to be able to compare unambiguously the advantages and disadvantages of analytical methods. To this end, a set of consistent definitions and methods for determining quantitative performance-characteristics (*e.g.*, precision, sensitivity, bias) is needed. The aim of this series of papers is to review the definition and determination of such parameters, and to suggest criteria for general use. This first paper discusses the general problem, considers those general aspects of analytical methods that are important, and establishes the performance-characteristics to be considered in detail.

KIRKBRIGHT[1] has pointed out the difficulties experienced by analysts when attempting to determine from the literature the most suitable spectrophotometric method or reagent for a particular purpose. These difficulties arise for two main reasons: (*a*) the nature and extent of investigation vary markedly from one paper to another; (*b*) authors use different approaches in defining, determining and expressing the quantitative characteristics of their methods. Kirkbright's paper is timely for, as he says, when new or modified methods are being presented in the literature at an ever-increasing rate, confusion and ambiguity are likely to increase so long as (*a*) and (*b*) persist. Conversely and desirably, greater uniformity will lead to more certain and efficient utilization of the vast amount of information appearing.

In an attempt to eliminate or reduce these problems, Kirkbright made a number of suggestions concerning the minimum amount of quantitative data that should be included in any publications describing new or modified reagents and methods. He dealt mainly with important experimental parameters in spectrophotometry but also recommended that data should be quoted for precision, sensitivity, selectivity, *etc.* Such parameters are of fundamental importance in defining the usefulness of all analytical methods. Garton *et al*[2] have used the term "performance-characteristics" to describe parameters of this nature. This term seems admirable, and is used throughout this series of papers.

Many authors, *e.g.*, refs. 2 and 3, have stressed the importance of uniformity in the definition and determination of performance-characteristics; otherwise, unambiguous comparison of analytical methods is either impossible or severely hindered. Nevertheless, analytical literature is notable for the multiplicity of methods used to describe performance-characteristics. This lack of uniformity is probably due to many factors among which may be included the following.

(*a*) Surprisingly, there appear to be no generally accepted definitions of several basic concepts such as "analytical method," "precision" and "interference."

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(*b*) A unified treatment of performance-characteristics is either absent, superficial or not comprehensive in the standard analytical texts, or in the journals. The most complete discussion known to the author is in Gottschalk's book,[4] which is in German, and tends to emphasize the statistical rather than the analytical aspects. Published papers generally present the views of their authors rather than attempt a critical review, and any suggestions made are often expressed in terms of a particular technique rather than in terms capable of general application.

(*c*) Statistical concepts must be used in consideration of many performance-characteristics. Many analysts seem unfamiliar with, or partially averse to, the use of such techniques, particularly when the topic is approached from the statistical rather than the analytical viewpoint.

For these reasons alone, it is not surprising that wide variations occur in the definition and determination of performance-characteristics. This series of papers has the following aims: (*a*) to discuss the characterization of analytical methods and propose performance-characteristics of general importance; (*b*) to consider the various definitions that have been suggested for these characteristics and to recommend definitions thought most suitable for general use; (*c*) to suggest suitable experimental techniques for determining these characteristics. These proposals are unlikely to meet with general agreement, but the author will be well satisfied if these papers provoke comment and discussion and perhaps help to lead to the general agreement that is so desirable and must ultimately be obtained. It should be emphasized that few of the individual ideas in this series are original; most if not all are to be found in the literature. The aim was not to provide a series of new observations but rather to attempt to weld existing concepts into a consistent whole.

The first part deals with several aspects that must be considered before individual performance-characteristics are discussed in detail. Throughout, only quantitative methods for analysing discrete samples are considered. Qualitative and continuous analysis are excluded; the former because quantitative treatment on the lines intended seems unnecessary and inappropriate, and the latter because a different type of treatment is preferable for some of the performance-characteristics.

DEFINITION OF ANALYTICAL METHOD

First it is essential to be clear on the meaning of the term "analytical method." The general concept seems clear at first sight but its very familiarity may conceal important differences in interpretation.

Analytical methods are of interest principally because they are, or may be, used in the production of analytical results. However, several other components are also involved in producing results. Thus, in addition to a description of the procedure to be used, an analyst, apparatus, reagents, laboratory and sample are all generally required. The question immediately arises—which combination of all or some of these components constitutes the analytical method? If none of the last five components affected analytical results, the question would be trivial. However, experience shows indisputably that each may markedly affect, for example, the precision and/or bias of analytical results. Thus, if any of these components were included with the procedure in a definition of "analytical method," it would follow that the method could change each time that a different analyst, apparatus, reagent, laboratory or sample was involved; such an ambiguous situation is to be avoided. It is concluded, therefore, that an unambiguous and useful definition can be framed only in terms of the procedure. A suggested definition is given below, and is recommended for general adoption.

Definition. An analytical method is to be regarded as the set of written instructions completely defining the procedure to be adopted by the analyst in order to obtain the required analytical result.

Surprisingly, only two definitions of the term "analytical method" have been found in the literature. Essentially the same definition as that proposed above has been given by the American Society for Testing and Materials (A.S.T.M.).[5] Kaiser and Specker[3] have suggested a different definition for "methods of measurement" and state that "analytical methods" are to be regarded as a special class of such methods. Their definition is "A method of measurement (Messverfahren) is embodied in the measuring arrangements and conditions (Messanordnung) and the specified procedure (Messvorschrift) which determines in every detail the operations (Messvorgang) to be carried out." The exact meaning of the term "Messanordnung" was not explicitly defined, and Kaiser[6] later emphasized that all details capable of affecting analytical results must be stated before the method can be considered to have been defined. This definition therefore leads to such detailed specification that the method would change each time the analyst, the laboratory, the reagents or the apparatus changed. Such a concept appears to the writer to be of little or no practical value, and, in addition, logically prevents consideration of one of the most important features of analytical methods, *i.e.*, their ability to allow good results to be obtained under a wide variety of experimental conditions. Sandell[7] and Maurice[8] have both mentioned the problem of defining the term "analytical method." Although neither gave a definition, they suggested that certain factors such as analysts and laboratories should be excluded from any definition. Their views thus support the definition proposed in this paper.

The definition proposed has two important consequences: (*a*) a distinction must be made between the errors of analytical methods and results; (*b*) great emphasis must be placed on accurate and complete specification of methods.

DISTINGUISHING BETWEEN ANALYTICAL METHODS AND RESULTS

Papers often contain such statements as "the precision (or other performance-characteristic) of the method is . . . ." Such statements would be incorrect if the proposed definition were adopted, because the concept of precision could not be applied to printed paper. The correct form would be "when the method was followed, analytical results were obtained with a precision of . . ." or more simply, "the precision of analytical results was . . . ." Thus emphasis is immediately placed on the quality of results; this can only help to stimulate more critical appraisal by analysts of the validity of their results. The shift of emphasis from methods to results should also encourage more searching investigations of the effects of the other five components involved in producing results.

It may be argued that any method has an associated limiting precision which cannot be bettered. In the author's opinion, such a concept is debatable but the question need not be laboured. In characterization of an analytical method, the precision obtained experimentally is crucial because it states what is known about the actual results rather than results relating to hypothetical conditions. Limiting precisions, if they exist, can easily be calculated for any set of hypothetical conditions. If experience with a particular method shows that the precision of results is essentially constant with time and in different laboratories, it may then be argued that the method rather than the results can be correctly associated with the experimentally determined precision.[9] Such an approach is considered undesirable because even extensive experience cannot guarantee universal applicability (as many analysts must know to their discomfort), though it is useful to think of such a method as a good one.

It is of interest that the A.S.T.M. propose the association of performance-characteristics such as precision and bias neither with methods nor with analytical results but with "measurement procedures." Such a procedure is defined[5] as "a method of measurement together with a system of causes." This "system of causes" represents a set of specified values for all the factors affecting performance-characteristics. This definition therefore leads logically to the same difficulties as Kaiser and Specker's proposed definition of "analytical method."[3] However, the term "error of an analytical method" retains a useful meaning in association with the definition proposed here, signifying an omission, ambiguity or mistake in the written procedure.

SPECIFICATION OF ANALYTICAL METHODS

It is vital that methods contain *all* experimental details of importance in achieving results of the quality obtained by the authors. This obvious but frequently neglected point has been emphasized by Kaiser[6] and often and eloquently by Youden.[9,10] Otherwise, different laboratories will use, in effect, different methods although each will state that the same method is employed. Analysts are well aware of the large effects that may be caused by apparently minor procedural variations. Such variations could easily lead to confusion concerning the quality of results obtainable, and hence to falsely severe judgment on the procedure or its description, and to further experimental investigations in a number of laboratories. If both consequences arise from inadequate description, it is correct to regard the method as unsuitable. Authors should therefore gladly accept the responsibility of attempting to specify their methods unambiguously. Youden,[9] in discussing interlaboratory comparative analyses, has stated "Unless and until a procedure has been adequately described, so that nearly all the laboratories show acceptable agreement for their averages, the question of agreement with a true value is hardly meaningful. If laboratories disagree, the procedure needs more careful specification." This view of an authority on the subject indicates the importance of satisfactory description of analytical procedures, and introduces the concept of "the true value."

Several authors (*e.g.*, Eisenhart[11]) have argued that a true value can be defined only in terms of the result of a measuring process—a further strong reason for unambiguous and complete description of analytical procedures. Such description meets two main difficulties.

First, many experimental and environmental factors may affect analytical results, and authors have the problem of deciding which factors should be specified in the method. Although it is not impossible to specify all the conditions, it is usually impracticable and often unnecessary. For example, it will usually be unimportant and unnecessarily restrictive to state in which direction the laboratory windows faced or which type of separating-funnel was used. It is customary not to specify such factors in analytical methods; they are left to the discretion of the analyst using the method. Nevertheless, the complete description of an analytical procedure ideally requires that the author should establish all those experimental conditions that may affect analytical results. This information can, in general, be obtained only by experimental study, and as this study is made more searching, so can the method be better defined.

Even if a full investigation is not possible, it is often of value to publish the method, but lack of knowledge should not then be taken as an excuse for an ambiguous analytical method. When the effects of certain factors are not known, authors should be even more careful to state exactly the procedures they have used. For example, if the effects of the intervals between reagent additions have not been determined, the author should state the range of intervals used during his work. Methods abound with common, basic procedures such as weighing and use of volumetric apparatus, of which complete details need not be given, because they are adequately described elsewhere. All procedural details peculiar to a particular method or not commonly known should be described in full. A related point has been emphasized by Youden;[9] he strongly condemns instructions such as "shake vigorously" and "clean thoroughly." Such wording is open to large differences in interpretation, and should always be expressed less ambiguously. All these points may appear so obvious as not to require stating, but so many published methods pay so little regard to them as to warrant their repetition. Editors could stimulate the improvement of analytical methods by striving still more keenly for unambiguous descriptions in published papers.

The second problem arises when authors have to specify the numerical values for experimental parameters such as weight, volume, time and temperature. In the writer's view, these numerical values should aim to define not only the optimum values but also the deviations from them that can be tolerated without causing more than a stated deterioration in the quality of results, thus ensuring a close enough approach to optimum values without waste of time, effort and money on unnecessarily fine control. As an example, consider the instruction "add 5 ml of reagent;" one analyst may painstakingly use a bulb pipette and add 5 ± 0·002 ml while another may use a graduated cylinder and add 5 ± 0·5 ml. The latter may be perfectly adequate (to achieve a stated precision) and in that case the instruction "add 5 ml (±0·5 ml)" is far more informative in indicating the degree of control required, but does not preclude the use of a pipette. Similarly, "add 5 ml (±0·002 ml)" immediately indicates that strict control is required, and that a graduated cylinder should not be used. The quantities in brackets may be called tolerances, and besides aiding choice of technique, serve as a guide to the critical factors of a method, so helping to prevent the false, assessment of importance of factors that is sometimes made by analysts presented with an unfamiliar method or technique. Analytical methods should always quote tolerances for each such parameter; the additional space required is a small price to pay for the extra information. Sometimes "add 5 ml" is taken to mean addition of 5 ± 1 ml or 5 ± 0·5 ml and "add 5·0 ml" to mean addition of 5·0 ± 0·1 ml or 5·0 ± 0·05 ml, and so on. However, there appears to be no universal agreement to this system, which is also much less flexible in defining tolerances, and it seems better to specify the tolerance.

Every method quoting tolerances should define the criteria used in deciding their values, *e.g.*, that the results were not affected by more than a certain amount by variations within the stated range; no strong reason appears for attempting more precise definition of tolerances. Tolerances should not be regarded as an excuse for careless or slipshod work; the aim should be to achieve the specified (optimum) value of the parameter; the tolerance indicates the necessary technique and degree of control required.

Tolerances should ideally be determined experimentally but the choice of values may not always be straightforward, and whenever there is any doubt as to the values to be specified or no investigations have been made, the best plan would be to quote the values observed during the development of the procedure. If an author gave falsely large tolerances there would be a tendency for results by other analysts to be of poorer quality (*e.g.*, less precise, more biased). Conversely, specification of too many extremely fine tolerances would tend to lead to rejection of a method. Thus, analysts would favour use of methods for which the tolerances had been reasonably chosen, a situation likely to encourage a more critical approach to the choice of tolerances and consequent improvement of analysis and analytical methods.

Consistent general application of this approach to definition and specification of analytical methods could be of great and increasing value to all analysts. General adoption of these suggestions is therefore recommended. Gottschalk[12] has argued for a standardized format for analytical methods and gives two examples. In the writer's opinion, his suggestions represent unnecessary standardization but indicate a possible line of development.

PERFORMANCE-CHARACTERISTICS

A primary aim of a new analytical method should be to improve the quality and/or efficiency with which samples (for which the method is relevant) can be analysed, and it is essential for authors to publish information giving the maximum possible assistance in deciding whether the method is likely to be of value for their purposes. Obvious examples are the bias and precision of the results. Such parameters may be called "performance-characteristics."

From what has been said above on analytical methods, it follows that performance-characteristics are not, in general, invariant properties of a method, and only show the performance obtained under a given set of experimental conditions. For that reason, it is essential to define these conditions closely, as emphasized by Garton *et al.*[2] and recommended by a British Standard[13] on the presentation of experimental results. Factors such as laboratory temperature, skill and experience of the analyst, and whether the work was carried out under research or routine conditions, may be important but are often omitted in papers, so that it becomes quite possible for different values for the one characteristic to be obtained when the same method is used by different workers. This possibility appears to be considered undesirable by many analysts, who seem to favour the concept of invariant performance-characteristics. It is worth briefly examining whether this concept has any advantages, as it is contrary to the approach recommended in this paper.

The practising analyst faces two main situations relevant to the point: (*a*) choosing a method for a particular sample, and (*b*) publishing a method or the results obtained by use of a published method. In (*a*), the analyst chooses that method apparently most suitable (on the basis of published performance-characteristics) for his particular problem. However, he would usually be ill-advised to assume that he will inevitably obtain the same values for all characteristics as those quoted in the method. In practice, he would always seek to obtain an estimate of some, at least, of the characteristics relevant to his own conditions, and this procedure in no way requires the concept of invariant performance-characteristics; indeed, it is clearly based on the contrary concept. If the performance with the chosen method is found to be satisfactory, the matter is at an end. If the performance turns out to be unsatisfactory, the analyst has either to select another method or attempt to locate the reasons why the performance under his conditions is not as good as that reported by others, and neither course of action is facilitated by the concept of invariant performance-characteristics. In (*b*), the analyst has merely, in effect, to quote experimental results. Clearly, he is then concerned solely with his observed performance-characteristics, and it is immaterial whether they are considered invariant or not. Different values for the performance-characteristics associated with a method may therefore be reported, which simply provide additional information for analysts facing situation (*a*) and present problems only if one tries to maintain a concept of invariant performance-characteristics; such a concept therefore appears to have no important advantages. In contrast, the concept of variable characteristics proposed in this paper should favour their more critical evaluation because the emphasis is placed on experimental estimation of performance rather than prediction.

On this basis, the following definition of performance-characteristics is proposed.

> *Definition*. The performance-characteristics of an analytical method used under a given set of experimental conditions are a set of quantitative and experimentally-determined values for parameters of fundamental importance in assessing the suitability of the method for any given purpose.

Although this definition includes all the elements required from the previous discussion, it has been deliberately put in very general terms. In this way, the same definition can be used if parameters other than those suggested in these papers are later considered to require inclusion.

There are, of course, several factors that are not included by the proposed definition, *e.g.*, the equipment and/or experience available in a particular laboratory, the care with which experimental operations need to be carried out, the ease or difficulty of making reagents and/or calibrating the analytical system. Quantitative expression of such factors is often impossible and in any case may be of little or no value to another analyst working under different conditions. Further, a well written method should itself allow any analyst to make an adequate assessment of such points without the need for any particular performance-characteristics. Performance-characteristics need, and should, refer only to the quality of the results obtained and the time required to make the analyses.

The literature dealing with analytical methods in general contains little discussion of the characteristics that should be quoted. Morrison and Skogerboe[14] state that sensitivity, accuracy, precision and selectivity are of primary importance in choosing a method. They mention that other factors such as scope, sampling and standards requirements, cost of equipment and time of analysis are also of great practical significance. Gottschalk[12] suggests eight factors required in evaluating a method, *viz.*, range, selectivity, errors, limit of determination, difficulty, apparatus required, cost and time of analysis. Kaiser and Specker[3] have proposed range, calibration function, systematic errors, precision, limit of detection, cost and time of analysis. These different suggestions can be summarized, once the factors excluded by the proposed definition have been omitted, by stating that information is required on the errors of analytical results, on the calibration curve, and on the time of analysis.

Analytical results are always affected by random errors, and systematic errors (*e.g.*, interferences) may also occur. Thus, performance-characteristics must aim to define the magnitude of both types of error. Random errors (precision) and the related concept of "limit of detection" will be considered in detail in Parts II and III of this series. Systematic errors (bias) and, in particular, the phenomenon of interference will be considered in detail in Part IV.

Mathematical expression of the calibration curve shows the relationship between the analytical measurement and the concentration (or amount) of the determinand.* This information is of value in revealing the range of concentrations covered by the method, the ease of calibration and the rate at which the magnitude of the analytical measurement changes with concentration. The last feature is of importance because it allows a check on unrealistic claims for precision. These aspects together with some comments on time of analysis and other miscellaneous factors will be dealt with in Part V, which also gives some detailed examples of a technique proposed for reporting performance-characteristics.

Acknowledgements—I should like to acknowledge the stimulating discussions with many of my colleagues and, in particular, Mr. I. R. Morrison.

Zusammenfassung—Der immer größer werdende Umfang der analytischen Literatur läßt es immer wichtiger erscheinen, Vor- und Nachteile analytischer Methoden zweifelsfrei gegeneinander abwägen zu können. Zu diesem Zweck braucht man einen Satz konsistenter Definitionen und Methoden, um quantitativ Gütekennzeichen (z.B. Genauigkeit, Empfindlichkeit, systematischer Fehler) ermitteln zu können. Das Ziel dieser Reihe von Publikationen ist es, einen Überblick über Definition und Bestimmung solcher Parameter zu geben und allgemein verwendbare Unterscheidungsmerkmale vorzuschlagen. Diese erste Arbeit diskutiert das Problem im allgemeinen, erörtert die allgemeinen Aspekte analytischer Methoden, die für dieses Problem wichtig sind, und gibt die Gütekennzeichen an, die im einzelnen betrachtet werden sollen.

Résumé—Le volume toujours croissant de la littérature analytique rend importante la possibilité de comparer sans ambiguïté les avantages et désavantages de méthodes analytiques. A cette fin, il est besoin d'un ensemble de définitions et de méthodes logiques pour la détermination de caractéristiques de performances quantitatives (par ex., précision, sensibilité, influences). Le but de cette série de mémoires est de passer en revue la définition et la détermination de tels paramètres, et de suggérer des critères d'emploi général. Ce premier mémoire discute du problème général, considère tels aspects généraux de méthodes analytiques qui sont importants, et établit les caractéristiques de performances que l'on doit considérer en détail.

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THE PERFORMANCE-CHARACTERISTICS OF ANALYTICAL METHODS—II*

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Summary—Statements on the errors of analytical results are an important aspect of characterizing the performance of analytical methods. The general nature of random and systematic errors is briefly discussed, and methods of numerically defining the former are considered. It is suggested that the standard deviation of analytical results be used exclusively as the quantitative measure of precision within the context of performance-characteristics. Techniques for, and precautions to be observed in, estimating standard deviation are critically discussed. On this basis, general principles are proposed that should be observed whenever possible in experimental tests to estimate standard deviation.

IN PART I[1] it was concluded that among the performance-characteristics of analytical methods should be included statements on the errors of analytical results. Although it seems that all analysts are in agreement on this, many different methods are used to determine and express analytical errors so that it is often difficult and sometimes impossible to interpret reported results quantitatively and/or unambiguously. Occasionally, the experiments reported do not allow even an estimate of the errors, despite the firm conclusions drawn. It seems most desirable to attempt to obtain greater uniformity in the determination and expression of errors.

NATURE OF ERRORS

Eisenhart[2] has given a particularly clear and illuminating discussion of this topic, and the brief outline below essentially follows his approach.

Consider the analysis of a stable, homogeneous sample for a substance with true concentration τ. When a number of identical portions of this sample are analysed, it is a matter of experience that the results ($x_1\, x_2 \ldots x_n$)‡ differ§ among themselves and in general from the true concentration. The error, E_i, of a result, x_i, is universally defined as the difference between the result and the true concentration, *i.e.*, $E_i = x_i - \tau$. The concept of a "true value" is of great importance, and will be discussed in more detail in Part IV. For the present, it suffices to think of the term in its literal sense.

There is experimental and mathematical[2] justification for the postulate that the mean of n analytical results approaches a definite value, μ, as the number of results is increased indefinitely provided that the analytical measurements are in "a state of statistical control" (*i.e.*, that all the causes of errors remain the same). That is to say, an analyst's results are meaningful estimates of the concentration to be determined. When the limiting mean concentration μ differs from the true concentration, results are said to be subject to bias or systematic error of magnitude B where $B = \mu - \tau$.

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‡ § See page 32.

The terms "bias" and "systematic error" are usually used synonymously, though Murphy[6] states that some regard systematic error as the cause of bias—a distinction that seems unimportant in the present context. The several sources of bias will be considered in Part IV; one familiar example is the effect of an interfering substance.

In the IUPAC recommendations[1] for presentation of results of chemical analysis, bias is defined as the difference between the mean of a series of results and the true value, *i.e.*, the experimental results define the bias exactly. Experimental results defined as in this paper provide only an estimate of the bias. For a given set of results, both definitions lead to the same numerical value for bias, but it seems inconsistent that IUPAC should imply that this experimental value has no uncertainty when this is quite contrary to the statistical approach. For example, according to the IUPAC definition the bias would, in general, vary with the number of results. Accordingly, the IUPAC definition is not followed in this series. *Analytical Chemistry*[7] recommends the term "mean error," defined in the same way as the IUPAC definition of bias. The use of mean error in this sense avoids the problem caused by the definition of bias in two different ways. Mean error is no more than a statement of experimental observation, and can be used as an estimate of bias in the sense used in this paper. It is unfortunate that the IUPAC and *Analytical Chemistry* definitions lead to two different terms for the identical concept. The IUPAC definition should be changed so that either bias is defined in the sense used in this paper or the term "bias" is replaced by "mean error."||

The magnitudes and signs of the deviations of individual results from their mean are found to vary randomly because of the inevitable variations in experimental conditions, such as slightly different amounts of reagents, differing reaction-times, temperatures, *etc.* These random variations are always present even if systematic errors are absent, and thus form a second source of error of profound importance.

Several different words are used to express this concept of the variability of results among themselves, *e.g.*, precision, reproducibility, repeatability. There seems to be little to choose etymologically between these terms. Precision has been recommended by IUPAC,[3] *Analytical Chemistry*[7] and ASTM.[8] A British Standard[9] favours reproducibility but recognizes that precision may ultimately be preferable. Usage in journals varies. It is desirable that one term be used consistently to avoid confusion.

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‡ In this series the term "analytical result" means the value obtained for the concentration (or amount) of the determinand when the procedure described in the analytical method is followed. It does not signify a primary "measured value" such as a weight, an electric current or voltage, a time. This usage follows the recommendations of IUPAC.[3] As Kaiser[4,5] points out, it is important to distinguish between a result obtained as described in a method and the mean result of replicate determinations. For example, a method may state that two portions of a sample must be analysed and the mean of the two determinations used to calculate an analytical result; the variability which characterizes the performance is then the variability of the means of duplicate determinations. Similarly, if a method specifies a single determination for each sample, variability should not be calculated for the means of a number of determinations.

§ Strictly, this statement is true only when one attempts to minimize any discrepancy between results and true values. Otherwise, identical results may be obtained if the analytical system is of such coarse discrimination that differences are concealed. In such cases, the excellent concordance of results is misleading because real differences between the concentration of samples will also pass undetected.

|| EDITORIAL NOTE: Unfortunately, the term "mean error" is ambiguous, since it could be interpreted as the average error; what is really meant is the error of the average, *i.e.*, the difference between the average and the true result, and the term "error of the mean" would be more correct.

Precision appears to be the most widely recommended and used, and is therefore used in this series and recommended for general adoption.

Thus, the terms bias and precision refer to the two types of error. Neither alone is capable of defining the total error of an analytical result, and it is useful to have a term connoting total error. There is concurrence on the use of the term "accuracy" for this purpose[3,7–9] This usage is followed in this series, and is recommended for general adoption. Eisenhart[2] has discussed the relative importance of bias and precision when methods of measurement are chosen.

Quantitative statement of precision

Random variations have the effect that the deviation of an analytical result from the limiting mean cannot be known exactly. Thus, each result must be regarded as an estimate to which attaches some uncertainty. Limits must be set on this uncertainty; otherwise the analytical result is worthless. For this purpose, statistical techniques are required. Of course, when an analyst's experience with a particular method shows that random variations have never been larger than r, and he is concerned only with detecting differences (between samples) that are very much larger than r, he is justified in not using formal statistical techniques. However, this approach is in essence the same as that required by statistics, and is a justifiable approximation. The basis of the statistical techniques has been covered in several books written especially for chemists and analysts.[10–13] The statistical approach requires calculation of an estimate of the variability of the results, and use of this estimate to calculate the likely maximum deviation of a result from the limiting mean.

To obtain a quantitative measure of precision corresponding to a given method and set of conditions, several parameters can be used, *e.g.*, the range of the results, the mean deviation from the mean, the standard deviation. The aim is to determine, from a finite number of results, the variability that would be observed in an infinite number of results, *i.e.*, an estimate is made of the true variability. The parameter used should therefore have as good precision and bias as possible, and the best parameter is variance. For a homogeneous set of n results, the estimate, V, of the true variance is given by the equation:

$$V = \frac{\sum_{1}^{n} (x_i - \bar{x})^2}{n - 1}$$

where $\bar{x}$ is the mean result.

The square root of the variance gives an estimate, s, of the true standard deviation, σ, which is used to calculate the likely deviation of a result from the limiting mean. The key role played by standard deviation in the characterization of precision has been generally recognized by analysts who have increasingly quoted it rather than other measures of precision such as range and mean deviation. There may however, be occasions when other parameters than s may allow better estimates of σ, *e.g.*, the mean deviation when results contain occasional gross deviations that are not representative of the normal precision.[12] Such possibilities do not alter the basic aim of obtaining as good an estimate as possible of the true standard deviation.

With an estimate of the true standard deviation *and* knowledge of the distribution* of the results, it is possible to calculate the range round the analytical result within

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* See page 34.

which the limiting mean is likely to lie. For a normal distribution, 68 % of results will, on average, lie in the range $\mu \pm \sigma$, and $\sim$95 % and 99·7 % in the ranges $\mu \pm 2\sigma$ and $\pm 3\sigma$, respectively. These facts and an analytical result x then allow such statements as "the limiting mean lies in the range $x \pm 2\sigma$" (95 % confidence).† The confidence level of 95 % implies that, on average, such statements will be correct on 95 occasions in every 100. If a greater or smaller degree of confidence is required for a particular application, the value of the factor used to multiply σ is changed accordingly. There is no reason why one confidence level should be suitable for all analytical work; indeed, quite the opposite is true. Thus, the confidence level must be chosen for each application and should not be fixed for the method. The confidence level is not a property of a set of results although their standard deviation is. For these reasons, it is undesirable to define a precision index as a fixed multiple of standard deviation as suggested in British Standard 4237:1967. The ASTM[8] has suggested that various indices of precision may be used provided that their bases are clearly indicated by added statements such as "2s limits," *etc*, but this may lead to misinterpretation. The best approach seems to be that recommended by IUPAC,[3] *i.e.*, to quote the experimentally estimated standard deviation. This estimate may then be interpreted appropriately for any particular problem.

Eisenhart[2] points out that s is really a measure of imprecision, for it increases with decreasing precision. He states that this was recognized by Gauss who remarked in 1809 that the parameter $1/(\sqrt{2} \,.\, \sigma)$ was more properly a measure of precision. Kaiser and Specker,[14] also recognizing this fact, tentatively suggested a parameter $\Gamma = \bar{x}/\sigma$ as an index of precision, and this was later repeated more definitely by Kaiser.[4] Murphy[6] and the ASTM[8] have discussed this and conclude that the normal usage is so entrenched that changes in nomenclature and usage are not justified. Further, it is highly desirable for numerical statements on precision to be in units directly of interest to the analyst, so definition of precision as an inverse function of s seems undesirable.

It is often of interest to quote s as a fraction of the mean of the results from which it was estimated. The term "coefficient of variation" has often been used but *Analytical Chemistry*[7] and IUPAC[3] recommend the term "relative standard deviation" be used.

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[*] "Distribution" denotes the relationship between the value of an analytical result and the probability of obtaining such a value; hence it is a fundamental indication of the variability of analytical results and is the best index of precision. Because the distribution usually cannot be estimated precisely from experimental results (and it is impracticable to quote all these) it is customary to postulate a given distribution (until evidence to the contrary is obtained) and to quote the experimental estimates of the parameters defining it. The normal (Gaussian) distribution is most frequently assumed. The distribution of experimental results often approximates to it, as expected from theory.[10] It is defined by the standard deviation, which thus becomes an index of precision and a convenient performance-charateristic. Nalimov[10] has discussed factors leading to non-normal distributions. Apparent non-normality may arise from the nature of the experimental design and interpretation of results, but the design proposed here should minimize this risk. Even when other distributions occur, they often approximate to the normal distribution, which therefore can usually be assumed. If some other distribution *is* postulated, experimental and/or theoretical grounds for doing so should be clearly stated, and its nature included with any statement of precision.

[†] The true standard deviation σ can never be known, and only the estimate s will be available. The uncertainty of this estimate means that broader confidence limits for an analytical result must be used, given by $\pm ts/n$ where t is the appropriate value of the parameter "Student's-t" (given in statistical tables), and n is the number of independent determinations on which the analytical result is based.

The former defines this parameter as 100 $s/\bar{x}$ while the latter recommends $s/\bar{x}$ so as to avoid confusion that might arise when analytical results are themselves expressed in per cent. On balance, the definition proposed in *Analytical Chemistry* seems preferable because it is in very common use, and the type of confusion postulated by IUPAC should be avoided so long as the word "relative" is placed before "standard deviation" whenever appropriate.

The term "precision," then, should be used when speaking generally of the degree of agreement among repeated results. For numerical definition of this degree of agreement, the parameters standard deviation or relative standard deviation should be used exclusively.

Factors affecting precision

Often, so little description of the experimental design and statistical interpretation of the results is given in published papers that it is impossible to assess the true significance of the reported precision. This section considers certain aspects of experimental design on the basis of performance-characteristics, and proposes a set of principles to be used whenever possible in experimental designs for estimating precision as a performance-characteristic. These principles are not intended to apply to the estimation of precision for other purposes which are likely to require individual consideration and other experimental designs.

Definition of analytical method. There is little point in quantifying precision if the analytical method is ill-defined. Therefore, as emphasised in Part I,[1] the analytical method must be complete and unambiguous before experimental estimation of precision is attempted.

Choice of experimental conditions. The magnitude of the random variations should be kept as constant as possible during the tests, which should be so designed that the results do not fall into groups between which systematic differences are likely; the effect of such grouping would be to give falsely large estimates of the standard deviation. If such grouping cannot be avoided or is of interest, the experimental design and the interpretation of results should be planned so that the standard deviations corresponding to variations within and between groups can be estimated independently.

First, the degree of control to be exercised over procedural details (reagent volumes, times, temperatures, voltages, *etc.*) must be decided and adhered to throughout. There is generally no need to seek extreme fineness of control; so long as the degree of control is specified when results are reported, s is a measure of the precision obtained with that degree of control.

Secondly, experience shows that analysts, apparatus and laboratories may all cause marked systematic deviations in both bias and precision so the basic unit for precision tests should be one analyst using one set of apparatus in one laboratory. The definition of performance-characteristics proposed in Part I[1] took account of this by associating the characteristics with a given set of experimental conditions. Of course, tests of precision may usefully be designed to involve several analysts, *etc*, but then the standard deviation associated with each combination should be estimated independently.

Even analytical results obtained solely by the basic combination (as defined above) may fall into groups. For example, in spectrographic analysis different photographic plates may cause systematic differences in results, and many other such grouping effects exist. Some confusion in published work is then possible unless the experimental design and statistical interpretation are clearly defined. For example, tests made on one plate would tend to give better precision than tests made on a number of plates—which of the two precisions is of interest for performance-characteristics? It is of value to know both, and their estimation is considered below.

Duration and number of tests. When the general experimental conditions have been decided, the number and duration of tests must be fixed. The latter factor is closely connected with the grouping effect just mentioned. Experience shows that the precision of results often worsens as the time period within which they were obtained increases. Aging of various components (*e.g.*, reagents, apparatus) of the analytical system may affect results, but increasing time periods will also usually give increasing chance of grouping effects. The analytical results may be regarded[2] as produced in batches which have essentially the same within-batch true standard deviation σ_w and a between-batch standard deviation σ_b, operating independently. In this model, the true standard deviation σ_t for any result in any batch is then given by:

$$\sigma_t = \sqrt{(\sigma_w^2 + \sigma_b^2)}.$$

Several points arise in connection with the validity of this model. First, the true standard deviation within a batch may vary from batch to batch. However, attention to the points mentioned earlier should normally ensure that such variations are unimportant. Minor variations will also tend to be averaged if the standard deviation is estimated from the variability within several batches. It is therefore reasonable to assume constancy of σ_w until evidence is obtained to the contrary. If such evidence were obtained, it would be better to seek and eliminate the source of variation than to employ the more complex statistical model that would be required.

Secondly, the differences between batches have been postulated as random, and though this is normally justifiable, the variations could be largely systematic, *e.g.*, if the ambient temperature increased from the first to last batch of results, and caused a systematic change in the results. This effect, however, would not call for any changes in the statistical model, but rather for elimination of the systematic effect, recalculation of s_b for the corrected results, and specification of the effect in the published method.

Thirdly, the between-batch standard deviation may not be constant. Again using the example of photographic plates, there may be systematic differences not only between plates from the same production batch but also between different production batches. This situation could be dealt with statistically, but in practice the problem is usually eliminated by recalibration of the analytical system.

Granted the model, it follows that σ_w represents the best precision achievable with the given experimental conditions, and is of interest when the analyst is concerned with the smallest concentration difference detectable between two samples, *e.g.*, in considerations of the limit of detection (see Part III) and the effects of other substances (see Part IV). The value of σ_t is of interest to analysts concerned with the regular analysis of samples of a particular type in order to detect changes in concentration. The value for σ_b is a measure of the between-batch variations occurring in the calibration curve for the method. Since it is preferable for the calibration curve to be constant, σ_b is also of interest.

On this basis, experimental designs for estimating precision should be chosen so that estimates, s_w and s_b, of the true standard deviations are obtained whenever possible, *i.e.*, designs in which n portions of a sample are analysed in each of m batches. The term "batch" requires amplification. The approach adopted implicitly defines a batch as that time during which the calibration curve remains constant. Such a definition is not practically useful, and a more pragmatic one is needed. The batches should be arranged so that there is likely to be reasonable correspondence between the between-batch variations in the precision tests and those that would be found in the regular analysis of samples of a given type. Often this will simply mean that a batch corresponds to the analysis of a number of samples more or less in parallel. No more rigorous definition of batch is considered necessary since the description of the experimental design ought to make clear the precise meaning in each particular case. Some analytical methods may allow the analysis of only one sample at a time; in that case all results obtained within one day might be regarded as a batch, but it would be more revealing to speak of within- and between-days standard deviations. Ambiguity can be avoided by clear description of the design and of the interpretation of results. It is important to ensure that any factors considered likely to have between-batch variations that may affect analytical results, are allowed to show these variations in the precision tests. Most often, these precautions in "batching" will lead to no more complication than the design already suggested, the analysis of n portions of the sample in each of m "batches."

Given this design m and n must be decided. Statistical considerations indicate that the larger m and n the better. However, it seems reasonable to obtain estimates of σ_w and σ_b with approximately the same numbers of degrees of freedom, and this is ensured by choosing $n = 2$. Then s_w and s_b will have m and $(m - 1)$ degrees of freedom, respectively. In choosing m, a compromise must be made between the uncertainty of the estimates and the time and effort available for the tests. A choice of $m = 10$ seems generally reasonable. For example, for normally-distributed results and at the 95% confidence level, the true within-batch standard deviation would lie in the range 0·7–1·8 s_w; it would also be possible to detect a statistically-significant between-batch variation such that $s_b = s_w$.

More detailed knowledge of likely sources of error can, of course, be used with advantage in choosing values for m and n. In trace analysis, contamination is often the dominant random error and may be unlikely to vary in general magnitude from one batch to another. In this situation, it would be more efficient in estimating σ_w to use the values $n = 5$ and $m = 4$ since the estimate s_w would then have 16 degrees of freedom as against 10 when $n = 2$ and $m = 10$. In general, it is suggested that the product nm should never be less than 10 and preferably not less than 20.

The final parameter to be fixed is the duration of the tests. Many arrangements are possible but, in general, it is considered reasonable to analyse one batch every 1–2 days. In this way, the design will usually give more opportunity for sources of between-batch variation to exert their effects than if all the tests had been completed in a much shorter period.

Choice of samples

It is important that the samples used be sufficiently stable and homogeneous for differences in the concentration of the determinand in the portions analysed not to cause any variations in results that are appreciable relative to analytical errors.

A further point of importance is the possible dependence of s on the concentration of the determinand, C. Numerous examples have been reported, and Nalimov[10] has suggested a general equation of the form:

$$s = aC + b$$

where a and b are constants for given experimental conditions.

The true functional relationship between s and C is unimportant in the present context; the prime point is that the precision cannot be characterized by estimating the standard deviation for only one concentration of the determinand, and at least two concentrations should be used. Concentrations at the extremes of the calibration curve are best if only two values are used, since interpolation rather than extrapolation can be used to estimate standard deviations for other concentrations. More information is obtained if several concentrations are used, and the linearity of the calibration curve can then be checked with good precision, but as with many other design parameters, there must be a compromise between information obtained and time and effort expended.

Samples for the tests must be homogeneous, stable, and available in sufficient amount and range of concentrations of the determinand; these requirements are usually best met by standards prepared by the analyst to contain accurately-known concentrations of the determinand. For certain techniques, *e.g.*, direct spectrography of metals and alloys, standards in the appropriate form can usually be more easily obtained commercially than prepared in the laboratory.

Usually, standards cannot be prepared with exactly the same physical form and chemical composition as the samples for which the method is intended. Differences in these factors may possibly affect precision so that the estimates obtained with standards do not apply to samples, and the extent to which standards are made to correspond with samples must be decided in each particular case. This point is less important if the precision for samples is also estimated as a check on the relevance of the estimates for standards. This check can be made with the same design as for standards if sufficient amounts of adequately stable samples are available. However, useful checks may be made even without such samples because it is not essential to estimate both s_w and s_b for samples. The latter (s_b) reflects between-batch variations in the calibration curve and these are validly estimated from standards. Thus, for samples it is mainly necessary to estimate s_w. For this, it suffices to make duplicate analyses on a sample in each batch. Different samples may be used in each batch but they should all contain approximately the same concentration of the determinand in case s_w varies with concentration. Two or more series of such samples may be used to check the dependence of s_w on concentration.

It is most desirable to include in each batch duplicate determinations on a sample or standard containing essentially none of the determinand (blank determination). It will be seen in Part III that the precision of such determinations is of great interest in connection with the smallest detectable concentration of the determinand.

Need to obtain independent analytical results

The analytical results used for estimating standard deviation should be statistically independent. This requirement involves two further aspects of experimental design both of which are apparently often ignored in the literature.

First, many methods call for a blank* determination, the result from which is used to correct the result obtained from a sample. Thus, the precision of both blank and

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* See page 39.

sample determinations affects the precision of analytical results. When the blank is subtracted from the sample result, the standard deviation of analytical results σ_R is given by:

$$\sigma_R = \sqrt{(\sigma_S^2 + \sigma_B^2)}$$

where σ_S and σ_B are the standard deviations (in units of concentration) for sample and blank results. Thus, an analytical result is derived from a pair of determinations, and independent determinations of such pairs should be made. For this experimental design, if *n* portions of *d* samples and standards are analysed in each of *m* batches, each batch must also contain *n* blank determinations; otherwise the estimated standard deviation will be falsely low by an amount depending on the values of σ_S and σ_B (*e.g.*, this bias will be approximately $-0{\cdot}4\sigma_S$ when $\sigma_B = \sigma_S$).

Secondly "randomization" must be used to ensure that unsuspected sources of variation during the tests in each batch do not cause bias in the statistical estimates. Suppose that some factor (*e.g.*, temperature) and hence the slope of the calibration curve varies systematically during a batch; then if samples were analysed in order of increasing concentration, the results might indicate a non-linear calibration curve, and the variability of the *n* replicate determinations of each sample would be smaller than if they had not been made one after the other. The first effect is clearly undesirable and the second leads, in general, to falsely optimistic estimates of the within-batch standard deviation. Both effects can be eliminated by analysing the samples, standards and blanks in a random order chosen from tables of random numbers, a new order for each batch. Other factors may also cause systematic effects, *e.g.*, one piece of apparatus may cause more contamination than another, or "memory" effects may exist leading to biased estimates for the slope of the calibration curve and to falsely optimistic estimates of precision. Therefore, the assignment of determinations in each batch to particular pieces of apparatus should also be randomized.

Conversion of measured values into concentrations

The standard deviations and analytical results are expressed in terms of the concentration (or amount) of the determinand. A calibration curve (or a factor) is required to convert the measured values into concentrations. For estimating precision, it is not generally necessary to establish the calibration with the best possible accuracy because errors as large as 10% in the standard deviations will usually be unimportant compared to the statistical uncertainties of the estimates. The results of the precision tests will establish the calibration sufficiently well except when few concentrations have been used and the calibration curve is markedly non-linear, in which case additional tests may be required for sufficiently accurate conversion.

In normal analysis the imprecision of results will lead, in general, to bias in the calibration curve used, but this error does not affect the precision of results, and can be made as small as desired by replication of the calibration determinations. Accordingly, if the analytical method specifies use of a fixed calibration curve (or factor), the error of the latter need not be considered further when quoting precision numerically. If, however, a fresh calibration is specified for each batch of analyses, the

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[*] Discussed in detail in Part III. For the present it suffices that the term "blank" be defined by the procedure called for by a method. This approach ensures a valid estimate of precision achieved when the method is used, although some approaches to blank determination lead to possibilities of bias in analytical results.

within-batch variations of the standards will cause the bias of the calibration to vary from batch to batch. The between-batch standard deviation for samples will then be greater than the true value for between-batch sources of variability; the difference is not considered important, and can be estimated from an estimate of the within-batch standard deviation for the standard. Accordingly, for methods involving within-batch calibration, it is considered adequate to obtain only one estimate for the calibration in each batch. Alternatively, this tendency to create apparent between-batch variability from within-batch variations can be avoided by making n independent estimates of the calibration in each batch, and analysing the analytical results so that s_w for samples includes the within-batch contribution from the calibration.

The relative values of s_w and s_b and their dependence on concentration are of basic importance in deciding whether or not a fixed calibration or a batch calibration should be used in normal analysis.

Precision of analytical and measurement systems

Many analytical methods proceed in two stages: (1) the sample is treated so that the determinand is brought into the required physical and/or chemical form in the required chemical environment (*e.g.*, dissolution of an alloy and separation of the determinand from other constituents): (2) the concentration or amount of the determinand in the treated sample is measured. The errors associated with each stage are often of interest, and though not strictly required for characterizing the precision obtained with the method, are often easily estimated. If s_A and s_M are the standard deviations associated with stages 1 and 2, respectively, and s is the overall standard deviation from the precision tests, then

$$s_A = \sqrt{(s^2 - s_M^2)}$$

The value of s_M can be obtained by applying the design principles already discussed to suitable standards or samples which are subjected only to stage 2 of the complete analytical procedure; s_A is then calculated from the equation above. As an example for spectrophotometric methods in which the coloured product is stable, duplicate measurement of the final solutions will give an estimate of s_M. Alternatively, if the colour is not stable, stable standard solutions with similar absorption spectra may be used.

Summary of suggested principles of experimental designs

The following set of principles is proposed for use in characterizing the precision achieved when a given method is used.

1. The analytical method should be complete and unambiguous.

2. Before any tests are made to estimate precision, the degree of control to be exercised over experimental factors should be decided, and adhered to throughout the tests.

3. Estimates of precision should be based on the results obtained by one analyst in one laboratory, using one set of apparatus.

4. The basic experimental design should allow estimates of within-batch and between-batch precision to be obtained. In general therefore, the tests should consist of the analysis of n portions of d samples and/or standards in each of m batches. Values of $n = 2$ and $m = 10$ are generally useful but other values may sometimes be more appropriate; d should be at least 2, and the samples and standards should always include two corresponding to the extremes of the calibration curve.

5. If standards are used so that the nature of the calibration curve and the variation of precision with concentration can both be estimated, the precision of analysing samples should be estimated for at least one concentration level.

6. Whenever the method calls for a blank determination, *n* such determinations should be made in each batch.

7. The order of analysis of samples, standards and blanks, and their assignment to particular pieces of apparatus, should be randomized in each batch.

8. The experimental design and methods of calculating statistical parameters must be described explicitly in published papers.

EXAMPLE OF STATISTICAL CALCULATIONS

The calculations may be made on the measured parameters (weight, absorbance, *etc*.,) or the final results (concentration or amount). The former is usually more convenient and has been used in the following example. There are several methods of calculation but the method given here is suitable for any values of m and n.

In the example, duplicate portions of 4 solutions were analysed spectrophotometrically in each of five batches, so $n = 2$ and $m = 5$. The results are first tabulated in logical order (assuming that the order of tests had been randomized), and then the blank correction is applied, Table I.

TABLE I.—EXPERIMENTAL RESULTS (AS ABSORBANCES) FOR ESTIMATING PRECISION

Concentration	1st Batch		2nd Batch		3rd Batch		4th Batch		5th Batch	
	Uncorrected	Corrected*	Uncorrected	Corrected*	Uncorrected	Corrected*	Uncorrected	Corrected*	Uncorrected	Corrected*
0	0·004	—	0·011	—	0·005	—	0·004	—	0·006	—
(blank)	0·002	—	0·005	—	0·004	—	0·005	—	0·006	—
C	0·211	0·207	0·211	0·200	0·213	0·208	0·210	0·206	0·211	0·205
	0·212	0·210	0·212	0·207	0·215	0·211	0·213	0·208	0·213	0·207
2*C*	0·416	0·412	0·414	0·403	0·412	0·407	0·416	0·412	0·413	0·407
	0·415	0·413	0·413	0·408	0·414	0·410	0·416	0·411	0·414	0·408
4*C*	0·820	0·816	0·821	0·810	0·821	0·816	0·819	0·815	0·818	0·812
	0·819	0·817	0·819	0·814	0·822	0·818	0·820	0·815	0·819	0·813

* In each batch, the first blank to be measured is assigned to the first portion measured of each of the other solutions; similarly for the second measurements of blank and other solutions, and for other measurements when $n > 2$.

The corrected results for each of the three solutions containing the determinand are now analysed as illustrated for the solution of concentration 2*C*. To simplify the arithmetic, it is convenient to transform the corrected results, x, to give a set of simpler numbers, X by using the equation $X = 1000\ (x - 0{\cdot}408)$, Table II.

TABLE II.—TRANSFORMED RESULTS FOR ESTIMATING PRECISION

	Batch					Sum	
	1	2	3	4	5		
Test 1	4	−5	−1	4	−1	1	$\Sigma X^2 = 97$
Test 2	5	0	2	3	0	10	$\Sigma B^2/n = 78{\cdot}5$
Sum (= *B*)	9	−5	1	7	−1	11	$(\Sigma B)^2/mn = 12{\cdot}1$
B^2	81	25	1	49	1	157	

If more than 2 tests are made on each sample in each batch the additonal corrected and transformed results are included in the appropriate batch columns of Table II and the summations carried out on all the results. In addition to these summations, the sum of the squares of the individual results

(ΣX^2) in Table II must also be calculated. An analysis of variance table is next drawn up for each solution, *e.g.*, Table III. For the results in Table II, the values of M_1 and M_0 are 16·6 ($N_1 = 4$) and 3·7 ($N_0 = 5$), respectively.

In these analysis of variance tables, $M_0 = s_W^2$ and $M_1 = ns_b^2 + s_W^2$, where s_W and s_b are the estimates of the within-batch and between-batch standard deviations. However, it is first necessary to test whether M_1 is statistically greater than M_0. For this purpose, the standard variance-ratio test (or Snedecor *F*-test) is used.

TABLE III—ANALYSIS OF VARIANCE OF TRANSFORMED RESULTS

Source of variability	Sums of squares (S_i)	Degrees of freedom	Mean squares
Between batches	$S_1 = \Sigma B^2/n - (\Sigma B)^2/mn$	$N_1 = m - 1$	$M_1 = S_1/N_1$
Within batches	$S_0 = \Sigma X^2 - \Sigma B^2/n$	$N_0 = m(n - 1)$	$M_0 = S_0/N_0$
Total	$S_t = \Sigma X^2 - (\Sigma B)^2/mn$	$N_t = mn - 1$	—

If M_1 is significantly greater (at the chosen probability level) than M_0, this is evidence of between-batch variations and then

$$ns_b^2 = M_1 - M_0$$

and

$$s_t^2 = s_W^2 + s_b^2.$$

If M_1 is not significantly greater than M_0, the evidence is too weak to assert that between-batch variations have been detected, and it is best to record s_b as non-significant (but not zero), and to calculate s_t^2 from

$$s_t^2 = [M_1 + (n - 1)\, M_0]/n$$

If M_1 is significantly smaller than M_0, the procedure and technique should be examined for abnormal sources of error since such a conclusion is inconsistent with the model used as a basis for the experimental design and calculations.

If M_1 is not significantly smaller than M_0, the best estimate for s_b is zero, and it is prudent to regard M_0 as the best estimate not only of s_W^2 but also of s_t^2.

These calculations and significances tests applied to the results in Table I lead to the conclusion shown in Table IV (after transformation of the results back to absorbance units).

TABLE IV—ESTIMATED STANDARD DEVIATIONS

Concentration	Standard deviation (absorbance units)			Average absorbance
	Within-batch	Between-batch	Total	
0	0·0020	—	—	0·005$_2$
C	0·0027	NS	0·0030	0·206$_9$
2*C*	0·0019	NS	0·0032	0·409$_1$
4*C*	0·0015	NS	0·0025	0·814$_6$

NS = not significant but not zero.

These standard deviations are then converted into concentration units to yield the final estimated standard deviations of analytical results. The figures in the first and last columns provide the conversion factor.

No estimates have been calculated for s_b and s_t for the blank determinations. This is because it has been assumed that a blank determination would be made with each batch of sample analysis, and therefore batch-to-batch variations of the blank should not affect analytical results. If a blank is not carried out with each batch of normal sample analyses, its between-batch variations are then of interest and s_b and s_t can be calculated by applying the same analysis of variance technique to the blank results.

REPORTING RESULTS OF PRECISION TESTS

If the experimental design used for precision tests is that proposed in this paper, Table IV illustrates a suitable method for summarizing the statistical results. To complete the table, it is necessary only to add a footnote stating the various numbers of degrees of freedom. The description of the experimental design will make it clear how many determinations were involved and how they were arranged in batches.

It is also useful to summarize concisely the main performance-characteristics. Table IV does this but a briefer statement giving concentration, s_w and s_t would indicate whether the method was worth consideration by a potential user. The concise statement of performance-characteristics will be dealt with in Part V.

CONCLUSIONS

Determination, reporting and discussion of the errors of analytical results are of great importance to all analysts, and it is clearly desirable that all analysts should use the same basic terminology in this field. The first part of this paper reviews some of the definitions proposed for the terms precision, bias and accuracy, and shows that differences existed between some of these definitions. These differences are both undesirable and easily avoidable. The definitions proposed by the American Society for Testing and Materials are very suitable, and it would be beneficial if they were used by all analysts.

Although there is general agreement that the term precision be used to denote the variability of analytical results, various suggestions have been made for the parameters to be used as quantitative indices of precision. There are two main aims for such quantification: (1) to characterize the precision achieved when a given method was used, and (2) to set confidence limits on particular analytical results; only the first is of interest in the context of performance-characteristics for which the best parameter for quantifying precision is the standard deviation.

The second part of this paper discusses factors that may affect precision, and proposes a set of principles for experimental designs of tests for estimating precision as a performance-characteristic. The aim has been to express these principles in such a way that they are applicable to all analytical methods. General adoption of these suggestions would help analysts in several ways: (1) by reducing problems arising in interpreting published data; (2) by facilitating comparison of the performances obtained with different methods, and (3) by encouraging a critical approach to experimental designs for precision tests.

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Zusammenfassung—Angaben über die Fehler analytischer Ergebnisse sind ein wichtiger Teil der Kennzeichnung analytischer Methoden. Die allgemeinen Eigenschaften zufälliger und systematischer Fehler werden kurz diskutiert und Methoden betrachtet, die zufälligen Fehler numerisch zu definieren. Es wird vorgeschlagen, die Standardabweichung analytischer Ergebnisse ausschließlich als quantitatives Genauigkeitsmaß im Rahmen der Gütekennzeichnung zu verwenden. Verfahren zur Ermittlung der Standardabweichung und dabei zu beobachtende Vorsichtsmaßregeln werden kritisch diskutiert. Auf dieser Grundlage werden allgemeine Regeln vorgeschlagen, die man bei Experimenten zur Ermittlung der Standardabweichung, wenn irgend möglich, beobachten sollte.

Résumé—Les rapports sur les erreurs de résultats analytiques sont un aspect important de la caractérisation des performances de méthodes analytiques. On discute brièvement de la nature générale des erreurs de hasard et systématiques, et considère des méthodes de définition numérique des premières. On suggère que l'écart-type de résultats analytiques soit utilisé exclusivement comme la mesure quantitative de la précision à l'intérieur du contexte de caractéristiques de performances. On discute de manière critique des techniques pour l'estimation de l'écart-type et des précautions à observer en ce domaine. Sur cette base, on propose des principes généraux que l'on devrait observer chaque fois que possible dans les essais expérimentaux pour estimer l'écart-type.

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N-ACETYLSALICYLOYL-*N*-PHENYLHYDROXYLAMINE AS AN ANALYTICAL REAGENT

DETERMINATION OF NIOBIUM AND TANTALUM IN THE PRESENCE OF EACH OTHER

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Summary—*N*-Acetylsalicyloyl-*N*-phenylhydroxylamine is proposed for the separation of niobium(V) and tantalum(V) and their gravimetric determination. Niobium is precipitated at pH 5·5–6·5 by the reagent and the complex is weighed directly. Tantalum is precipitated from 1–2*M* hydrochloric acid solutions and the complex is ignited to tantalum pentoxide. The method is fairly selective. In the presence of thiocyanate the reagent forms an extractable complex with niobium. The reaction forms the basis of a selective and sensitive spectrophotometric determination of niobium.

SOME of the derivatives of hydroxamic acid have proved most useful for the determination of niobium and tantalum in the presence of each other. Thus, *N*-benzoyl-*N*-phenylhydroxylamine has been used for the spectrophotometric determination of niobium, in the absence of titanium and tantalum,[1] for the separation of niobium from tantalum by precipitation[2] and for the gravimetric determination of tantalum. Improvements in selectivity might be brought about by the introduction of suitable substituents into *N*-benzoyl-*N*-phenylhydroxylamine. *N*-Benzoyl-*N*-*o*-tolylhydroxylamine[3] has been used for the separation of niobium from tantalum, and in this paper we show that *N*-acetylsalicyloyl-*N*-phenylhydroxylamine can be used for the separation and gravimetric determination of niobium and tantalum in presence of a number of other associated ions.

EXPERIMENTAL

Reagents

N-*Acetylsalicyloyl*-N-*phenylhydroxylamine*. The reagent is prepared by condensing acetylsalicyloyl chloride and phenylhydroxylamine in the presence of sodium hydrogen carbonate, by the method of Bamberger,[4] modified by Lutwick and Ryan,[5] the acetylsalicyloyl chloride being prepared by the method of Riegel and Wittcoff.[6] The white needle-shaped crystals of the reagent (recrystallized from ethanol–water) melt at 128°. Found: C, 66·9%; H, 4·8%; N, 5·1%; calculated for $C_{15}H_{13}O_4N$: C, 66·42%; H, 4·79%; N, 5·16%.

A 0·3% w/v solution of the reagent in purified chloroform is used for spectrophotometric work. For gravimetric experiments a 4% solution of the reagent in ethanol is prepared.

Ammonium thiocyanate, 4*M*. Prepared just before use.

Chloroform for spectrophotometric work. Purified by washing several times with half its volume of distilled water and finally distilled.

Solutions of metal ions. Standard niobium and tantalum solutions are prepared by fusing about 1 g of the appropriate pentoxide with about 10 g of potassium hydrogen sulphate in a silica crucible and extracting the cooled melt with 500 ml of 1*M* tartaric acid solution. The metal ion content is determined gravimetrically with cupferron.

Ammonium acetate, 1*M*.

Procedures

Separation and gravimetric determination of niobium. Take an aliquot of a tartrate solution of niobium(V) containing 10–20 mg of the metal and up to 16 times as much tantalum(V). Neutralize the solution to Methyl Red with 1*M* ammonia. Dilute the solution to about 100 ml and adjust the pH to 5·5–6·5 with 0·1*M* ammonia or 0·1*M* hydrochloric acid, then add 25 ml of 1*M* ammonium acetate as buffering agent. Precipitate niobium in the cold by slow addition of the alcoholic solution of the reagent. The dull white precipitate coagulates quickly. Stir for a few minutes, then filter off on Whatman No. 42 paper. Wash several times with water containing 0·2% reagent and 5% ammonium acetate. Dissolve the precipitate in the minimum quantity of 1*M* ammonia and dilute to about 150 ml with water. Acidify to 0·1–0·5*M* with hydrochloric acid. Heat to 70–80° and add 2–3 times the theoretical quantity of the 4% alcoholic solution of the reagent, with stirring. Immediate precipitation of niobium as a yellow granular complex results. Boil for 1 min and allow to settle for 2 hr at room temperature. Filter off on a porosity 4 sintered-glass crucible with decantation. Wash several times with cold water containing 0·1% reagent and dry to constant weight at 105–115°. Calculate the niobium content, using the conversion factor 0·1011.

Gravimetric determination of tantalum. Evaporate the filtrate from separation of niobium until the metal concentration is about 1 mg/ml. Acidify to 1–2*N* with either hydrochloric acid or sulphuric acid. Heat to 70–80° and add the reagent in alcohol in the proportion of 7–8 mg reagent per mg of tantalum. Boil the solution for a few minutes and then allow it to stand at room temperature for 2 hr. Filter off on Whatman No. 42 paper and wash with cold water. Dry the precipitate in the filter for 1 hr at 110° and ignite in a silica crucible at above 900° to constant weight. Weigh as Ta_2O_5.

Spectrophotometric determination of niobium. Take an aliquot of tartrate solution of niobium, containing 0·0125–0·875 mg of the metal, in a separatory funnel and add 2–3 ml of freshly prepared 4*M* ammonium thiocyanate followed by enough hydrochloric acid to make the solution 5–9*M* with respect to the acid. Add 2–3 ml of 0·3% w/v solution of the reagent in chloroform and equilibrate gently for 2 min with two 5-ml portions of chloroform. Dry the combined extracts with sodium sulphate and dilute to 25 ml with dry chloroform. Measure the absorbance at 400 nm against a reagent blank.

RESULTS AND DISCUSSION

Gravimetric procedures

Conditions. For quantitative separation of niobium, the pH should be kept in the range 5·5–6·5. At low pH tantalum is also precipitated and at higher pH the precipitation of niobium is not quantitative. Table I shows the effect of pH on the precipitation of 15 mg of niobium in the presence of 150 mg of tantalum. For the final precipitation of niobium at 70–90°, the acid strength should be 0·1–0·5*M* with respect to hydrochloric acid. The precipitate formed in sulphuric acid media is charred on drying. It is found that for quantitative precipitation of tantalum, the medium should be 1–2*N* hydrochloric or sulphuric acid.

TABLE I.—PRECIPITATION OF 15 mg OF Nb IN PRESENCE OF 150 mg OF Ta

pH	Nb found, *mg*	Error *mg*	pH	Nb found, *mg*	Error *mg*
1·2	23·28	+8·28	6·0	15·00	0·00
2·5	18·86	+3·86	6·5	14·99	−0·01
3·0	17·62	+2·62	7·0	14·60	−0·40
4·0	16·84	+1·84	8·0	10·80	−4·20
5·0	15·86	+0·86	9·0	2·28	−12·72
5·5	15·00	0·00	9·5	0·00	−15·00

When the temperature is raised above 35° the precipitate of niobium formed at pH 5·5–6·5 disintegrates and passes through the filter. Therefore it is always necessary to keep the temperature below 35° for the separation of niobium. However, for the final precipitation of niobium, the temperature should be above 70° because the yellow complex formed at 60° and below is partially melted on drying. The precipitation of tantalum is slow at low temperatures. Therefore it is always advantageous to conduct the precipitation at 70–80° with vigorous stirring.

For the separation of niobium about 15–20 mg of the reagent per mg of the metal is enough. The optimum concentration of the reagent in the final precipitation is 2–3 times the theoretical quantity. A large excess should be avoided because the reagent is soluble in water at 30° only to the extent of 0·25%. A large excess of the reagent may be used for the precipitation of tantalum. But about 7–8 mg of the reagent per mg of tantalum is enough to effect quantitative precipitation.

Effect of foreign ions. Separation of niobium is quantitative in the presence of almost all the cations examined except titanium(IV). Up to a 16-fold amount of tantalum(V) can be tolerated, and zirconium, iron(III) and cerium(IV) can be masked by EDTA. The effect of various foreign ions in the determination of 15 mg of niobium is given in Table II.

TABLE II.—INTERFERENCE OF FOREIGN IONS IN DETERMINATION OF 15 mg OF Nb

Ion, *mg*		Niobium found, *mg*	Error, *mg*	Ion, *mg*		Niobium found, *mg*	Error, *mg*
Fe(II)	200	15·0	0·00	Ce(IV)	100	14·99	−0·01
Cu(II)	200	15·02	+0·02	V(IV)	100	14·98	−0·02
Co(II)	200	15·01	+0·01	Th	100	15·00	0·00
Ni	200	15·00	0·00	Ti(IV)	15	15·04	+0·04
Be	200	14·99	−0·01	Mo(VI)	50	15·01	+0·01
Zn	200	15·01	+0·01	W(VI)	50	15·00	0·00
Al	250	14·98	−0·02	Citrate	250	15·00	0·00
Cr(III)	200	14·98	−0·02	Oxalate	100	14·90	−0·10
Fe(III)	300	15·03	+0·03	EDTA	500	15·01	+0·01
Zr	100	15·04	+0·04	Fluoride	50	14·28	interferes

To eliminate the interference of small amounts of titanium(IV), niobium is precipitated in the presence of 2–3 ml of 20-vol hydrogen peroxide. The precipitate of niobium is then dissolved in ammonia and reprecipitated in the presence of 1 ml of hydrogen peroxide. An equal amount of titanium can then be tolerated.

Most of the ions examined are without effect in the determination of tantalum, but tungsten(VI) and molybdenum(VI) interfere seriously. Zirconium and cerium(IV) can be complexed by EDTA and vanadium(V) by thiocyanate. Titanium(IV) can be masked (up to 50-fold amount) by fluoride. Other cations such as Mn(II), Cu(II), Co(II), Fe(II), Fe(III), Al, Cr(III), Th, V(IV) and U(VI) will not interfere even in 50-fold amount even in the absence of complexing agents. Complexing agents such as oxalate, fluoride, citrate and EDTA are tolerated in still larger quantities.

The complex formed between niobium(V) and the reagent in 0·1–0·5*M* hydrochloric acid solutions was determined by analysis to be $NbO(C_{15}H_{12}O_4N)_3$ (found: N, 4·9%; Nb, 10·1%; required N, 4·56%; Nb, 10·10%). The conversion factor is 0·1011.

Spectrophotometric determination. The complex shows no absorption maximum in the range 370–560 nm, but 400 nm is chosen as the wavelength for photometric measurements because the absorbance of the reagent is then negligible (Fig. 1).

For maximum colour development 5–9*M* hydrochloric acid medium is required. In sulphuric acid medium of the same acidity, the intensity of the colour is considerably less. For maximum colour development 2·5 ml of 4*M* ammonium thiocyanate is required. Lower amounts cause decreased sensitivity and stability, whereas no change is noticed with larger concentration of thiocyanate. The optimum concentration of the reagent is found to be 2–3 ml of 0·3% w/v solution of the reagent in

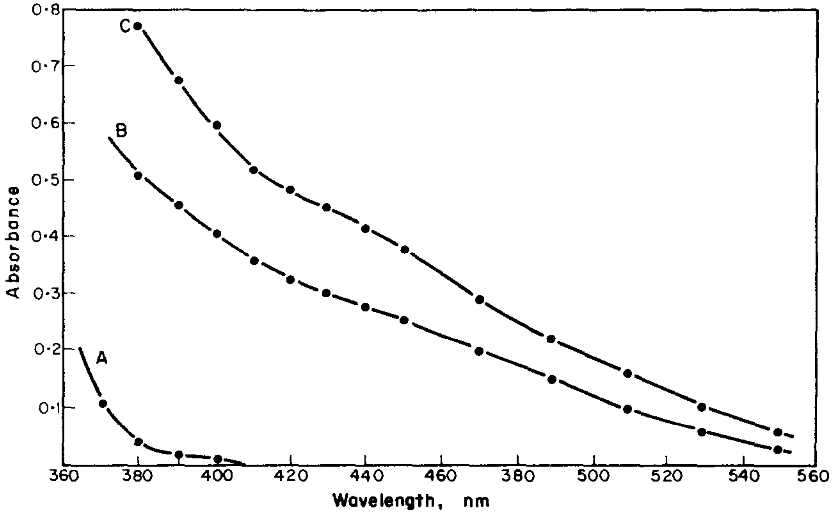

FIG. 1.—Absorption spectra.
A. 2 ml of 0·5% w/v reagent in 25 ml against chloroform blank
B. 2 ppm niobium against reagent blank
C. 3 ppm niobium against reagent blank.

chloroform. In all experiments, the blanks should contain the same amount of reagent as in the test solution.

The complex is stable at room temperature for 18 hr and afterwards the absorbance increases slightly and a turbidity results. Variation in temperature from 15 to 50° has no marked effect if the volume change of the solution with temperature is allowed for.

The system obeys Beer's law from 0·25–4 ppm of niobium at 400 nm. The optimum concentration range according to Ringbom's method[7] is from 0·5–3·5 ppm, the relative analytical error per 1% absolute photometric error calculated from Ayres's equation[8] being 2·3%. The molar absorptivity of the complex is $17 \cdot 7 \times 10^3$ $\text{l.mole}^{-1} . \text{mm}^{-1}$.

The complex is highly unstable and insensitive in the absence of a very large excess of thiocyanate, so that methods for the determination of composition in solution with respect to thiocyanate failed. Therefore Job's method[9] and the molar ratio method[10] were applied with equimolar solutions of the reagent and niobium, a constant excess of thiocyanate being kept. These methods indicate (Figs. 2 and 3) that the ratio of metal to reagent is 1:2.

The solid complex formed between niobium, reagent and thiocyanate in hydrochloric acid medium was isolated and analysed (found: N, 6·0%; S, 4·5%; Nb, 13·1%; $NbO(C_{15}H_{12}O_4N)_2SCN$ requires N, 5·94%; S, 4·53%; Nb, 13·14%).

Interferences. It was found during this study that 25 μg of Nb can be determined in the presence of 25 mg each of Tl(I), Hg(II), Cd, Ni, Co(II), Fe(II), Ca, Ba, Sr, Be, Mg, Zn, Fe(III), Cr(III), Al, Sb(III), As(III), Bi, La, V(IV), Zr, Ce(IV), Th, V(V), W(VI), Mo(VI), U(VI) and Os(VIII). Copper(II) present in up to a 1000-fold amount can be masked by EDTA. Tantalum(V) forms a colourless complex which is not extractable with chloroform and a 200-fold amount can be tolerated. Only titanium(IV) causes a serious interference, and it is best to eliminate titanium, by prior removal with the reagent. Of the various anions, oxalate and fluoride cause serious interference. Citrate, tartrate, borate and EDTA are tolerable in 1000-fold amounts.

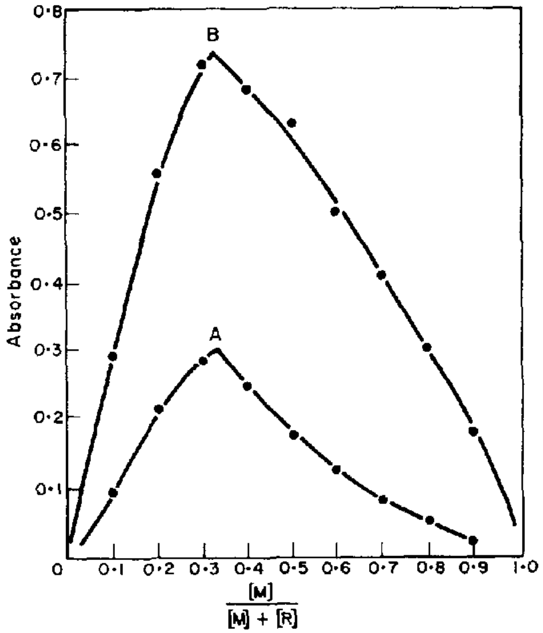

FIG. 2.—Job's method for composition.
A. Niobium = Reagent = $0{\cdot}25 \times 10^{-3}M$
B. Niobium = Reagent = $0{\cdot}5 \times 10^{-3}M$

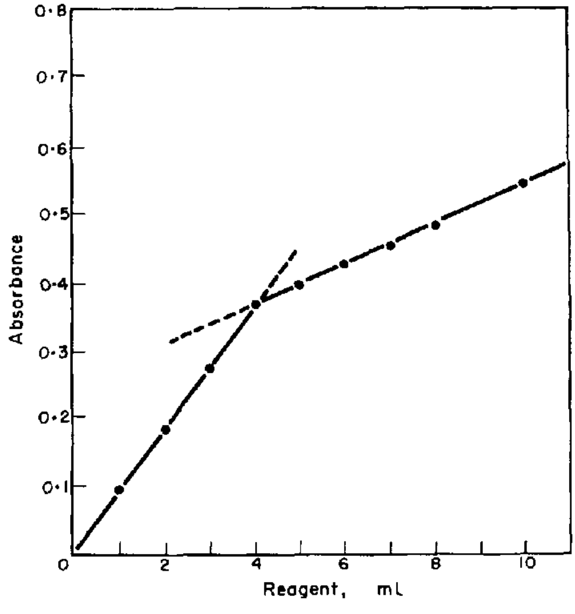

FIG. 3.—Molar ratio method for composition.
Niobium = Reagent = $0{\cdot}5 \times 10^{-3}M$; 2 ml of niobium solution taken.

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Zusammenfassung—*N*-Acetylsalicyloyl-*N*-phenylhydroxylamin wird zur Trennung von Niob(V) und Tantal(V) und deren gravimetrischer Bestimmung vorgeschlagen. Niob wird durch das Reagens bei pH 5,5–6,5 gefällt und der Komplex direkt gewogen. Tantal wird aus 1–2*M* salzsauren Lösungen gefällt und der Komplex zu Tantalpentoxid verglüht. Die Methode ist vergelichsweise selektiv. In Gegenwart von Rhodanid bildet das Reagens mit Niob einen extrahierbaren Komplex. Die Reaktion bildet die Grundlage für eine selektive und empfindliche spektrophotometrische Bestimmung von Niob.

Résumé—On propose la *N*-acétylsalicyloyl *N*-phénylhydroxylamine pour la séparation de niobium(V) et tantale(V) et leur détermination gravimétrique. On précipite le niobium par le réactif à pH 5,5–6,5 et pèse directement le complexe. On précipite le tantale de solutions en acide chlorhydrique 1–2*M* et calcine le complexe en pentoxyde de tantale. La méthode est moyennement sélective. En la présence de thiocyanate, le réactif forme un complexe extractible aved le niobium. La réaction forme la base d'une détermination spectrophotométrique sélective et sensible du niobium.

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DETERMINATION OF DEUTERIUM IN HEAVY WATER BY SECONDARY DEUTERON ACTIVATION

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Summary—The deuterium concentration of heavy water was determined by utilizing recoiling deuterium nuclei from *n–d* collisions to induce the reaction $^{16}O(d, n)^{17}F$. The internal ratio of 66-sec fluorine-17 to 7·35-sec nitrogen-16 activity, formed by the reaction $^{16}O(n, p)^{16}N$, was found to vary linearly with deuterium concentration. When such an internal ratio of activities is measured, the neutron flux and sample weight need not be known. Deuterium was determined over the range from 2·6 to 94·5 atom %, with a relative standard deviation of 2·8%. The effect of sample size was investigated and it was found that the relative amount of fluorine-17 activity formed became less as sample size decreased, due to the loss of recoiling deuterons from the sample. A simple relationship to account for this effect was obtained.

MANY of the lighter elements and their isotopes cannot readily be determined by neutron activation.[1,2] These nuclides do, however, yield suitable measurable activities during charged particle activation, and several investigators[3–9] having access to nuclear reactors but not to charged particle accelerators have consequently explored the possibility of using secondary nuclear reactions for charged particle activation. Tritons and alpha particles have been produced in reactors by utilizing the $^{6}Li(n, \alpha)t$ reaction, whereas protons and deuterons have been obtained for n–p and n–d "knock-on" reactions induced by epi-cadmium neutrons. These secondary charged particles have been successfully used for the determination of deuterium,[3] lithium-6,[4,5] oxygen-16[6,7,8] and oxygen-18.[9] Although the charged particle flux obtained by these methods is much smaller than fluxes obtained from accelerators, the technique does have the advantage that relatively large samples can be irradiated uniformly. Furthermore, target preparation and heating, which can be serious problems in charged particle activation, are almost totally eliminated.

Amiel and Peisach[3] have determined the deuterium concentration in heavy water by the reaction $^{16}O(d, n)^{17}F$ utilizing knock-on deuterons produced by reactor fast neutrons. In the present work the feasibility of using 14-MeV neutrons from a neutron generator has been investigated.

When a water sample containing D_2O is irradiated with 14-MeV neutrons the following reactions take place.

(*i*) $^{2}H(n, d)n$

(*ii*) $^{16}O(d, n)^{17}F$

(*iii*) $^{16}O(n, p)^{16}N$

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The amount of fluorine-17 ($t_{1/2} = 66$ sec) and nitrogen-16 ($t_{1/2} = 7{\cdot}35$ sec) activity formed is given by:

$$A_{^{17}\mathrm{F}} = N_0\sigma_2\phi_\mathrm{d}(1 - e^{-\lambda_2 t}) \tag{1}$$

$$A_{^{16}\mathrm{N}} = N_0\sigma_3\phi_\mathrm{n}(1 - e^{-\lambda_3 t}) \tag{2}$$

where the indices refer to the specific nuclear reactions, and

A = activity produced, disintegrations/sec
N = number of atoms
σ = cross-section, mm^2
ϕ = flux, particles/mm^2 . sec
λ = decay constant
t = irradiation time, sec.

If the neutron flux stays constant during the irradiation, the ratio of activities formed (R_A) can be expressed as

$$R_A = \frac{A_{^{17}\mathrm{F}}}{A_{^{16}\mathrm{N}}} = C_1\frac{\phi_\mathrm{d}}{\phi_\mathrm{n}} \tag{3}$$

where C_1 is a constant.

From reaction (1) we have that the number of prompt deuterons per sec (P_d) can be written as:

$$P_\mathrm{d} = N_\mathrm{d}\sigma_1\phi_\mathrm{n}. \tag{4}$$

The number of deuterons per unit volume of the sample ($N_\mathrm{d}/V_\mathrm{s}$) is directly proportional to the deuterium concentration (a) of the sample expressed in atom % (atom % deuterium is here defined as the percentage of hydrogen atoms in the sample which have mass = 2). This assumption is true, because the change in volume caused by replacing the hydrogen atoms of water molecules with deuterium atoms is negligible [the difference between the ratio of the density of D_2O to that of water (1·107) and the ratio of their molecular weights (1·111) is negligible in comparison to the relative standard deviation of 2·8% for the method (Table II)]. Thus

$$\phi_\mathrm{d} = C_2\frac{P_\mathrm{d}}{V_\mathrm{s}} = C_3 a\sigma_1\phi_\mathrm{n} \tag{5}$$

where C_2 and C_3 are constants. By substituting for ϕ_d in equation (3) the following expression is obtained:

$$R_A = \frac{A_{^{17}\mathrm{F}}}{A_{^{16}\mathrm{N}}} = C_4 a. \tag{6}$$

It can thus be seen that the ratio of fluorine-17 and nitrogen-16 activities is directly proportional to the deuterium concentration of the sample expressed in atom %. It should be noted that this ratio is independent of sample size and neutron flux (if the neutron flux stays constant during irradiation).

Some of the usual methods for determining deuterium in water are mass spectrometry, interferometry, and optical and density measurements.[10] The only methods currently available utilizing nuclear properties, other than the 'knock-on" technique, are those based on photoneutron emission[11,12] and prompt neutron detection during irradiation with deuterons.[13]

EXPERIMENTAL

Samples weighing approximately 1 g were prepared by mixing known weights of heavy water, containing 94·5 atom % deuterium, with natural water. The deuterium concentration of the prepared samples ranged from 2·6 to 94·5 atom % deuterium. The samples were contained in cylindrical polyethylene vials which were heat-sealed before use. Natural water samples similarly prepared were used as blanks.

Irradiations were carried out with a 150-keV Cockcroft-Walton accelerator (Texas Nuclear Corporation) producing 14-MeV neutrons by bombarding a tritiated titanium target with a deuteron beam of 150–500 μA. A neutron flux of approximately 10^6n . mm^{-2} . sec^{-1} was obtained. The neutron output was monitored by a proton recoil detector connected to a ratemeter. The beam current of the neutron generator was varied when necessary during irradiation in an effort to maintain a constant neutron flux. All samples and standards were irradiated for 2 min.

The samples were transferred to and from the irradiation terminal through a polyethylene pneumatic tube by means of compressed air. The gamma-rays from the radioisotopes produced were detected by two matched 75 × 75 mm NaI(Tl) crystals positioned 25 mm apart. The detectors were connected to a 400-channel pulse-height analyser operated in the multiscaler mode. Counting was started 30 sec after the end of each irradiation in order to allow the 7·35-sec nitrogen-16 activity to cool sufficiently, thereby minimizing dead-time effects.

RESULTS AND DISCUSSION

The decay of the activity produced in a sample containing 58·0 atom % deuterium is shown in Fig. 1, from which the relative contribution of 7·35-sec nitrogen-16, 66-sec fluorine-17 and 9·96-min nitrogen-13 can be seen; prolonged counting reveals the presence of 110-min fluorine-18 as well. The stripping of all the decay curves was done by computer, using the CLSQ program of Cumming.[14] The possible origin of the activities found is given in Table I.

TABLE I.—REACTIONS LEADING TO ACTIVITIES FOUND IN FAST NEUTRON IRRADIATED HEAVY WATER SAMPLES

Source	Reaction	Q-value, *MeV*	Half-life
Sample	$^{16}O(n, p)^{16}N$	−9·639	7·35 sec
	$^{16}O(d, n)^{17}F$	−1·631	66 sec
	$^{16}O(p, \gamma)^{17}F$	0·596	
	$^{16}O(p, \alpha)^{13}N$	−5·208	9·96 min
	$^{16}O(d, \gamma)^{18}F$	7·538	110 min
	$^{16}O(p, n)^{16}F$	−2·450	
Container	$^{12}C(p, \gamma)^{13}N$	1·941	9·96 min
	$^{12}C(d, n)^{13}N$	−0·286	
	$^{13}C(p, n)^{13}N$	−3·005	

The activity ratio (R_A) of fluorine-17 to nitrogen-16 at the end of the irradiation was found to change linearly with deuterium concentration, as expected from equation (6), and to go through the origin of the calibration curve so that one standard sample is sufficient to fix the calibration. The activity ratio per atom % deuterium was $8{\cdot}47 \times 10^{-5}$. The linearity of the calibration curve over the concentration range studied indicates that fluorine-17 is predominantly formed by the $^{16}O(d, n)^{17}F$ reaction. The contribution of fluorine-17, formed by knock-on protons (see Table I), is negligibly small even at low deuterium concentrations. Other reactions induced in pure water samples are unlikely to yield fluorine-17. Amiel and Peisach[3] found that their calibration curve started to deviate from proportionality for deuterium concentrations below about 7 atom %. That such a deviation was not observed in this work can be ascribed to the fact that most of the epi-cadmium neutrons used in

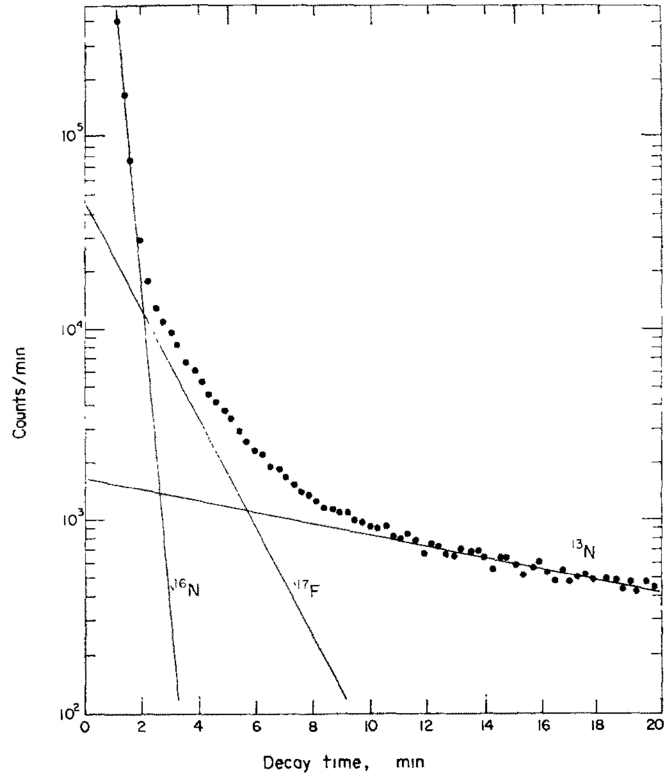

FIG. 1.—Decay of a sample containing 58·0 atom % deuterium, showing the relative amounts of 7·35-sec nitrogen-16, 66-sec fluorine-17 and 9·96-min nitrogen-13 formed.

their investigation have energies considerably below 14 MeV. Higher energy neutrons would thus favour the formation of fluorine-17 by the ^{16}O(d, n)^{17}F reaction rather than the ^{16}O(p, γ)^{17}F reaction, as the threshold for the former reaction is much higher (see Table I).

The results of some determinations of deuterium are shown in Table II, showing an average relative standard deviation of 2·8 % over the concentration range studied. The error distribution (Table II) indicated the absence of bias. The mean value of the activity ratio per atom% deuterium was $8{\cdot}50 \times 10^{-5}$, which is in agreement with the calibration value within the precision of the measurements. The deuterium concentration expressed as w/w% D_2O can be obtained from the concentration in atom % (a) by the relationship:

$$\text{w/w\% } D_2O = \frac{20a}{18 + 0{\cdot}02a}\,. \qquad (7)$$

The precision of the method is not affected by the reproducibility of sample position at the irradiation terminal, because the activity ratio (R_A) is independent of flux. A variation of neutron flux does however affect the precision, owing to the large difference in half-lives of the two activities determined. This is thought to be the main source of error of the method, as the relative standard deviation due to statistical errors is about 0·8 % (for a sample having a deuterium content of 50

Table II.—Determinations of deuterium

Known deuterium concentration, *atom %*	^{17}F zero activity, *cpm*	^{16}N zero activity *cpm*		Activity ratio		Activity ratio per *atom %*		Deuterium concentration found, *atom %*	Error, *atom %*	Relative error, %
2·60	2237	9·440		0·237		9·12		2·79	+0·19	7·3
4·34	2980	8·514		0·350		8·07		4·13	−0·21	4·8
5·77	4642	9·375		0·495		8·58		5·84	+0·07	1·2
8·07	6163	9·171		0·672		8·33		7·93	−0·14	1·7
14·12	10880	9·179		1·185		8·39		13·99	−0·13	0·9
15·43	12288	9·380		1·310		8·49		15·47	+0·04	0·3
18·3	16230	10·187		1·593		8·70		18·8	+0·5	2·7
24·4	16810	8·288	× 10^6	2·03	× 10^{-3}	8·32	× 10^{-5}	24·0	−0·4	1·6
34·9	22742	7·536		3·02		8·65		35·6	+0·7	2·0
49·2	36051	8·549		4·22		8·58		49·8	+0·6	1·2
58·0	44684	9·351		4·78		8·24		56·4	−1·6	2·8
67·5	47530	8·168		5·82		8·62		68·8	+1·3	1·9
76·6	51067	7·962		6·41		8·37		75·7	−0·9	1·2
89·9	51831	6·870		7·55		8·40		89·1	−0·8	0·9
94·5	57318	7·054		8·13		8·60		96·0	+1·5	1·6

Mean value of activity ratio per atom % deuterium = 8·50 × 10^{-5}.
Relative standard deviation = 2·8%.

atom %) as compared to a value of 2·8 % found. Even though the half-lives of nitrogen-16 and nitrogen-13 differ greatly from that of fluorine-17 (see Table I), their formation introduces a source of error in the determination of the fluorine-17 activity, which becomes appreciable in samples of very low deuterium content, (below about 2 atom %) and may be considered a limiting factor of the method. It is estimated that samples with a deuterium concentration of about 1 atom % can only be analysed with a relative standard deviation of approximately 20%. The sensitivity of the method, based on the criterion that the net measured fluorine-17 activity should be twice the standard deviation of the background, is about 0·6 atom % deuterium.

The effect of sample size was investigated and it was found that the activity ratio (R_A) became smaller as sample size decreased, because the relative amount of fluorine-17 activity formed decreased owing to the loss of recoiling deuterons from the sample. To a first approximation the loss of recoiling deuterons from the sample is directly proportional to the area (A) of the sample; therefore the fluorine-17 activity formed in a sample with weight W is given by

$$A_{^{17}\mathrm{F}} = k_1(W - k_2\mathrm{A}) \tag{8}$$

where k_1 and k_2 are constants. The relationship between the area (A) and weight (W) of a sample (expressed in mm^2 and g respectively) contained in a cylindrical container with a radius of r mm is given by the expression

$$\mathrm{A} = 2\pi r^2 + 2W/rD$$

where D is the density of the sample, in g/mm^3. By substitution for A in equation (8) and from the fact that the activity ratio (R_A) is proportional to the fluorine-17 activity per unit weight of sample, the relationship between R_A and sample weight can be found.

$$R_A = C_1 - C_2/W. \tag{9}$$

The values of the constants C_1 and C_2 were obtained by measuring the activity ratios (R_A) for different size samples and were found to be $8{\cdot}68 \times 10^{-5}$ and $0{\cdot}368 \times 10^{-5}$ respectively for the conditions of this experiment, which differed slightly from those prevailing during the actual analyses. Therefore

$$R_A = \left(8{\cdot}68 - \frac{0{\cdot}368}{W}\right) \times 10^{-5} \tag{10}$$

The maximum energy attained by knock-on deuterons during 14-MeV neutron irradiation can be determined from momentum considerations, and is about 12·5 MeV. The range of such deuterons in water is approximately 1·2 mm.[15] Equation (10) is not applicable in cases where any of the linear dimensions of the sample are less than twice the range of the maximum energy of the knock-on deuterons. This corresponds to sample weights less than approximately 0·16 g, for the sample holders used in this experiment.

The effect of sample size on activity ratio (R_A) is shown in Fig. 2. The smooth curve was calculated from equation (10) and the points were measured for sample sizes between 0·18 and 1·1 g. It can be seen that as sample size increases the activity ratio per atom% increases asymptotically to the maximum value of $8{\cdot}68 \times 10^{-5}$. It is also clear that small variations in sample size below about 0·5 g (see Fig. 2) will

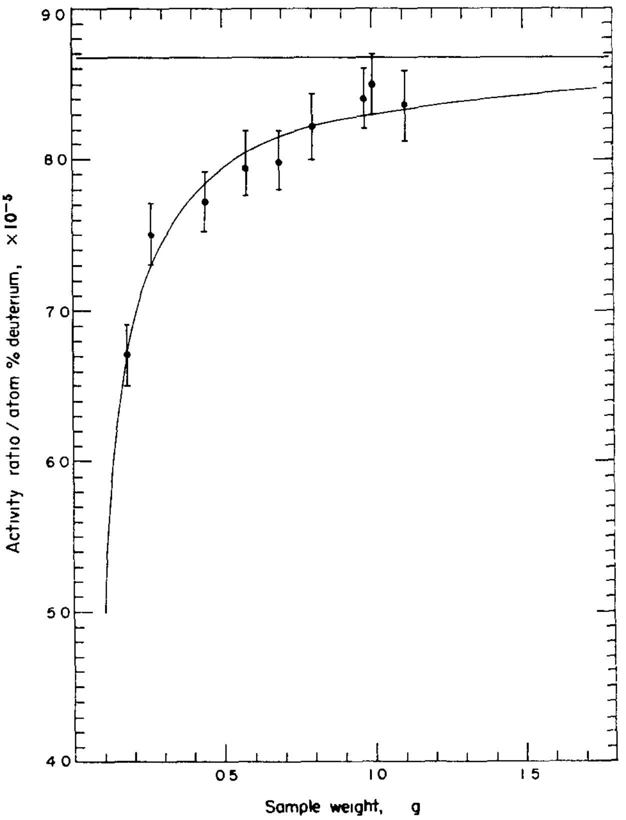

FIG. 2.—The effect of sample size on the activity ratio ($^{17}F/^{16}N$) measured, for a sample containing 94·5 atom % deuterium.

considerably affect the precision of the method, owing to the loss of recoiling deuterons from the sample. Variation of sample size between samples and standards weighing more than 0·5 g will, however, not appreciably add to the errors of the method.

The flux obtainable from neutron generators is about four orders of magnitude smaller than the epi-cadmium flux of a reactor. This is somewhat compensated for by the fact that all the neutrons from a 14-MeV generator can contribute to the formation of fluorine-17, whereas a large majority of epi-cadmium neutrons have energies lower than that necessary to produce knock-on deuterons with energies above the threshold of the $^{16}O(d, n)^{17}F$ reaction. From the yield of fluorine-17 activity per atom % deuterium, obtained during reactor irradiation[8] and in this work, it is estimated that the effective cross-section for the production of fluorine-17 by 14-MeV neutrons is approximately 200 times larger than that for reactor epi-cadmium neutrons. Furthermore, reactor thermal neutrons which do not contribute to knock-on activation products, do form serious interfering activities, owing to activation of impurities either in the sample or sample vial. This necessitates enclosing the samples in cadmium covers during irradiation. Care must also be taken to prevent cross-contamination from the cadmium covers. Although the cross-sections of many common impurities for 14-MeV neutrons can be appreciable, the activities produced are usually not positron emitters and can be discriminated against if necessary by coincidence counting of annihilation gammas in the case of fluorine-17. The nitrogen-16 activity formed in the sample can also be measured very specifically by suitable energy discrimination, as this nuclide emits very high energy gamma-rays.

The present method provides a simple and rapid non-destructive method for determining heavy water concentrations. Furthermore, irradiation flux and sample weight need not be determined, as use is made of an internal ratio of activities. The relative amounts of deuterium and oxygen in the sample are measured directly; impurities which do not form interfering activities but which may affect other methods of heavy water determination (such as density measurements) do not present any problem when this method is used.

Recent developments[16] in 14-MeV neutron generator technology have made it possible to obtain fluxes of up to 10^9 n.mm^{-2} . sec^{-1}. The availability of such a generator would greatly improve the sensitivity of the analysis described here and would in general greatly increase the scope and applicability of secondary charged particle activation analysis. Furthermore, the low cost of neutron generators as compared to nuclear reactors makes them more readily available to smaller analytical laboratories.

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Zusammenfassung—Die Deuteriumkonzentration in schwerem Wasser wurde bestimmt; dabei wurden Rückstoß-Deuteriumkerne aus n–d-Stößen zu der Reaktion $^{16}O(d, n)^{17}F$ verwendet. Das innere Verhältnis der Aktivitäten von Fluor-17 (66 sec) und Stickstoff-16 (7,35 sec) der sich durch die Reaktion $^{16}O(n, p)^{16}N$ bildet, änderte sich linear mit der Deuteriumkonzentration. Mißt man ein solches inneres Aktivitätsverhältnis, dann braucht man weder Neutronenfluß noch Probengewicht zu kennen. Deuterium wurde im Bereich 2,6–94,5 Atom-% mit einer relativen Standardabweichung von 2,8% bestimmt. Der Einfluß der Probengröße wurde untersucht; mit fallender Probengröße wurde die relative Fluor-17-Aktivität kleiner, da Rückstoßdeuteronen aus der Probe verloren gingen. Zur Berücksichtigung dieses Effekts wurde ein einfacher Ausdruck gefunden.

Résume—On a déterminé la concentration en deutérium de l'eau lourde en utilisant les noyaux deutérium de recul des collisions n–d pour induire la réaction $^{16}O(d, n)^{17}F$. On a trouvé que le rapport interne de l'activité du fluor-17 66 s à celle de l'azote-16 7,35 s, formé par la réaction $^{16}O(n, p)^{16}N$, varie linéairement avec la concentration en deutérium. Lorsqu'un tel rapport interne d'activités est mesuré, le flux de neutrons et le poids d'échantillon n'ont pas besoin d'être connus. On a déterminé le deutérium dans le domaine allant de 2,6 à 94,5 atomes%, avec un écart-type relatif de 2,8%. On a étudié l'influence de la dimension de l'échantillon et l'on a trouvé que l'importance relative de l'activité du fluor-17 formé devenait moindre quand la dimension de l'échantillon décroissait, par suite de la perte de deutérons de recul de l'échantillon. On a obtenu une relation simple pour rendre compte de cette influence.

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RAPID SPECTROPHOTOMETRIC DETERMINATION OF BORON IN STEEL*

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Summary—A rapid spectrophotometric method is presented for the determination of boron in steel by use of the fluoborate–Methylene Blue complex. The method is in principle similar to that of Rosotte, but modifications simplify the operation, obviate contamination and avoid problems with emulsion formation. Up to 20% Cr, 10% Ni, and 1% each of V, Mo and W present either individually or collectively do not interfere in the determination, making it applicable to alloy steels. The determination limit of the method has been lowered from 5 to 0·2 ppm boron. Samples are dissolved at room temperature in polythene bottles, solubilizing all forms of boron including boron nitride, and avoiding loss of relatively volatile boron compounds. The precision of the method is good. Six samples can be analysed in less than 2 hr.

SEVERAL reagents have been used for the photometric determination of boron in steel. Amongst the most frequent are 1,1-dianthrimide, quinalizarin and curcumin. A critical evaluation of these reagents has been made by the B.I.S.R.A. Methods of Analysis Committee,[1] who adopted the reagent 1,1-dianthrimide for use after a preliminary separation of iron by cation-exchange. However, the conditions established for the colour development are critical and so less useful for routine work. The present ASTM method[2] involves a prior distillation of methyl borate in an expensive all-quartz apparatus, and there is a great possibility of contamination from the relatively large quantities of reagents required in the procedure.

Takeuchi[3] and co-workers described a method for determining boron in steel by pyrohydrolysis and constant-current coulometry. This approach was unsuccessful in our laboratory; even with pure synthetic solutions containing microgram amounts of boron, the yields were erratic. Harrison and Cobb[4] used the boron–curcumin complex in an acetic anhydride medium. The dissolution at 80° in 20% sulphuric acid, recommended in the procedure, required excessive time. Further, the blanks were high, and calibration was inconsistent. Very recently Tolk *et al.*[5] also used curcumin for determining boron. The method appears to be time-consuming in the sample dissolution step and requires an additional 3 hr for subsequent treatment and colour development. Further the authors reported a serious limitation of the method in that no oxidizing agents could be used, which leaves uncertain the treatment of the carbides *etc* inherent in iron and steel. No alternative is offered.

The triple complex of Methylene Blue, fluorine and boron in dichloroethane medium has been proposed by many workers[6–9] for the determination of boron in steel. Rosotte[9] successfully dissolved steel directly in a fluorine-containing medium, with the obvious advantage of reducing the amount of reagents capable of affecting the blank. Ammonium hydrogen fluoride, hydrofluoric acid *etc* were used to achieve

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both the rapid dissolution and the conversion of boron into BF_4^- (the active species) at room temperature.

However the extraction technique recommended by her, involving a pneumatic separator, was found far from satisfactory in our laboratory. Polyethylene separatory funnels proved to be successful both in providing a quick separation of the two phases and in equilibrating the excess of reagents into the aqueous phase without emulsion formation. As will be illustrated the method presented here is suitable down to 0·2 ppm of boron, with satisfactory precision.

EXPERIMENTAL

Apparatus

Nalgene 4-oz (125-ml) narrow-mouth bottles with polypropylene screw closures (Canlab, Cat. 5-803 or equivalent). Nalgene 60-ml bottles with dropper assembly and polypropylene closures (Canlab, Cat. 6-251 or equivalent). Nalgene Squibb pear-shape separatory-funnels (polypropylene, Teflon plug, polyethylene stopper, capacity 125 ml (Canlab, Cat. 37-287 or equivalent). These bottles and funnels should be kept filled with demineralized distilled water until just before use, and refilled after use and washing. Polyethylene measuring cylinders, funnels and beakers. Mohr pipette graduated to 0·01 ml.

Reagents

Use demineralized distilled water throughout, and chemically pure reagents. Prepare reagents in plastic or polyethylene ware and transfer immediately to polyethylene containers with screw closures.

Hydrofluoric acid, 5%. Carefully add 10 ml of 50% HF (27*M*) to 90 ml of water in a polyethylene beaker.

Boron stock solution, 50 *μg/ml*. Dissolve 0·287 g of boric acid in water and dilute to a litre in a volumetric flask.

Standard BF_4^- *solution A*, 1 *μg of boron/ml*. Transfer 5 ml of boron stock solution into a 125-ml polyethylene bottle, add 20 ml of water and 2·5 ml of 5% hydrofluoric acid. Mix, let stand for 24 hr and dilute to 250 ml in a volumetric flask. This solution is stable for 6 months.

Standard BF_4^- *solution B*, 0·1 *μg of boron/ml*. Transfer 10 ml of solution A into a polyethylene beaker. Add 1 ml of 5% hydrofluoric acid followed by 80 ml of water. Mix, transfer, and dilute to 100 ml in a volumetric flask with water. Prepare this solution fresh as needed.

Ammonium hydrogen fluoride, 8*M*. Dissolve 91 g of $NH_4F.HF$ in 150 ml of boiling water. Filter.

Phosphoric acid (3 + 2). Dilute 3 parts of phosphoric acid (sp. gr. 1·69) with 2 parts of water.

Hydrogen peroxide, 100-*vol*.

Hexamethylenetetramine solution, 40%. Dissolve 40 g of hexamethylenetetramine in water by slight warming. Filter and dilute to 100 ml with water. Prepare fresh as needed.

Methylene Blue solution, 0·01*M*. Dissolve 0·8 g of "medicinal Methylene Blue" in 200 ml of water. Filter through a glass filter (fine porosity) and dilute to 250 ml with water.

1,2-*Dichloroethane*. Distilled.

Pure iron chips, boron-free. NBS 55e is suitable.

The ammonium hydrogen fluoride, phosphoric acid, hydrogen peroxide, Methylene Blue and conc. hydrofluoric acid solutions should be kept in bottles fitted with droppers to facilitate transfer. Volumes can be measured by counting drops or graduating the droppers.

Procedure

Calibration. Weigh 0·100 g of pure iron or NBS 55e chips into a series of 6 polyethylene bottles (narrow mouth) and add in the following order (making sure the sample remains in contact with the reagents): 1 ml of ammonium hydrogen fluoride solution, 1 ml of phosphoric acid (3 + 2), 0·5 ml of concentrated hydrofluoric acid, and 2·0 ml of 100-vol hydrogen peroxide. Cap the bottle immediately after the addition of hydrogen peroxide and tap gently to bring the sample in contact with the reagents. It takes 5–10 min for complete dissolution. Let stand for an additional 15 min. Transfer the contents to separatory-funnels, using 10, 9·5, 9, 8, 7 and 6 ml of water for rinsing. Add (by pipette) 0, 0·5, 1·0, 2·0, 3·0 and 4·0 of standard boron solution A to the respective separatory-funnels (to give the same total volume in each) and mix (this covers the range 5–40 ppm boron; to cover the range lower than 5 ppm use standard solution B). Add 5 ml of hexamine solution and mix, then add 1 ml of Methylene Blue solution and mix. Add 15·0 ml of dichloroethane (from a burette). Stopper and manipulate the separatory-funnels so that no aqueous phase is trapped under the organic layer. Clamp the funnels in a mechanical wrist-action shaker and shake for 5 min. Let settle for 2–4 min. Tap the funnels, if necessary, to ensure complete separation of the two phases.

Transfer the (lower) organic phase into another separatory-funnel, add 10 ml of water, stopper the funnel, mix very gently for 30 sec to extract the excess of Methylene Blue into the aqueous phase (excessive shaking may produce an emulsion; this must be avoided). A clear separation is achieved. Let settle for about 5 min, drain off about 1 ml to flush the stem and then transfer the organic layer through a 70-mm fast filter paper (*e.g.*, Whatman No. 541) supported on a dry 50-ml beaker, leaving about 1 ml of it in the separatory-funnel.

Transfer an appropriate aliquot of the extract into a dry 25-ml volumetric flask and dilute to the mark with dichloroethane. In the range 0·2–1·0 ppm boron no dilution with dichloroethane is needed. Measure the absorbance in a 10-mm cuvette, with dichloroethane as reference, at 650 nm, using a red-sensitive phototube. Obtain the net absorbance by subtracting the blank (0 μg boron). Plot absorbance *vs.* μg of boron or calculate a conversion factor.

Samples. Weigh sample and add boron-free iron as follows.

Boron, *ppm*	Sample wt., *g*	Boron-free iron, *g*	Final extract aliquot, *ml*
Blank	nil	0·1000	As in example
0·2–1	0·1000	nil	No dilution
1–5	0·1000	nil	10
5–40	0·1000	nil	5
40–70	0·0500	0·0500	5
70–100	0·0300	0·0700	5

Carry out the procedure as described (including blank) under calibration except for the addition of boron standard solution; instead use 10 ml of water for rinsing.

RESULTS AND DISCUSSION

Interferences

Residual elements in steel such as Cu, Cr, Ni, V, Mo and W did not present any problem in the boron determination, but their effect was investigated to ensure that the method would be applicable to alloy steels. Table I shows the interference study with British Chemical Standards steel 273 containing 25 ppm boron, which was used to provide the steel matrix. Potassium dichromate and nickel ammonium sulphate were used to provide 20 mg of Cr and 10 mg of Ni, and ammonium vanadate, ammonium molybdate and sodium tungstate were used to provide 1 mg each of V, Mo and W, added to a 0·1 g sample.

TABLE I.—INTERFERENCE STUDY WITH BCS STEEL STANDARD, CERTIFIED 25 ppm BORON

Element added	Boron found, *ppm*
nil	23
nil	25
20% Cr	24
10% Ni	22
1% V	24
1% Mo	25
1% W	23
20% Cr + 10% Ni + 1% V + 1% Mo + 1% W	24

Evidently 20% Cr, 10% Ni, and 1% each of V, Mo and W added either individually or collectively do not interfere in the boron determination.

Range of application

Extension of the lower limit of the method from 5 ppm down to 0·2 ppm of boron by use of a bigger sample weight did not give encouraging results. The alternative—use of a larger proportion of the Methylene Blue extract—proved satisfactory, as shown in Table II. The blanks were similarly carried out with a 10-ml aliquot.

TABLE II.—RECOVERY TESTS

Boron, *ppm*			Boron, *ppm*		
Present	Found*	Range	Present	Found†	Range
1·0	1·1	0·8–1·1	0·2	0·3	0·25–0·3
2·0	2·4	2·0–2·5	0·5	0·5	0·3–0·55
3·0	2·8	2·6–3·1	0·8	0·8	0·7–0·9
4·0	3·9	3·5–4·0	1·0	1·0	0·9–1·1
5·0	5·1	4·7–5·2			

* 10 ml of extract diluted to 25 ml for absorbance measurement.

† Absorbance of undiluted extract measured.

The procedure described was applied to a number of British Chemical Standard steels. The results are recorded in Table III. The wide spread in the range of values listed in the certificates prevents knowledge of the "true" content but the precision of the present method is good throughout.

TABLE III.—BORON IN BCS STEEL STANDARDS

BCS No.	Certificate		Boron found, *ppm*	Standard deviation, *ppm*	No. of detns.
	Value, *ppm*	Range, *ppm*			
272	40	30–40	30	1·1	5
273	25	15–30	23	1·8	5
275	10	10–25	11	1·1	5
326	10	10	6	1·3	8
327	30	25–40	38	1·7	5
328	40	35–50	44	0·8	6
329	80	70–80	65	1·4	4
330	70	70–80	71	2·0	7

Conclusions

In the determination of boron as described under the procedure the active species is BF_4^-, which forms the ion-association complex with Methylene Blue. Normally it takes about 18 hr to convert boron into BF_4^-. However, iron catalyses this reaction, which is completed in 5–10 min, the time needed to dissolve the steel. The incorporation of phosphoric acid prevents the formation of anionic complex iron fluorides capable of entering into extractable combination with Methylene Blue. Attack with ammonium hydrogen fluoride destroys boron nitride, solubilizing the boron; hence total boron is obtained.[9] Addition of hydrogen peroxide speeds up the dissolution and oxidizes the iron. The dissolution at room temperature avoids risk of loss of boron compounds volatile at higher temperatures (*e.g.*, ~70°).

The partition coefficient of the ion-association complex is such that the volume of both the aqueous and organic phases must be precise, as indicated in the method, otherwise variable errors will occur.

It is advisable to clean the polyethylene ware initially with a mixture of ammonia solution (1 part) and dichloroethane (2 parts) and to rinse with water. It is of the utmost importance subsequently to keep the apparatus clean and filled with water between tests. It has been reported that some batches of dichloroethane, usually with a slight yellowish tinge, interfere with the extraction of the fluoborate–Methylene Blue complex. Strizovic and Caldwell[8] purified the dichloroethane by treating it with small portions of sodium hydroxide until colourless. Excess of alkali was removed by washing with dilute sulphuric acid and then water.

Up to 20% Cr, 10% Ni, 1% each of V, Mo and W present either individually or collectively do not interfere in the boron determination, showing the feasibility of applying the method to alloy steels. The method can also be applied to determine trace amounts of boron in fertilizers containing phosphate, or in glass, but it is then necessary to use boron-free iron, as indicated in the method, to catalyse the BF_4^- formation. The lower limit of the method is 0·2 ppm of boron. Sample dissolution is carried out at room temperature, solubilizing all forms of boron including boron nitride. This avoids loss of relatively volatile boron compounds. The precision of the method is good and six samples can be analysed in less than 2 hr. The method has been in use in our laboratory for the last 2 years.

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Zusammenfassung—Ein schnelles spektrophotometrisches Verfahren zur Bestimmung von Bor in Stahl mit Hilfe des Fluoborat-Methylenblau-Komplexes wird angegeben. Es ähnelt im Prinzip der Methode von Rosotte, aber Änderungen vereinfachen die Handlung und vermeiden Verunreinigung und Probleme der Emulsionsbildung. Bis 20% Cr, 10% Ni und je 1% V, Mo und W stören einzeln oder gemeinsam bei der Bestimmung nicht; dadurch wird das Verfahren auf legierte Stähle anwendbar. Die Nachweisgrenze wurde von 5 auf 0,2 ppm Bor gesenkt. Die Proben werden bei Raumtemperatur in Polythene-Flaschen aufgeschlossen, wobei alle Formen von Bor auch Bornitrid, in Lösung gehen und der Verlust von relativ flüchtigen Borverbindungen vermieden wird. Die Genauigkeit des Verfahrens ist gut. Sechs Proben können in weniger als zwei Stunden analysiert werden.

Résumé—On présente une méthode spectrophotométrique rapide pour la détermination du bore dans l'acier par l'emploi du complexe fluoborate-bleu de méthylène. La méthode est en principe similaire à celle de Rosotte, mais des modifications simplifient l'opération, évitent la contamination et écartent les problèmes de formation d'émulsion. Des quantités allant jusqu'è 20% Cr, 10% Ni et 1% de chacun des métaux V, Mo et W présents soit individuellement, soit collectivement, n'interfèrent pas dans le dosage, le rendant applicable aux aciers alliés. La limite de dosage de la méthode a été abaissée de 5 à 0,2 ppm de bore. Les échantillons sont dissous à température ordinaire dans des bouteilles en polythène, solubilisant toutes les formes du bore y compris l'azoture de bore, et évitant la perte de composés du bore relativement volatils. La précision de la méthode est bonne. On peut analyser six échantillons en moins de 2 h.

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ANION-EXCHANGE SEPARATION AND SPECTROPHOTOMETRIC DETERMINATION OF MOLYBDENUM AND TUNGSTEN IN SILICATE ROCKS

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Summary—A combined ion-exchange spectrophotometric method has been developed for the determination of molybdenum and tungsten in silicate rocks. After the decomposition of samples with a mixture of sulphuric, nitric and hydrofluoric acids, traces of molybdenum and tungsten are separated from other elements by anion-exchange in acid sulphate media containing hydrogen peroxide. The adsorbed molybdenum and tungsten can easily be stripped from the column by elution with sodium hydroxide–sodium chloride solution. The adsorption and desorption steps provide selective concentration of molybdenum and tungsten, allowing the simultaneous spectrophotometric determination of the two metals with dithiol. Results on the quantitative determination of molybdenum and tungsten in the U.S. Geological Survey standard samples are included.

MOLYBDENUM is quite frequently reported in the routine spectrochemical analysis of common types of rocks, although its concentration often borders on the spectrochemical detection limits. Unlike molybdenum, the abundance of tungsten in most rocks and sediments is below the limits of detection by direct spectrochemical methods. A number of photometric methods have been described for the determination of molybdenum in silicate rocks. Recent progress in concentration and the subsequent photometric determination of molybdenum in rocks has been reviewed by Chan and Riley.[1] The colorimetric method developed by Stanton and Hardwick[2] for molybdenum in soils, sediments and rocks is primarily intended to provide a rapid procedure for field work, involving fusion of samples with potassium hydrogen sulphate.

There are fewer photometric methods for tungsten in silicate rocks. For photometric determination with the tin(II) chloride–thiocyanate method, Sandell[3] first removed iron and titanium by a double precipitation, and molybdenum by hydrogen sulphide precipitation, using antimony(V) sulphide as a carrier. Jeffery[4] concentrated molybdenum and tungsten by extraction with α-benzoinoxime into chloroform after alkali fusion of silicates, the two metals being determined simultaneously with dithiol. Chan and Riley[5] co-precipitated tungsten with manganese dioxide from a perchloric acid solution of rocks, purified it by cation-exchange, and finally determined it spectrophotometrically with dithiol. Since the carrier, co-precipitating agent or organic extracting agent has generally to be removed before tungsten can be determined spectrophotometrically, the procedures are tedious and time-consuming.

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It has been demonstrated that comparatively few metal ions, including molybdenum and tungsten, adsorb on a strongly basic anion-exchange resin in the sulphate form from sulphuric acid or sulphate media.[6,7,8] This behaviour of molybdenum and tungsten may offer a good basis for separating them from many other metals in silicate rocks before photometric determination. However, we found that even though the distribution coefficients of both metals are sufficiently high in sulphuric acid or sulphate media, a considerable portion of the two metals appears in the effluent from the sample solution, probably because of hydrolysis and the slow kinetics of the exchange reactions involved.

This difficulty can be overcome by allowing the two metals to adsorb on the resin from sulphuric acid or sulphate media containing a small amount of hydrogen peroxide. Thus, selective anion-exchange in sulphuric acid media coupled with simultaneous determination with dithiol allows the development of a simple, rapid, and highly selective method for the determination of molybdenum and tungsten in a variety of silicate rocks.

EXPERIMENTAL

Reagents and apparatus

Stock solutions. Molybdenum(VI): an appropriate amount of ammonium molybdate was dissolved in water to give *ca.* 10 mg of Mo/ml. The solution was standardized against EDTA. Tungsten(VI): an appropriate amount of sodium tungstate was dissolved in water to give *ca.* 10 mg of W/ml. The solution was standardized gravimetrically. From these stock solutions, standard solutions were freshly prepared by dilution with water.

Ion-exchange resin. A strong base anion-exchange resin, Dowex I-X8, SO_4-form, 100–200 mesh, was used. An appropriate amount of resin (Cl-form) was purified by placing it in a large column and backwashing with water to remove fine particles. Then it was washed with 3*M* sulphuric acid (to convert it into the sulphate form) until the effluent gave a negative test with silver nitrate. Finally the resin was washed thoroughly with water until the effluent gave a negative test with barium chloride. After drying at 60° for several hours the resin was stored in a desiccator containing a saturated potassium bromide solution.

Dithiol solution. An appropriate amount of toluene-3,4-dithiol was dissolved in 0·25*M* sodium hydroxide to yield a *ca.* 0·1% solution, and a few drops of thioglycollic acid were added. This solution was freshly prepared, when needed.

Column. Dried resin (5 g) was slurried with water and poured into a conventional glass column, 15 mm bore, drawn to a tip and with a plug of glass wool at the outlet. The resulting resin bed was about 50 mm long.

Equilibrium study

The distribution coefficient, K_d, for molybdenum(VI) and tungsten(VI) was determined by a batch method.[9] Portions of dried resin (1 g each) were weighed and placed in glass stoppered conical flasks, to which 41-ml portions of ammonium sulphate solution were added. The solution was previously adjusted to 0·025*M* in sulphuric acid and contained varying amounts of ammonium sulphate and 1·03 mg of molybdenum(VI) or 1·04 mg of tungsten(VI). After mechanical shaking for 20 hr at room temperature, the two phases were separated by filtration. An aliquot of the filtrate was analysed colorimetrically for the respective element with dithiol. The K_d was calculated from the formula

$$K_d = \frac{\text{amount of ion in resin phase/g of resin}}{\text{amount of ion in solution phase/ml of solution}}$$

The K_d values for molybdenum(VI) and tungsten(VI) on the resin as a function of concentration of sulphuric acid were determined in the same manner. The K_d values were also determined in the presence of hydrogen peroxide at selected concentrations of sulphuric acid.

Procedure

Weigh out about 2 g of powdered sample in a platinum dish. Add 10 ml of 5*M* sulphuric acid, 4 ml of nitric acid and 10 ml of hydrofluoric acid. Heat on a hot-plate and evaporate to dryness. Continue the heating until no further fumes of sulphuric acid are evolved. Repeat the fuming with a further 2 ml of sulphuric acid and 20 ml of water in order to remove all traces of fluoride. Add a further 2 ml of sulphuric acid and 20 ml of water and digest at slightly below the boiling point for 30 min while stirring at intervals. Dilute to about 150 ml and boil gently until a clear solution results. After cooling, add 4 ml of 30% hydrogen peroxide and dilute to 200 ml with water. Pass the solution through the resin column at a flow-rate of 1–2 ml/min. After washing the column with 50 ml of $1M$ ammonium sulphate–$0{\cdot}025M$ sulphuric acid solution, strip the molybdenum and tungsten by elution with 50 ml of $0{\cdot}5M$ sodium hydroxide–$0{\cdot}5M$ sodium chloride solution at a flow-rate of 0·5 ml/min. Discard the first 20-ml fraction of the effluent and collect the subsequent 25-ml fraction for the determination of both elements.

Transfer the fraction containing molybdenum and tungsten into a Kjeldahl flask. Add 2 ml of sulphuric acid and heat until dense white fumes of sulphuric acid are evolved. After cooling add a few drops of 30% hydrogen peroxide and heat again until white fumes evolve. Add a few ml of water and three drops of 85% phosphoric acid, make alkaline with ammonia and expel the excess of ammonia by boiling. Add 1 ml of $5M$ sulphuric acid to the resulting solution and dilute to about 18 ml with water. Add 3 ml of the dithiol solution and warm on a steam-bath for 30 min. After cooling, extract the dithiol complexes of molybdenum and tungsten with 5 ml of n-butyl acetate and filter into a 10-mm cell. Measure the absorbance of the extract at 630 and 670 nm against the blank solution. Calculate the amounts of molybdenum and tungsten from the following equations

$$\mathrm{Mo} = A_{670} \,.\, a_{\mathrm{W}}^{630} - A_{630} \,.\, a_{\mathrm{W}}^{670}/a_{\mathrm{Mo}}^{670} \,.\, a_{\mathrm{W}}^{630} - a_{\mathrm{Mo}}^{630} \,.\, a_{\mathrm{W}}^{670}$$

$$\mathrm{W} = A_{630} \,.\, a_{\mathrm{Mo}}^{670} - A_{670} \,.\, a_{\mathrm{Mo}}^{630}/a_{\mathrm{Mo}}^{670} \,.\, a_{\mathrm{W}}^{630} - a_{\mathrm{Mo}}^{630} \,.\, a_{\mathrm{W}}^{670}$$

where A_{630} and A_{670} are the absorbances at 630 and 670 nm, respectively, a_{W}^{630}, a_{W}^{670}, a_{Mo}^{630} and a_{Mo}^{670} are constants which are determined experimentally with standard solutions, and the result is expressed in μg.

RESULTS AND DISCUSSION

Adsorption on Dowex I ion-exchange resin

K_{d} values for molybdenum(VI) and tungsten(VI) in acid sulphate media on Dowex I are tabulated in Table I as a function of the sulphate concentration. K_{d} values for the two metals in sulphuric acid media of varying concentration are listed in Table II. The values in parentheses indicate the K_{d} values for molybdenum and tungsten in the presence of 0·8% hydrogen peroxide. The K_{d} values for molybdenum and tungsten generally decrease monotonically with increasing sulphate or sulphuric acid concentration in the range covered. It can be seen that the K_{d} values for molybdenum and tungsten in slightly acidic sulphate media are much higher than the respective values in sulphuric acid media. The presence of hydrogen peroxide makes molybdenum favour the resin phase to a greater extent, but lowers the K_{d} values for tungsten in sulphuric acid media.

TABLE I.—DISTRIBUTION COEFFICIENTS OF Mo(VI) AND W(VI) AS A FUNCTION OF CONCENTRATION OF AMMONIUM SULPHATE
(Free acid concentration kept constant at $0{\cdot}025M$ H_2SO_4)

	$(NH_4)_2SO_4$, M	0·050	0·10	0·25	0·50	1·00
K_{d}	Mo(VI)	$4{\cdot}0 \times 10^3$	$2{\cdot}5 \times 10^3$	$2{\cdot}0 \times 10^3$	$1{\cdot}2 \times 10^3$	$0{\cdot}8 \times 10^3$
	W(VI)	$>10^4$	$>10^4$	$>10^4$	$>10^4$	$>10^4$

TABLE II.—DISTRIBUTION COEFFICIENTS OF Mo(VI) AND W(VI) AS A FUNCTION OF CONCENTRATION OF SULPHURIC ACID

	H_2SO_4, M	0·050	0·25	0·50	0·75	1·00
K_{d}	Mo(VI)	937	187(625)	52(227)	28	12(72)
	W(VI)	2130	566(353)	229(153)	125	21(63)

Values in parentheses are the distribution coefficients in the presence of 0·8% H_2O_2.

Over a wide range of sulphate or sulphuric acid concentration, the K_d values for molybdenum and tungsten should be sufficiently high to allow the two metals to adsorb on the column, but an attempt to adsorb molybdenum and tungsten quantitatively on the column failed with 200 ml of 0·5*M* ammonium sulphate–0·025*M* sulphuric acid solution containing 52 μg each of molybdenum and tungsten; a small fraction of both metals (3–4%), passed through. Similarly the uptake of molybdenum and tungsten from sulphuric acid solutions is only partial; when 200 ml of 0·45*M* sulphuric acid solution containing the two metals (52 μg each) is loaded onto the column, approximately 50% of molybdenum and 70% of tungsten pass through the column. The partial breakthrough of molybdenum and tungsten may be accounted for as due to the slow kinetics of the exchange reactions involving the hydrolysis products.

The partial breakthrough can be avoided by introducing a small amount of hydrogen peroxide into the sulphuric acid or sulphate solution containing the two metals. The concentration of hydrogen peroxide in sulphuric acid (pH 1) which is necessary to retain molybdenum and tungsten on the column covers a range from at least 0·3 to 6% peroxide in the final solution. However, a higher concentration of peroxide should be avoided, particularly if iron(III) is present, as this acts as a catalyst for deterioration of the resin.

Interferences

Adsorption of molybdenum and tungsten on the Dowex I column from sulphuric or sulphate media, and the subsequent elution with sodium hydroxide solution provides a selective removal of molybdenum and tungsten from a number of metals including alkali and alkaline earth metals, titanium, iron(II), iron(III), aluminium, beryllium, cadmium, cobalt, copper, gallium, germanium, nickel, vanadium and zinc.[7] Uranium(VI), thorium, zirconium and scandium, which are retained strongly

TABLE III.—DETERMINATION OF MOLYBDENUM AND TUNGSTEN IN 2-g SAMPLES OF SILICATE ROCKS

Sample (location collected)	Added, μg		Found, μg		Content in original sample, μg	
	Mo(VI)	W(VI)	Mo	W	Mo	W
Granite (Gunma)	—	—	1·54	1·32	1·54	1·32
	—	—	1·39	1·63	1·39	1·63
	—	—	1·56	1·54	1·56	1·54
	2·06	—	3·56	1·17	1·50	1·17
	—	2·08	1·39	3·46	1·39	1·38
					Av. 1·48 ± 0·07	Av. 1·41 ± 0·16
Andesite (Gunma)	—	—	1·73	0·07	1·73	0·07
	—	—	1·74	0·08	1·74	0·08
	—	—	1·72	0·06	1·72	0·06
	2·06	—	3·62	0·10	1·56	0·10
	—	2·08	1·50	2·21	1·50	0·13
					Av. 1·65 ± 0·10	Av. 0·09 ± 0·01
Basalt (Hiyōgo)	—	—	1·17	0·95	1·17	0·95
	—	—	1·24	0·85	1·24	0·85
	—	—	1·24	0·85	1·24	0·85
	2·06	—	3·19	0·82	1·13	0·82
	—	2·08	1·22	2·89	1·22	0·81
					Av. 1·20 ± 0·04	Av. 0·86 ± 0·05

TABLE IV.—DETERMINATION OF MOLYBDENUM AND TUNGSTEN IN STANDARD ROCKS

G-1 (Granite)	W-1 (Diabase)	G-2 (Granite)	GSP-1 (Granodiorite)	AGV-1 (Andesite)	PCC-1 (Peridotite)	DTS-1 (Dunite)	BCR-1 (Basalt)	Method	Author
MOLYBDENUM, ppm									
5·44, 5·45 6·23*	0·52	0·15, 0·15	0·32, 0·28	1·68, 1·64	0·02, 0·04	0·02, 0·06	1·20, 1·21	Photometric	This work
7	0·5								Fleischer[11]
		1·9	2·6	4·6	0·2	1·3	2·9	Photometric	Chan and Riley[13]
		<0·1	0·2	1·7	<0·1	<0·1	1·2	Spectrochemical	LeRiche†
		1·4	1·5	5·5	6·5	8·2	6·5	Spectrochemical	Kulbicki *et al.*†
		0·94	1·6	3·0	—	—	1·4	Spectrochemical	Champ†
TUNGSTEN, ppm									
1·21, 1·40 0·51*	0·45	0·00, 0·00	0·29, 0·32	0·64, 0·62	0·06, 0·06	0·06, 0·03	0·53, 0·55	Photometric	This work
0·4	0·45								Fleischer[10]
—	—								Fleischer[11]
		0·4	0·5	1·1	0·2	0·2	0·7	Photometric	Chan and Riley[13]

* Molybdenum and tungsten separated chromatographically with a DEAE column.[14]

† Quoted by Flanagan.[12]

on the resin, may not be stripped from the column by elution with 0·5M sodium hydroxide–0·5M sodium chloride solution. It will not generally be necessary to purify the eluted fraction of molybdenum and tungsten, particularly if the two metals are determined spectrophotometrically with dithiol.

Precision and accuracy

Results of repeated determinations of molybdenum and tungsten in three types of rocks, which represent the igneous rocks, are given in Table III. A known amount of molybdenum or tungsten was added to each rock sample, and the overall recoveries were estimated. The results are also quoted in Table III. The averages and errors (expressed as the standard deviation) are based on all determinations including addition tests. In general, the overall precision is satisfactory, the relative standard deviations ranging from 6 to 11%.

To obtain information about the accuracy of the method, the U.S. Geological Survey standard rock samples were analysed by the proposed procedure, the results being quoted in Table IV. For comparison, recommended values for G-1 and W-1 given by Fleischer, and some recent literature values cited by Flanagan for the new series of rock samples are also listed in Table IV. With respect to W-1 our values for molybdenum and tungsten are in good agreement with recommended values. Since the molybdenum concentration in G-1 is unusually high, causing a high concentration ratio of molybdenum to tungsten, considerable uncertainty may be introduced into the simultaneous dithiol determination of molybdenum and tungsten.[4] Our values obtained after the separation of molybdenum and tungsten are close to recommended values.

For the new series of standard rocks our values for molybdenum agree with spectrochemical results given by Le Riche. For tungsten the photometric values given by Chan and Riley are distinctly higher than our values, the disagreement being particularly marked for granite G-2 and two ultrabasic rocks PCC-1 and DTS-1.

Zusammenfassung—Ein kombiniertes spektrophotometrisches Ionenaustauschverfahren zur Bestimmung von Molybdän und Wolfram in Silikatgesteinen wurde entwickelt. Nach Aufschluß der Proben mit einem Gemisch von Schwefel-, Salpeter- und Flußsäure werden Molybdän- und Wolframspuren von anderen Elementen durch Anionenaustausch in saurem, Sulfat und Wasserstoffperoxid enthaltendem Medium getrennt. Das adsorbierte Molybdän und Wolfram kann durch Elution mit Natriumhydroxid-Natriumchloridlösung leicht von der Säule gelöst werden. Die Adsorptions- und Desorptionsschritte bewirken selektive Anreicherung von Molybdän und Wolfram; die gleichzeitige spektrophotometrische Bestimmung beider Metalle mit Dithiol wird möglich. Ergebnisse der quantitativen Bestimmung von Molybdän und Wolfram in Standardproben vom U.S. Geological Survey sind beigefügt.

Résumé—On a élaboré une méthode associée échange d'ions–spectrophotométrie pour la détermination du molybdène et du tunstène dans des roches aux silicates. Après la décomposition des échantillons avec un mélange d'acides sulfurique, nitrique et fluorhydrique, les traces de molybdène et de tungstène sont séparées des autres éléments par échange anionique dans des milieux de sulfate acide contenant de l'eau oxygénée. On peut aisément détacher de la colonne les molybdène et tungstène adsorbés par élution avec une solution de soude-chlorure de sodium. Les stades d'adsorption et de désorption fournissent une concentration sélective du molybdène et du tungstène, permettant la détermination spectrophotométrique simultanée des deux métaux au dithiol. On inclut les résultats sur la détermination quantitative du molybdène et du tungstène dans des échantillons étalons du U.S. Geological Survey.

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USE OF 3-HYDROXY-1,3-DIPHENYLTRIAZINE IN THE SPECTROPHOTOMETRIC DETERMINATION OF COPPER, PALLADIUM, IRON, COBALT, NICKEL, AND MOLYBDENUM

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Summary—3-Hydroxy-1,3-diphenyltriazine (HDPTA) forms brightly coloured complexes with copper, palladium, iron, cobalt and nickel ions, which are readily extractable in benzene. The deep yellow molybdenum complex is completely soluble in 60% ethanol. All the chelates have a definite absorption maximum between 398 and 422 nm, the reagent absorption being negligible above 415 nm. The molar composition of the chelates is ML_2, except for iron and cobalt which form ML_3 complexes. Microquantities of these metals can be determined spectrophotometrically with HDPTA.

3-HYDROXY-1,3-DIPHENYLTRIAZINE (HDPTA) was suggested by Shome[1] as an analytical reagent in which the nitroso group of cupferron was replaced by the benzenediazonium group. Later Sogani and Bhattacharya[2] used this reagent for the gravimetric determination of palladium, copper and nickel. The reagent was subsequently employed by Shome, Das and Das[3] for the spectrophotometric determination of thallium. In the present study, HDPTA was used for the extraction and subsequent photometric determination of copper, palladium, iron, cobalt and nickel in benzene medium.

Molybdenum was determined previously by Kaimal[4] and Shome by precipitation with HDPTA followed by ignition and weighing as oxide. The present investigation was carried out to examine the possibility of spectrophotometric determination of the metal in 60% ethanol, with HDPTA as the colour-forming reagent.

EXPERIMENTAL

Reagents

Solutions of the metals were prepared by dissolving their chlorides, nitrates or sulphates in water; acids were added wherever necessary and the metal contents were determined by the usual methods. Weighed amounts of ammonium or alkali metal salts of various anions were dissolved in water and made up to standard volumes. Sodium acetate, ammonia or hydrochloric acid solutions were used for the regulation of pH. All the reagents and chemicals used were analytical reagent grade.

HDPTA ($C_{12}H_{11}N_3O$) was crystallized twice from alcohol, and ~0·01 *M* solutions of the compound were prepared in spectroscopic grade ethanol.

Dry benzene and spectroscopic grade ethanol were prepared and stored in the usual manner.

Extraction and spectrophotometric determination of copper, palladium, iron, cobalt and nickel in benzene

An aliquot of the metal solution was taken in a 100-ml separatory funnel, diluted, and adjusted to an optimum pH value (Table I); 2–5 ml of the ethanol solution of HDPTA were then introduced into the funnel and shaken thoroughly. The metal chelate was then extracted with 2 or 3 successive

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TABLE I.—PHOTOMETRIC DETERMINATION OF COPPER, PALLADIUM, IRON, COBALT, NICKEL AND MOLYBDENUM WITH HDPTA (TEMPERATURE 25°C)

Metal ion	λ,* *nm*	Time limit for colour stability hr.	Range for adherence to Beer's law, *μg/ml*	Molar absorptivity × 100	Optimum concentration range, *μg/ml*	pH range
Cu^{2+}	415	24	1·0 –10·2	50	2·5 –9·3	3·8–5·4
Pd^{2+}	415	48	0·2 –5·5	219	0·7 –3·4	3·6–5·6
Fe^{3+}	418	24	0·5 –3·9	98	1·15–4·0	4·0–5·7
Co^{2+}	420	36	0·45–3·25	148	0·6 –2·8	6·8–8·3
Ni^{2+}	422	72	0·4 –3·5	152	0·75–2·7	6·4–8·0
Mo^{6+}	420	6	1·0 –15·0	51	3·6 –13·0	2·0–4·0

* Appropriate wavelength for the determination.

5-ml portions of benzene. The combined organic extracts were then diluted to the mark with benzene in a 25-ml volumetric flask and dried with a pinch of anhydrous sodium sulphate. A corresponding blank solution was prepared and the absorbance of the complex was measured against the reagent blank at an appropriate wavelength (Table I).

Spectrophotometric determination of molybdenum in 60% ethanol

A measured volume of molybdenum solution was adjusted to pH 2·5–3·5, the reagent (2–5 ml) was added and the volume was made up with ethanol and water so that the final solution contained 60% of alcohol. The pH was checked and the absorbance was measured at room temperature against a reagent blank prepared under the same conditions.

RESULTS

Characteristics of the complexes

The molybdenum, nickel and palladium complexes are yellow, the copper and cobalt complexes brownish yellow, and the iron complex blue-violet. Each has a well defined absorption maximum in the visible region (Fig. 1).

Conformity to Beer's law was tested at the appropriate λ_{max} or at a longer wavelength. Longer wavelengths were preferred when the reagent interfered with measurements at λ_{max} because it also absorbed at that wavelength. The ranges of metal concentration for adherence to Beer's law and of optimum concentration for photometric determination[5] are listed in Table I.

The metal complexes were extracted with benzene from solutions adjusted to different pH values, the other conditions remaining the same, and the pH ranges for complete extraction were determined from absorbance studies (Fig. 2). The colour of the molybdenum complex in 60% ethanol was found to be independent of the acidity in the pH range 2·0–4·0.

When a definite amount of $\sim 10^{-3}M$ metal solution was treated with varying amounts of $10^{-3}M$ ethanolic HDPTA solution and the complex was extracted into benzene, the absorbances of the extracts showed that extraction is quantitative only when at least a 5-fold excess of the reagent is used. Molar ratio studies[6] indicated the composition of the chelates as ML_2, except for the iron and cobalt complexes which were ML_3 (M = metal, L = ligand). For molybdenum a 60% ethanol medium was used for these studies, and the complex was found to be ML_2.

The colour of the metal–HDPTA complexes was stable for at least 24 hr except for the molybdenum complex, the colour of which gradually decreased after 6 hr. Time limits for colour stability are given along with the molar absorptivities, in Table I.

Solvents such as chloroform, carbon tetrachloride, ether and ethyl acetate could

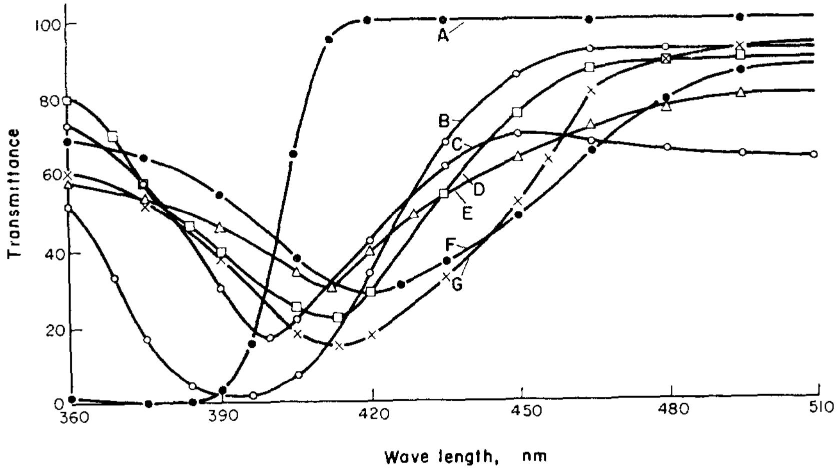

FIG. 1.—Transmittance curves of HDPTA complexes.
A—$10^{-3}M$ reagent; *B*—Cu, 10·2 μg/ml; *C*—Fe, 2·61 μg/ml; *D*—Mo, 10·3 μg/ml; *E*—Co, 1·36 μg/ml; *F*—Ni, 2·0 μg/ml; *G*—Pd, 3·7 μg/ml; concentrations refer to metal ions.

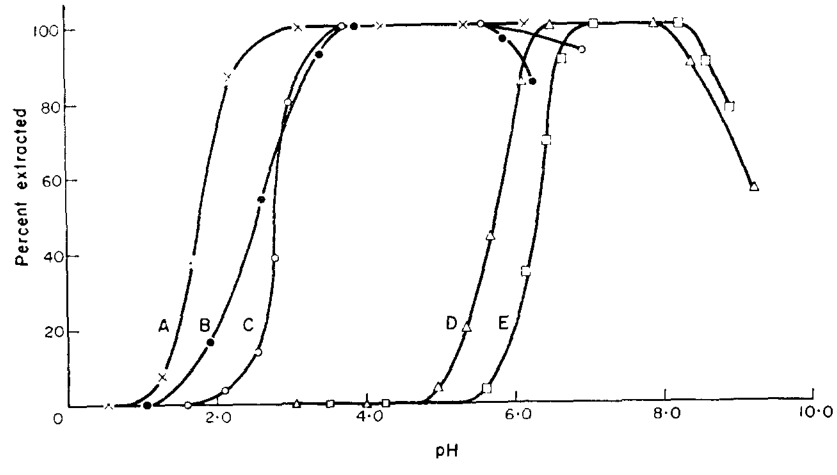

FIG. 2.—Extraction of HDPTA complexes as a function of pH.
A—Pd; *B*—Fe; *C*—Cu; *D*—Ni; *E*—Co.

not be used for the extraction of metal–HDPTA complexes, because the reagent was found to be unstable in these media. Toluene and xylene appeared to be usable. The molybdenum complex could be extracted with benzene, but the colour intensity was less than that in alcoholic medium. Moreover, the molybdenum–HDPTA chelate showed a tendency to decompose in benzene solution.

Interferences

The effect of a number of foreign ions on the spectrophotometric determination of the metals was studied; the procedure involved approrpriate pH adjustments and use

TABLE II.—EFFECT OF DIVERSE IONS ON THE PHOTOMETRIC ANALYSIS OF METALS

Foreign ion	Amount tolerated (*mg*) in the determination of					
	Iron (Fe^{3+} = 65·25 μg)	Cobalt (Co^{2+} = 45·3 μg)	Nickel (Ni^{2+} = 50·0 μg)	Copper (Cu^{2+} = 127·5 μg)	Palladium (Pd^{2+} = 57·5 μg)	Molybdenum (Mo^{6+} = 193·5 μg)
Ni^{2+}	1·4†	—	—	1·4†	1·42	1·25
Zn^{2+}	1·25	0·18	0·26	1·45	1·55	1·5
Cd^{2+}	1·2	0·10	0·12	1·4	1·5	1·6
Hg^{2+}	2·0	2·0	2·0	2·0	2·0	1·2
Mn^{2+}	1·2	0·075*	0·18*	1·25	1·25	0·75
Co^{2+}	1·0†	—	—	1·5†	1·4	1·4
Cu^{2+}	Nil	0·50‡	0·50‡	—	Nil	0·20§
Pd^{2+}	Nil	0·75‡	0·75‡	Nil	—	0·25§
Pb^{2+}	0·75†	1·0†	1·0†	1·2†	1·25†	0·15
Bi^{3+}	0·50†	1·45†	1·7†	1·45†	1·7†	Nil
Al^{3+}	1·4	0·60*	0·80*	1·4	1·6	1·6
Ga^{3+}	0·23	—	—	—	—	0·35§
In^{3+}	0·60	—	—	1·1¶	1·1¶	0·60
Fe^{3+}	—	0·32*	0·60*	1·1¶	1·2¶	0·010
Th^{4+}	1·0	0·80*	1·25*	0·58	0·70	1·2
Ti^{4+}	0·025	1·0*	1·0*	0·90¶	0·90¶	0·80§
Sn^{4+}	—	0·25*	0·30*	0·75	0·30	0·40
V^{5+}	0·15†	0·25‖	0·25‖	0·30†	0·30‖	0·050 (V^{4+})
Mo^{6+}	0·65†	0·95*	1·2*	0·90¶	0·90¶	—
W^{6+}	0·65	0·80	0·80	0·65	0·80†	1·4
U^{6+}	0·90	0·75	1·0	1·0	1·0	0·45
F^-	Nil	100	100	100	100	0·10
oxalate	0·10	10	10	100	10	Nil
tartrate	10	10	10	10	10	0·18
$EDTA^{4-}$	Nil	Nil	Nil	Nil	Nil	0·40

* Citrate–fluoride as masking agent.
† Tartrate as masking agent.
‡ Prior extraction of the foreign ions with HDPTA.
§ Filtration before measurement.
¶ Oxalate as masking agent.
‖ Fluoride as masking agent.

of masking agents. In some cases, especially in the interference studies in the determination of molybdenum, the solutions were filtered before the absorbance measurements. The results are shown in Table II. A 2% error was considered tolerable.

Precision and accuracy

The precision and accuracy of determination of each of the metals with HDPTA according to the recommended procedures were obtained by employing a set of five solutions of a particular concentration for each, and the results are shown in Table III.

DISCUSSION

A great many organic reagents have been proposed for the colorimetric determination of copper, palladium, iron, cobalt, nickel and molybdenum. Most suffer from

TABLE III.—PRECISION AND ACCURACY

Metal ion	Concentration, *μg/ml*	Coefficient of variation, %	Mean relative error, %
Fe^{3+}	2·61	0·5	−0·3
Co^{2+}	1·36	0·8	−0·3
Ni^{2+}	1·52	0·1	−0·4
Cu^{2+}	2·55	0·1	−0·4
Pd^{2+}	1·47	0·8	−0·4
Mo^{6+}	5·16	0·9	−0·2

some drawback such as lack of specificity, selectivity, sensitivity, precision, and stability of complexes. HDPTA is superior to some of the commonly used reagents.

Although HDPTA was long ago introduced as an analytical reagent it has not previously been used successfully for the colorimetric determination of metals, owing mainly to the low solubility and the unstable nature of the reagent and its metal chelates in aqueous and many non-aqueous solvents. However, benzene has now been found an appropriate solvent for the purpose. The HDPTA-complexes of copper, palladium, iron, cobalt and nickel can be rapidly extracted into benzene and the colour of the extracted complexes is sufficiently stable to permit spectrophotometric determination of these metals. In some cases the reagent is selective, but difficulties arise in the determination of iron in the presence of copper and palladium, and in separation of copper and palladium, or cobalt and nickel.

Zusammenfassung—3-Hydroxy-1,3-diphenyltriazin (HDPTA) bildet kräftig gefarbte Komplexe mit Kupfer, Palladium, Eisen, Kobalt und Nickel, die sich leicht in Benzol extrahieren lassen. Der tiefgelbe Molybdänkomplex ist in 60% Athanol vollständig löslich. Alle Chelate haben ein deutliches Absorptionsmaximum zwischen 398 und 422 nm; die Absorption des Reagens ist über 415 nm zu vernachlässigen. Die Zusammensetzung der Chelate ist ML_2 außer bei Eisen und Kobalt, die ML_3-Komplexe bilden. Mikromengen dieser Metalle können mit HDPTA spektrophotometrisch bestimmt werden.

Résumé—La 3-hydroxy 1,3-diphénytriazine (HDPTA) forme des complexes vivement colorés avec les ions cuivre, palladium, fer, cobalt et nickel, qui sont aisément extractibles en benzène. Le complexe jaune foncé du molybdène est complètement soluble en éthanol à 60%. Tous les chélates ont un maximum d'absorption défini entre 398 et 422 nm, l'absorption du réactif étant négligeable au-dessus de 415 nm. La composition molaire des chélates est ML_2, à l'exception des complexes de fer et de cobalt qui forment des complexes ML_3. On peut déterminer spectrophotométriquement des microquantités de ces métaux avec le HDPTA.

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A SEPARATION SCHEME FOR THE ANALYSIS OF MULTICOMPONENT SAMPLES*

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Summary—A sequential separation scheme has been devised for the quantitative analytical separation of 27 different metal ions. Five different chromatographic and ion-exchange columns are used to separate the metal ions into groups. The metal ions of each group are eluted separately from each column by means of selective eluents. Following separation, the metal ions are determined by titrimetry, flame spectrometry or other appropriate analytical methods. The reliability of the proposed scheme has been demonstrated by extensive testing, including the analysis of U.S. National Bureau of Standards samples. The scheme can be used for macro or micro quantities.

ALTHOUGH efficient methods can usually be worked out for the analysis of large numbers of samples of similar chemical composition, the incidental analysis of samples of different types often presents a difficult problem. The selection of a plan for analysis of a multicomponent sample requires an experienced, trained chemist. Even then, the myriads of analytical methods in books and journals are often confusing, and selection of methods is apt to be a hit and miss proposition. All too often a method will not be successful the first time it is tried on a particular sample. Minor difficulties are often encountered and the method will work only after some modification. Therefore, the analysis of new or non-routine samples is frequently slow and costly. Each new type of sample often becomes a research project in itself.

A more systematic approach to the analysis of analytical samples, particularly those of a non-routine nature, is clearly called for. The aim of the present work is to provide at least a start in that direction. A systematic scheme for the separation of some 27 different metal ions by column chromatographic techniques is presented. Once each metal ion component of the sample has been separated, measurement by appropriate titrimetric, spectral or other method is easily accomplished. Sometimes the measurement method used will permit determination of two or more elements without mutual interference, thereby reducing the number of separations required and simplifying the analytical process. Extensive testing has shown that this separation scheme is dependable and provides quantitative separations for both macro and trace amounts of the various metal ions.

The classical hydrogen sulphide scheme is a somewhat systematic approach to chemical analysis, but the methods are often slow and subject to co-precipitation errors. More recently, several comprehensive separation schemes using solvent extraction, chromatography and ion-exchange have been described.[1-7] However, these are largely schemes for radiochemical separations and the separations are not always quantitative. Chalmers and co-workers[8,9] have approached the analysis of

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metal ion mixtures systematically using solvent extraction with cupferron and other complexing reagents. Their method uses spectrophotometric and polarographic measurement of separated elements and is intended for 100 μg or less of each element.

EXPERIMENTAL

Reagents

Amberlyst XAD-2, an inert cross-linked polystyrene polymer, was obtained from Rohm & Haas as 20–50 mesh beads. The beads were ground in a Waring blender and sieved to obtain the proper mesh sizes. This product was washed successively with $6M$ hydrochloric acid and methanol, and air-dried.

Amberlyst A-26 macroreticular anion-exchange resin was obtained from the same source and was similarly ground and sieved. It was then washed with $2M$ perchloric acid, $1M$ hydrochloric acid, and then with water.

Dowex 50W-X8 cation-exchange resin, 100–200 mesh was purified by washing with 10% ammonium citrate solution, $3M$ hydrochloric acid, and finally with water.

Indicators were 0·5% w/v aqueous solutions of Xylenol Orange, 8-hydroxy-7-(6-sulpho-2-naphthylazo)-5-quinoline sulphonic acid (NAS) and Arsenazo I.

Isopropyl ether (IPE) and isobutyl methyl ketone (IBMK) were redistilled before use. Trioctylphosphine oxide (TOPO) was obtained from Eastman Organic Chemicals and used as received.

Column preparation

Conventional columns were used. The flow was controlled by a 1-mm bore stop-cock and the column support was held in place by a small plug of glass wool. Columns with Amberlyst XAD-2 as the inert support were all prepared by the same method. The requisite amount of XAD-2 slurried in methanol was added to the column and the methanol was allowed to drain rapidly just to the top of the support. A perforated Teflon disk was then placed on the top of the support to prevent disturbance of the column bed. Next the support was impregnated with the extractant by adding 3–5 column volumes of equilibrated IPE, IBMK or $0{\cdot}5M$ TOPO in cyclohexane and allowing the extractant to displace the methanol by gravity flow. Then the interstitial organic liquid was removed with equilibrated $8M$ hydrochloric acid. This is best accomplished by using some air pressure and a rapid flow-rate (10–20 ml/min).

The stripping solvent used to remove sorbed metal ions from the IPE and IBMK columns is $0{\cdot}1M$ hydrochloric acid in 98% methanol. After the metal ions have been stripped from the column, the support is in essentially the same condition as when the methanol slurry was first added to the column. Therefore it can be made-ready for the next sample by repetition of the procedure above.

Since elutions from the TOPO column are carried out with aqueous solutions, the column can be used a dozen times or more without reconditioning. When reconditioning is necessary it is sufficient to pass a few ml of $0{\cdot}5M$ TOPO–cyclohexane through the column to replace any lost extractant and then displace the interstitial TOPO solution with $8M$ hydrochloric acid as described above.

Any three of the first four columns used in the separation scheme may be connected so that the effluent from one flows directly into the next. A flow-rate of approximately 1 ml/min was used for elutions requiring up to 20 ml per element. Elements requiring a larger volume were eluted at a flow-rate of approximately 2 ml/min.

Analytical procedures

Antimony was determined by an oxidation-reduction method. Add 10 ml of hydrochloric acid and 20 ml of 10% potassium bromide solution to a 30–50-ml sample containing antimony(V). If the solution contains tartrate, also add 4 ml of sulphuric acid. If an organic solvent is present, remove it by boiling. Add excess 8% sulphurous acid and boil for 10 min to reduce to antimony(III). Remove any excess of sulphur dioxide by bubbling air through the solution for 5 min. Cool and titrate with standard potassium bromate, using α-naphthoflavone indicator.

Most elements were titrated with $0{\cdot}02M$ EDTA; solutions as dilute as $0{\cdot}001M$ were used to titrate very small quantities of separated metal ions. Conditions for EDTA titrations are given in Table I. Ammonia–ammonium chloride buffers were used for pH 9–10 and pyridine for pH 6.

Chromium was determined by a standard oxidation-reduction method employing ammonium persulphate.[10] To solutions also containing citrate, add 5 ml of sulphuric acid and evaporate until sulphur trioxide fumes appear and the sample becomes charred. Cool slightly, add 10 ml of nitric acid and again evaporate to sulphur trioxide fumes. Cool, wash down the beaker walls with distilled water and again evaporate to fumes. Dilute and determine the chromium by the persulphate oxidation procedure.

TABLE I.—SUMMARY OF EDTA TITRATION METHODS

Element	Method	pH	Indicator	Notes
Ga(III)	back-titn. Zn	6	NAS	
Fe(III)	back-titn. Th	2	Xylenol Orange	
Sn(IV)	back-titn. Cu	3·5	NAS	1
Cu(II)	direct	6	NAS	
Co(II)	direct	6	NAS	
Zn(II)	direct	6	NAS	
Cd(II)	back-titn. Cu	6	NAS	
Bi(III)	direct	2	Xylenol Orange	2
Ti(IV)	back-titn. Cu	4·5	NAS	3
Th(IV)	direct	2	Xylenol Orange	
Zr(IV)	back-titn. Th	2	Xylenol Orange	4
V(IV)	back-titn. Zn	6	NAS	5
Pb(II)	back-titn. Cu	6	NAS	
Mn(II)	direct	9	Arsenazo I	6
Al(III)	back-titn. Cu	6	NAS	7
Ni(II)	back-titn. Zn	6	NAS	8
Mg(II)	direct	10	Arsenazo I	Photometric end-point, 565 nm
Re(III)	direct	6	Arsenazo I	9
Ca(II), Sr(II), Ba(II)	direct	10	Arsenazo I	Photometric end-point, 565 nm

Notes 1. Acidify to pH 1 or below to prevent hydrolysis. Add 2 g of sodium chloride and a 50–100% excess of standard EDTA, and boil for 5 min. Cool, buffer with ammonium acetate to pH 3·5 and back-titrate.

2. If sulphate or chloride is present add excess of standard EDTA to solution at pH 2 and boil for 5 min. Cool, buffer to pH 6, back-titrate with standard copper(II), using NAS indicator.

3. Add excess of standard EDTA, buffer to pH 4·5 with ammonium acetate, add several drops of 30% hydrogen peroxide, and boil for 5 min. Cool and back-titrate.

4. Add 100% excess of standard EDTA to a pH 1 solution and boil for 10 min. Cool, adjust pH to 2·0 with ammonia and back-titrate.

5. If hydrogen peroxide is present, boil to remove. Then add a small amount of 8% sulphurous acid or ascorbic acid to reduce to V(IV). Then determine as indicated in the table.

6. Titrate with DCTA (1,2-diaminocyclohexanetetra-acetic acid) instead of EDTA. Add several drops of 8% sulphurous acid to ensure complete reduction to Mn(II). A spectrophotometric end-point (565 nm) is more accurate than the visual end-point.

7. Add 50–100% excess of standard DCTA, buffer to pH 6 with pyridine and ammonia, and boil for 5 min. Cool and back-titrate. If hydrofluoric acid is present, add 2–3 ml of sulphuric acid and evaporate to heavy fumes. Cool and redissolve the aluminium sulfate with water, heating if necessary.

8. For successive titration of nickel(II) and magnesium(II) in mixtures, first determine nickel(II) at pH 6 by zinc(II) back-titration, using a minimum amount of NAS indicator. Then adjust the pH to 10 with ammonia, add Arsenazo I indicator and titrate the magnesium(II). Best results are obtained by using a spectrophotometric end-point at 565 nm.

9. Total rare earths and alkaline earths in mixtures may be successively titrated, first the rare earths at pH 6, then the alkaline earths at pH 10. A spectrophotometric end-point is recommended for the latter titration.

Atomic-absorption methods were used to analyse for metals when a good microtitration method was not available or where more than one component was to be measured without further separation. A Perkin–Elmer model 290 atomic-absorption unit was used and the procedures followed were those recommended by the manufacturer. In general, standard solutions were prepared in the solvent used to elute the metal of interest from the chromatographic column.

SELECTION OF SYSTEMS

Among the various methods of separating metal ions from one another, ion-exchange and extraction chromatography (liquid-liquid partition chromatography) are outstanding. Many separations have been reported, that use these two multistage techniques; the separations are quantitative and can usually be used with one element (or more) present in large excess over the others. Several systems have been studied extensively and the behaviour of a number of elements is well known. These systems include anion-exchange with aqueous hydrochloric acid,[11] hydrochloric acid in non-aqueous solvents,[12,13] aqueous hydrofluoric acid,[14] and cation-exchange with hydrochloric acid in acetone.[15,16] In extraction chromatography aqueous hydrochloric acid–ketone systems,[17] trioctylphosphine oxide (TOPO),[18,19] bis(2-ethylhexyl)phosphoric acid[20–22] and others have been studied extensively. Any single system works well for certain elements but either fails or is not advantageous for separation of other elements. For example, anion-exchange with aqueous hydrochloric acid separates many elements very well but tin(IV) is difficult to remove quantitatively from the column. Iron(III) and uranium(VI) are difficult to separate from each other; if the hydrochloric acid concentration is too high manganese is retained, albeit weakly, and is difficult to elute quantitatively. A number of elements are not retained by an anion-exchange column from hydrochloric acid solutions.

Some general requirements of an efficient separation scheme may be listed.

1. The separations should be quantitative with each element being strongly retained by the chromatographic column or not retained at all.
2. The separations should be quick and the elution volumes small.
3. The eluting media should be easily volatilized and should keep all elements in solution. Any incompatible combinations of metal ions and eluting media should be avoided by a separation earlier in the scheme.
4. Sufficient information should be available for prediction of the behaviour of many elements under the conditions used.
5. The sequence of steps should be such that a minimum number of changes in eluent composition is required for group separations.

The separation scheme presented in the next section fits these requirements very well. The first four group separations are carried out on chromatographic and ion-exchange columns, each using $8M$ hydrochloric acid as the eluent. The columns are small to minimize elution volumes, and the flow-rates employed are reasonably fast. Following a single evaporation, the remaining elements are separated on a cation-exchange column.

The column support is an important consideration in any chromatographic separation. Special halogenated polyethylene supports have been successfully used in the past. However, we have found that Amberlyst XAD-2, a porous polystyrene, sorbs significantly larger quantities of organic solvents than polyfluoroethylene supports and yet is hard and mechanically strong. For this reason XAD-2 was used in the present work.

For anion-exchange separations, Amberlyst A-26 macroreticular resin was employed. This is similar to Amberlyst XAD-2 but has quaternary ammonium functional groups to provide sites for anion-exchange. The highly porous, rigid structure of the A-26 resin permits somewhat faster flow-rates and smaller elution volumes than the ordinary gel-type resins. Dowex 50W-X8 was selected as the cation-exchange resin for this study. It was found that some metal ions are more easily eluted from this resin than from a column of the macroreticular cation-exchange resin, Amberlyst 15.

SEPARATION SCHEME

A flow chart summarizing the separation of sample mixtures into groups and the column methods of separating the metal ions in the individual groups is given in Table II. Elements listed under each group are retained by that column and are later eluted by the eluents listed at the right. The elements not retained by a column are washed from the column with $8M$ hydrochloric acid (for columns 1–4). Several notes on various details concerning the group separations are given in footnotes in Table II.

Methods for measurement of individual metal ions (once they are separated) are outlined under *Experimental* above. However, several additional details regarding separation and determination of some of the metal ions should be mentioned.

1. No reliable method was found for separating antimony(V), iron(III) and gallium(III) on the IPE column. Antimony(V) can be separated from iron(III) and gallium(III) by passing an acidic solution containing excess of tartrate through a short Dowex-50 column. Antimony(V) passes through while iron (III) and gallium(III) are retained. After stripping from the column, iron and gallium may be separated from each other on an A-26 column, a small amount of ascorbic acid being used to reduce the iron to iron(II), and $0{\cdot}45M$ hydrobromic acid in 90% methanol being the eluent.[23]
2. When copper(II) and cobalt(II) (Group 3) are both present in the sample, the cobalt(II) will be sorbed onto the column above the copper(II) band. When the eluting solvent is changed to $0{\cdot}5M$ hydrochloric acid in 65% ethanol, the order of elution is reversed and cobalt is eluted from the column ahead of the copper. Because copper(II) is also slowly eluted by this eluent, extra care must be taken to ensure use of a column of sufficient size to allow a clean separation.
3. The separation of copper(II) from uranium(VI) (Group 3) by elution with $2{\cdot}5M$ hydrochloric acid is marginal.
4. Several good methods are available for separating zirconium and hafnium (Group 4) should it be desirable to separate these two elements.[24,25]
5. When $0{\cdot}6M$ hydrobromic acid is added to the column (Group 5), lead bromide is initially precipitated at the top of the column. If the amount of lead(II) is small this precipitate readily redissolves on continued elution. When larger amounts of lead are present, the dissolution of the precipitate may be hastened by using heated eluent or by using a hot water-jacket on the exchange column.
6. If aluminium(III) is eluted with $0{\cdot}3M$ hydrofluoric acid, a column of Kel F (or another plastic) is used in place of a glass column.
7. A method for successive titration of nickel(II) and magnesium(II) in mixtures is outlined in Table I.
8. A method for successive titration of total rare earths and alkaline earths is outlined in Table 1.

The probable effect of several additional elements on the separation scheme was also considered.

Arsenic(III), germanium(IV). These elements should be retained by the IPE column. However, separation of arsenic and germanium from a large number of elements by extraction into benzene from 10–$12M$ hydrochloric acid has been reported;[26] this separation has also been accomplished by using a column of benzene sorbed onto a porous solid support.[27]

Niobium(V), tantalum(V), tungsten(VI). A separation scheme for these three

TABLE II.—FLOW CHART FOR SEPARATION SCHEME

Abbreviations: IPE = isopropyl ether, IBMK = isobutyl methyl ketone,
TOPO = trioctylphosphine oxide

Data in parentheses are recommended column bed volumes for trace (T) and macro (M) amounts of metal ions.

Sample in 8*M* HCl

↓

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1. IPE on XAD-2 column* (T 5 ml; M 6 ml + 1 ml/additional 0·1 mmole)

Sb(V) Ga(III) Fe(III)	Strip with 0·1*M* HCl in MeOH

↓

---

2. IBMK on XAD-2 column (T 5–10 ml; M 15 ml + 2 ml/additional 0·1 mmole)

Mo(VI)	Elute with 1*M* HCl–3*M* H_2SO_4
Sn(IV)	Strip with 0·1*M* HCl in MeOH

↓

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3. Amberlyst A-26 column,† (T 4–5 ml; M 6ml + 1 ml/additional 0·1 mmole)

Co(II)	Elute with 0·5*M* HCl in 65% EtOH
Cu(II)‡	Elute with 2·5*M* HCl
U(VI)	Elute with 1·0*M* HCl
Zn(II)	Elute with 0·05*M* HBr
Cd(II)	Elute with 1·0*M* HNO_3–0·01*M* HBr
Bi(III)	Elute with 2·0*M* $HClO_4$

↓

---

4. TOPO–cyclohexane on XAD-2 column§ (T 5–10 ml: M 15 ml + 2 ml/additional 0·1 mmole)

Ti(IV) Sc(III)	Elute with 5·0*M* HNO_3
Th(IV)	Elute with 12*M* HCL
Zr(IV) Hf(IV)	Elute with 1·0*M* HCl

↓

Evaporate to near dryness. Add HNO_3 and re-evaporate. Dissolve in 20 ml of H_2O.

↓

If Cr present add citrate, pH 4, boil, cool, adjust to pH 2.¶**

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5. Dowex 50W-X8 column (T 4 ml; M 6 ml + 1 ml/additional 0·1 mmole)

V(IV)	Elute with 1% H_2O_2–0·01*M* $HClO_4$
Pb(II)	Elute with 0·6*M* HBr
Mn(II)	Elute with 1·0*M* HCl in 92% acetone
Al(III)	Elute with 0·3*M* HF
Ni(II) Mg(II)	Elute with 3·0*M* HCl in 60% EtOH
Ca(II) Ba(II) Sr(II) RE(III)	Strip with 4·0*M* HNO_3

elements has been reported, that uses a hydrofluoric acid medium and a chromatographic column containing IBMK on a solid support.[28] These separations appear to be selective, but extensive testing would be needed to determine how well such a separation would fit into the present scheme.

Indium. Published extraction data[29] (and work by the present authors) indicated that indium(III) should be quantitatively retained by the IBMK column from $8M$ hydrochloric acid. However, experimentation showed that indium is only partly retained by this column; the remainder is sorbed by the A-26 column.

Gold(III). Gold is easily extracted from hydrochloric acid solution and will be retained by the IPE column. Platinum, rhodium, osmium and iridium have not been tested at all.

Mercury(II). Mercury passes through the IPE and IBMK columns, although a larger volume of $8M$ hydrochloric acid than normal is needed for complete elution.[17] Mercury(II) is retained by the A-26 column.

Silver (I). Silver forms an anionic chloride complex that is reasonably soluble in $8M$ hydrochloric acid. Thus moderate amounts of silver will remain in solution and will pass quantitatively through the first four columns. Evaporation of the eluate from the TOPO column, followed by dilution with water, should permit quantitative gravimetric separation of silver from the remaining elements. Interference from lead can be avoided by repeated washing of the precipitated silver chloride with hot dilute nitric acid.[30]

Alkali metals. These will pass quantitatively through the first four columns, but some of the alkali metals may be retained by the Dowex-50 column.

EVALUATION OF SEPARATION SCHEME

The reliability of any comprehensive analytical separation scheme can only be established by thorough testing. The likelihood of an actual sample containing macro amounts of all 27 elements is negligible. Most samples will contain only a few

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Footnotes to Table II

* The best eluting solvent here is a 1:1 mixture of equilibrated $8M$ hydrochloric acid and non-equilibrated acid. Otherwise when the eluting solvent is first added to the column some of the dissolved IPE may be salted out of solution, causing streaking of the sorbed metal bands and bleeding of the extracting agent from the column.

† Manganese(II) and lead(II) are weakly extracted by the resin. The elution volume required for these two metals is greater than for the other metals considered. An elution volume equivalent to 8 column volumes is sufficient to elute these metals from the column.

‡ Copper(II), although retained by the resin, has a sufficiently low distribution coefficient for it to move slowly down the column. Therefore, when large amounts of copper(II) are present in the sample, care must be taken to ensure the column is of sufficient size to perform the desired separations.

§ If a larger than usual IPE or IBMK column is used, the effluent from the A-26 column should be heated for a few minutes to remove any dissolved organic solvent. This avoids the possibility of removal of any TOPO from the column by dissolved organic IPE or IBMK.

¶ Omit the citrate step if chromium is absent. A vanadium residue from the evaporation step may be redissolved by adding a few drops of hydrogen peroxide.

** A faster method may be used for separation of small amounts of chromium(III) (<1%), provided sulphate will not interfere with subsequent operations. After removing hydrochloric acid, add a small amount of sulphuric acid and evaporate to fumes. This converts the chromium(III) into an anionic sulphate complex. Cool, dilute with water to reduce the sulphuric acid concentration to $0{\cdot}1$–$0{\cdot}25M$, then transfer to the Dowex-50 column that has been conditioned with $0{\cdot}1M$ sulphuric acid. Elute the chromium(III) sulphate complex from the column with $0{\cdot}1M$ sulphuric acid. This method will recover approximately 99% of the chromium present in the sample.

elements, but the variety of combinations is very large. The following testing programme was used to demonstrate the validity of the proposed separation scheme.

1. Each element was separated on an appropriate column from the elements immediately preceding and following it in the scheme. Spot tests (or other qualitative tests) were used to determine the point of complete elution of an element and to ascertain that breakthrough of the next element did not occur with a reasonable additional volume of eluent. This general procedure has proven to be a dependable test of separation efficiency and is much more reliable than using only batch distribution coefficients to predict actual column separations.

2. Several synthetic samples were separated and analysed quantitatively. The sample compositions were chosen to test the reliability of various portions of the separation scheme. Results, together with actual separation conditions, are summarized in Table III.

TABLE III.—SEPARATION AND ANALYSIS OF METAL ION MIXTURES
Approximately 0·1 mmole of each element is present. Flow-rate 1 ml/min if element requires 20 ml or less; otherwise 2 ml/min.

Metal ion mixture	Column *mm, type*	Wash,* *ml*	Elution *ml, eluent*	Recovery, %
Gallium(III)	60 × 12, IPE	10	20, MeOH	100·3
Lead(II)	60 × 10, A-26		15, 8*M* HCl	100·3
Zinc(II)			25, H_2O	99·8
Nickel(II)	140 × 10, A-26	—	25, 8*M* HCl	100·4
Cobalt(II)			30, 0·5*M* HCl/65% EtOH	100·4
Copper(II)			20, 1*M* HCl	99·8
Zinc(II)			100, 0·5*M* HBr	100·0
Cadmium(II)			100, 1*M* HNO_3/0·01*M* HBr	100·4
Titanium(IV)	110 × 14, TOPO	30	20, 0·05*M* HCl	99·9
Vanadium(IV)	60 × 12, Dowex-50		20, 1% H_2O_2	99·6
Aluminium(III)			25, 3*M* HCl	99·9
Nickel(II)	100 × 13, TOPO	—	20, 8*M* HCl	100·0
Titanium(IV)			50, 5*M* HNO_3	99·4
Thorium(IV)			100, 0·2*M* HCl	99·6
Lanthanum(III)	130 × 12, TOPO	—	20, 8*M* HCl	100·2
Titanium(IV)			40, 5*M* HNO_3	100·0
Thorium(IV)			50, 12*M* HCl	100·0
Zirconium(IV)			125, 1*M* HCl	100·4
Nickel(II)	70 × 12, Dowex-50	—	100, 3*M* HCl/60% EtOH	99·8
Magnesium(II)				100·2
Calcium(II)			40, 4*M* HNO_3	100·2

* "Wash" is the volume of 8*M* HCl needed to wash elements of later groups (see Table II) from the column.

3. Several U.S. National Bureau of Standards samples were analysed by using the separation methods of the present scheme. Some of these samples contain many different elements and their analysis is ordinarily quite complicated. Results are given in Table IV.

A simple statistical evaluation of the results obtained for separation and analysis of all synthetic and NBS samples is summarized in Table V. The average recoveries

TABLE IV.—ANALYSIS OF U.S. NATIONAL BUREAU OF STANDARDS SAMPLES
Flow-rate 1 ml/min if element requires 20 ml or less; otherwise 2 ml/min

Sample number	Metal determined	Column *mm, type*	Wash,* *ml*	Elution *ml, eluent*	Certificate value %	Found,† %
54d	Sb	60 × 10, IPE	7	20, IPE	7·04	7·06
	Sn	120 × 14, IBMK	9	30, IBMK	88·57	88·4$_1$
	Cu	50 × 10, A-26	10	20, H_2O	3·62	3·61
	Pb			10, 8*M* HCl	0·62	0·61
124d	Fe	50 × 10, IPE	6	15, MeOH	0·18	0·19
	Sn	150 × 10, IBMK	10	30, MeOH	4·56	4·51
	Cu	130 × 12, A-26	50	30, 1*M* HCl	83·60	83·6$_0$
	Zn			50, H_2O	5·06	5·05
	Pb	30 × 10, Dowex-50		30, 0·6*M* HBr	5·20	5·22
	Ni			15, 3*M* HCl	0·99	1·00
173a	Fe	70 × 10, IPE	10	20, MeOH	0·15	0·15
	Ti	300 × 14, TOPO	30	50, 0·5*M* HCl	—	—
	V	60 × 12, Dowex-50		15, 1% H_2O_2	4·06	4·04
	Al			20, 3*M* HCl	6·47	6·49
20f	Fe	100 × 13, IPE	15	—	—	—
	Mo	80 × 10, IBMK	10	—	—	—
	Cu	50 × 10, A-26	30	30, H_2O	0·239	0·24$_8$
	Mn	50 × 10, Dowex-50		30, 1*M* HCl/92% acetone	0·754	0·76$_4$
	Ni			50, 3*M* HCl/60% EtOH	0·243	0·25$_8$
	Cr‡			0·1*M* H_2SO_4	0·097	0·097
101e	Fe	100 × 10, IPE	20	—	—	—
	Mo‡	80 × 10, IBMK	5	10, MeOH	0·43	0·40
	Co‡	50 × 10, A-26	30	20, 0·001*M* HCl	0·18	0·19
	Cu‡				0·36	0·36
	Mn	70 × 10, Dowex-50	20	50, 1*M* HCl/92% acetone	1·77	1·74
	Ni			25, 3*M* HCl	9·48	9·44
	Cr			20, H_2O	17·98	17·8$_9$
1a	Fe§	60 × 10, IPE	10	20, MeOH	1·63	1·60
	Ti§	80 × 10, TOPO	15	20, 0·5*M* HCl	0·16	0·17
	Al§	120 × 10, Dowex-50		60, 0·3*M* HF	4·16	4·12
	Mg§			100, 3*M* HCl/60% EtOH	2·19	2·27
	Ca¶			40, 4*M* HNO_3	41·44	41·2$_6$

* The volume of 8*M* HCl needed to remove elements from later groups.
† Average of 3 determinations.
‡ Determined by atomic absorption.
§ Reported as the metal oxide.
¶ Calcium plus strontium, calculated as CaO.

Dissolution Methods

No. 54 d (tin-base alloy). Dissolve 250 mg in 10 ml of 8*M* HCl, 0·5 ml of HNO_3, 1 ml of 3% H_2O_2. Dilute to 25 ml with 8*M* HCl, take 4-ml aliquot (40 mg of sample).

No. 124d (copper-base alloy). Dissolve 250 mg in 10 ml of 8*M* HCl, 1 ml of 30% H_2O_2. Dilute to 25 ml with 8*M* HCl, take 4-ml. aliquot (40-mg sample).

No. 173a (titanium-base alloy). Dissolve 50 mg in 5 ml of 8*M* HCl (90°, 2 hr). Add 0·25 ml of 30% H_2O_2 to oxidize Ti to Ti(IV), boil to remove H_2O_2. Add 0·5 ml of 6% H_2SO_3 to reduce V to V(IV). Adjust sample volume to about 5 ml with 8*M* HCl.

No. 20f (steel). Dissolve 1 g in 10 ml of HCl, 1 ml of HNO_3. Evaporate almost to dryness. Dilute to 100 ml with 8*M* HCl, take 10 ml (100-mg sample).

No. 101e (alloy steel). Dissolve 500 mg in 10 ml of HCl, 1 ml of HNO_3. Evaporate almost to dryness. Dilute to 100 ml with 8*M* HCl, take 5 ml (25-mg sample).

No. 1a (limestone). Weigh 500-mg sample, ignite for 30 min at 1000°. Dissolve in 5 ml of H_2O, 4 ml of $HClO_4$, 5 ml of HF. Evaporate to $HClO_4$ fumes. Dilute to 25 ml with 8*M* HCl, take 5 ml (50-mg sample).

TABLE V.—SUMMARY OF ANALYTICAL DATA

Type of sample	Number of samples	Average recovery, %	Relative standard deviation, %
Synthetic samples	25	100·1	0·3
NBS samples, components greater than 2% of sample	14	99·7	0·4
NBS samples, components less than 2% of sample	14	101·0	3·5

and relative standard deviations for major sample components are considered quite good, especially since most samples were only 40 or 50 mg. The average recovery of minor components of NBS samples is a bit high, but again it should be remembered that emphasis was placed on using small samples, which makes the accurate determination of minor constituents more difficult.

A study of the samples analysed (Tables III and IV) shows that for any given sample the separation scheme can usually be shortened considerably. If the sample contains no elements of certain groups, the column separation for those groups can be dispensed with. Stripping of the last element in the A-26 column group with water (or dilute acid), in the TOPO column group with 0·5*M* hydrochloric acid, or in the Dowex-50 column group with 3–4*M* hydrochloric acid often permits a more rapid elution than indicated by the scheme in Table II. Often the method of analysis will not require the separation of each element from the others. For example the analysis of an aluminium alloy for traces of iron, copper, zinc and bismuth by a flame method might require only the isolation of the minor elements from the aluminium matrix by the IBMK and A-26 columns or by an A-26 column alone. Automation of the separation steps by suitable pumps, valves and timers would further improve the convenience of the separations.

The scheme is incomplete to the extent that it does not include *all* metallic elements and does not cover the separation of some closely related elements such as the individual rare earths. However, it is felt that the proposed scheme is a useful step towards a systematic approach to the analysis of samples containing metallic elements. The scheme appears to be reliable and the separations are convenient and reasonably quick to carry out.

Zusammenfassung—Ein Trennungsgang zur quantitativen analytischen Trennung von 27 verschiedenen Metallionen wurde entworfen. Fünf verschiedene chromatographische und Ionenaustauschsäulen dienen zur Auftrennung der Metallionen in Gruppen. Die Metallionen jeder Gruppe werden von jeder Säule durch selektive Elutionsmittel einzeln eluiert. Nach der Trennung werden die Metallionen durch Titration, Flammenphotometrie oder andere geeignete analytische Verfahren bestimmt. Die Zuverlässigkeit des vorgeschlagenen Trennungsganges wurde durch eingehende Erprobung demonstriert; auch Proben vom US National Bureau of Standards wurden analysiert. Der Trennungsgang kann für Makro- und Mikromengen verwendet werden.

Résumé—On a établi un schéma de séparation séquentielle pour la séparation analytique quantitative de 27 ions métalliques différents. On utilise cinq colonnes chromatographiques et échangeuses d'ions différentes pour séparer les ions métalliques en groupes. Les ions métalliques de chaque groupe sont élués séparément de chaque colonne au moyen d'éluants sélectifs. A la suite de la séparation, les ions métalliques sont dosés par titrimétrie, spectrométrie de flamme ou d'autres méthodes analytiques appropriées. On a démontré l'exactitude du schéma proposé par un examen étendu, incluant l'analyse d'échantillons du U.S. National Bureau of Standards. On peut utiliser le schéma pour des macro- ou micro-quantités.

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METALLEXTRAKTIONEN MIT ALIPHATISCHEN ALKOHOLEN

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Zusammenfassung—Eine Reihe von Metallen wird mit den Alkoholen 2-Äthyl-1-butanol, 4-Methyl-2-pentanol und 1-Butoxy-2-propanol aus jodidhaltigen schwefelsauren Lösungen quantitativ, ein anderer Teil unvollständig und einige Elemente werden überhaupt nicht extrahiert. Die Durchführung der Extraktion wird beschrieben. Es ergeben sich eine Fülle von Trennungsmöglichkeiten; zwei davon, die Trennungen Zink-Cadmium und Indium-Gallium werden besprochen und an technischen Produkten erprobt. Am Beispiel des Quecksilbers wird mittels konduktometrischer Extraktionstitration die Zusammensetzung der extrahierten Metallkomplexe bewiesen.

IN LETZTER Zeit haben Verteilungsverfahren zur Anreicherung und Trennung von Elementen erhebliche Bedeutung erlangt. Die Flüssig-Flüssig-Extraktion zeichnet sich gegenüber Fällungsreaktionen durch einige Vorteile aus, die es gestatten, diese Arbeitsweise in der analytischen Praxis bevorzugt gegenüber anderen Methoden zu verwenden.

Wir haben eingehende Untersuchungen über die Extrahierbarkeit von Metallen mit den Alkoholen 2-Äthyl-1-butanol, 4-Methyl-2-pentanol und 1-Butoxy-2-propanol in jodidhaltigen schwefelsauren Lösungen durchgeführt. Diese Solventien sind nicht oder nur sehr wenig wasserlöslich und stellen sich preismäßig kaum höher als etwa Äthanol oder Methanol. Wie bekannt, werden hohe Verteilungskoeffizienten in jodidhaltigen Systemen schon bei geringeren Konzentrationen des komplexbildenden Halogenidions erreicht als in chlorid- und bromidhaltigen Lösungen.[1] Auch wirkt sich der Einfluß des Gegenkations (H^+, Li^+, Na^+ usw.) weniger aus als in chloridhaltigen Systemen. Neben den komplexbildenden Liganden haben aber das organische Solvens und die Acidität der Lösung einen entscheidenden Einfluß auf das Extraktionsvermögen. Hierfür geeignet sind alle organischen Lösungsmittel, deren Molekül ein Sauerstoffatom enthält und Oxoniumsalze bilden können.

Aliphatische Alkohole und Äther, die von sich aus keine mesomeren Oxoniumkationen bilden können, werden mit starken Säuren zu einer Protonenaddition gezwungen, wobei pro Molekül Alkohol, das als Base mit Schwefelsäure zu einem Oxoniumsalz reagiert, zwei Ionen gebildet werden. Die Metalle können dann aus wäßriger Phase über den Sauerstoff gebunden als undissoziiertes Molekül oder komplexe Metallsäure extrahiert werden. Bemerkenswert erscheint, daß einfach negativ geladene Komplexe allgemein gut extrahiert werden, gegenüber zwei- oder mehrfach negativ geladenen. Systematische Untersuchungen über das Extraktionsverhalten von mit Wasser nicht mischbaren aliphatischen Alkoholen bezüglich Metallen aus jodidhaltigen Medien wurden bisher nicht durchgeführt. Es war nun interessant zu erfahren, ob unsere Arbeiten Vorteile in der analytischen Praxis bezüglich Extrahierbarkeit, Trennungsmöglichkeiten, Säurekonzentration usw. ergeben.

EXPERIMENTELLER TEIL

Durchführung der Extraktion

Die Untersuchungen wurden in zylindrischen Schütteltrichtern von 250 ml Inhalt bei Raumtemperatur vorgenommen. Da die meisten Elemente nach einmaliger Extraktion mit 20 ml Lösungsmittel nicht vollständig in die organische Phase überführt werden, verwendeten wir ein Lösungsmittelgemisch von 20 ml Alkohol und 25 ml Tetrachlorkohlenstoff. Durch die Beschwerung des organischen Extraktionsmittels war eine schnelle Phasentrennung gewährleistet, wobei sich die organische Phase im unteren Teil des Schütteltrichters sammelt. Das Extraktionsvermögen dieses Lösungsmittelgemisches wird dadurch zwar etwas verschlechtert, es ist jedoch auf diese Art eine 2–3 fache Ausschüttelung ohne größeren Arbeitsaufwand möglich.

Die Extraktion wurde durch 2 Minuten dauerndes Schütteln bewerkstelligt. Längeres Schütteln hatte auf den Extraktionseffekt keinerlei steigernden Einfluß. Nach vollständiger Phasentrennung wurde der organische Anteil zur weiteren Aufarbeitung abgetrennt. Die wäßrige Schicht kam nun in einen 250-ml Titrierkolben, wobei der Restanteil des Lösungsmittels verkocht wird. Durch anschließenden Zusatz von 5 ml conz. Salpetersäure und Aufkochen der Lösung konnte das Jodid entfernt werden. Die Analysen wurden nach üblichen Verfahren durchgeführt.

Die Bestimmung der Metalle in der organischen Phase erfolgte nach zwei Methoden.

1. Die in ein Becherglas überführte organische Schicht wurde mit Wasser versetzt und auf dem Sandbad eingeengt. Waren im Rückstand noch organische Anteile vorhanden, so wurde er mit 5 ml conz. Schwefelsäure und 5 ml conz. Salpetersäure aufgenommen und zum Sieden gebracht. In dieses Säuregemisch wurde solange tropfenweise Perhydrol zugesetzt, bis alle organischen Reste zerstört waren.

2. Die Methode der Rückextraktion des Metalls aus organischer Phase mit Natronlauge ist zeitsparend und gut reproduzierbar, wobei diese Phase in einem 250 ml-Schütteltrichter gesammelt und mit 20 ml 20% iger Natronlauge 1 Minute lang geschüttelt wurde. Zur besseren Schichttrennung wurden dann 50 ml Wasser zugesetzt und nochmals kurz geschüttelt. Nach dieser Extraktion befinden sich die Metalle quantitativ in wäßriger Phase. Diese wird nach Trennung in einem Titrierkolben gesammelt und Lösungsmittelreste durch Verkochen entfernt. Nach Erkalten der Lösung werden zur Entfernung des Jodids 20 ml conz. Salpetersäure zugegeben und zum Sieden erhitzt.

DISKUSSION DER ERGEBNISSE

Wie Abb. 1 zeigt, lassen sich die Elemente Indium, Thallium, Zinn, Antimon, Wismut, Tellur, Kupfer, Silber, Gold, Quecksilber, Cadmium, Palladium und Platin nach ein- oder höchstens dreimaliger Extraktion zu 98–100% in die organische Phase überführen. Blei, Arsen und Zink konnten trotz aller Variationsversuche, die Jodidkonzentration, Säuregrad und Extraktionsmittelgemisch betrafen, nur zu 80–90% extrahiert werden. Die Metalle Titan, Zirkonium, Hafnium, Vanadin, Niob und Molybdän waren nur zu einem geringen Prozentsatz, Aluminium, Gallium, Chrom, Mangan, Eisen, Kobalt, Nickel, Rhodium und Uran überhaupt nicht auszuschütteln.

Indium wurde bereits mit Diäthyläther, Methylisobutylketon und Cyclohexanon aus jodidhaltigen Lösungen als Tetrajodoindat $[InJ_4]^-$ extrahiert.[1,2,3] Geringere Mengen Kaliumjodid als in Tab. I angegeben, ergaben unvollständige Ergebnisse.

Thallium(I) läßt sich nur schlecht extrahieren, mit Tl^{3+} hingegen erhielten wir sehr gute Resultate. Dieses wird nach Specker und Pappert[4] entweder als Thalliumjodid oder im Überschuß von Jodid als Tetrajodothallat $[TlJ_4]^-$ vorliegend, mit Cyclohexanon und Tributylphosphat extrahiert.

Zinn. Bei Verteilungsversuchen von Sn^{2+} ergaben sich bedeutende Unterschiede je nach eingesetztem Lösungsmittel. Aus 0,5*M* kaliumjodidhaltiger- und 2*N* schwefelsaurer Lösung konnte Zinn nach dreimaliger Extraktion mit 1-Butoxy-2-propanol vollständig in das organische Solvens überführt werden. Auch 2-Äthyl-1-butanol und 4-Methyl-2-pentanol aus 4*N* schwefelsaurer Lösung extrahierten

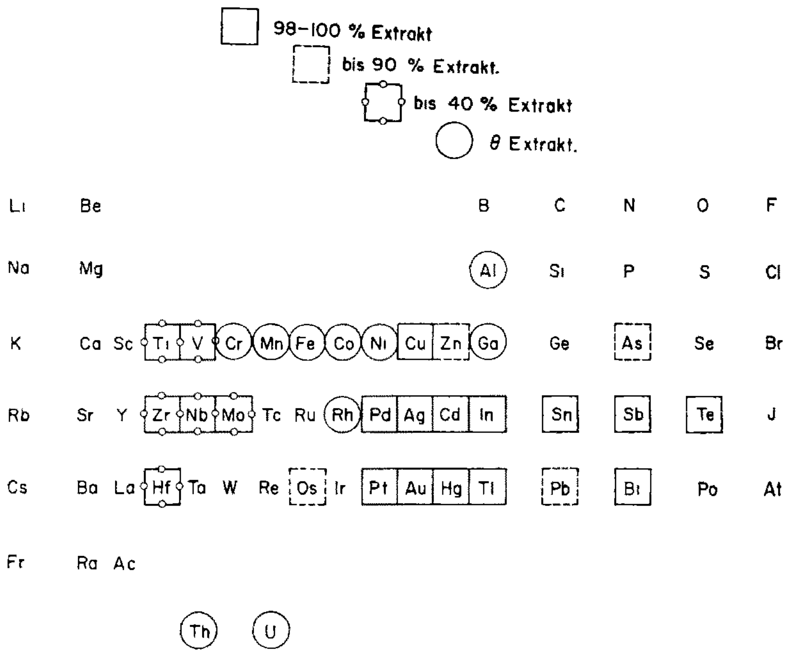

ABB. 1.—Extraktionsvermögen der Alkohole 2-Äthyl-1-butanol, 4-Methyl-2-pentanol und 1-Butoxy-2-propanol.

TABELLE I.—OPTIMALE SÄURE- UND JODIDKONZENTRATION FÜR EINE QUANTITATIVE EXTRAKTION DER ELEMENTE

Element	$[H_2SO_4]$, *N*	[KJ], *M*	Analytische Bestimmung
Indium	2	0,75	komplexometrisch,[13] oder Fällung als In $(OH)_3$[14]
Thallium	1	0,9	komplexometrisch[12]
Zinn	4	0,5	komplexometrisch[12]
Antimon	3	0,75	Fällung als Sulfid; Auflösung in HCl und jodometrische Bestimmung[14]
Wismut	7	0,75	komplexometrisch[12]
Tellur	1	0,75	Fällung als Sulfid[14]
Kupfer	8	0,75	komplexometrisch[12]
Silber	8	0,75	komplexometrisch[8,13]
Gold	1	0,75	komplexometrisch[8]
Cadmium	5	0,071	komplexometrisch[8,12]
Quecksilber	7	0,75	komplexometrisch[8,12]
Palladium	5	0,75	komplexometrisch[12]
Platin	6	0,75	photometrisch[15]

Die Extraktionen wurden einheitlich bei einer Konzentration von 20 mg Metall in 40 ml wäßriger Phase durchgeführt.

quantitativ. Aus 6*N* schwefelsaurer Lösung, nicht jedoch bei geringerer Säurekonzentration, fällt ein Niederschlag, vermutlich Zinn(II)-jodid aus.

Antimon läßt sich aus 0,25*M* jodidhaltiger und 1–6*N* schwefelsaurer Lösung mit Methylisobutylketon zu 99,4% extrahiern.[5]

Wismut liegt bei Jodidüberschuß als $[BiJ_4]^-$ vor und läßt sich mit einem Gemisch von 15% Tributylphosphat in Octan gut extrahieren.[6] Wir erzielten aus 6*N* salzsaurer Lösung gute Ergebnisse.

Tellur. Nach einmaliger Extraktion mit 20 ml Lösungsmittel, ohne Zusatz von Tetrachlorkohlenstoff, läßt sich Tellur als Pentajodotellurat $[TeJ_5]^-$ quantitativ extrahieren. Ein ähnliches Ergebnis war bei Verwendung von Methylisobutylketon festzustellen.[5]

Kupfer. Die Angaben von Specker und Hartkamp[6] sowie Specker und Pappert[4] über das Extraktionsverhalten von Elementen der ersten Nebengruppe zeigen auch mit unseren Ergebnissen gute Übereinstimmung. Kupfer wird als $[CuJ_2]^-$ oder in konzentrierteren Lösungen als $[Cu_2J_3]^-$ nach dreimaliger Schüttelung extrahiert.

Silber konnten wir aus schwach saurer Lösung nicht quantitativ in die organische Phase überführen, wie dies mit Cyclohexanon geschieht.[7] Das in wäßriger Phase

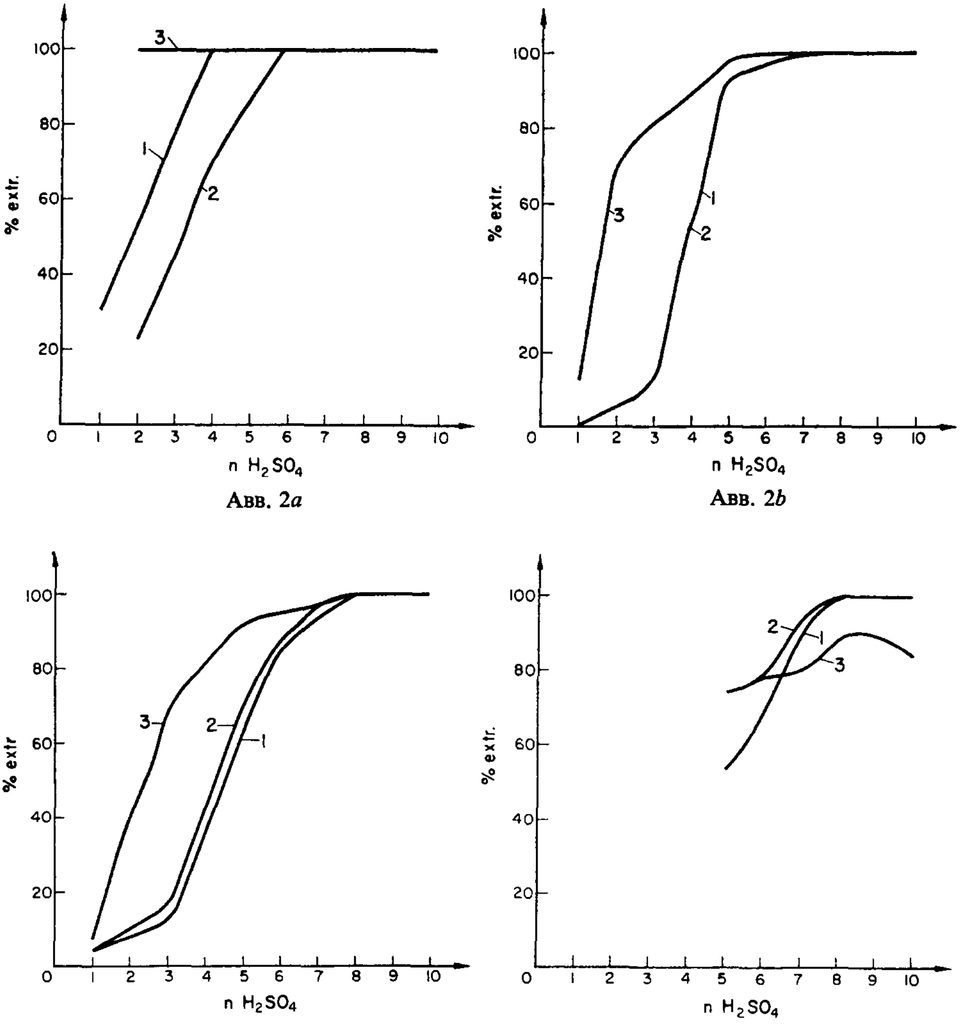

ABB. 2*a*

ABB. 2*b*

ABB. 2*c*

ABB. 2*d*

ABB. 2.—Abhängigkeit der Alkoholextraktion von der Säurenormalität: *1*: 2-Äthyl-1-butanol; *2*: 4-Methyl-2-pentanol; *3*: 1-Butoxy-2-propanol. (*a*)-Zinn; (*b*)—Wismut; (*c*)—Kupfer; (*d*)—Silber; (*e*)—Cadmium; (*f*)—Quecksilber; (*g*)—Platin.

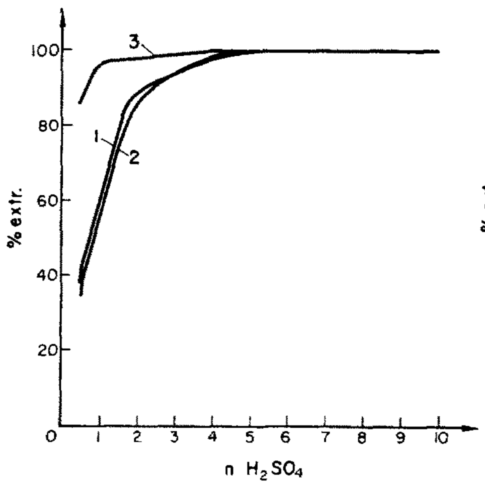

Abb. 2*e*

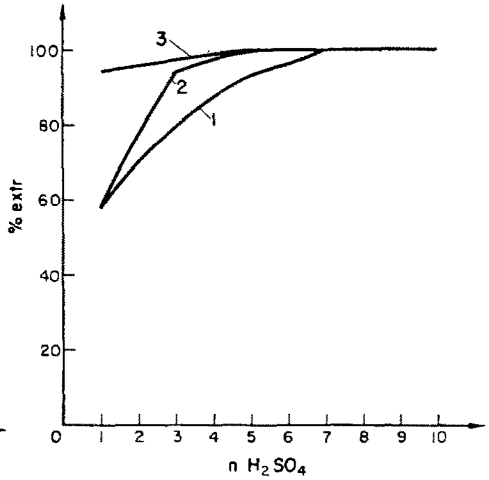

Abb. 2*f*

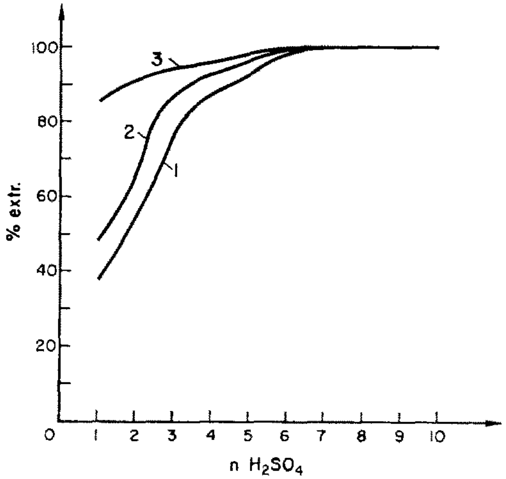

Abb. 2*g*

ausgefallene Silberjodid wird von den Alkoholen leicht gelöst und liegt in der organischen Phase als $[AgJ_2]^-$ oder $[Ag_2J_3]^-$ vor.

Gold. Das als $[AuJ_4]^-$-Komplex in der organischen Phase vorliegende Metall kann nicht mit Natronlauge reextrahiert werden, da es dabei als Kolloid ausfällt. Nach Abdampfen des Lösungsmittels wird der Rückstand mit 15 ml Salzsäure und 5 ml Salpetersäure versetzt. Man kocht kurz und nimmt mit Wasser auf, neutralisiert mit Natronlauge und bringt die Lösung in einen 250 ml-Meßkolben. Hieraus werden aliquote Anteile entnommen und mit 5 ml 0,1*M* Komplexon-III-Lösung, 1 ml 1*M* Kaliumcyanoniccolat-Lösung, 1 ml Ammoniak (25%ig) und SAS-SN als Indikator versetzt. Die Rücktitration erfolgt mit 0,1*M* Zinksulfatlösung.

Cadmium. Die Elemente der zweiten Nebengruppe sind mit verschiedenen Extraktionsmitteln eingehend untersucht und Angaben über die Zusammensetzung derjewe ils extrahierten Verbindung gemacht worden.[8,9,10] Wir konnten 100 mg

Cd^{2+} aus 0,071*M* Kaliumjodid- und 5*N* schwefelsaurer Lösung extrahieren. In diesem Fall liegt ein Verhältnis Cadmium : Jodid = 1 : 3 vor. Aber auch bei einem Verhältnis von 1 : 2 läßt sich Cadmium noch quantitativ extrahieren.

Quecksilber wird als Quecksilberjodid HgJ_2 oder als Komplex $[HgJ_3]^-$ extrahiert. Bei großem Überschuß an Jodid nimmt die Extrahierbarkeit wieder ab, da sich dann Tetrajodomercurat $[HgJ_4]^{2-}$ bildet.

Platinmetalle. Von diesen Elementen wurden Palladium(IV), Platin(IV), Rhodium(III) und Osmium(VIII) auf ihr Verteilungsverhalten untersucht. Palladium wird durch einmalige Extraktion mit Alkohol allein (ohne CCl_4) aus 0,75*M* Kaliumjodid- und 5*N* schwefelsaurer Lösung extrahiert. Ist der Alkohol mit Tetrachlorkohlenstoff "verdünnt", kann man das Metall durch dreimalige Extraktion bei gleicher Jodidkonzentration aus 3*N* schwefelsaurer Lösung in die organische Phase uberführen.

Unter gleichen Bedingungen wurden Verteilungsversuche am Platin ausgeführt. Das Extraktionsmaximum von 98% wurde in 6*N* schwefelsaurem Medium ermittelt. Eine weitere Erhöhung der Säure- und Jodidkonzentration ergab eine Erniedrigung des Verteilungskoeffizienten.

Bei Osmium ergaben sich Schwierigkeiten bei der nach der Extraktion folgenden analytischen Bestimmung, da Verbindungen dieses Metalls bekanntlich sehr flüchtig sind. Mit Bestimmtheit kann jedoch gesagt werden, daß Osmium zum Großteil, Rhodium dagegen überhaupt nicht extrahiert wird.

Bei Palladium und Platin wurde der Metallgehalt nach der Extraktion jeweils in beiden Phasen analysiert. Nach Zusatz von 5 ml conz. Salpetersäure zur Entfernung des Jodids mußten die Elemente mit 5 ml conz. Salzsäure wieder in Lösung gebracht werden.

Konduktometrische Extraktionstitration

Diese dient der Aufklärung der Zusammensetzung des extrahierten Metallkomplexes, wobei es notwendig ist, daß das zu extrahierende Kation gut meßbare Änderungen der Leifähigkeit in der organischen Phase hervorruft.

Am Beispiel des Quecksilber-(II)-nitrates, das schon mit Cyclohexanon als Extraktionsmittel untersucht wurde,[6] konnten wir die Zusammensetzung der Quecksilberjodidverbindungen, wie sie von den Alkoholen extrahiert werden, nachweisen. Aus den Knickpunkten der Leitfähigkeitskurven ist zu entnehmen, daß Quecksilber als HgJ_2 und $[HgJ_3]^-$ extrahiert wird. Quecksilber(II)-jodid hat nur eine geringe Leitfähkeit in der organischen Phase, erst bei weiterer Zugabe von Kaliumjodid ist ein steiler Anstieg der Leitfähigkeit zu beobachten, wobei sich das Quecksilber(II)-jodid zum Trijodomercurat umsetzt.

Die Untersuchungen wurden in einem 150-ml Meßzylinder ausgeführt. Zu 20 ml einer 7*N* schwefelsauren Lösung, die 0,77 mMol Quecksilber enthielt, werden 40 ml Alkohol zugesetzt. Dann wird portionsweise 0,1*N* Kaliumjodidlösung zugegeben. Nach jeder Zugabe wird durch kräftiges Durchmischen beider Phasen das Verteilungsgleichgewicht eingestellt und die Leitfähigkeit in der organischen Phase gemessen.

Trennungen

Cadmium-Zink Diese beiden Metalle konnten mit Cyclohexanon bzw. einem Gemisch von Cyclohexanon und Tetrahydrofuran aus jodidhaltigen, schwach

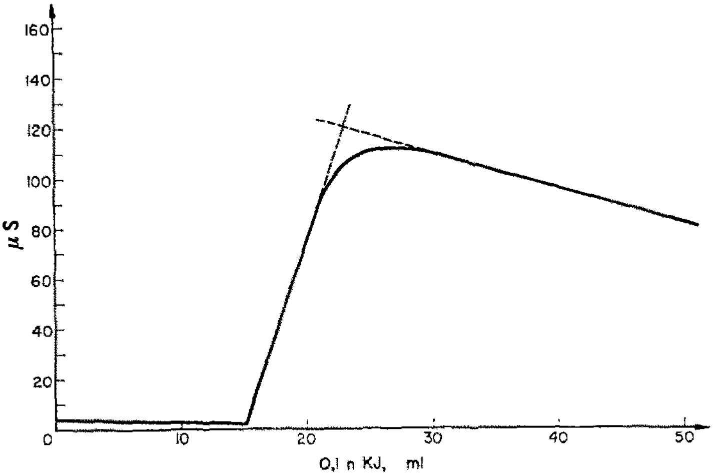

ABB. 3*a*

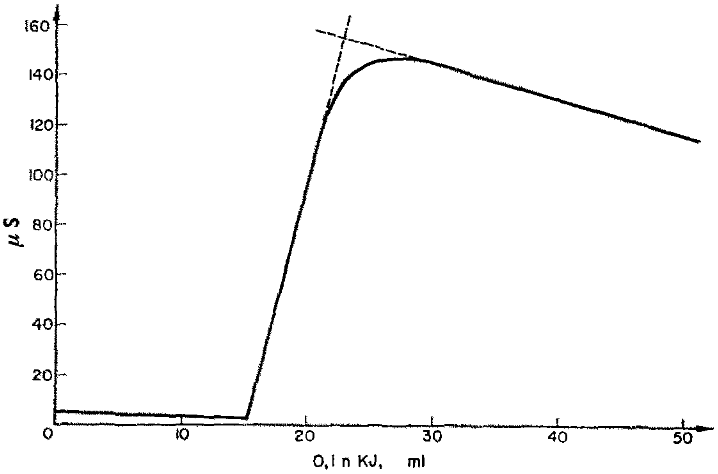

ABB. 3*b*

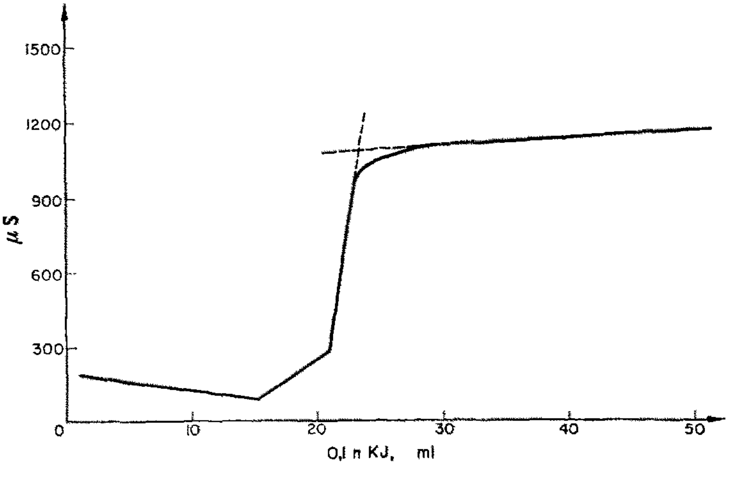

ABB. 3*c*

ABB. 3.—Konduktometrische Extraktionstitration von Quecksilber (II) mit (*a*)—2-Äthyl-1-butanol; (*b*)—4-Methyl-2-pentanol; (*c*)—1-Butoxy-2-propanol.

schwefelsauren bzw. ammoniakalischen Lösungen getrennt werden.[10] Auch Isoamylalkohol, Isobutylalkohol, n-Butylalkohol, Diäthyläther und Isoamylacetat aus schwach schwefelsaurer jodidhaltiger Lösung werden als Extraktionsmittel angegeben, wobei Cadmium zu 100%, aber auch ein hoher Prozentsatz (10–20%) Zink in die organische Phase übergeht.[11]

Eigene Versuche ergaben, daß mit 1-Butoxy-2-propanol aus 0,071*M* Kaliumjodid- und 5*N* schwefelsaurer Lösung nach dreimaliger Ausschüttelung 100% Cadmium und 5% Zink extrahiert wurde. Die Beobachtung, daß auch Zink in die organische Phase überführt wird, konnte mit 2-Äthyl-1-butanol und 4-Methyl-2-pentanol nicht gemacht werden, weshalb diese beiden Alkohole zur Trennung dieser beiden Metalle Verwendung fanden. Es war jedoch notwendig, den Konzentrationsbereich von Cadmium zu ermitteln, bei dem dieses Metall aus einer konstant gehaltenen jodid- und schwefelsäurehaltigen Lösung mit einem bestimmten Volumen Alkohol extrahiert wird.

TABELLE II.—EXTRAKTIONSFÄHIGKEIT DER ALKOHOLE GEGENÜBER CADMIUM BEI GLEICHER JODIDKONZENTRATION

Cadmium, *mg*		
	gefunden	
vorgelegt	wäßrige Phase	organische Phase
5	0	5
20	0	20
50	0	49,9
100	0	100,2
200	71,6	129,4

Die angegebenen Zahlen sind Mittelwerte aus fünf Bestimmungen mit 20 ml 2-Äthyl-1-butanol und 4-Methyl-2-pentanol gelöst in 25 ml Tetrachlorkohlenstoff.

Wie Tab. II zeigt, lassen sich 100 mg Cadmium noch quantitativ extrahieren. Bei weiterer Erhöhung der Metallkonzentration muß auch die Jodidkonzentration entsprechend gesteigert werden. Die Trennung des Cadmiums vom Zink ist vollständig und gut reproduzierbar, wie aus Tab. III zu ersehen ist.

TABELLE III.—2-ÄTHYL-1-BUTANOL UND 4-METHYL-2-PENTANOL ALS EXTRAKTIONSMITTEL

vorgelegt		gefunden, nach der Extraktion	
Cadmium, *mg*	Zink, *mg*	Cadmium (org.), *mg*	Zink (wäß.), *mg*
10,1	11,6	10,3	11,6
10,1	47,2	10,1	47,2
10,1	94,2	10,4	94,1
5	94,2	5	94,2
50,5	9,5	50	9,5
101	9,5	99,2	9,8

Das in der wäßrigen Phase befindliche Zink wurde komplexometrisch bestimmt.[12]

Um diese Ergebnisse auch *in praxi* an technischen Produkten, Hüttenerzeugnissen etc. zu überprüfen, haben wir einen Blei-Cadmium-Flugstaub und Blei-Cadmium-Rückstände der Firma Dr. L. C. Marquart, Beuel/Rhein untersucht. Die Ergebnisse sind in Tab. IV zu sehen.

TABELLE IV.—ANALYSENWERTE NACH DER EXTRAKTION MIT 2-ÄTHYL-1-BUTANOL UND 4-METHYL-2-PENTANOL

	Blei-Cadmium Flugstaub		Blei-Cadmium Rückstände	
	gegeben, %	gefunden, %	gegeben, %	gefunden, %
Zink	6,43	6,25	10,06	10,18
Blei	18,24	—	41,05	—
Kupfer	0,05	—	0,3	—
Cadmium	18,57	18,35	11,19	11,19
Arsen	0,24	—	1,6	—
Antimon	0,78	—	—	—
Silber	23 ppm	—	40 ppm	—
Schwefel	—	—	2,08	—
SiO_2	—	—	0,6	—

Die angegebene Fehlervarianz des Analysenattestes der Firma ist ±0,5%

Es wurde 1 g Substanz in conz. Salzsäure gelöst und auf dem Sandbad bis zur Trockene eingeengt, sodann mit 1*N* Schwefelsäure aufgenommen, um das Blei als Sulfat zu fällen, worauf filtriert und die Lösung in einem 100 ml-Meßkolben gesammelt wird; man füllt bis zur Marke mit Wasser auf und verwendet 20 ml dieser Lösung für die nachfolgende Extraktion.

Indium-Gallium. Wie Hartkamp und Specker[1,2] berichten, lassen sich die beiden Metalle aus jodidhältiger und mindestens 0,2*N* schwefelsaurer Lösung mit Cyclohexanon und mit Methylisobutylketon trennen.

Die optimalen Bedingungen für die Trennung fanden wir aus 0,75*M* kaliumjodidhaltiger und 2*N* schwefelsaurer Lösung, mit 2-Äthyl-1-butanol, 4-Methyl-2-pentanol und 1-Butoxy-2-propanol. In schwefelsaurer Lösung bei gleichbleibender Jodidkonzentration war Gallium in dem von uns untersuchten Bereich in keinem Fall in die organische Phase extrahiert worden.

Tabelle V gibt die Mittelwerte von 8 Bestimmungen für Indium und Gallium nach dreimaliger Extraktion wieder. Das in wäßriger Phase befindliche Gallium wurde entweder als Oxinat bestimmt, oder auch Galliumoxinat in heißer Salzsäure gelöst und bromatometrisch bestimmt.[5]

TABELLE V.—2-ÄTHYL-1-BUTANOL, 4-METHYL-2-PENTANOL UND 1-BUTOXY-2-PROPANOL ALS EXTRAKTIONSMITTEL

vorgelegt		gefunden nach der Extraktion	
Indium, *mg*	Gallium, *mg*	Indium (org.), *mg*	Gallium (wäß.), *mg*
19,23	18,4	19,23	18,12
98,75	18,67	99,4	18,51

Summary—A number of metal ions may be extracted quantitatively from iodide-containing sulphuric acid solutions by 2-ethyl-1-butanol, 4-methyl-2-propanol, or 1-butoxy-2-propanol, some partially extracted, and others not at all. There are many possibilities for separations, two of which—zinc-cadmium and indium-gallium—are described, and have been tested in technical products. The determination of the composition of the extracted metal complexes is described with reference to those of mercury, a conductimetric extraction titration being used.

Résumé—Un certain nimbre d'ions métalliques peuvent être extraits quantitativement, quelques-uns partiellement et d'autres pas du tout à partir de solutions d'acide sulfurique contenant de l'iodure au moyen de 2-éthyl 1-butanol, 4-méthyl 2-propanol ou 1-butoxy 2-propanol. Il y a de nombreuses possibilités pour les séparations dont deux: zinc–cadmium et indium–gallium sont décrites et ont été essayées sur des produits techniques. On décrit la détermination de la composition des complexes métalliques extraits par rapport à ceux du mercure, en utilisant un titrage conductimétrique par extraction.

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SHORT COMMUNICATIONS

Spectrophotometric determination of niobium(V) with n-propyl 3,4,5-trihydroxybenzoate

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MANY attempts have been made to determine niobium spectrophotometrically,[1-12] but none avoid direct interference by such elements as platinum metals, nickel, copper, iron, hafnium, zirconium, tantalum, and manganese, which are likely to be present in niobium alloys. This paper describes the spectrophotometric determination of niobium in the presence of the commonly interfering elements, with n-propyl 3,4,5-trihydroxybenzoate (PTB).

EXPERIMENTAL

Reagents

All reagents and chemicals were analytical grade.

PTB solutions. A 0·1*M* solution was prepared by dissolving 21·2 g of reagent in 200 ml of acetone and diluting, with constant stirring, to one litre with water. Lower concentrations were prepared by proper dilution with 1:4 acetone–water mixture. These colourless solutions were stable for at least one week.

PTB solutions (0·1*M*) in t-pentanol or in isobutanol were colourless, and stable for at least two weeks.

Metal ions. An $8\cdot0 \times 10^{-3}M$ stock solution of niobium was obtained by fusing in a silica crucible the calculated quantity of niobium pentoxide and 14 g of potassium pyrosulphate until a clear colourless liquid was formed. To the cooled melt 20 ml of 20% tartaric acid solution and 0·5 ml of concentrated sulphuric acid were added and the mixture was brought to boiling. Unbroken bits of melt were disintegrated with a stout platinum rod. The resulting solution was diluted to 1 litre with 2% tartaric acid solution. Blank solutions were similarly prepared but without niobium pentoxide.

Phosphate buffer. A mixture of 250·0 ml of 0·2*M* sodium dihydrogen phosphate and 37·0 ml of 0·2*M* sodium hydroxide was diluted to 1 litre with water, adjusted to pH 6·1 and stored in polythene bottles.

Procedure

An aliquot of the neutralized niobium solution, containing 0–100 μg of Nb, is treated in a small Kjeldahl flask with 10 ml of pH 6·1 phosphate buffer solution and 5 ml of $10^{-3}M$ PTB in acetone–water, and gently boiled for 2 mins. Two methods are then available.

A. The cooled solution is quantitatively transferred to a 25-ml volumetric flask, diluted to the mark with water and mixed, and the absorbance of the solution is measured at 333 nm against a reagent blank prepared similarly.

B. The cooled solution is placed in a separating-funnel, treated with 1 ml of 1*M* sodium chloride, and extracted successively with three 5-ml portions of $10^{-3}M$ PTB in t-pentanol. The combined extract is filtered, the filter paper is washed with 5 ml of the solvent and the volume is made up to 25 ml with t-pentanol. The absorbance is measured at 333 nm against a blank similarly prepared.

Procedure for alloys

A 0·1-g sample of the alloy is dissolved in 20 ml of 1:1 concentrated hydrochloric and nitric acids. The solution is evaporated to dryness and the residue is fused in a silica crucible with 2 g of potassium pyrosulphate. The cooled melt is dissolved in 20 ml of 20% tartaric acid solution containing a few drops of concentrated sulphuric acid. The resulting solution is diluted with water to 100 ml, and an aliquot that contains up to 100 μg of Nb is treated according to the recommended procedure.

RESULTS AND DISCUSSION

Conditions

Preliminary experiments showed that when a slightly acid solution, about pH 6·1, of niobium in tartrate solution was treated with PTB dissolved in acetone–water mixture a bright yellow to deep orange colour appeared, depending on the concentrations of the metal and ligand. The coloured species reached maximum intensity on boiling for 2 min and was stable in diffused light for at least three weeks. Among the common oxygen-containing organic solvents, t-pentanol and isobutanol were the most efficient extractants.

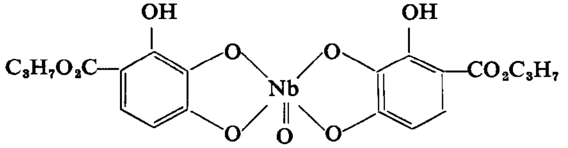
The niobium-PTB complex had a constant λ_{max} between pH 5·4 and 6·3 with a constant molar absorptivity at 333 nm over the pH range 5·5–6·5. A minimum 3:1 ligand:metal concentration ratio was needed in acetone–water medium for full colour development, and an 8:1 ratio for the reaction with PTB in either isobutanol or t-pentanol; both solvents will extract the complex. The absorbance was higher if the metal ion solution was buffered to pH 6·1 before addition of the reagent.

To find the temperature conditions for maximum absorbance, each solution was brought to the required temperature (Table I), kept there for 2 min, then cooled to 20°. During heating the solution became pale yellow, and intensified in colour on cooling.

TABLE I—EFFECT OF TEMPERATURE ON ABSORBANCE OF COMPLEX

Temp., °*C*	Absorbance	Temp., °*C*	Absorbance	Temp., °*C*	Absorbance
20	0·40	50	0·42	80	0·45
30	0·40	60	0·44	90	0·45
40	0·42	70	0·45	100	0·48

Beer's law was valid over the niobium concentration range of 0–100 μg/ml for either acetone–water or t-pentanol media, but the molar absorptivity is lower in the latter. Two methods were used to establish the composition of the Nb–PTB complex in solution, the continuous variations[13] and the mole-ratio method.[14–16] The results showed that an ML_2 complex is formed. The stability constant was evaluated from the results [log $K = 10{\cdot}00$ (continuous variations[14]); log $K = 9{\cdot}50$ (mole-ratio[13]); 10 results each]. The structure of the chelate was tentatively proposed as:



Electrophoresis and adsorption of the complex on the anion-exchange resin Amberlite IR-45(OH) showed the anionic nature of the complex. No explanation is offered for the solubility of the complex in t-pentanol and isobutanol.

Precision and accuracy

To find the repeatability of the procedure devised, 50 μg of niobium in pure solution were determined 11 times in acetone–water and t-pentanol media; the mean absorbances were 0·48 and 0·45 and the coefficients of variation for a single absorbance measurement were 2·3% and 3% respectively. Table II indicates the results (average of three) of determination of niobium in synthetic sample solutions which contained the commonly interfering ions. Analysis of an Alcomax IV sample (Al 8·0%, Ni, 13·5%, Co 24·0%, Cu 3·0%, Fe, 48·7%, Nb 2·8%) gave 2·65% Nb (5 results, relative standard deviation 1%).

TABLE II—INTERFERENCES

Metal added, μg							Nb, μg	
Al	Co	Cr	Cu	Fe	Ni	Ta	Added	Found
200	200		200			500	50·0	48·2
	200	200		500			100·0	97·5
		500			500		100·0	98·2
150	500		150		300		50·0	47·8
		300		200		300	50·0	48·5

Effect of foreign ions

Measurements of the absorbances of the coloured species developed from 50-μg of niobium in the presence of 1-mg amounts of Al, Co(II), Cu(II), Fe(III), Ta, Ba, Ca, Li, Na, Rh(III), Ir(IV), Os(IV), Ni, Cr(III), Au(III), K, Zn, Re(VII), Ag, Hg, Pb, Hf and Zr, resulted in ±3·8% relative error. The error caused by the presence of 1-mg amounts of the following ions are given in parentheses: U(VI) (+52%), Sn(II) (+15%), Mo(VI) (+50%), Ti(III) (+15%), Pt(II) or (IV) (+20%) and Au(III) (+18%).

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Summary—The use of n-propyl 3,4,5-trihydroxybenzoate (PTB) for the spectrophotometric determination of niobium is investigated. PTB yields a yellowish-orange ML_2 chelate with Nb(V) at pH 6·1. The formation constant at pH 6·1 is about 10^{10}. Beer's law is obeyed over the range 0–100 μg of Nb per ml.

Zusammenfassung—Die Verwendung von n-Propyl-3,4,5-trihydroxybenzoat (PTB) zur spektrophotometrischen Bestimmung von Niob wird untersucht. PTB bildet bei pH 6,1 mit Niob(V) ein gelborange gefärbtes ML_2-Chelat. Die Bildungskonstante bei pH 6,1 beträgt etwa 10^{10}. Das Beersche Gesetz gilt im Bereich 0–100 μg pro ml.

Résumé—On étudie l'emploi du 3,4,5-trihydroxybenzoate de *n*-propyle (PTB) pour le dosage spectrophotométrique du niobium. Le PTB donne un chélate orangé-jaunâtre ML_2 avec Nb(V) à pH 6,1. La constante de formation à pH 6,1 est d'environ 10^{10}. La loi de Beer est suivie dans le domaine 0–100 μg de Nb par ml.

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Determination of gadolinium in sodium borate glasses

(*Received* 24 *April* 1969. *Accepted* 29 *May* 1969)

INCREASING use of rare-earth doped glasses[1] as lasers has made analytical determination of their composition a matter of urgency. Likewise the increasing use of inorganic glasses as matrices for trapped radicals and ions in unusual oxidation states[2] necessitates development of a non-destructive analytical method for the determination of impurities. Gadolinium(III) introduced into inorganic crystals exhibits ultraviolet fluorescence under short wavelength excitation.[3] Stimulated emission by

Effect of foreign ions

Measurements of the absorbances of the coloured species developed from 50-μg of niobium in the presence of 1-mg amounts of Al, Co(II), Cu(II), Fe(III), Ta, Ba, Ca, Li, Na, Rh(III), Ir(IV), Os(IV), Ni, Cr(III), Au(III), K, Zn, Re(VII), Ag, Hg, Pb, Hf and Zr, resulted in $\pm 3{\cdot}8\%$ relative error. The error caused by the presence of 1-mg amounts of the following ions are given in parentheses: U(VI) (+52%), Sn(II) (+15%), Mo(VI) (+50%), Ti(III) (+15%), Pt(II) or (IV) (+20%) and Au(III) (+18%).

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Summary—The use of n-propyl 3,4,5-trihydroxybenzoate (PTB) for the spectrophotometric determination of niobium is investigated. PTB yields a yellowish-orange ML$_2$ chelate with Nb(V) at pH 6·1. The formation constant at pH 6·1 is about 10^{10}. Beer's law is obeyed over the range 0–100 μg of Nb per ml.

Zusammenfassung—Die Verwendung von n-Propyl-3,4,5-trihydroxybenzoat (PTB) zur spektrophotometrischen Bestimmung von Niob wird untersucht. PTB bildet bei pH 6,1 mit Niob(V) ein gelborange gefärbtes ML$_2$-Chelat. Die Bildungskonstante bei pH 6,1 beträgt etwa 10^{10}. Das Beersche Gesetz gilt im Bereich 0–100 μg pro ml.

Résumé—On étudie l'emploi du 3,4,5-trihydroxybenzoate de *n*-propyle (PTB) pour le dosage spectrophotométrique du niobium. Le PTB donne un chélate orangé-jaunâtre ML$_2$ avec Nb(V) à pH 6,1. La constante de formation à pH 6,1 est d'environ 10^{10}. La loi de Beer est suivie dans le domaine 0–100 μg de Nb par ml.

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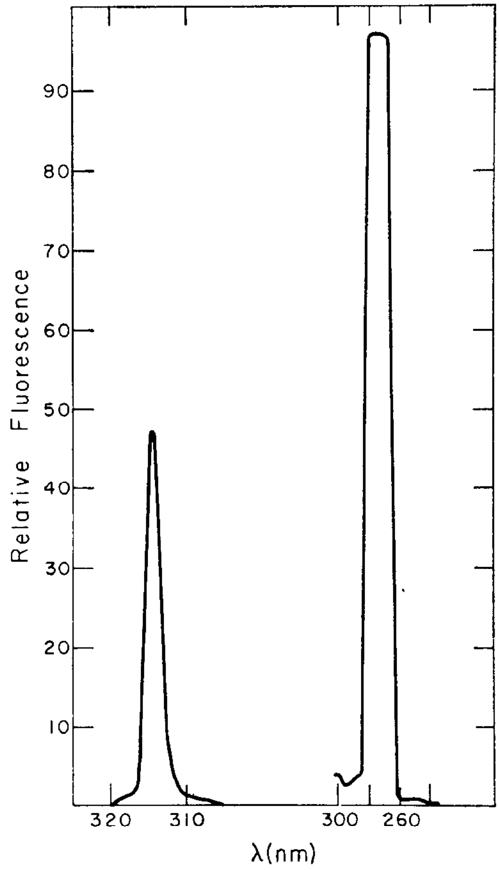

FIG. 1.—Fluorescence spectrum of a glass containing 1% w/w gadolinium.
Left—emission (excitation 273 nm)
Right—excitation (emission 312 nm)

TABLE I.—RELATIVE FLUORESCENCE OF GADOLINIUM IN GLASSES CONTAINING GADOLINIUM ONLY

Gd^{3+}, *ppm*	Relative fluorescence, I_0	Gd^{3+}, *ppm*	Relative fluorescence, I_0
10	5	5000	2600
50	24	6500	3350
100	48	8000	4500
500	250	10000	4800
1000	500	13000	6400
2000	1200	20000	10000
4000	2250		

gadolinium(III) in lithium magnesium aluminium silicate glass was measured by Gandy and Ginther,[4] who observed fluorescence at 312·5 nm. Dependence of fluorescence intensity on concentration was used in this work for the quantitative determination of gadolinium.

EXPERIMENTAL

Apparatus

The spectrofluorimeter used for the measurement of excitation and fluorescence emission spectra was constructed in this laboratory and will be described in detail elsewhere.[5] Briefly, it consists of a

500-W xenon arc lamp (Mazda), interchangeable with a medium pressure 100-W mercury lamp, an excitation monochromator (Bausch & Lomb, 250-mm focal length), the sample compartment, an analysing monochromator (Bausch & Lomb, 500-mm focal length), an EMI 9558 Q/B photomultiplier connected through a 16-ohm resistor to an EIL Vibron electrometer, and a Kipp & Zonen recorder. Slow drifts in intensity were corrected by frequent measurement of a reference glass. Fast fluctuations were filtered out. The fluorescence was viewed from the front (illuminated) side of the glass at an angle of 35°. The photomultiplier was cooled to −20° for all measurements.

Reagents

Sodium tetraborate and boric acid, 99·5% purity. Gadolinium chloride, 99·9% purity.

Preparation of glasses

Dry gadolinium chloride, was mixed with borax and boric acid (in which were taken ratio 123:62 w/w) in plastic vials containing glass balls, by means of an electric vibrator. The mixture contained gadolinium in concentrations ranging from 10 to 20000 ppm. It was established that homogeneous mixtures were obtained after 10 min. These mixtures were found to melt at temperatures lower than 1000°, but clear transparent solutions resulted only after heating at 1100° for at least 15 min. The melts were made in platinum crucibles. Drops of the hot melt were allowed to fall directly onto a clean white glazed ceramic surface. The drop was placed inside a ring 1-mm thick and pressed with a second ceramic tile so as to obtain glasses of constant 1-mm thickness. The glasses were inserted into a glass holder with a circular opening of 12-mm diameter and their excitation and fluorescence spectra were measured at room temperature.

RESULTS AND DISCUSSION

The excitation spectrum for fluorescence measured at 312 nm and the emission spectrum for 273 nm excitation are shown in Fig. 1. The 312 nm emission results from the transition from the $^6P_{7/2}$ state to the $^8S_{7/2}$ ground state of the $4f^7$ electronic configuration of Gd^{3+}. The excitation at 273 nm is due to the transition from the ground state to the levels in the ^6I multiplet.

Table I presents relative fluorescence at 312 nm on excitation at 273 nm as a function of gadolinium concentration in glasses in which the only rare earth was gadolinium. Linear dependence was observed in the total range from 10–20000 ppm. The conditions of measurement were excitation 273 nm; emission 312 mμ; voltage applied to photomultiplier 1250 V; slitwidths—excitation, entrance and exit both 0·6 mm; emission, entrance 1·0 mm, exit 0·5 mm.

TABLE II.—RELATIVE FLUORESCENCE OF GADOLINIUM AS A FUNCTION OF CONCENTRATION IN GLASS CONTAINING EQUAL AMOUNTS OF Gd AND Sm

Gd^{3+}, *ppm*	Relative fluorescence, I	I_0/I
500	180	1·38
1000	390	1·28
2000	720	1·66
4000	1440	1·56
5000	1920	1·35
6500	1980	1·69
10000	2000	2·40
20000	2000	5·0

In order to test the effect of the presence of another rare earth, the fluorescence of gadolinium was measured in glasses with equal concentrations of samarium. The results are presented in Table II, conditions of measurement being as above. At concentrations up to 6500 ppm, the gadolinium fluorescence decreased by a factor of 2/3, and dependence was linear. At higher concentrations of samarium and gadolinium, quenching of fluorescence was observed.

It is therefore assumed that a non-radiative energy transfer takes place from gadolinium to samarium. Low concentrations up to 6000 ppm provide the best conditions for the analytical determination.

Thanks are due to the National Bureau of Standards, Washington, D.C., for grant No. NBS(G)-83, under which this work was performed.

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Summary—A method for the determination of gadolinium in sodium borate glasses is described which utilizes the 312-nm fluorescence of gadolinium under 273-nm excitation. A linear dependence of fluorescence on concentration is found for the concentration range 10–20000 ppm. Quenching of gadolinium fluorescence by samarium is examined.

Zusammenfassung—Eine Methode zur Bestimmung von Gadolinium in Natrium Borat Gläsern, unter Benutzung der 312 nm Fluoreszenz des Gadoliniums mittels 273 nm Erregung, wird beschrieben. Eine lineare Abhängigkeit der Fluoreszenz von der Konzentration im Bereich von 10–20000 ppm wurde gefunden. Quenching der Gadolinium Fluoreszenz durch Samarium wurde untersucht.

Résumé—On décrit une méthode pour la détermination du gadolinium dans les verres au borate de sodium, qui utilise la fluorescence 312 nm du gadolinium sous l'excitation 273 nm. On trouve une relation linéaire entre la fluorescence et la concentration pour le domaine de concentrations 10–20000 ppm. On examine l'extinction de la fluorescence du gadolinium par le samarium.

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Polarographic determination of impurities in high-purity phosphorus

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Several methods have been developed for the determination of trace impurities in high-purity phosphorus used in the semiconductor industry.[1,2] These include spectrophotometric, fluorimetric, spectrographic, voltammetric and radioactivation techniques. However, no simple method has been reported for determining copper, lead and cadmium at the ppM (parts per milliard) level. This paper describes the application of square-wave (S.W.) and radio-frequency (R.F.) polarography in a phosphoric acid base electrolyte to the simultaneous determination of these elements down to 0·1 ppm. For cadmium, higher sensitivity is achieved by the use of cation-exchange separation before polarographic determination in a potassium sulphate base electrolyte.

EXPERIMENTAL

Apparatus

Polarograph. A Yanaco PF-501 R.F./S.W. polarograph (Yanagimoto Mfg. Co., Kyoto, Japan) was used in this study. The instrumental parameters were as follows—S.W. frequency: 200 Hz; amplitude: 20 mV; time constant: 52; amplifier sensitivity: 1/2; recorder sensitivity: 0·02 or

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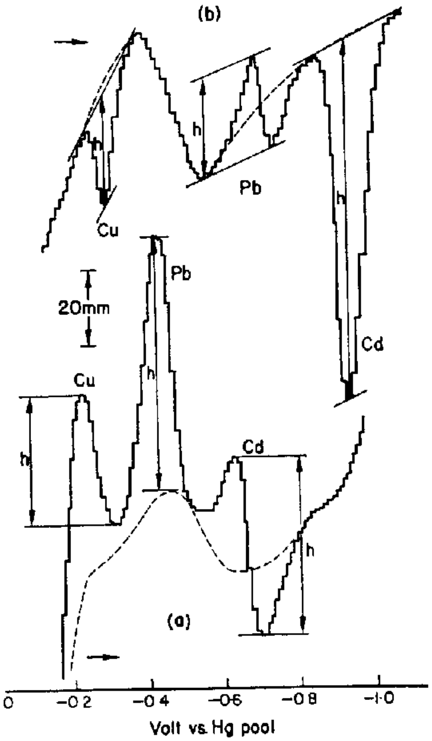

FIG. 1.—R.F. polarograms
(*a*) $3M$ H_3PO_4–$0{\cdot}2M$ KCl containing 0·05 μg of Cu, 0·16 μg of Pb and 0·08 μg of Cd/ml (7·5 × $10^{-7}M$ each, Cu, Pb and Cd).
(*b*) $0{\cdot}4M$ K_2SO_4 containing 0·05 μg each of Cu, Pb and Cd/ml (*ca.* 7·5 × $10^{-7}M$ Cu, 2·5 × $10^{-7}M$ Pb and 4·5 × $10^{-7}M$ Cd).
Broken lines: base electrolyte alone. *h*: peak height.

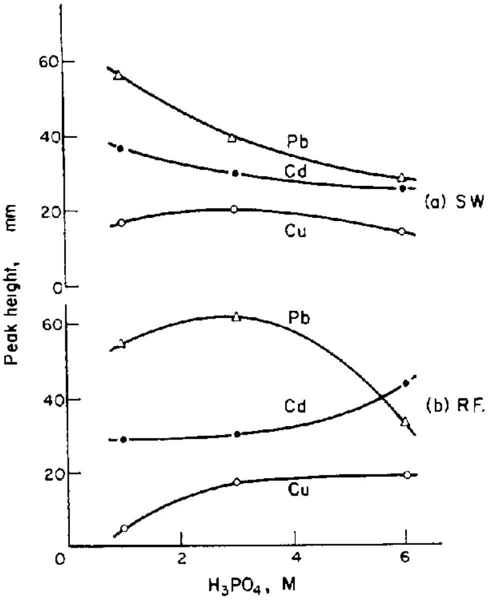

FIG. 2.—Effect of phosphoric acid concentration on peak-height in $0{\cdot}2M$ KCl. (0·03 μg of Cu, 0·1 μg of Pb and 0·06 μg of Cd/ml)

0·04 (for the S.W. polarography); and R.F. frequency: 455 kHz; S.W. modulation: 200 Hz; amplitude: 4 V; amplifier sensitivity: 1/1; recorder sensitivity: 0·02 or 0·04 (for the R.F. polarography). All measurements were carried out at 20 or 25 ± 0·5° after deaeration with nitrogen for 15 min.

Cation-exchange column. Columns were prepared from Amberlite IR 120 B strongly acidic cation-exchange resin, 30–50 mesh. After careful conditioning, the resin was converted into the hydrogen form with 3*M* hydrochloric acid and washed free from acid with water. The flow-rate was adjusted to *ca.* 1 ml/min.

Reagents

Water was purified by ion-exchange followed by repeated distillation. *Nitric acid* was purified by distillation; *ca.* 5 ppM of copper and 0·6 ppM of lead were found after purification. *Potassium sulphate*, 0·5*M*, was purified by electrolysis with a mercury cathode.

Potassium chloride. Potassium chloride solution (100 ml, 3*M*) was shaken with two lots of 4 ml of 0·1% sodium diethyldithiocarbamate solution and 20 ml of chloroform, and then with 20 ml of chloroform. The aqueous phase was evaporated to dryness in a quartz beaker and heated to *ca.* 400° to destroy organic matter.

Phosphoric acid 6M. Phosphoric acid (90 ml, 6*M*) was poured onto a 14-mm diam. × 150-mm cation-exchange column. The first 10-ml fraction of the effluent was discarded, and the following 80-ml fraction was collected for use. The breakthrough capacity of the column was *ca.* 100 ml.

All the reagents used were of reagent grade. A quartz condenser was used in the distillations.

Procedure

Dissolution of sample. Elementary phosphorus was converted into phosphoric acid as follows. Place a weighed sample (0·5–2 g) in a 50-ml quartz tall beaker, add 5 ml of water and then 10 ml of nitric acid per g of sample, in small portions, and heat gently until the sample has dissolved. Continue heating to evaporate the solution to 1–2 ml. Add 10 ml of water, evaporate to 1–2 ml, and repeat this operation twice more. To minimize airborne contamination, carry out the dissolution and evaporation inside a small chamber, which is continuously flushed with purified nitrogen.

Cation-exchange separation of copper, lead, and cadmium in phosphoric acid. Pour a sample (5–20 ml of 3*M* phosphoric acid) onto a 12-mm diam. × 60-mm cation-exchange column, and wash the column with 20 ml of water. Pass 30 ml of 4*M* hydrochloric acid through the column, and collect the effluent in a 50-ml silica dish. Evaporate the effluent to dryness.

RESULTS AND DISCUSSION

Because copper(II) gives low peak-heights in S.W. and R.F. polarograms in 3*M* or 6*M* phosphoric acid, a small amount of potassium chloride was added (0·2*M*). A typical R.F. polarogram is shown in Fig. 1(*a*). The effect of phosphoric acid concentration on peak-height is summarized in Fig. 2.

TABLE I.—DETERMINATION OF IMPURITIES IN 99·9999% RED PHOSPHORUS

Expt. no.	Sample taken, *g*	Base electrolytes	Polarography	Found, *ppm*		
				Cu*	Pb	Cd
1	0·91	3*M* H_3PO_4–0·2*M* KCl	S.W.	0·1	0·1	Not detected
			R.F.	0·1	0·1	Not detected
2	1·12	3*M* H_3PO_4–0·2*M* KCl	S.W.	0·1	0·1	Not detected
			R.F.	0·1	0·1	Not detected
3	2·06	6*M* H_3PO_4–0·2*M* KCl	R.F.	0·1$_2$	—	—
4	0·59	0·4*M* K_2SO_4, 2·5 ml	R.F.	—	—	0·01
5	0·90	0·4*M* K_2SO_4, 2·5 ml	R.F.	—	—	0·00$_6$

* Blank values, 0·1–0·2 μg, were subtracted. No correction was required for the other two elements.

As reproducibility of R.F. polarograms of lead and cadmium in 6*M* phosphoric acid–0·2*M* potassium chloride was poor, 3*M* phosphoric acid–0·2*M* potassium chloride was chosen as the base electrolyte for the simultaneous determination of the three elements.

The lower limits of determination in 3*M* phosphoric acid–0·2*M* potassium chloride were (in μg/ml): 0·005 (S.W.) 0·01 (R.F.) for Cu, 0·01 (S.W., R.F.) for Pb, and 0·01 (S.W., R.F.) for Cd. The calibration curves (peak-height *vs.* concentration) were linear up to at least 0·1 μg/ml, with a maximum deviation of *ca.* 5% at 0·05 μg/ml. All of them passed through the origin except for R.F. polarograms of copper. However, in 6*M* phosphoric acid–0·2*M* potassium chloride, R.F. polarographic peak heights were proportional to copper concentrations over the range 0·005–0·1 μg/ml.

In S.W. and R.F. techniques in 3*M* phosphoric acid–0·2*M* potassium chloride, the following elements may be present in at least the amounts (μg/ml) indicated without causing appreciable error: Pb, 10; Cd, 5; As(III), 0·7; Fe(III), 5; Sb(III), 0·04 (in the determination of 0·03 μg of Cu/ml); Cu, 6; Cd, 5; As(III), 0·4; Fe(III), 2·5; Sb(III), 0·05 (in the determination of 0·1 μg of Pb/ml): Cu, 3; Pb, 1; As(III), 0·7; Fe(III), 2·5; Sb(III), 0·05 (in the determination of 0·05 μg of Cd/ml). Also, nitric acid more dilute than 0·1*M* does not interfere with the determination.

A sample of high-purity red phosphorus was analysed by these techniques with the results shown in Table I (Expts. 1–3). Phosphorus, *ca.* 1 or 2 g, was converted into *ca.* 10 ml of 3*M* or 6*M* phosphoric acid as described above. As little as 0·1 ppm of these elements can be determined simultaneously within 5–6 hr.

In order to extend the lower limits of determination, cation-exchange separation was combined with the polarographic determination in a small volume of 0·4*M* potassium sulphate. A typical R.F. polarogram in this base electrolyte is shown in Fig. 1(*b*). The lower limits of determination in 0·4*M* potassium sulphate were (in μg/ml): 0·002 (S.W.) 0·01 (R.F.) for Cu, 0·01 (S.W., R.F.) for Pb, and 0·005 (S.W.) 0·002 (R.F.) for Cd. In both S.W. and R.F. techniques, peak-heights of copper, lead, and cadmium were proportional to concentrations of the elements up to at least 0·1 μg/ml, with a maximum deviation of *ca.* 5% at 0·05 μg/ml.

In the cation-exchange separation described above, the breakthrough capacity of the column for the desired impurity elements was *ca.* 50 ml in 3*M* phosphoric acid, and these elements were completely eluted with *ca.* 25 ml of 4*M* hydrochloric acid. Copper and lead, 0·1–1 μg each, and cadmium, 0·01–1 μg, added to 10–20 ml of purified 3*M* phosphoric acid, were almost completely recovered. Because of the relatively large contamination of copper and lead, this method was successfully applied only to the determination of cadmium in high-purity phosphorus. The results are given in Table I (Expts. 4 and 5). Since cadmium contamination is negligible, less than 5 ppM of cadmium in phosphorus can be determined by this technique. The time required for a determination is approximately 8 hr.

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Summary—Square-wave and radio-frequency polarographic techniques in phosphoric acid–potassium chloride media are applied to the simultaneous determination of copper, lead and cadmium in high-purity red phosphorus down to a level of 0·1 ppm. In addition *ca.* 0·01 ppm of cadmium is determined by R.F. polarography in potassium sulphate base electrolyte after cation-exchange separation.

Zusammenfassung—Square-wave- und Radiofrequenzpolarographie in Phosphorsäure-Kaliumchlorid-Medien werden zur gleichzeitigen Bestimmung von Kupfer, Blei und Cadmium in hochreinem rotem Phosphor bis herunter zum Bereich 0,1 ppm verwendet. Ferner läßt sich etwa 0,01 ppm Cadmium nach Kationenaustausch-Abtrennung in Kaliumsulfat-Trägerelektrolyt durch Radiofrequenzpolarographie bestimmen.

Résumé—On applique les techniques polarographiques d'onde carrée et de radio-fréquence en milieux acide phosphorique-chlorure de potassium à la détermination simultanée des cuivre, plomb et cadmium dans le phosphore rouge de haute pureté jusqu'à des teneurs aussi faibles que 0,1 ppm. De plus, on détermine environ 0,01 ppm de cadmium par la polarographie R.F. en électrolyte de base sulfate de potassium après séparation par échange cationique.

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Submicro determination of cobalt, manganese or nickel in organometallic compounds

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Little attention has been devoted to the determination of metals in organometallic compounds on the submicro scale. A method for the determination of iron[1] appears to be the only one studied so far; in this method, the organic material was digested in a sealed tube with a nitric/sulphuric acid mixture and the iron determined spectrophotometrically.

It has subsequently been shown[2,3] that a more rapid mineralization procedure, with a perchloric/sulphuric acid mixture in an open tube, is effective in the submicro determination of phosphorus. Some photometric EDTA titration methods for microgram quantities of various metals have recently been described[4] and it was suggested that these might be applicable to the analysis of organometallic compounds.

These techniques have been examined for the analysis of compounds containing cobalt, manganese or nickel.

EXPERIMENTAL

Photometric titration

Standard solutions, which had been treated to simulate the residues from digestion of organometallic materials, gave variable, high results when titrated by the methods described previously,[4] probably because titratable impurities were introduced during the processing of the solutions. Some improvement might be achieved by the use of purified reagents, masking agents or more selective titrations. In refining the titrimetric methods, however, much of their simplicity might be lost and it was considered better to seek suitable spectrophotometric methods; titrimetry, including the use of the mercury electrode,[5] would only be reconsidered if spectrophotometry proved unsuitable.

Spectrophotometric methods

Cobalt. Nitroso-R-salt[6] was found to be a satisfactory reagent.

Manganese. Attempts to determine manganese by the catalytic method of Almássy and Dezsö[7] failed to achieve the desired repeatability. Satisfactory precision was obtained by oxidation to permanganate with ammonium hexanitratocerate.[8] Owing to the poor sensitivity of this method, however, the largest final volume that could be used was 10 ml, which allows barely sufficient volume for washing digestion vessels. The formaldoxime method proposed by Marczenko[9] gave a precision as good as the permanganate method and, because of its higher sensitivity, was preferred.

Nickel. Sodium diethyldithiocarbamate[10] was briefly examined for nickel determination, but results were very erratic. The dimethylglyoxime method proposed by Yamasaki and Matsumoto[11] had been used previously with some success; it was found that the higher pH recommended by Blackwell *et al.*[12] was preferable and consistency of results was improved by an alteration in the order of addition of the reagents.

Mineralization procedures

Portions of aqueous solutions of metal salts containing 4–20 μg of metal were evaporated in digestion tubes and treated by the open- and sealed-tube mineralization procedures. Excellent recoveries were obtained with both for all three metals tried, the spectrophotometric finishes being used. However, when the open-tube digestion was applied to organometallic compounds, consistent but slightly low recoveries were obtained from cobalt and nickel compounds and variable, high results from a manganese compound. Variations in the amounts of acids and time and temperature of heating did not consistently improve results, so the lengthier sealed-tube digestion procedure was adopted.

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Submicro determination of cobalt, manganese or nickel in organometallic compounds

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Little attention has been devoted to the determination of metals in organometallic compounds on the submicro scale. A method for the determination of iron[1] appears to be the only one studied so far; in this method, the organic material was digested in a sealed tube with a nitric/sulphuric acid mixture and the iron determined spectrophotometrically.

It has subsequently been shown[2,3] that a more rapid mineralization procedure, with a perchloric/sulphuric acid mixture in an open tube, is effective in the submicro determination of phosphorus. Some photometric EDTA titration methods for microgram quantities of various metals have recently been described[4] and it was suggested that these might be applicable to the analysis of organometallic compounds.

These techniques have been examined for the analysis of compounds containing cobalt, manganese or nickel.

EXPERIMENTAL

Photometric titration

Standard solutions, which had been treated to simulate the residues from digestion of organometallic materials, gave variable, high results when titrated by the methods described previously,[4] probably because titratable impurities were introduced during the processing of the solutions. Some improvement might be achieved by the use of purified reagents, masking agents or more selective titrations. In refining the titrimetric methods, however, much of their simplicity might be lost and it was considered better to seek suitable spectrophotometric methods; titrimetry, including the use of the mercury electrode,[5] would only be reconsidered if spectrophotometry proved unsuitable.

Spectrophotometric methods

Cobalt. Nitroso-R-salt[6] was found to be a satisfactory reagent.

Manganese. Attempts to determine manganese by the catalytic method of Almássy and Dezső[7] failed to achieve the desired repeatability. Satisfactory precision was obtained by oxidation to permanganate with ammonium hexanitratocerate.[8] Owing to the poor sensitivity of this method, however, the largest final volume that could be used was 10 ml, which allows barely sufficient volume for washing digestion vessels. The formaldoxime method proposed by Marczenko[9] gave a precision as good as the permanganate method and, because of its higher sensitivity, was preferred.

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Mineralization procedures

Portions of aqueous solutions of metal salts containing 4–20 μg of metal were evaporated in digestion tubes and treated by the open- and sealed-tube mineralization procedures. Excellent recoveries were obtained with both for all three metals tried, the spectrophotometric finishes being used. However, when the open-tube digestion was applied to organometallic compounds, consistent but slightly low recoveries were obtained from cobalt and nickel compounds and variable, high results from a manganese compound. Variations in the amounts of acids and time and temperature of heating did not consistently improve results, so the lengthier sealed-tube digestion procedure was adopted.

Recommended procedures

Mineralization. Digest the samples, containing 4–20 μg of metal, in sealed tubes by the procedure described elsewhere.[1,8] It is particularly important to ensure that the last traces of nitric acid are removed from the opened tube before nickel is determined.

Determination of cobalt. Transfer the residue from the digestion tube into a 50-ml conical flask with about 10 ml of water. Add 25 μl of concentrated sulphuric acid followed by 2 ml of 50% sodium acetate trihydrate solution and 2 ml of 0·05% nitroso-R-salt solution. Boil the contents of the flask for 1 min, add 1 ml of concentrated nitric acid and again boil for 1 min. Cool the solution rapidly in running water and transfer it into a 25-ml volumetric flask. Dilute to the mark and measure the absorbance at 500 nm in a 40-mm cell against a reference blank solution taken through the whole procedure. Prepare a calibration curve by evaporating portions of standardized[13] cobalt solution to dryness in digestion tubes, and applying the complete procedure.

Determination of manganese. Transfer the residue from the digestion tube into a 25-ml volumetric flask with about 10 ml of water. Add 1 ml of formaldoxime solution (8·4 ml of 36% formaldehyde + 70 ml of 10% hydroxylamine hydrochloride solution diluted to 100 ml) followed immediately by 3 ml of 1·25*M* sodium hydroxide. After 10–15 min, dilute to the mark and measure the absorbance at 455 nm in a 40-mm cell against a reference blank solution taken through the whole procedure. For the calibration curve apply the whole procedure to portions of standardized[14] manganese solution, diluted to 10 ml and to which concentrated sulphuric acid has been added to make the total acid volume 5 μl.

Determination of nickel. Transfer the residue from the digestion tube into a 25-ml volumetric flask with about 10 ml of water. Add 1 ml of 20% tartaric acid solution and 0·5 ml of saturated bromine water. Allow the solution to stand for 1–2 min, add concentrated ammonia solution dropwise to decolorize the solution and then 5 or 6 drops in excess. Allow the solution to stand for 1–2 min, then add, in quick succession, 1 ml of 3*M* sodium hydroxide, 5 ml of buffer solution (100 ml of 0·2*M* disodium hydrogen phosphate + 65 ml of 0·2*M* sodium hydroxide) and 1 ml of 1% ethanolic dimethylglyoxime solution, swirling the flask well during each addition. After 15 min, dilute to the mark and measure the absorbance at 466 nm in a 40-mm cell against a reference blank solution subjected to the whole procedure. Prepare a calibration curve by applying the colour development procedure to a standard nickel solution.

Note. The bromine water should be prepared daily and allowed to stand for 1 hr before use. The 3*M* sodium hydroxide should be renewed weekly and the tartaric acid and buffer solutions monthly.

RESULTS AND DISCUSSION

The results of the analysis of a number of organometallic compounds are summarized in Table I. Only two of the forty determinations done came outside the normally accepted limits, of ±0·3% absolute, for analysis of organic materials. The range of compounds listed is limited; other materials analysed by the recommended methods were either of uncertain composition, in which case similar precision was obtained, or were clearly inhomogeneous.

TABLE I.—ANALYSIS OF ORGANOMETALLIC COMPOUNDS

Compound	Range of weight, μg	Metal, %		No. of detns.	Range of errors % *absolute*
		Calc.	Found (mean)		
Ni–dimethylglyoxime	28·0–69·4	20·32	$20{\cdot}3_0$	4	$-0{\cdot}3_8$ to $+0{\cdot}1_7$
Ni–nioxime	48·1–100·5	17·21	$17{\cdot}2_1$	4	$-0{\cdot}0_6$ to $+0{\cdot}1_2$
Ni–oxine	27·3–91·5	16·91	$16{\cdot}8_9$	4	$-0{\cdot}1_1$ to $+0{\cdot}0_6$
Ni–α-naphthol	34·7–98·5	14·01	$14{\cdot}0_9$	4	$+0{\cdot}0_1$ to $+0{\cdot}1_6$
Ni–di-isopropyl-dithiophosphate	46·7–92·5	12·10	$12{\cdot}0_7$	4	$-0{\cdot}1_8$ to $+0{\cdot}2_7$
Co–anthranilic acid	32·0–69·8	17·79	$17{\cdot}8_6$	4	$-0{\cdot}2_7$ to $+0{\cdot}0_7$
Co–α-nitroso-β-naphthol	63·4–89·9	9·95	$9{\cdot}9_5$	4	$-0{\cdot}0_5$ to $+0{\cdot}0_7$
Co–acetylacetone	30·1–85·8	16·54	$16{\cdot}5_4$	4	$-0{\cdot}0_4$ to $+0{\cdot}0_7$
Mn–acetylacetone	43·3–84·4	15·60	$15{\cdot}6_1$	4	$-0{\cdot}0_8$ to $+0{\cdot}1_0$
Mn–anthranilic acid	33·7–90·7	16·79	$16{\cdot}9_0$	4	$-0{\cdot}1_4$ to $+0{\cdot}3_1$

The reason for the failure of the open-tube digestion procedure is not known. Deviations from the mean for the cobalt and nickel compounds mineralized by this technique were similar to those obtained by sealed-tube digestion but mean recoveries of only about 98% were obtained. The manganese compound tested gave a mean recovery of about 107% and results were very variable. It is thought that higher oxidation states of manganese may be formed during the digestion.

TABLE II.—POOLED STANDARD DEVIATIONS FOR TITRIMETRIC AND SPECTROPHOTOMETRIC DETERMINATION OF METALS

	Pooled standard deviation, μg		
	Co	Mn	Ni
Spectrophotometry	0·06	0·09	0·05
Photometric titration	0·13	0·09	0·13

A comparison of the pooled standard deviations for the two finishes is of interest and is shown in Table II. In each case the figures are based on 8 determinations at 4 levels of metal content in the range 4–20 μg. The improvement in precision by the spectrophotometric procedure is significant for cobalt and nickel, although no improvement is obtained for manganese.

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Summary—Methods for the determination of cobalt, manganese or nickel in samples of organometallic compounds weighing 30–100 μg have been developed. Spectrophotometric determination following digestion with nitric and sulphuric acids in a sealed tube is recommended, all results obtained from the analysis of standard compounds being within ±0·4% absolute error. Digestion in an open tube with perchloric and sulphuric acids gives slightly low results for cobalt and nickel compounds and is inappropriate for manganese compounds.

Zusammenfassung—Verfahren zur Bestimmung von Kobalt, Mangan oder Nickel in Proben metallorganischer Substanzen mit 30–100 μg wurden entwickelt. Nach Aufschluß mit Salpeter- und Schwefelsäure im abgeschmolzenen Rohr wird spektrophotometrische Bestimmung empfohlen; alle Ergebnisss der Analyse von Standardverbindungen lagen innerhalb von 0,4% absolutem Fehler. Aufschluß im offenen Rohr mit Überchlor- und Schwefelsäure gibt für Kobalt- und Nickelverbindungen etwas zur niedrige Werte; für Manganverbindungen ist er nicht geeignet.

Résumé—On a élaboré des méthodes pour la détermination du cobalt, du manganèse ou du nickel dans des échantillons de composés organométalliques pesant 30–100 μg. On recommande le dosage spectrophotométrique suivant la digestion avec les acides nitrique et sulfurique en tube scellé, tous les résultats obtenus de l'analyse de composés étalons étant compris dans les limites d'erreur absolue ±0,4%. La digestion en tube ouvert avec les acides perchlorique et sulfurique donne des résultats légèrement faibles pour les composés du cobalt et du nickel et ne convient pas aux composés du manganèse.

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Spectrophotometric extractive titrations—VII.* Titrations with di-2-naphthylthiocarbazone

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DITHIZONE has been successfully applied as titrant in extractive titrations.[1–4] It was considered that the use of its analogue, di-2-naphthylthiocarbazone (DNZ), would be advantageous: the molar absorptivities of the reagent and its chelates are higher than those of dithizone and of dithizonates,[5,6] and DNZ does not form secondary chelates. Thus, it would be most advantageous to use DNZ in the analysis of samples readily soluble in alkaline medium and for the consecutive titration of two metal ions, because it is more likely that there will be a pH range within which both metal ions are extracted successively than in the case of dithizone, and the titration employing the measurement of absorbance due to free reagent should be easier because of the lower tendency of DNZ to pass into ammoniacal aqueous solutions from organic solvents such as carbon tetrachloride or chloroform. The disadvantages that were envisaged stemmed from the lower stability of DNZ solutions and the lack of reliable equilibrium constants to enable prediction of optimum conditions.[7]

The reagent was evaluated by titrating traces of silver in germanium dioxide and successively titrating mercury and zinc. During the titrations, the solutions were kept in a dark bottle placed in a Dewar flask kept cold by being filled with water with ammonium chloride dissolving in it.

EXPERIMENTAL

Apparatus

As described earlier.[1,8]

Reagents

The common reagents and solutions were as indicated earlier.[1,8]

Standard silver solution, 100 ppm. Reagent grade silver sulphate was dissolved in water on the day of use and diluted to the required concentration.

Di-2-naphthylthiocarbazone. A sample was prepared by the procedure of Grzhehorzhevsky[9] and was purified by dissolving 0·1 g in 50 ml of carbon tetrachloride, then re-extracting with five 50-ml portions of aqueous ammonia (1 + 9). The combined aqueous phases were cooled in an ice-bath, and then acidified with dilute acetic acid. The green precipitate was filtered off on filter paper and dried in the dark at room temperature. The DNZ so precipitated was dissolved in 25-ml of freshly distilled, water-free chloroform or carbon tetrachloride and this stock solution was stored in a dark bottle in a refrigerator. Solutions of DNZ, $1-^{6} \times 10^{-5}M$, were prepared by diluting the stock solution with either chloroform or carbon tetrachloride. The titre of solutions was checked absorptiometrically, by taking the absorptivity at 650 nm to be $6{\cdot}70 \times 10^{4}$ $l.mole^{-1}cm^{-1}$.[10,11]

Procedures

Titration of silver. Ten ml of chloroform were placed in the titration cell, followed by 50 ml of the solution to be analysed, containing up to 10 μg of silver, and 1 ml of 0·1% sodium ethylenedinitrilotetra-acetate. The solution was adjusted with $2M$ ammonia to a suitable pH between 3 and 11.

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In the comparison cell, 10 ml of chloroform and 50 ml of water were placed. The solutions were agitated with a mixer for 2 min, then the titration was started. After each addition of DNZ, the mixer was applied for 1 min. When the organic phase in the lower arm of the titration cell clarified, the absorbance at 650 nm was measured against a blank of pure chloroform. During the titration the absorbance rises negligibly up to the end-point, but thereafter it increases markedly with each addition of titrant.

Consecutive titration of mercury and zinc. Thirty ml of the solution to be analysed, containing up to 5 μg of mercury and 2 μg of zinc, were placed in the titration cell, followed by 20 ml of 30% w/v sodium acetate trihydrate solution. Ten ml of carbon tetrachloride were added to the comparison and titration cells, then the comparison cell was filled with aqueous sodium acetate solution and the phases were equilibrated for 2 min. When the phases settled, the spectrophotometer was checked with the comparison cell, and then the titration, with $5 \times 10^{-5}M$ DNZ, was begun. After each increment of titrant was added, the solutions were agitated for 100 sec and then the absorbance of the organic layer was measured at either 580 or 590 nm. It was observed that during the titration of mercury there is a slight increase in the absorbance until the end-point is reached and thereafter it increases markedly until the second end-point is reached. Thereafter the slope of the curve decreases sharply, but remains positive.

The buffers and the vessels used were carefully purified with a solution of DNZ in chloroform.

RESULTS AND DISCUSSION

Silver

In order to find the pH range for titration of silver with DNZ it was necessary to reinvestigate the pH-dependence of the extraction of this element, because the reported data are contradictory.[6,12] A series of 50-ml aliquots of $0{\cdot}015M$ EDTA, each containing 20 μg of silver, were either acidified with a few drops of $1M$ sulphuric acid or made ammoniacal and, after measurement of pH, transferred into 100-ml separatory funnels and shaken for 30 sec with 5 ml of $1{\cdot}3 + 10^{-5}M$ DNZ in chloroform. The absorbance of the extracts was measured at 500 and at 650 nm. Treatment of the results in the manner described by DuBois and Knight[11] showed that DNZ is quantitatively bound over the pH range 2–11. The discrepancy between these findings and those of earlier authors might be due to the replacement of sodium hydroxide with aqueous ammonia, which suppresses the precipitation of silver oxide.

The procedure for spectrophotometric extractive titration of silver with DNZ was designed by taking into account this pH range. Because of addition of EDTA, the procedure should be selective against interferences other than mercury(II) and gold(III).[12] In order to check the accuracy of the method the absorptiometric titre was compared with that obtained by the titration of standard silver sulphate solution. The technique of simultaneous titration of the standard sample and of the blank solution was applied, and the shape of the titration curve was quite similar to that reported earlier,[4] if the absorbance of the blank was measured with the spectrophotometer zero being set for the sample. The results of titrations listed in Table I indicate that the DNZ was still not pure; it obviously contained some metal chelate which absorbs negligibly at 650 nm and which is less stable than the chelate of silver with DNZ. Further purification of DNZ by adsorption might seem useful, but it might result in another shortcoming—lower stability of titrant solutions.[11]

TABLE I.—TITRATION OF SILVER

Silver present, μg	Volume of DNZ solution, *ml* calculated,* *A*	found, *B*	Difference, % $100(A - B)/A$
7·0	0·389	0·348	10·5
5·0	0·298	0·260	6·5
4·5	0·250	0·230	8·0
3·5	0·194	0·170	12·4
2·5	0·139	0·128	7·9
1·0	0·056	0·050	10·7

* Using Beer's law and molar extinction coefficient $6{\cdot}70 \times 10^4$ l.mole^{-1}.cm^{-1} at 650 nm.

With the application of the procedure for silver to the analysis of germanium dioxide being in mind, the extraction of silver with DNZ from $1M$ ammonium tartrate in 0·5% EDTA solution was investigated. It was found that DNZ is bound by silver quantitatively only between pH 8·6 and 11. The narrowing of the pH range cannot be explained by the complexing effect of tartrate ions; it is more likely that the ammonium tartrate contains an anionic impurity which binds silver more strongly than tartrate does. Fortunately, even the narrower pH range coincides with that best suited for dissolution of germanium dioxide,[4] at the same time the measurement of the absorbance at the wavelength of maximum absorptivity of free DNZ remains possible because of the large partition coefficient of DNZ between chloroform and water. The application of the prodedure for silver, modified by addition of ammonium tartrate, to the analysis of germanium dioxide was proven to be satisfactory, the only shortcoming being the necessity to check frequently the titre of DNZ solutions by titration of standard silver solution.

Consecutive titration of mercury and of zinc

The choice of suitable wavelength and organic solvent for the consecutive titration of mercury and of zinc with DNZ was made on the basis of measurements of absorption spectra of equimolar solutions of pure mercury and zinc chelates in chloroform and in carbon tetrachloride. It was found that the ratio of absorbance of the zinc and mercury chelates is most favourable at 585 nm with carbon tetrachloride as solvent.

There must be a large difference between the stability of the chelates involved for successful successive titration.[8] The ratio of the extraction constant of the mercury chelate to that of the zinc one is $>10^{16}$ with chloroform as solvent.[11] This high value, which presumably applies also to carbon tetrachloride systems, indicates that in consecutive titration at any pH zinc will be titrated only after all mercury has been completely extracted. The titration of zinc may then be treated as if it is present alone and the minimum pH for successive titration may be calculated according to equations derived earlier,[7] but with modification taking into account the complexing effect of buffer.

$$\mathrm{pH_t} = 2{\cdot}14 - \frac{1}{2}\log K^{\mathrm{CCl_4}}_{\mathrm{Zn(DNZ)_2}} + \frac{1}{2}\log\,(1 + K_{\mathrm{ZnAc}}[\mathrm{Ac}]) \tag{1}$$

Here K_{ZnAc} is the stability constant of zinc acetate. Employing the value of the extraction constant found by Grzehorzhevsky[5] and the stability constant of zinc acetate referred to by Jazimirski and Wasiljew,[13] the threshold pH for consecutive titration of mercury and of $10^{-6}M$ zinc solutions in $0{\cdot}88M$ acetate medium is 6·72.

These predictions were verified experimentally (Table II). For the reasons mentioned in connection with silver, the DNZ solutions were standardized by separately titrating either mercury or zinc standard solutions.

TABLE II.—CONSECUTIVE TITRATION OF MERCURY AND ZINC

Mercury, μg		Zinc, μg	
present	found	present	found
5·0	4·9	0·8	$0{\cdot}7_3$
3·2	3·4	1·1	$1{\cdot}1_5$
3·2	3·3	1·1	1·2
2·2	2·2	2·0	$2{\cdot}0_6$
1·9	1·8	0·6	0·5
0·9	$0{\cdot}7_7$	0·6	$0{\cdot}6_6$

Lead and thallium(I), in 50-μg amounts, did not interfere with the titration, but metal ions such as nickel, cobalt and copper, or large amounts of citrate, did. The consecutive titration therefore requires the separation of mercury and of zinc from the bulk of any sample.

It may be concluded that the spectrophotometric extractive titrations with DNZ are feasible; in comparison with titrations with dithizone they have advantages mainly related to the absence of the formation of secondary chelates, so that, e.g., silver can be determined in an ammoniacal medium. The higher values of molar absorptivity of DNZ chelates did not lead to higher absolute sensitivity, because of the limiting effect of the variability of blanks. A serious shortcoming of titrations with DNZ is the necessity of carefully protecting the titrant both from light and heat.

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Summary—An investigation of the possibilities of the use of di-2-naphthylthiocarbazone as titrant in spectrophotometric extractive titrations has been undertaken. A selective procedure for successive titration of silver in an ammoniacal medium has been developed and applied to the analysis of germanium dioxide. It has been established that the consecutive titration of mercury and zinc in the microgram range is possible. Because of low selectivity of this titration, a separation of mercury and zinc from other ions is necessary.

Résumé—On a entrepris une investigation des possibilités d'emploi de la di-2-naphtylthiocarbazone comme agent de titrage dans les titrages par extraction spectrophotométriques. On a élaboré une technique sélective pour le dosage courant de l'argent dans un milieu ammoniacal et on l'a appliquée à l'analyse du bioxyde de germanium. On a établi que le titrage consécutif du mercure et du zinc dans le domaine du microgramme est possible. A cause de la faible sélectivité de ce titrage, une séparation des mercure et zinc des autres ions est nécessaire.

Zusammenfassung—Die Verwendungsmöglichkeiten von Di-2-naphthylthiocarbazon als Titrant bei spektrophotometrischen extraktiven Titrationen wurden untersucht. Eine selektive Vorschrift zur Titration von Silber in ammoniakalischem Medium wurde entwickelt und auf die Analyse von Germaniumdioxid angewandt. Es wurde festgestellt, daß die Titration von Quecksilber und Zink nacheinander im Mikrogrammbereich möglich ist. Da die Titration wenig selektiv ist, müssen Quecksilber und Zink von anderen Ionen abgetrennt werden.

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Determination of atmospheric iron particulates by X-ray fluorescence spectroscopy

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ATMOSPHERIC iron particulates as iron oxides present a serious hazard to human beings. Iron oxide fumes are generated, for example, in welding operations. It has been shown that continued exposure to concentrations above 30 mg/m^3 may cause chronic bronchitis.[1,2] Atmospheric iron particulates have been determined by emission spectrography[3] and by atomic-absorption spectroscopy.[4] The former has relatively poor precision and accuracy compared with the latter, though that suffers from inter-element effects.

The good precision and accuracy of X-ray fluorescence spectroscopy have been well documented in other articles[5–9] on trace analysis. The inter-element effects in the present method were neglected because of the lack of heavy elements, the abundance of lighter elements as matrix, and the thinness[10] of samples collected on membranes.

Summary—An investigation of the possibilities of the use of di-2-naphthylthiocarbazone as titrant in spectrophotometric extractive titrations has been undertaken. A selective procedure for successive titration of silver in an ammoniacal medium has been developed and applied to the analysis of germanium dioxide. It has been established that the consecutive titration of mercury and zinc in the microgram range is possible. Because of low selectivity of this titration, a separation of mercury and zinc from other ions is necessary.

Résumé—On a entrepris une investigation des possibilités d'emploi de la di-2-naphtylthiocarbazone comme agent de titrage dans les titrages par extraction spectrophotométriques. On a élaboré une technique sélective pour le dosage courant de l'argent dans un milieu ammoniacal et on l'a appliquée à l'analyse du bioxyde de germanium. On a établi que le titrage consécutif du mercure et du zinc dans le domaine du microgramme est possible. A cause de la faible sélectivité de ce titrage, une séparation des mercure et zinc des autres ions est nécessaire.

Zusammenfassung—Die Verwendungsmöglichkeiten von Di-2-naphthylthiocarbazon als Titrant bei spektrophotometrischen extraktiven Titrationen wurden untersucht. Eine selektive Vorschrift zur Titration von Silber in ammoniakalischem Medium wurde entwickelt und auf die Analyse von Germaniumdioxid angewandt. Es wurde festgestellt, daß die Titration von Quecksilber und Zink nacheinander im Mikrogrammbereich möglich ist. Da die Titration wenig selektiv ist, müssen Quecksilber und Zink von anderen Ionen abgetrennt werden.

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The good precision and accuracy of X-ray fluorescence spectroscopy have been well documented in other articles[5–9] on trace analysis. The inter-element effects in the present method were neglected because of the lack of heavy elements, the abundance of lighter elements as matrix, and the thinness[10] of samples collected on membranes.

EXPERIMENTAL

Reagents

All chemicals used were of reagent grade. Distilled demineralized water was used throughout.

Preparation of standards

Pure iron wire (1·000 g) was dissolved in 10 ml of hydrochloric acid (1 + 1) and diluted to 1 litre with water. This solution contained 1000 μg of iron per ml, and was diluted further as required. Portions containing 1000, 300, 100, 30 and 10 μg of iron, were added each to 10 ml of water, and ammonia solution was then added dropwise to precipitate hydrous iron(III) oxide. After checking by atomic-absorption spectroscopy for completeness of precipitation, the precipitates were filtered off on membranes which could be used as iron standards with or without a Mylar film covering[11] and which were reasonably permanent.

Apparatus

A Norelco air-path X-ray fluorescence spectrometer with tungsten tube operated at 50 kV and 40 mA, lithium fluoride analyser crystal and scintillation counter was used. For the preparation of the standards, a Pyrex filter holder (Millipore Corp. cat. no. XX10 047 00) with 47-mm PH membranes of 0·30 μm pore size was used.

Procedure

An inverted polyethylene cup is pressed on to the membrane disk so that the precipitate of hydrous iron(III) oxide or unknown sample is exposed through the opening. The sample holder with disk and sample backing is then inverted in the X-ray unit and the intensity of the Fe*K*α line is measured. A blank membrane is used to obtain a correction for background.

RESULTS AND DISCUSSION

Background interference

Since blanks may cause significant errors in trace analysis, an investigation was made into the contribution of Fe*K*α intensity from the tungsten target tube, Mylar, precipitating reagent, membrane and sample backing. Compared with about 5 cps from 10 μg of iron in the sample, none of the blanks showed any significant contribution to the Fe*K*α signal.

A similar study was also made on various filters. Neither regular filter paper nor a Millipore membrane showed any detectable iron while a glass-fibre filter appeared to contain about 5 μg of iron. A silver membrane also showed very little iron but the back-scattering was so serious that the metallic membrane was considered unsuitable for the present work.

Back-scattering

In order to improve signal-to-noise ratio a sample backing was sought which would give the least back-scattering. Of those studied an inverted polyethylene cup was found to be the most suitable. Metallic backings enhanced the Fe*K*α radiation by approximately 15 %, but were unsuitable because of their higher back-scattering.

Inter-element effects

Based on information about the chemical compositions of the atmospheric particulates reported,[12] a study was made of some inter-element effects. No significant inter-element effects were observed that were greater than the experimental error of approximately 5 % (Table I).

Working curve

The count-rate was plotted on a log-log scale for amounts of iron between 10 and 1000 μg. The recorded peaks and the calibration curve are shown in Fig. 1. It appears that the working curve is

TABLE I.—INTENSITIES (*cps*) OF Fe*K*α LINE FROM 100 μg OF IRON IN THE PRESENCE OF SOME OTHER ELEMENTS

Element	Amount added, μg			
	0	100	500	1000
Silicon	49·5	45·6	45·9	47·8
Aluminium	47·5	45·5	48·2	46·2
Magnesium	47·5	48·2	48·0	46·5
Calcium	49·5	48·2	46·5	47·0

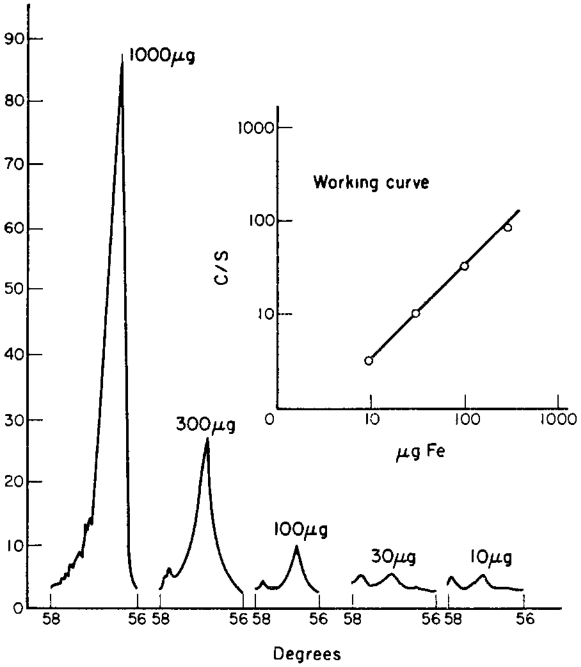

FIG. 1.—X-ray fluorescence spectra of iron standards, and the calibration graph.

linear up to 1000 µg of iron as hydrous iron(III) oxide, but it is doubtful whether the linearity will still hold up to 1000 µg of iron in actual atmospheric samples, because of increasing thickness of the samples collected on the membranes. No further attempt was made to ascertain the linearity beyond 1000 µg of iron.

Precision and accuracy

The precision for five different standard samples of 100 µg of iron determined by this method was checked, and a relative standard deviation of ±5·4% was obtained at a concentration level of 100 µg of iron, with an average count-rate of 46·5 cps.

Table II shows the results of analyses by this method and by a wet chemical method for various collected samples. Samples 1–4 were taken in a wet-chemical laboratory for the analysis of alloys, and samples 5–10 were taken near a machine workshop. The average error of ±6·7% in the concentration ranges shown compares favourably with that of atomic-absorption spectroscopy[4] for this concentration range.

TABLE II.—ACCURACY OF THE X-RAY FLUORESCENCE METHOD

	Iron found, *µg/m*^{3}		
Sample No.	X-ray method	Chemical method	Difference, %
1	23	25	−8·0
2	29	32	−9·4
3	42	40	+5·0
4	45	49	−8·2
5	88	82	+7·3
6	87	91	−4·4
7	125	115	+6·1
8	141	133	+6·0
9	265	282	−6·0
10	340	359	−5·3

In conclusion the present method was found to be suitable for the determination of iron in the atmospheric samples with satisfactory precision and accuracy. The sensitivity of the method could be improved by using a thinner beryllium window in the X-ray chamber, by utilizing smaller membranes for sample-collection and by the use of a better detector system. The disadvantages of the X-ray fluorescence method are the complications due to inter-element effects, especially when large amounts of sample are collected, and the difficulty in preparing proper standards.

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Summary—A method is described for the determination of atmospheric iron particulates by X-ray fluorescence spectroscopy. Samples are collected, with a low-volume air sampler, on organic membranes which are used directly for measurement by comparison with standards prepared by precipitation of hydrous iron(III) oxide on similar membranes. The method is simple and rapid, and offers a precision and error of about 6% for the range 10–200 μg of iron.

Zusammenfassung—Ein Verfahren zur Bestimmung atmosphärischer Eisen-Schwebeteilchen durch Röntgenfluoreszenzspektroskopie wird beschrieben. Die Proben werden mit einem kleinvolumigen Luft-Probenahmegerät auf organischen Membranen gesammelt; diese werden direkt zur Messung verwendet und mit Standards verglichen, die durch Fällen von Eisen(III)oxidhydrat auf gleichartige Membranen hergestellt werden. Das Verfahren ist einfach und schnell. Genauigkeit und Fehler betragen etwa 6% im Bereich 10–200 μg Eisen.

Résumé—On décrit une méthode pour la détermination de particules de fer atmosphérique par spectroscopie de fluorescence de rayons X. Les échantillons sont collectés, avec un échantillonneur d'air de faible volume, sur des membranes organiques que l'on utilise directement pour la mesure par comparaison avec des étalons préparés par précipitation d'oxyde de fer(III) hydraté sur des membranes similaires. La méthode est simple et rapide, et offre une précision et une erreur d'environ 6% dans le domaine 10–200 μg de fer.

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NUCLEATION AND CRYSTAL GROWTH OF COPPER(II) 8-HYDROXYQUINOLINATE PRECIPITATED FROM MIXED SOLVENTS

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Summary—The precipitation kinetics of copper(II) 8-hydroxyquinolinate, formed in water–acetone mixtures, have been studied in a stop-flow apparatus by spectrophotometric techniques. Three factors are found to be important in improving the physical characteristics of crystals precipitated from mixed solvents. Supersaturation and growth rate can be controlled uniformly by slow rate of change in solvent composition; the presence of acetone significantly reduces the number of effective nuclei; thirdly, large amounts of organic solvent cause a change in the crystal form and its growth mechanism. At room temperature, copper(II) 8-hydroxyquinolinate is precipitated as a dihydrate from water–acetone mixtures containing 0–60% acetone, and the crystal growth is limited by a diffusion-controlled process. Anhydrous copper(II) 8-hydroxyquinolinate is formed in 70% acetone solutions by a surface-controlled reaction.

EARLIER work reported from this laboratory[1] has demonstrated the possibility of precipitating metal chelates from solutions containing large amounts of organic solvents. The technique involves the addition of about an equal volume of a miscible organic solvent, such as ethanol or acetone, to an aqueous solution of the metal ion. Following the addition of the chelating agent, the solution is warmed to approximately 70°, and the preferential volatilization of the organic solvent is accompanied by the formation of the precipitate.

Particularly striking is the increased size of these crystals as compared to the chemically identical particles obtained by a direct addition procedure. Further, co-precipitation is significantly lowered. These results compare favourably with other, more common methods of precipitation from homogeneous solution.[2,3] The initial speculation was that these alterations arose solely from the increased solubility of the metal chelates in the mixed solvent media. The gradual and uniform decrease in solubility, caused by the preferential evaporation of the organic solvent component, allowed the crystals to grow under conditions closer to equilibrium, so that the formation of more perfect crystals was favoured.

However, other factors may be more important. It is possible that the presence of the organic solvent may markedly reduce the rate of the chelation reaction and thereby reduce the initial supersaturation. Alternatively, the organic solvent may cause a change in the crystal growth mechanism or may reduce the rate of the slowest step which, again, would permit the development of more perfect crystals. A third possibility is that nucleation processes are altered by the presence of the organic solvent; *e.g.*, the effectiveness of foreign nuclei may be reduced.

The precipitation kinetics of copper(II) 8-hydroxyquinolinate were studied under conditions of varying solvent composition and solution supersaturation in order to obtain experimental data which could be used to distinguish between these various control factors. It had been reported earlier[4] that the colour and crystal habit of precipitated copper(II) 8-hydroxyquinolinate were particularly dependent upon the presence of organic solvents. A much different precipitate was formed from solutions containing over 60% of the organic solvent. Supersaturated solutions of this compound, in solvents varying from 0 to 70% v/v acetone, were formed in the chamber of a 4-jet mixer and passed into a stop–flow observation chamber where they were observed spectrophotometrically. Data, collected at wavelengths at which the predominant interaction with the light-beam was the scattering by solid particles, were treated by fitting various crystal growth equations.

EXPERIMENTAL

Apparatus

Stop–flow apparatus. The all-glass apparatus used for obtaining kinetic data[5] consisted essentially of four storage cylinders, an efficient 4-jet mixing chamber based on Hartridge and Roughton's device[6] and a Pyrex precision bore observation tube with an accurate inside diameter of 2 mm. This tube was mounted horizontally and passed directly through the cell compartment of a spectrophotometer. Its position was fixed by an aluminium block which had been adjusted to the dimensions of the cell holder.

Reagents

Water. Distilled water, passed through a "Bantam Demineralizer" containing cation- and anion-exchange resins, was used to prepare all solutions. Monitored water impurities were 0·05 ppm or less.

Acetone. Reagent grade acetone was distilled through a 300-mm Vigreux column. The high- and low-boiling fractions were discarded.

Ammonium acetate buffer solutions. A 2*M* stock solution was prepared by dissolving 154·2 g of reagent grade ammonium acetate in water, filtering and diluting to 1 litre. All 0·2*M* solutions used for precipitation reactions were prepared by appropriate dilution of the stock solution.

Copper solutions. A 6·354-g sample of purified electrolytic copper metal (pellets, 99·99% pure) was dissolved in 120 ml of nitric acid (1 + 4). The resulting copper nitrate solution was evaporated almost to dryness, then diluted with water, filtered through a fine porosity Whatman filter paper, and diluted to 1 litre with water.

8-Hydroxyquinoline solutions. Reagent grade 8-hydroxyquinoline was recrystallized from ethanol, and dissolved in appropriate solvents.

Copper 8-hydroxyquinolinate solutions. The desired amount of copper standard solution was transferred by pipette into a 500-ml graduated cylinder and the necessary amount of 1*M* nitric acid added to yield a pH of 2. This solution was then diluted to 500 ml with water and transferred to a 1-litre volumetric flask. The same cylinder was used to measure the desired amount of acetone in which a weighed amount of 8-hydroxyquinoline was dissolved. This solution was then transferred into the rapidly stirred copper solution, and the final volume was adjusted to 1 litre with water.

When aqueous solutions were prepared, the nitric acid was added to the 8-hydroxyquinoline solution in order to dissolve the reagent.

Procedure

Manipulation and testing of the stop–flow apparatus. The reactant solutions were placed in the storage cylinders as follows: 0·2*M* buffer solution in cylinder 1, copper 8-hydroxyquinolinate solution in cylinder 2, a blank solution of buffer and acetone in cylinder 3, and 4*M* hydrochloric acid cleaning solution in cylinder 4.

The simultaneous outflow of the reactant and buffer solution was maintained for 5 sec by applying a constant nitrogen pressure of 9·6 kN/m^2. Two sec before the flow was stopped, a sample was collected at the end of the observation tube and used to determine the initial reactant concentration. The stop-cock at the end of the observation tube was closed first to prevent the formation of bubbles in the observation tube. The pressure was then removed as rapidly as possible in order to follow the crystal growth processes at atmospheric pressure. An electric stop-watch was started when the flow was stopped. The recorder was switched on before the flow started.

The efficiency of the mixing chamber was tested with an acid-base reaction and phenolphthalein indicator. Under an applied pressure of 9·6 kN/m^2 (corresponding to a flow-rate of 10 ml/sec or a flow-speed of 3·2 m/sec) mixing was found to be complete in 3·5 msec.

Preliminary precipitation experiments with copper 8-hydroxyquinolinate were carried out with the observation tube vertical, and the absorbance was measured at different heights along the tube. It was found that the final absorbance of a particular run did not depend on the position of measurement, and that it remained constant. This indicated that the growing particles did not migrate or settle, but remained where they formed.

Copper determination. The sample collected after each run was analysed for copper, by a technique described by Reilley[7] but with several modifications. The 8-hydroxyquinoline interfered in the determination; it was therefore necessary to oxidize it first. After addition of 2 ml of 30% hydrogen peroxide, each sample was heated until a colour change occurred. The temperature was then raised until all of the excess of hydrogen peroxide was removed. The copper was titrated with EDTA at pH 4, with PAN as indicator. The result of this titration determined the value for the initial concentration (C_0) of the run.

THEORETICAL CONSIDERATIONS

Any crystallization process may involve three basic phases: achievement of supersaturation, formation of crystal nuclei, and growth of the nuclei into visible crystals. A comprehensive theoretical treatment, dealing with the overall growth rate of a large number of distinct crystals growing from a supersaturated solution, must be very complex.

The growth process alone may involve such diverse events as diffusion of the solute particles from the bulk of the solution to the crystal surface, adsorption of solute material at the solid–liquid interface, diffusion across the face of the crystal, and dehydration and incorporation of the precipitated material into the crystal lattice. Depending upon experimental conditions, each one of these processes may become the rate-controlling factor. Certainly, the rate laws are not always sufficiently described by one mechanistic step (*e.g.*, within transition regions) and furthermore, complications arising from competing dissolution and agglomeration phenomena may tend to obscure the actual growth laws.

Theoretical treatments which apply to specific growth paths can generally be found. It should be emphasized, however, that extreme care is required in selecting a particular theoretical treatment, for it may involve making unwarranted assumptions about prospective growth paths. The distinction between a diffusion-controlled and a surface-controlled reaction generally serves as a first approach to give some insight into a particular crystal growth system.

The theoretical and practical aspects of diffusion-controlled growth kinetics have been treated by several authors.[8,9] Careful reconsiderations by Ham[10] confirmed earlier findings that a diffusion-limited process may be approximately described by an expression of the form:

$$C_t = C_0 \exp [-t/\tau]^n \tag{1}$$

Where C_0 = initial concentration of solute at time $t = 0$
C_t = solute concentration at any time t
C_s = equilibrium solubility
n = exponent depending upon the growth mechanism
τ = time constant, depending upon the diffusion coefficient D, the sink radius r_s, the final particle radius $r_{0(\infty)}$*, and C_0.

Equation (1) is an approximation,[10] valid for small t when

$$\frac{C_t - C_s}{C_0} > \frac{1}{2}$$

---

* Shape and size of the actual crystals are approximated by a sphere of equal volume.

It also requires that the dimensions of the precipitate particles remain small compared to their distance of separation, *i.e.*, $r_c/r_s \ll 1$. The latter requirement may be fulfilled for a large number of small particles as well as for a few widely spread large particles.

As long as the particle growth is strictly diffusion-controlled, and the particles are incorporated into the crystal at the point where they are absorbed, the crystal will grow with constant eccentricity. Qualitatively similar rate laws are then predicted for crystals of different shapes, *e.g.*, spheres and spheroids. For this growth mechanism the exponent n of equation (1) will be between 1·0 and 1·5.

There is, however, at least one other, perhaps even more important, possibility by which crystals can grow under diffusion-controlled conditions. In this case, the entire crystal surface is thought to be active in capturing solute material; but the captured particle may be incorporated into the crystal lattice only at certain specific sites. This requires the adsorbed particle to migrate across the face of the crystal, and this process must be sufficiently faster than the diffusion of the solute to the surface layer to maintain the assumed rate-determining mechanism. Under these conditions, the exponent n of equation (1) depends to a larger extent on the shape of growing crystals and varies between 1·0 and 2·0.[11]

The exponent n would approach a value of 3·0 if a process at the crystal surface should become rate determining. Equation (1) may, therefore, be used to distinguish between diffusion-controlled and surface-controlled precipitation reactions.

Particularly at low supersaturations, crystal growth often proceeds by way of screw dislocations. Burton, Cabrera and Frank [12] have developed rate laws for this type of growth by considering a system of non-dissociated species growing from the vapour phase. Basically the same theory was subsequently applied by Chernov[13] to crystallization models, involving liquid–solid phase transitions. Recently, this theory was further extended by Reich and Kahlweit[14] to include surface-controlled reactions.

The following simple relationship was derived by Reich and Kahlweit:

$$C_t - C_s = \frac{j}{k_D} + \left(\frac{j}{k_R}\right)^{1/2}. \tag{2}$$

The rate constant k_D of a diffusion-limited process, and k_R, the rate constant of a surface-controlled reaction, may be evaluated if the flux j (in mole.sec^{-1}) of the deposited material can be determined as a function of time. Equation (2) should be most relevant during the latter part of the precipitation process where the supersaturation changes only slowly with respect to time.

For $k_D > k_R$ or for $j \to 0$, the flux is mainly determined by:

$$j \approx k_R(C_t - C_s)^2. \tag{3}$$

On the other hand, for large flux values:

$$j \approx k_D(C_t - C_s). \tag{4}$$

Equation (2) predicts, therefore, a second-order rate law in the case of a surface-controlled reaction and a first-order rate law for diffusion-limited precipitations.

Similar equations have been developed previously.[9,16] However, equation (3) differs from Walton's suggestion[17] that the kinetic order should always be equal to the number of ions required to form a neutral molecule. Equation (3) predicts a second-order rate law for surface-controlled precipitations, regardless of whether the solute species are ions or molecules.

According to Reich and Kahlweit,[15] the flux j may be found from:

$$j = -\frac{\mathrm{d}c/\mathrm{d}t}{(C_0 - C_t)^{2/3}} \cdot \frac{r_{c(\infty)}}{3\bar{V}(C_0 - C_s)^{1/3}}\,. \tag{5}$$

The molar volume is indicated in equation (5) by $\bar{V}$. Letting

$$k' = \frac{r_{o(\infty)}}{3\bar{V}} \tag{6}$$

we have:

$$\frac{j}{k'} = \frac{\mathrm{d}c/\mathrm{d}t}{(C_0 - C_t)^{2/3}} \cdot \frac{1}{(C_0 - C_t)^{1/3}} = Y. \tag{7}$$

From equations (3) and (4), we see that, depending upon the rate controlling step,

$$Y \approx \frac{k_D}{k'}(C_t - C_s) \tag{8}$$

or

$$Y \approx \frac{k_R}{k'}(C_t - C_s)^2. \tag{9}$$

Equation (7) is particularly useful for data interpretation of experiments in which the particle sizes have not been determined.

RESULTS AND DISCUSSION

Initial experiments with unsaturated solutions of copper 8-hydroxyquinolinate revealed that the absorption spectrum was time-independent and appreciably different from the combined spectra of the reactants. While a possible effect of solvent composition upon the rate of chelation cannot be discounted, the chelation reaction must nevertheless be very fast compared to crystallization rate. From flow experiments it was estimated that the chelation in aqueous solution must be complete in less than 1 msec. For this system, then, chelate formation cannot be effective in controlling the crystal growth process.

Turbidimetrically determined crystallization curves of transmittance *vs.* time are shown in Fig. 1. These curves reveal a steady induction period which is terminated rather abruptly and is followed by a rapid crystal growth, which later on becomes slower and slower as the reaction is approaching equilibrium conditions. Many similarly shaped curves have been reported.

Figure 1 reveals that there exists a definite relationship between the initial concentration (C_0) and the final absorbance (A_e). To find this relationship, final absorbance values were plotted against the initial concentrations (Fig. 2). A straight-line relationship is observed in all cases.

The straight-line equation calculated by least-squares serves to evaluate the concentration terms C_t and C_s; the solubility (C_s) of copper 8-hydroxyquinolinate in a

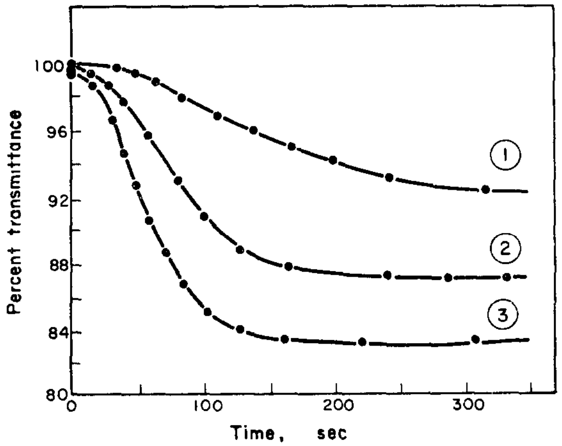

FIG. 1.—Precipitation curves of copper(II) 8-hydroxyquinolinate formed in aqueous solution; concentration dependence.
C_0: ①—0·883; ②—1·090; ③—1·25 (mole/l. × 10^4).

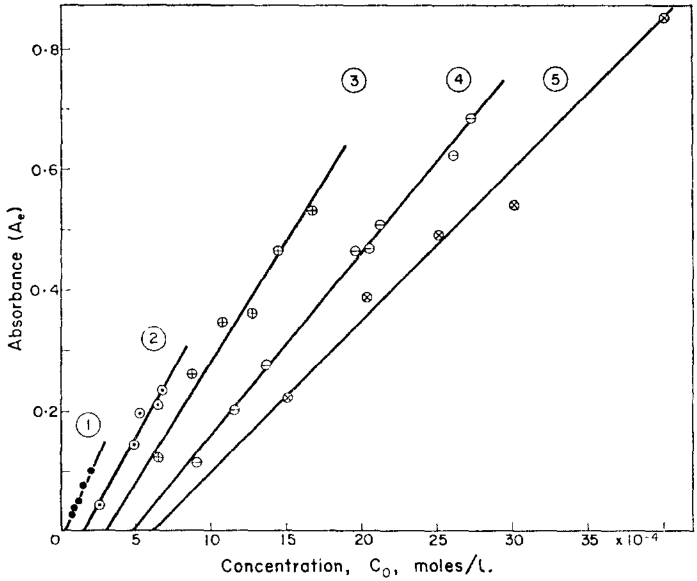

FIG. 2.—Turbidimetric calibration lines for copper(II) 8-hydroxyquinolinate precipitated from different solvent media.
Acetone content, % v/v: ① ●—0%; ② ○—20%; ③ ⊕—40%; ④ ⊖—50%; ⑤ ⊗—60%.

given solvent system is obtained from the intercept of the corresponding calibration line with the abscissa.

Combining absorption and scattering laws, Wells[18] derived an expression which is of the same form as Beer's law. A straight-line relationship may, therefore, be expected for cases approaching ideal conditions. It must be pointed out, however, that Wells's expression is at most an approximation since it neglects such important factors as how closely the particles are packed.

The turbidimetric detection method was chosen because ordinary absorption measurements of coloured species in solution were unsuccessful, owing to strong interference from the growing particles. Conductometric measurements, often used for this purpose, were unsuitable, too, since the particles in solution were neutral molecular species.

Figure 3 shows typical experimental data plotted in log–log form according to equation (1). The horizontal lines on each run terminate the region for which this type of data treatment is expected to be best applicable. The lower limit corresponds to the value calculated by setting $C_t = 0{\cdot}9C_0$, and the upper limit generally indicates the point of the reaction at which $C_t = \frac{1}{2}C_0$. Straight lines are obtained within these limits, which extend over a large portion of the precipitation process. The slope of these lines appears to be independent of the reaction rate. The average slope of all runs considered at a given solvent composition, therefore, may be used to determine the exponent n of equation (1).

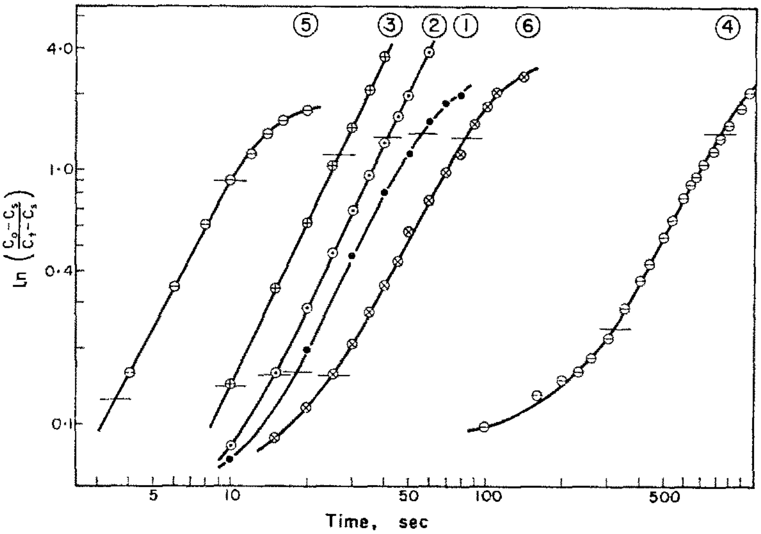

FIG. 3.—Experimental crystal growth data for copper(II) 8-hydroxyquinolinate in different solvent media, plotted according to equation (1).
C_0 (mole/l. × 10^4): ①—0·9688; ②—4·456; ③—11·15; ④—9·10; ⑤—31·07; ⑥—15·00.

Table I summarizes the results obtained in the different solvent media. The time constant τ is obtained from the intercept of the precipitation lines with the 1·0 line (ordinate value) of Fig. 3. The minimum and maximum τ value of a given solvent system may serve as a first indication of the range of reaction times studied. It should be noted that the total concentration and the τ value range in run 59 cover approximately two orders of magnitude.

The constancy of the $\bar{n}$ values in Table I is remarkable. There are no significant differences in the average slope values, nor is there an indication of a trend in the values. This suggests clearly that the precipitation mechanism does not change within the entire solvent and concentration range investigated. These data, however do not give a complete answer as to what mechanism is involved in the rate determining

Table I

Acetone content, % *v/v*	Number of runs averaged	Concentration range C_0 min., *mole.l.*$^{-1}$ × 10^4	C_0 max., *mole.l.*$^{-1}$ × 10^4	Time range τ min., *sec*	τ max., *sec*	Slope range $n_{\min}$	$n_{\max}$	Average slope $\bar{n}$	Standard deviation of $\bar{n}$
0	9	0·6545	2·080	7·0	64·0	1·40	2·50	1·89	0·37
20	12	2·349	6·809	10·6	86·0	1·43	2·10	1·87	0·21
40	16	6·412	17·16	11·7	71·0	1·38	2·30	2·02	0·22
50	11	9·10	31·07	9·3	700·0	1·54	2·54	1·95	0·32
60	11	15·00	40·00	6·1	130·0	1·55	2·30	1·88	0·22

step, since the $\bar{n}$ values were found to lie near 2 (*i.e.*, between 1·5 and 3·0). Had these values been consistently less than 2, the growth could be classified as diffusion-controlled. Conversely, values consistently above 2 would clearly indicate surface-control. With the data obtained, it is only clear that the mechanism does not change and that the particles are not incorporated into the crystal at their adsorption sites.

Reich and Kahlweit's treatment was then applied to the same experimental data. $(C_t - C_s)$ *vs.* t values of individual runs were plotted and the instantaneous rates (dc/dt) were determined from the slopes. These rates were used as input data in a computer programme used to calculate the necessary parameters to construct the plots shown in Figs. 4*a* and 4*b*.

These two figures illustrate that the plots of j/k' *vs.* supersaturation are linear in all five solvent systems. On the other hand, plots of $(j/k')^{1/2}$ *vs.* supersaturation were curved. Only one run is shown for each solvent system. Actually, 7–10 runs performed under various precipitation conditions were evaluated in this manner for each solvent system, and similar curve shapes were obtained in all cases. Under the conditions investigated, the precipitation of copper 8-hydroxyquinolinate appeared to be a diffusion-controlled process.

Figure 4*a* also reveals that the slope of the straight lines obtained varies with changing solvent composition. The slope of these lines, being equal to $k_D/k' = k_D'/r_{c(\infty)}$, is inversely proportional to the final particle size. The general trend observed, therefore, indicates that the final particle size increased with increasing acetone content. Such an effect could be explained in two ways. The increase in particle size could simply result from the larger amount of material which is precipitated from the increasingly concentrated acetone solutions. This possibility was eliminated by the proposed method of plotting the data, which accounted for such an effect. Alternatively, it could be explained by a real decrease in the number of growing particles in solvent media containing more acetone. We believe the latter to be the case. In fact, without counting particles it was qualitatively observed that the number of growing particles per unit volume decreased rapidly with increasing acetone content. For solutions containing 40% or more acetone, it was also found that the number of particles was dependent upon the initial solute concentration C_0. The number of particles generally increased with increasing supersaturation although C_0 was kept well below the range where homogeneous nucleation could occur. Table II gives a more complete representation of the data and clearly shows the effect of acetone concentration on particle size. It should be emphasized, however, that nucleation, although generally influenced by the supersaturation and by the acetone content, was

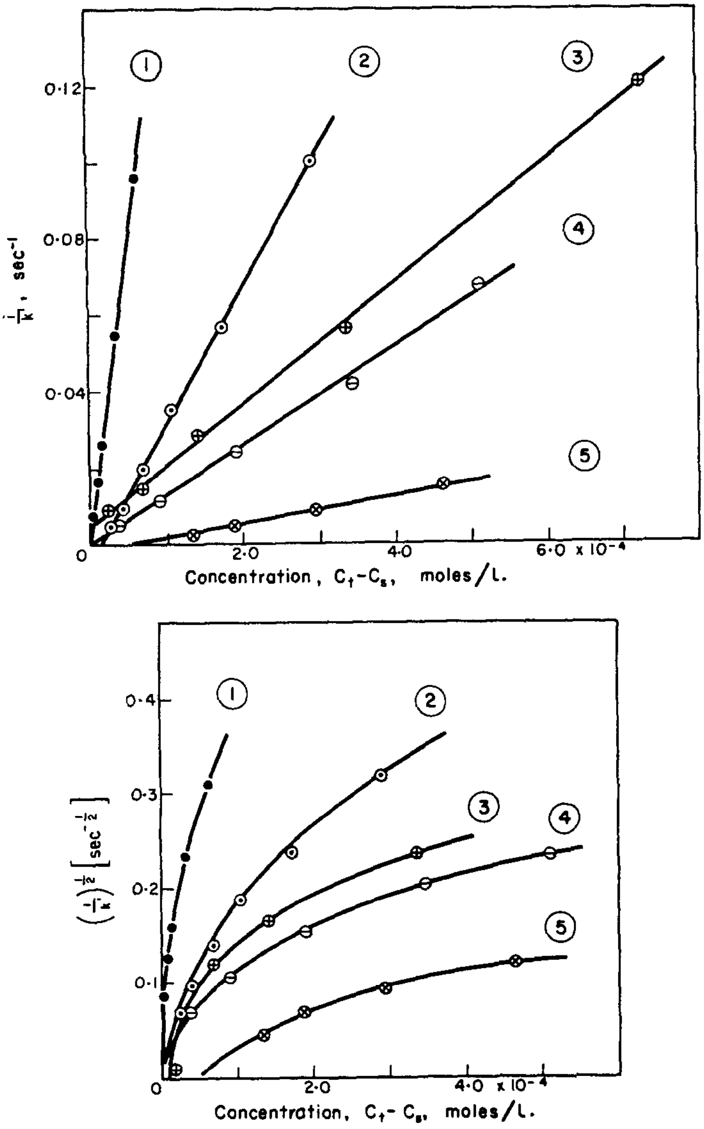

FIG. 4.—Experimental crystal growth data for copper(II) 8-hydroxyquinolinate in different solvent media.

(*a*) First-order rate plots according to equation (8).

(*b*) Second-order rate plots for the same runs.

C_0 (mole/l. × 10^4): ①—2·080; ②—5·996; ③—14·49; ④—27·10; ⑤—15·00.

a somewhat unpredictable process. Differences in the number of particles did occur even under seemingly identical conditions of successive experiments.

Within this restriction it still appears that the trends in the k_D/k' values are sufficiently uniform to justify interpretation. The 40, 50, and 60% acetone data, despite some scatter, display a clear trend to larger values with increased supersaturation. Since the solutions of higher supersaturations contain more material, one might expect larger particles to be formed. These data indicate exactly the opposite effect.

TABLE II

Acetone content, % v/v	Concentration C_0 *mole.l.*$^{-1}$ × 10^4	Supersaturation $S = \frac{C_0}{C_s}$	$\frac{k_D}{k'} = \frac{k_D \,.\, 3\bar{V}}{r_{c(\infty)}}$	Aver. $\frac{k_D}{k'}$
0	0·6545	2·014	0·146	
	0·7439	2·289	0·148	
	0·9265	2·855	0·163	
	0·9688	2·981	0·112	0·151
	1·670	5·138	0·166	
	2·080	6·400	0·159	
	2·117	6·605	0·161	
20	2·857	2·012	0·0238	
	2·997	2·110	0·0250	
	4·456	3·138	0·0250	
	5·276	3·715	0·0458	0·0323
	5·996	4·222	0·0360	
	6·515	4·588	0·0337	
	6·809	4·793	0·0369	
40	6·412	2·15	0·0018	
	6·678	2·24	0·0014	
	9·281	3·12	0·0065	
	12·65	4·25	0·0117	0·00977
	14·35	4·82	0·0192	
	14·49	4·87	0·0159	
	16·56	5·56	0·0119	
50	9·10	1·88	0·00087	
	11·51	2·37	0·00203	
	12·70	2·62	0·00178	
	19·60	4·04	0·00156	0·00467
	26·40	5·44	0·00173	
	27·10	5·59	0·01262	
	31·07	6·41	0·01210	
60	15·0	2·46	0·00386	
	20·0	3·28	0·00177	
	25·0	4·10	0·00270	
	25·0	4·10	0·00422	0·00555
	30·0	4·92	0·00518	
	40·0	6·56	0·01139	
	40·0	6·56	0·00973	

The larger k_D/k' values require a smaller $r_{c(\infty)}$. The only way in which smaller $r_{c(\infty)}$ values may be obtained with increasing amounts of material is by an even greater increase in the number of growing particles. Since heterogeneous nucleation certainly predominates, the number of foreign particles that may effectively serve as crystal growth sites must increase with increasing supersaturation. This effect has been observed previously for ionic precipitates.[19,20] The data obtained at 20% acetone concentration may or may not be displaying this trend and the aqueous solutions obviously do not. Therefore, the implication is drawn that the higher acetone concentrations cause the number of effective foreign nuclei to be more supersaturation-dependent.

A comparison of the average k_D/k' values for various solvent compositions shows a pronounced trend toward decreasing values with increasing acetone content. Since this change is much larger than any expected changes in diffusion coefficients, the change must relate to increased particle sizes, which must be caused by a decrease in the number of effective foreign nuclei. There is no rational basis for expecting a decrease in the total number of foreign nuclei in these solvent systems, which leads to the postulate that the ability of the nuclei to act as effective crystal growth sites must be decreased by the presence of the acetone. The fact that this change is most pronounced with the first addition of acetone (*i.e.*, from 0 to 20 %) and decreases until disappearing at about 50 % acetone suggests a Langmuir type adsorption of the acetone on the active crystal growth sites. This postulate is also consistent with the supersaturation dependence of particle size since at the high acetone concentrations the more weakly held acetone molecules may be displaced by the precipitating particles at the higher supersaturations.

The practical significance of this effect should not be overlooked. The reduced number of effective nuclei in the mixed solvent media favours the formation of larger crystals, which are more easily separated. In this respect, the technique of precipitation from mixed solvents has a definite advantage over other more common methods of precipitation from homogeneous solution, where it was found that the number of particles produced is often little different from the number obtained by direct mixing of suitable, dilute solutions.[20]

Precipitation of anhydrous copper(II) 8-hydroxyquinolinate

While precipitations from 60% acetone solutions were being performed, it was observed that in some runs, crystals of different appearance and behaviour were formed in addition to the normally occurring crystals. The ordinary crystals were yellow, star-shaped, and did not move in the observation tube. The other crystals were bright green and more compact.

X-Ray powder diffraction data clearly established that the unit cells of the two materials were different. Gravimetric analysis of the two crystal forms confirmed the expected fact that the difference observed arose from a change in the degree of hydration. The yellow form was found to be a dihydrate, while the green crystals were an anhydrous form of copper 8-hydroxyquinolinate.

The anhydrous crystal form became predominant in precipitations from 70% acetone. These crystals tended to settle rapidly even at sizes barely visible under strong illumination of the observation tube. The decrease in transmittance due to the presence of these crystals, therefore, never exceeded 2% at a wavelength of 500 nm and was too small to be useful for following the course of reaction. The disappearance of the green chelate complex from solution was therefore used to study the precipitation kinetics, a wavelength of 445 nm being used.

The interpretation of the kinetic data was undertaken as for the dihydrate. No correction was made to take into account any absorption changes due to the presence of precipitate, and runs in which both crystal types occurred were excluded from further considerations. For the runs with 70% acetone solutions, plots identical to those shown in Fig. 3 yielded an average exponent and standard deviation of $\bar{n} = 2{\cdot}53 \pm 0{\cdot}16$. This value, being significantly different from $\bar{n}$ for the dihydrate, would indicate that another reaction step, such as a process at the crystal surface, may have become rate-determining.

This first indication was confirmed by applying Reich and Kahlweit's treatment. It can be seen on Fig. 5 that $(j/k')^{1/2}$ *vs.* $(C_t - C_s)$ now approached a straight line rather than the simple first-order function. The precipitation of anhydrous copper 8-hydroxyquinolinate must, therefore, be governed by a surface-controlled reaction.

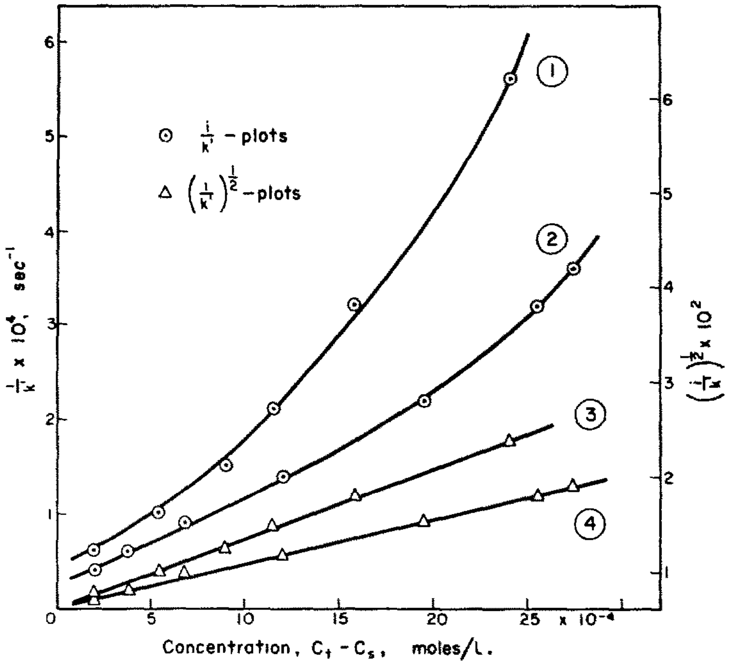

FIG. 5.—Experimental crystal growth data of anhydrous copper(II) 8-hydroxyquinolinate precipitated from 70% acetone–water solutions; first- and second-order rate plots according to equations (8) and (9).
C_0 (mole/l. × 10^4): ① and ③—74·50; ② and ④—38·50.

The difference of three orders of magnitude in the ordinate scales of Figs. 4 and 5, together with determined τ values ranging from 2000 to 10000 sec, indicated that the precipitation of the anhydrous form was a much slower process. As it appears very unlikely that diffusional rates are much affected in going from 60% to 70% acetone solutions, the crystal growth of the anhydrous form cannot be limited by diffusion.

CONCLUSIONS

This study has shown three major factors to be of importance in causing an improvement of the physical characteristics of copper(II) 8-hydroxyquinolinate crystals when these are precipitated from mixed solvents. First, the presence of organic solvents such as acetone increases the solubility of this chelate compound sufficiently to permit a controlled precipitation in which the supersaturation and growth rate are conveniently regulated by the evaporation of the organic solvent. Secondly, the number of growing particles is reduced, which leads to the formation of larger, more easily manipulated crystals. The presence of acetone inhibits a considerable number of heterogeneous nuclei from becoming effective growth sites. Thirdly, the actual growth mechanism and crystal composition are altered in the presence of large amounts of acetone. Copper(II) 8-hydroxyquinolinate is precipitated at room temperature as a dihydrate in water–acetone mixtures containing from 0 to 60% v/v acetone. Within this range of solvent composition, the precipitation kinetics do not change, and the crystal growth is governed by a diffusion-limited process. Anhydrous copper(II) 8-hydroxyquinolinate is produced from 70% acetone solutions.

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Zusammenfassung—Die Fällungskinetik von Kupfer(II)-8-hydroxychinolat, das sich in Aceton-Wasser-Gemischen bildet, wurde in einer stopped-flow-Apparatur spektrophotometrisch untersucht. Drei Faktoren wurden gefunden, die zur Verbesserung der physikalischen Eigenschaften von aus Lösungsmittelgemischen gefällten Kristallen wichtig sind. Übersattigung und Wachstumsgeschwindigkeit können durch langsame Änderung der Lösungsmittelzusammensetzung kontrolliert werden; die Gegenwart von Aceton vermindert die effektive Keimzahl erheblich; große Mengen des organischen Lösungsmittels bewirken einen Wechsel in der Kristallform und dem Wachstumsmechanismus. Bei Zimmertemperatur fällt Kupfer(II)-8-hydroxychinolat als Dihydrat aus Gemischen mit bis zu 60% Aceton; das Kristallwachstum ist diffusionskontrolliert. In 70% Aceton bildet sich wasserfreies Kupfer(II)-8-hydroxychinolat nach einem oberflächenkontrollierten Mechanismus.

Résumé—Les cinétiques de précipitation du 8-hydroxyquinoléinate de cuivre(II), formé en mélanges eau-acétone, ont été étudiées dans un appareil 'stop-flow' par des techniques spectrophotométriques. On a trouvé que trois facteurs sont importants dans l'amélioration des caractéristiques physiques des cristaux précipités à partir de mélanges de solvants. On peut contrôler uniformément la sursaturation et la vitesse de croissance par la vitesse lente de changement dans la composition du solvant; la présence d'acétone réduit notablement le numbre de germes efficaces; troisièmement, de grandes quantités de solvant organique causent un changement dans la forme du cristal et son mécanisme de croissance. A température ordinaire, le 8-hydroxyquinoléinate de cuivre(II) est précipité à l'état de dihydrate à partir de mélanges eau-acétone contenant 0–60% d'acétone et la croissance du cristal est limitée par un processus régi par la diffusion. Le 8-hydroxyquinoléinate de cuivre(II) anhydre est formé en solutions à 70% d'acétone par une réaction régie par la surface.

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SOLVENT EXTRACTION OF Ga(III) AND In(III) FROM AQUEOUS HALIDE MEDIA BY ADOGEN-364

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Summary—Adogen-364 has been used for the extraction of gallium(III) and indium(III) from halogen acid solutions, and the dependence of the extraction on chloride, bromide and iodide ion concentration studied. The separation of Ga(III), In(III) and Al(III) is reported and some conclusions have been drawn about the stoichiometry of the extracted species.

AMINES have found wide application for analytical separations.[1–4] The extraction of a variety of metal complexes from halogen acids has been reported.[5–7] Good *et al.*[8,9] used long chain alkylamines and quaternary ammonium salts for the extraction of iron(III), cobalt(II), gallium(III) and indium(III) from aqueous chloride solutions. Application of high molecular weight amines for the extraction of some metal iodides including gallium and indium has been reported by Suzuki.[10]

The aim of this investigation is to achieve separation of gallium(III), indium(III) and aluminium(III) ions from each other by amine extraction, using Adogen-364 in toluene.

EXPERIMENTAL

Reagents

Adogen-364. Obtained from Archer-Daniels-Midland Co., Minneapolis. It is a water-insoluble trialkyl tertiary amine mixture of C_8 and C_{10} chains with C_8 predominating: average molecular weight 390; sp. gr. 0·802. Solutions of Adogen-364 were prepared by dilution with toluene.

Gallium and indium solutions. The metal was dissolved in concentrated hydrochloric acid and the solution evaporated almost to dryness to give the chloride. Metal sulphate solutions were prepared by precipitation of gallium and indium hydroxide followed by dissolution in the minimum quantity of concentrated sulphuric acid. Both gallium and indium stock solutions were standardized against EDTA. The metal bromide or iodide was obtained in solution by addition of the corresponding acid to the sulphate solution.

Procedure

The extraction experiments were performed in separating-funnels; 10 ml of the aqueous phase containing gallium and indium at concentration levels of about $10^{-3}M$ at different halogen acid concentrations were shaken for 2 min with an equal volume of Adogen-364 (1% v/v) in toluene. After equilibration the phases were separated and analysed for metal ion concentration.

Each of the separated phases was heated to dryness and the organic residue was destroyed by a mixture of nitric and sulphuric acids. The metal concentration was determined spectrophotometrically with gallion[11] for gallium, and Alizarin-S[12] for indium.

RESULTS AND DISCUSSION

Extraction of indium and gallium

Gallium, indium and aluminium were extracted by Adogen-364 from their solutions in halogen acids (HCl, HBr, HI). The results obtained showed that it is possible to separate them.

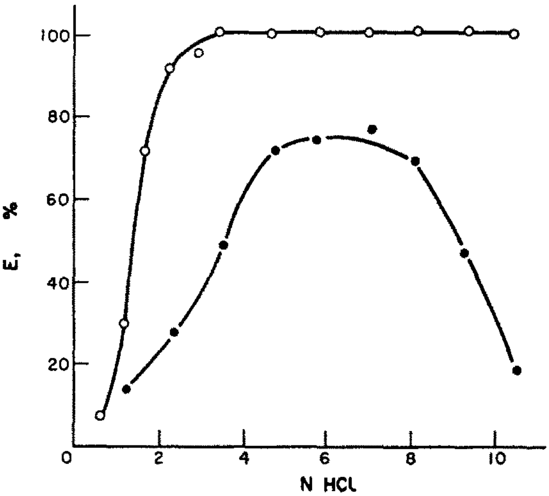

FIG. 1.—Variation of the degree of extraction of Ga(III) and In(III) as function of HCl concentration.
1% solution of Adogen-364 in toluene.
O—Ga(III); ●—In(III)

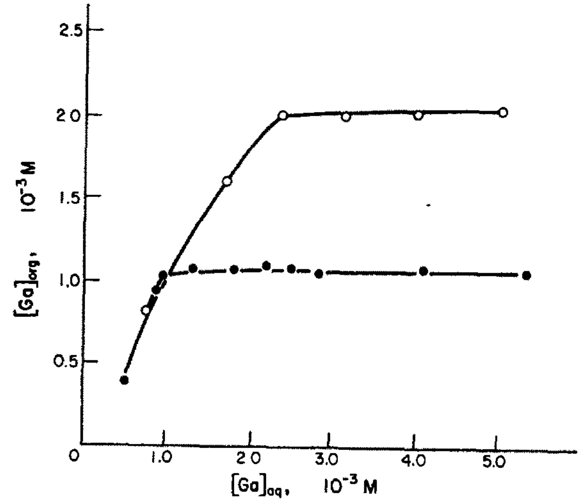

FIG. 2.—Extraction isotherm for Ga(III) and 2·0 × $10^{-3}M$ Adogen-364 in toluene.
O—From 6*M* HCl; ●—From 5·5*M* HBr

The degree of extraction of gallium and indium metal complexes increases with hydrochloric acid concentration as shown in Fig. 1, but the extraction of indium passes through a maximum at higher acid concentration.

The extraction isotherm for the gallium-chloride system (Fig. 2) indicates that the limiting ratio of amine hydrochloride to gallium is 1:1. The data of Woodward[13] and Kraus[14] indicate that tetrachlorogallate is the predominant species in aqueous hydrochloric acid solutions so that the ion-pair $R_3NH{\cdot}GaCl_4$ may be the extractable species.

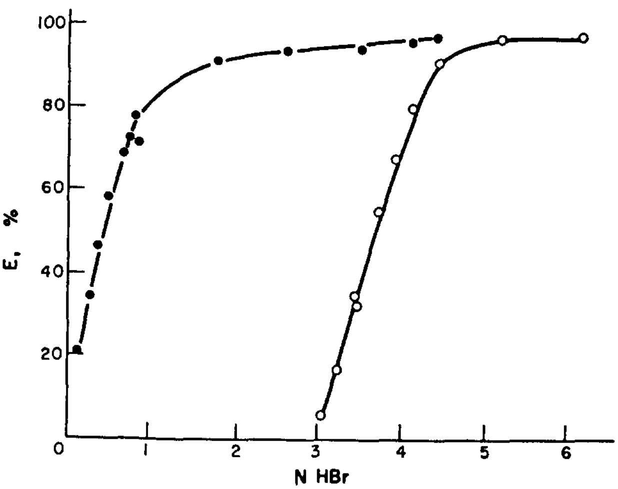

FIG. 3.—Dependence of the degree of extraction of Ga(III) and In(III), on HBr concentration.
1 % solution of Adogen-364 in toluene.
○—Ga(III); ●—In(III)

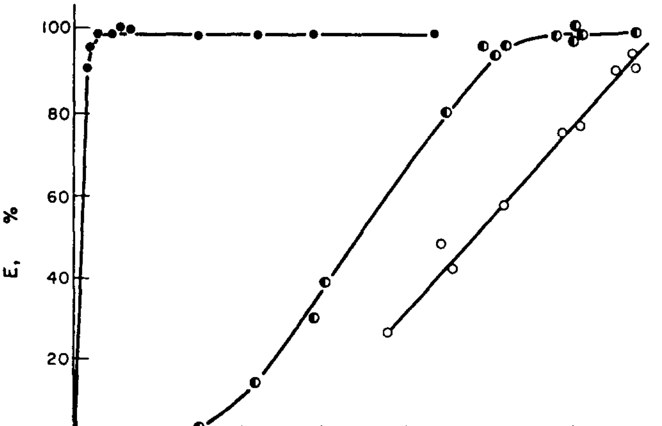

FIG. 4.—Dependence of the degree of extraction of Ga(III) and In(III), on HI concentration.
●—In(III), extraction by 1 % amine solution.
◐—Ga(III), extraction by 1 % amine solution.
○—Ga(III), extraction by 5 % amine solution.

The variation of degree of extraction of gallium and indium bromide complexes with the concentration of the acid in the aqueous phase is shown in Fig. 3. The indium bromide complex is extracted at lower acidity than the corresponding gallium complex; 50 % extraction is reached for indium at an acidity of 0·5*M*, whereas with gallium 50 % extraction is reached only at 3·7*M*. There is no decrease in extractability of indium with increasing concentration of the acid, such as is observed in the chloride system. The extraction isotherm of gallium bromide shows a 2:1 ratio of amine hydrobromide to gallium (Fig. 2), and the ion-pair $(R_3NH)_2 \cdot GaBr_5$ may be extracted. The extraction isotherm of the indium–bromide system indicates that the ratio of

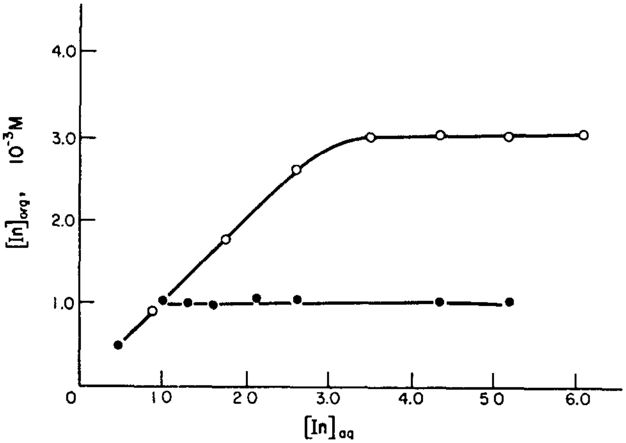

FIG. 5.—Extraction isotherm for In(III) and $3\cdot0 \times 10^{-3}M$ Adogen-364 in toluene. ○—From $2M$ HI; ●—From $2\cdot5M$ HBr

TABLE I.—SEPARATION OF INDIUM FROM GALLIUM IN $2M$ HBr

Ratio of Ga:In	Gallium		Indium	
	Taken, *mg*	found, *mg*	Taken, *mg*	Found, *mg*
1:1	2·58	2·60	2·90	2·96
1:1	2·58	2·57	2·90	2·90
1:1	2·58	2·58	2·90	—
1:1	2·58	2·57	2·90	2·86
10:1	0·50	0·50	0·05	0·05
10:1	5·00	5·00	0·50	0·50
100:1	10·00	9·92	0·10	0·10
1:10	—	—	0·50	0·53

TABLE II.—SEPARATION OF INDIUM FROM GALLIUM IN $1\cdot5M$ HI

Ratio of Ga:In	Gallium		Indium	
	Taken, *mg*	Found, *mg*	Taken, *mg*	Found, *mg*
1:1	2·50	2·47	2·00	1·97
1:10	0·50	0·50	5·00	4·94
1:100	0·05	0·05	5·00	5·00
1:1	2·50	2·43	2·00	1·94
1:100	0·05	0·05	5·00	4·94
1:10	0·50	0·49	5·00	5·00

amine hydrobromide to metal is 3:1 (Fig. 5), and that the ion-association compound $(R_3NH)_3\cdot InBr_6$ may be extracted.

From hydriodic acid solution, indium is more readily extracted than gallium (Fig. 4). The extraction isotherm of indium iodide was obtained (Fig. 5), indicating an amine hydriodide to metal ratio of 1:1.

From the results obtained, it can be seen that in the case of gallium, with increasing acid concentration, the order of extractability of the various complexes is $Cl^- > Br^- > I^-$, and in the case of indium it is $I^- > Br^- > Cl^-$. These results agree with those obtained by ion-exchange,[15,16] and solvent extraction methods.[17]

TABLE III.—SEPARATION OF GALLIUM FROM ALUMINIUM IN 6·5*M* HBr

Ratio of Ga:Al	Gallium	
	Taken, *mg*	Found, *mg*
1:10	0·50	0·50
1:1	2·50	2·49
1:10	0·50	0·50
1:100	0·50	0·49
1:1	0·50	0·49
1:10	0·50	0·48
1:100	0·50	0·48

TABLE IV.—SEPARATION OF GALLIUM FROM ALUMINIUM IN 7·0*M* HCl

Ratio of Ga:Al	Gallium	
	Taken, *mg*	Found, *mg*
1:1	2·50	2·45
1:10	0·50	0·49
1:100	0·50	0·48
1:1	2·50	2·50
1:10	0·50	0·50
1:100	0·50	0·49

TABLE V.—SEPARATION OF INDIUM FROM ALUMINIUM IN 5·0*M* HBr

Ratio of In:Al	Indium	
	Taken, *mg*	Found, *mg*
1:10	1·00	1·03
1:100	1·00	0·98
1:1	1·00	0·99
1:10	2·00	1·96
1:100	1·00	0·94
1:1	1·00	0·94

Extraction of aluminium by Adogen-364 in all the systems mentioned is negligible over the concentration range studied.

SEPARATION OF GALLIUM, INDIUM AND ALUMINIUM

The extraction results show that it is possible to separate indium and gallium from both 2*M* hydrobromic acid and 1·5*M* hydriodic acid; gallium and aluminium from both 7·0*M* hydrochloric acid and 6·5*M* hydrobromic acid; indium and aluminium from both 5*M* hydrobromic acid and 2*M* hydriodic acid.

The separation of the three elements from each other could be achieved by the extraction of indium from 1·5*M* hydriodic acid followed by the extraction of gallium from 7*M* hydrochloric acid.

Synthetic mixtures of the metal salts were prepared and the suitable acidity of the aqueous phase for the extraction of one component was established by the addition of the corresponding acid. The aqueous phase was shaken twice, each time for 2 min,

TABLE VI.—SEPARATION OF INDIUM FROM ALUMINIUM IN 2·0M HI

Ratio of In:Al	Indium	
	Taken, *mg*	Found, *mg*
1:10	1·00	0·97
1:100	1·00	1·02
1:1	2·02	2·02
1:10	1·00	0·98
1:100	1·00	0·98
1:1	2·00	1·96

with an equal volume of 1% v/v amine solution in toluene. For the separation of gallium from aluminium in hydrobromic acid medium, 5% v/v amine solution in toluene was used. Results of the separations are listed in Tables I–VI. Every element separated was tested spectroscopically for the presence of other cations.

Determination of gallium and indium after separation was carried out spectrophotometrically by means of the reagents mentioned above.

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Zusammenfassung—Adogen-364 ist zur Ausscheidung von Gallium(III) und Indium(III) aus Halogen Säurelösungen benutzt worden und die Abhängigkeit von Chlorid, Bromid und Jodid-Ionen bei der Ausscheidung wurde studiert. Ein Bericht über die Trennung von Ga(III), In(III) und Al(III) wird gegeben und einige Schlüsse wurden über die Stöchiometrie der ausgeschiedenen Arten getroffen.

Résumé—On a utilisé l'Adogen-364 pour l'extraction du gallium(III) et de l'indium(III) à partir de solutions d'hydracides, et l'on a étudié la dépendance de l'extraction par rapport à la concentration en ion chlorure, bromure et iodure. On rapporte la séparation de Ga(III), In(III) et Al(III) et l'on tire quelques conclusions sur la stoechiométrie de l'espèce extraite.

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VERSATILE SPECTROPHOTOMETRIC METHOD FOR THE DETERMINATION OF SILICON*

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Summary—A versatile spectrophotometric method is described for the determination of microgram levels of silicon, as molybdenum blue. It combines the desirable features of existing spectrophotometric methods with three pretreatment procedures, namely (*a*) the removal of cations with a cation-exchange resin in the H^+-form, (*b*) the conversion of all silicon species into the reactive monomer with an alkaline treatment, and (*c*) the decomposition of silicon fluoride with boric acid in the presence of cation-exchange resin. These pretreatments coupled with the colour development provide five procedures which are applicable to a wide variety of samples including natural and industrial waters and solutions of various nuclear reactor fuels and components. Provisions are included for the selective determination of total silicon.

MICROGRAM amounts of silicon are usually determined by the familiar molybdenum blue colorimetric method. Many variations of this method[1–6] were investigated in an attempt to establish a reliable, sensitive spectrophotometric method for silicon with sufficient versatility for application to a wide diversity of samples. All the methods investigated, though sufficiently sensitive, had several shortcomings, foremost of which was the low tolerance for diverse ions, especially common anions. To circumvent this major defect, most of the methods were oriented to specific analytical problems and used with close control of sample preparation and with calibration under the same conditions as the samples.

The desirable features of these molybdenum blue procedures have now been combined with three simple pretreatments (see Table I) to provide a truly versatile spectrophotometric method that is free from the limitations mentioned. The pretreatments are (*a*) conversion of non-reactive silicon species into the reactive monomer with hot sodium hydroxide solution, (*b*) removal of cations and excess of sodium hydroxide with cation-exchange resin, and (*c*) complexation of fluoride with boric acid. The basic molybdenum blue method is used alone and in various combinations with these three pretreatments to give five separate procedures. The proposed method has high tolerance for diverse ions and is applicable to a wide variety of samples including natural and industrial waters, and solutions of various nuclear fuels and components. Provisions are made for the selective determination of the sum of the reactive monosilicic and disilicic acids and for the determination of total silicon.

EXPERIMENTAL

Apparatus

Because of the limited but non-negligible solubility of silica in water, especially that which is alkaline, plastic ware was used wherever possible in treatment of samples and to store reagents. Most of the items recommended are commercially available. For filtration, 0·45-μm membrane

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filters were supported on a 25-mm Millipore filter holder used in conjunction with a Fisher filtrator. The base of the filter holder was extended to a total length of 180 mm with 6-mm tubing to permit direct filtration into a beaker or a 50-ml polyethylene bottle.

Reagents

Silicon-free ammonia solution, ~*6M*. Expose distilled water to twice its volume of conc. ammonia solution in a sealed polyethylene bag for 12–24 hr, stirring the water constantly by magnetic stirring during the equilibration.

TABLE I.—APPLICABILITY OF THE VARIOUS PROCEDURES

Procedure	Applicability	Diverse ion effect*
I.	Molybdenum blue procedure. Determination of reactive silicon in aqueous solution devoid of fluoride. Samples containing much Cu(II) must be analysed by procedure III. Samples containing Fe are conveniently analysed by procedure III.	The tolerance levels, expressed as diverse ion to silicon molar ratio, are at least 950 for Al; at least 185 for Co, Cr(III, VI), Fe†, lanthanides‡, Mn, Ni, and Zn; 25 for As(V), Hg, Sn(IV), U(VI), and V(V). Copper(II) absorbs at 810 nm, hence its tolerance ratio is only 20. Tin(II) immediately reduces the molybdate and must be absent. The alkaline earths require the use of HNO_3 instead of H_2SO_4 for pH adjustment. Up to 10 mmole of Cl^-, ClO_4^-, NO_3^-, and SO_4^{2-}, and 0·005 mmole of phosphate per sample aliquot do not interfere. Citrate, fluoride, oxalate, and tartrate must be absent.
II.	Alkaline pretreatment followed by molybdenum blue procedure. Determination of total silicon in low-salt aqueous solutions devoid of fluoride. Samples containing much Cu(II) must be analysed by procedure IV.	Anions same as procedure I. Cations which form insoluble hydroxides must be absent. Use procedure IV for samples containing cations that form insoluble hydroxides.
III.	Cation-exchange resin treatment followed by molybdenum blue procedure. Determination of the sum of reactive silicon in aqueous metal salt solutions devoid of fluoride.	Anion tolerance same as for procedure I. Metals, except those in the form of anionic complexes, are removed by the cation-exchanger; *e.g.*, 2 mmole of Al, 1·5 mmole of equimolar Fe, Cr, Ni mixture, 0·8 mmole of U, and 0·5 mmole of Bi are removed sufficiently to permit application of the alkaline treatment. The tolerance for metals that form anionic complexes is the same as for procedure I.
IV.	Cation-exchange resin treatment followed by alkaline treatment followed by molybdenum blue procedure. Determination of total soluble silicon in aqueous metal salt solutions devoid of fluoride.	As for procedure III.
V.	Cation-exchange resin–boric acid treatment followed by molybdenum blue procedure. Determination of total silicon in metal salt solutions containing fluoride.	Except for those that exist as stable anionic complexes, cations are removed by the resin. This procedure has been applied successfully to fluoride solutions of "Zircaloy" and to mixtures of Al-U and Zr-U fuel solutions. Niobium at 10 and Sn(IV) and Ti at 25 molar ratio to silicon do not interfere. At least 5 mmole of fluoride can be present in the sample aliquot without adverse effect.

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* Based on diverse ion studies at a silicon level of 30 μg (1 μmole) The interference level was established on the basis of a *t*-test at the 95% confidence level.

† Because the molybdenum blue colour is slow to form, the minimum colour development time is 1·5 hr.

‡ Lanthanide oxalates are insoluble, so the sample solution must be centrifuged or filtered.

Ammonium molybdate reagent. Dissolve 50 g of ammonium heptamolybdate tetrahydrate in water, filter the solution through a 0·45-μm membrane filter, then dilute the solution to 500 ml.

Oxalic acid–tartaric acid complexing reagent, 0·75*M* in each component.

Reducing agent. Dissolve 27 g of sodium hydrogen sulphite, 2 g of sodium hydroxide, and 0·50 g of 1-amino-2-naphthol-4-sulphonic acid in 225 ml of water, filter, and dilute to 250 ml.

Cation-exchanger. Dowex 50W-X8 (or equivalent), 50–100-mesh, in the H$^+$-form. The resin must be washed with 6*M* hydrochloric acid and then with water, then stored without water in a plastic container.

Silicon stock solution, 1·000 mg/ml. Fuse 0·5350 g of pure silica with 2 g of sodium carbonate in a platinum crucible, cool, dissolve the melt and dilute to 250 ml with water containing 0·4% sodium hydroxide. Prepare working standards from the stock solution by dilution with the same sodium hydroxide solution.

Procedures

The basic molybdenum blue method for the determination of silicon is used alone or in various combinations with sodium hydroxide, cation-exchange resin, and boric acid pretreatments to provide five procedures for different types of samples and different determinations (Table I). In all cases, two appropriate standards and a blank are processed simultaneously and the results for the samples are calculated by comparison with the standards.

Procedure I. Place a sample aliquot of 75 ml or less, containing 5–100 μg of reactive silicon, into a 100-ml polyethylene beaker. Adjust the pH to 1·1 ± 0·1 with 6*N* sulphuric or nitric acid, then add 10 ml of ammonium molybdate reagent. Adjust the pH to 1·3 ± 0·1 with either 6*N* sulphuric acid or ammonia, and let stand for 10 min. Add 10 ml of the complexing reagent, mix, and after 30 sec but within 1 min of the addition of complexer, add 2 ml of the reducing solution. Wait 20 min for colour development, then dilute the solution to 100 ml with water in a volumetric flask. Measure the absorbance against water at 815 nm (infrared source and detector) or at 795 nm (visible source and detector) in 10- or 50-mm cells.

Procedure II. Place a sample aliquot of 50 ml or less, containing 5–100 μg of silicon, into a 50-ml polyethylene bottle. Add 2 drops of phenolphthalein indicator, then 50% sodium hydroxide solution until the solution turns pink, plus an additional 5 drops. Heat in a boiling water-bath for 20 min and chill to room temperature. Add H$^+$-form cation-exchange resin until the solution is neutral, then add approximately 5 ml more. Filter the sample through a 0·45-μm membrane filter and collect the filtrate and water rinses in a 100-ml polyethylene beaker. Continue with the determination as in Procedure I. If much precipitate appears when the sample is made basic, the results will be low and the sample should be analysed by Procedure IV.

Procedure III. Add approximately 10 ml of H$^+$-form cation-exchange resin to a 50-ml polyethylene beaker. Transfer a sample aliquot of 25 ml or less, containing 5–100 μg of reactive silicon, onto the resin and mix. Filter the solution through a 0·45-μm membrane filter and collect the filtrate and water rinses in a 100-ml polyethylene beaker. Continue with the determination as in Procedure I.

Procedure IV. Carry the sample through the cation-exchange resin treatment and the alkaline treatment as in Procedures III and II and finish by Procedure I. As there is a filtration before the alkaline treatment, particulate silicon is not determined.

Procedure V. Add approximately 10 ml of H$^+$-form cation-exchange resin to a 50-ml polyethylene beaker. Transfer a sample aliquot of 5 ml or less, containing 5–100 μg of silicon, onto the resin and mix. Add 40 ml of saturated boric solution, mix, and let stand for 30 min with intermittent mixing. Filter the sample through a 0·45-μm membrane filter and collect the filtrate and water washes (which must not exceed 70 ml) in a 100-ml polyethylene beaker. Conclude the determination by Procedure I. In fluoride medium, silicon generally exists only as the fluoride-complexed monomer so only total silicon is determinable.

RESULTS AND DISCUSSION

The widely used molybdenum blue procedure for the determination of silicon involves initial formation of the yellow silicomolybdic acid complex, reduction of the yellow complex to the more sensitive molybdenum blue complex, and spectrophotometric measurement of the blue colour. The existing molybdenum blue methods have these three basic steps in common but vary in the specific conditions used to develop and measure the molybdenum blue species. For example, various pH values and molybdenum reagents have been recommended for the formation of the silicomolybdate complex, various organic complexing reagents have been suggested for masking the excess of molybdate and destroying extraneous molybdate complexes, and many reducing reagents have been used to produce the blue complex. The measurement of the blue complex has been made at several different wavelengths.

The many variations in the colour development phase of the method were studied and evaluated. A discussion of the pertinent variables, pH, reagents, and measurement of the blue complex follows.

Formation of silicomolybdate

The critical variables in the formation of the silicomolybdic acid complex are the chemical state of the silicon, the pH, the quantity and composition of the molybdate reagent, and the presence of anions.

In an aqueous medium, silicon exists as monosilicic acid, disilicic acid, a variety of higher polysilicic acids, and silica. One or any combination of these species may be present, depending on such factors as temperature, pressure, pH, and the presence of various electrolytes.

Monosilicic acid and disilic acid are reported to react quantitatively with ammonium molybdate in 75 sec and 10 min, respectively.[7] Polysilicic acids and silica react slowly or not at all and must be converted into the reactive monomer if they are to be determined. The conversion can be accomplished by reaction with hydrofluoric acid, by a basic fusion, or by reaction with a hot sodium hydroxide solution. The decomposition in a hot alkaline solution at pH 12–13 is employed in this method. In solutions containing fluoride, the silicon exists predominantly as a fluorosilicate which yields the reactive monomer upon reaction with boric acid, so no conversion is deemed necessary.

The optimum pH for the reaction of monosilicic acid and molybdate has been reported as 1·2–1·3,[8] 1·6[9] and 1·6–2·0.[10] Based on a pH study over the range 1·0–2·0, a pH of 1·3 ± 0·1 is recommended, corresponding to formation of α-silicomolybdic acid.[11] The simplest method of achieving these conditions is to add the ammonium molybdate solution to a sample acidified to pH 1·1 ± 0·1. If the pH is too high, colour formation is incomplete.

Previous investigators have recommended different amounts of ammonium molybdate in the form of a water solution or a sulphuric acid solution. All variations gave satisfactory production of the yellow silicomolybdate in low-salt media; however, without exception, the suggested conditions did not provide adequate tolerance for the common anions chloride, nitrate, perchlorate, and sulphate. These ions could be tolerated in quantities only up to about 2 mmole, above which serious negative interference is observed. A much more practical tolerance of about 10 mmole is obtained by using a water solution of molybdate and maintaining the molybdate at 0·85 mmole per test sample. At this molybdate level, phosphomolybdate resists dissociation by oxalic acid and tartaric acid; however, if the amount of oxalic and tartaric acids added is increased to 7·5 mmole of each, satisfactory results are obtained.

Complexation of excess of molybdate and destruction of extraneous molybdate complexes

After the silicomolybdic acid has been formed, an organic complexing reagent is introduced to mask residual molybdate and destroy other molybdate complexes. A 0·75*M* oxalic acid–0·75*M* tartaric acid complexing solution is used in this method.

The complexer also slowly breaks up the silicomolybdic acid complex so the interval between the addition of the complexing solution and the addition of the reducing reagent must be kept between 30 and 60 sec. The absorbance of the sample decreases at the rate of 0·005/min. The complexing reagent and the reducing solution may not be added simultaneously because complete dissociation of the phosphomolybdate complex is then not attained.

Reduction of silicomolybdate to molybdenum blue

Chlorostannous acid, iron(II) ammonium sulphate, sodium sulphite, and various mixtures of sodium sulphite, sodium bisulphite, and 1-amino-2-naphthol-4-sulphonic acid have been used to reduce silicomolybdate to the molybdenum blue complex.[1,2] The last of these, prepared according to Banks and Carlson,[6] was confirmed to be the most reliable from the standpoint of stability of the reduced species, stability of the reducing solution (shelf life is at least one month), and colour reproducibility. Quantitative colour development is obtained in 20 min and the colour is stable for at least 16 hr.

Under the recommended colour development conditions, the absorbance spectrum of the molybdenum blue complex has a maximum at 815 nm with an infrared source and detector and 795 nm with a visible source and detector. Best results are obtained with the infrared source and detector.

TABLE II.—RESULTS OF THE ANALYSIS OF SILICON STANDARDS AND DIFFERENT TYPES OF SYNTHETIC SAMPLES BY THE VARIOUS PROCEDURES

Procedure	Salt or matrix added	Amount	Recovery*, %
I	None	—	100·0 ± 1·2 (19)
	Various metal salts individually (See Table I)	0·2 mmole	99·9 ± 1·2
II	None	—	98·3 ± 0·4 (4)†
III	None	—	100·8 ± 1·0 (4)
	7:2:1 Fe–Cr–Ni mixture as nitrates	1·5 mmole total	100·6 ± 0·6 (4)
IV	None	—	99·9 ± 1·2 (2)
	$Bi(NO_3)_3$	0·5 mmole	98·0
	$Cu(NO_3)_2$	1·0 mmole	99·5
	$Hg(NO_3)_2$	0·5 mmole	98·0
	7:2:1 Fe–Cr–Ni mixture as nitrates	1·5 mmole total	101·7
	0·4M $SnCl_4$—2M HCl	1·0 ml	91·0‡
V	0·01M $KNbO_3$—4·6M HF	1·0 ml	100·5
	0·08 M $SnCl_4$—4·6M HF	0·25 ml	100·0
		1·0 ml	91·0‡
	0·02M Ti(IV) in HF–HNO_3	1·0 ml	99·5
	2·0M $Al(NO_3)_3$—0·014M $UO_2(NO_3)_2$—0·4M ZrF_4—3M HF	1·0 ml	99·5 ± 0·9 (5)

* The recoveries are quoted relative to the average silicon recovery in procedure I for pure silicon standards, with the associated standard deviation (number of replicates given in brackets). The silicon level was 30–40 μg throughout.

† The silicon was initially converted into a non-reactive form by evaporation with nitric acid.

‡ In chloride or fluoride media, the anionic Sn(IV) complexes are not completely removed by the resin. Residual Sn(IV) precipitates molybdate.

Use of cation-exchange resin to circumvent diverse ion effects

In an overall silicon method that includes alkaline conversion of inert silicon into reactive silicon, colour development and measurement, metal ions affect the determination in many ways. They may precipitate as the hydroxide, molybdate, oxalate, or other salts during colour development. They may prevent complete conversion of inert silicon species into the determinable monosilicate by precipitating at high pH and occluding silicon. They may, like copper, absorb at the working wavelength. Finally they may consume reductant. Cation-exchange resin in the H^+-form can be used effectively to avoid most, if not all, of these undesirable side-effects. The cation-exchange resin is also used to neutralize the sodium hydroxide introduced in the alkaline conversion treatment. This practice keeps the introduction of anions to a minimum. In many laboratories, including this one, highly radioactive samples must often be analysed. Use of the resin enables sufficient reduction of the activity level to permit removal of the sample from the shielding facility.

Effects of diverse ions; method reliability

The effects of diverse ions on the various procedures and the applicability of the various schemes to different types of samples have been studied. Table I summarizes the effects of diverse ions and Table II lists the results for silicon standards processed by the various schemes. Some of the standards were mixed with metal salts or acid–metal salt matrices known to be troublesome. It can readily be seen that the three pretreatments have little effect on the recovery of silicon and that each procedure produces highly satisfactory results within its limitations.

Based on results collected over a 2-month period, the attainable precision at the 30–40-μg silicon level is 1·25% relative standard deviation.

Zusammenfassung—Ein vielseitiges spektrophotometrisches Verfahren zur Bestimmung von Silicium im Mikrogrammbereich als Molybdänblau wird beschrieben. Es verbindet die Vorteile bekannter spektrophotometrischer Verfahren mit drei Vorschriften zur Vorbehandlung: (a) der Entfernung von Kationen mit einem Kationenaustauschharz in der H^+-Form; (b) der Überführung aller Silicium-Spezies durch Alkalibehandlung in das reaktionsfähige Monomere; (c) die Zersetzung von Siliciumfluorid mit Borsäure in Gegenwart von Kationenaustauschharz. Diese Vorstufen ergeben zusammen mit der Farbentwicklung fünf Verfahren, die auf viele verschiedenartige Proben anwendbar sind, darunter natürliche und industrielle Wässer und Lösungen verschiedener Kernreaktorbrennstoffe und-bestandteile. Die selektive Bestimmung von Gesamtsilicium ist berücksichtigt.

Résumé—On décrit une méthode spectrophotométrique polyvalente pour le dosage du silicium à des teneurs de l'ordre du microgramme, en tant que bleu de molybdène. Elle combine les caractères désirables de méthodes spectrophotométriques existantes avec trois techniques de prétraitement, nommément (*a*) l'élimination des cations avec une résine échangeuse de cations sous la forme H^+, (*b*) la conversion de toutes les espèces du silicium en le monomère réactif par un traitement alcalin, et (*c*) la décomposition du fluorure de silicium par l'acide borique en la présence d'une résine échangeuse de cations. Ces prétraitements associés avec le développement de la coloration fournissent cinq techniques qui sont applicables à une large variété d'échantillons comprenant l'eau naturelle et industrielle et des solutions de divers combustibles et constituants de réacteurs nucléaires. On inclut des dispositions particulières pour la détermination sélective du silicium total.

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END-POINT EVALUATION IN INSTRUMENTAL TITRIMETRY—I
LINEAR EXTRAPOLATION OF HYPERBOLIC TITRATION CURVES

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Summary—A method is described for the estimation of a systematic titration error which is introduced by linear extrapolation of hyperbolic titration curves in amperometric, photometric, and other instrumental titrations. It is assumed that the titration is based upon a single-step ion-association reaction $mA + nB \rightleftharpoons A_mB_n$ and that the measured physical property falls within known minimum and maximum values. The procedure is suitable for end-point determination, even when the titration curves have extensive curvature, and for predicting the choice of optimum experimental conditions for a given titration.

In many instrumental titrations, such as conductometric, amperometric, spectrophotometric, thermometric, and other titrations, the measured physical property represents a summation of partial contributions which are directly proportional to molar concentrations of the individual species involved in the equilibrium. The appropriate proportionality constants can be defined according to the method under consideration (see *e.g.*, ref. 1). Usually, their values depend upon the experimental conditions employed and may even be zero. In all these titrations hyperbolic titration curves are obtained with linear segments on both sides of a more or less pronounced bend in the vicinity of the equivalence point. The linear segments of the curve are extrapolated and the point of intersection is taken to be both the end-point and the equivalence point.

Such graphical end-point extrapolation presents no problem if the curvature around the equivalence point is insignificant and the linear segments are long enough. In practice, however, titration curves with extensive curvatures are fairly common. Tyrrell,[2] for example, presented a family of thermometric titration curves discussing the necessary criteria to obtain a sharp end-point. Usually, (Figs. 1 and 2) the extrapolated end-point deviates considerably from the true equivalence point. Thus, systematic titration errors may occur, their magnitude depending upon the concentration of the substance to be determined and upon the completeness of the reaction.

Most of the discussion of the problems of end-point extrapolation has been limited to the simple ion-combination reaction

$$A + B \rightleftharpoons AB$$

Langer and Stevenson[3] advocated two procedures for the end-point evaluation, using chords of the hyperbola. The first is based on the fact that if one asymptote to the titration curve is known, the second can easily be constructed by means of the theorem saying that on any chord the parts between the hyperbola and the two asymptotes are of equal length. The second procedure is based on the theorem that the bisector of any pair of parallel chords of the hyperbola goes through the intersection point of the asymptotes. Thus, the end-point of a hyperbolic titration curve is found as the point of intersection of the bisectors of two different pairs of parallel chords. Grunwald[4] has used a method of end-point calculation based on the curvature of the titration curve. If the mathematical expression of the titration curve is known, the equivalence point can be calculated as an intersection point of two secants. One of them is drawn across the curvature before the equivalence point, the second is given by a pair of points beyond the equivalence point. Again, one point is chosen, the other is calculated. This procedure may be easily applied only if the equilibrium is of a simple type. An easy but approximate way of systematic error estimation in photometric titrations based on the formation of a simple complex AB is given in the monograph by Ringbom,[5] and the expression derived by him is discussed below [*cf.* equation (10)]. The problem of the end-point evaluation when one of the asymptotes is known has been solved by Khadeev.[6] The estimation of the amperometric titration error has been studied by Gordienko and co-workers[7] for cases where one of the equilibrium species is not involved in the electrode reaction. Klas[8,9] has examined the titration curve and the end-point evaluation in radiometric precipitation titrations in which one of the ions forming the precipitate is labelled. He has also treated the problem of the systematic errors[10] in these titrations.

Less attention has been paid to the titration curves for a general case of reaction

$$mA + nB \rightleftharpoons A_mB_n$$

despite the known fact that the linear extrapolation of such a curve is subject to greater systematic errors. Brinkman has given expressions for the estimation of this error, but we have been unable to discover a full explanation of their derivation or value.[11] A rigorous investigation of the conditions required for the existence of extrema on titration curves and their locations was undertaken by Goldman and Meites.[1] They considered the general ion-combination reaction in which the product did not make any contribution to the physical property measured. The practical application of their expressions involves a detailed knowledge of the equilibrium itself and of the individual proportionality constants. A general equation of the amperometric precipitation curve for the above-mentioned equilibrium was also derived by Mar'yanov,[12] who also discussed the conditions for the existence of an extremum. Klas[13] evaluated a correction of the consumption of titrant in relation to the solubility of a precipitate A_mB_n in a radiometric titration.

The present paper deals with the problem of systematic errors arising in linear extrapolations of titration curves with considerable curvature. It is supposed that the titration is based on a one-step reaction and that the measured property is directly proportional to the concentration of the product A_mB_n and reaches a limiting constant value beyond the equivalence point, so that the position of the horizontal asymptote parallel to the abscissa is known. These conditions are often encountered in practice and the treatment permits easy end-point evaluation, even if the titration curve has pronounced curvature.

Derivations of equations

Consider the case of a titrimetric determination of a substance A with a standard solution of substance B in which the product A_mB_n is formed, essentially in one step. It is supposed that equilibrium is attained after each addition of the titrant, and is characterized by a formation constant

$$K_{mn} = \frac{[A_mB_n]}{[A]^m[B]^n} \tag{1}$$

which is usually the conditional (effective) stability constant.

The equations for the analytical concentrations of the constituents A and B are

$$c_A = [A] + m[A_mB_n] \tag{2}$$

$$c_B = [B] + n[A_mB_n] = ac_A \tag{3}$$

the parameter a (equivalent fraction) representing the ratio of the added titrant to the total amount of the substance A being titrated. To obtain the equation expressing the dependence of the measured equilibrium concentration of the product A_mB_n, terms from equations (2) and (3) are substituted into (1):

$$K_{mn} = \frac{[A_mB_n]}{(c_A - m[A_mB_n])^m(ac_A - n[A_mB_n])^n}\,. \tag{4}$$

This rearranges to give

$$F(a, [A_mB_n]) = K_{mn}(c_A - m[A_mB_n])^m(ac_A - n[A_mB_n])^n - [A_mB_n] = 0 \tag{5}$$

The derivative of this function forms the basis of a general equation of the tangent to the curve $[A_mB_n] = f(a)$ with the variables X and Y

$$\begin{aligned} &X\{nc_AK_{mn}(c_A - m[A_mB_n])^m(ac_A - n[A_mB_n])^{(n-1)}\} - Y\{K_{mn}(c_A - m[A_mB_n])^{(m-1)} \\ &\quad\times (ac_A - n[A_mB_n])^{(n-1)}[m^2(ac_A - n[A_mB_n]) + n^2(c_A - m[A_mB_n]) + 1\} \\ &\quad + mK_{mn}c_A(ac_A - n[A_mB_n])^n(c_A - m[A_mB_n])^{(m-1)} - (m + n - 1)[A_mB_n] = 0. \end{aligned} \tag{6}$$

Of more interest is an expression for the intersection of a given extrapolation tangent with the abscissa, $Y = c_A/m$. This straight line corresponds to the limiting value for the measured physical quantity, if the substance A is quantitatively converted into the complex A_mB_n. Substitution for Y and for the parameter a from equation (4), gives

$$X = \frac{n}{m} + \frac{c_A + m(m + n - 1)[A_mB_n]}{mnc_A[A_mB_n]}\sqrt[n]{\frac{[A_mB_n]}{K_{mn}(c_A - m[A_mB_n])^m}}\,. \tag{7}$$

It is convenient to introduce a new variable, *i.e.*, the distribution coefficient $\delta_{mn} = m[A_mB_n]/c_A$, which represents the relative amount of the substance A bound into the complex, or the relative part of the maximum change in the physical quantity to be measured during the titration. Then equation (7) may be rewritten

$$X = \frac{n}{m} + \frac{1 + (m + n - 1)\delta_{mn}}{n\delta_{mn}}\left(\frac{\delta_{mn}}{m(1 - \delta_{mn})^m}\right)^{1/n}(K_{mn}c_A{}^{(m+n-1)})^{-1/n} \tag{8}$$

or

$$X = \frac{n}{m} + f_{mn}(K_{mn}c_A^{(m+n-1)})^{-1/n} = \frac{n}{m} + \Delta a. \tag{9}$$

Thus, the deviation from the equivalence point $X = n/m$ is obtained as a product of the function f_{mn} and a constant which involves the value of the stability constant K_{mn} and the analytical concentration of the substance A to be titrated.

Systematic error in linear extrapolations of hyperbolic titration curves

To show the significance of the deviations which are inherent in the common procedure of extending the linear segments of the titration curve plot, values of c_A and K_{mn} were chosen so that the curvatures of the theoretical curves Figs. 1 and 2 were pronounced. The titration curve in Fig. 1 is calculated for the formation of AB, ($m = n = 1$) and it is seen that the linear branch extends as far as $\delta_{11} = 0{\cdot}4$. If this segment is used to extrapolate the end-point, a deviation $(\Delta a)_{0{\cdot}2} = 0{\cdot}15$ results. When the tangent is drawn from a point in the middle of the maximum attainable change, the deviation $(\Delta a)_{0{\cdot}5} = 0{\cdot}30$ is obtained which, in its turn, represents a positive 30% systematic error.

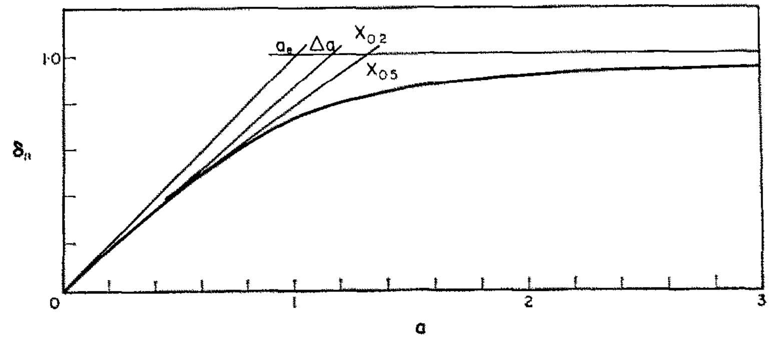

FIG. 1.—Dependence of distribution factor upon the equivalent fraction for the formation of complex AB; $K_{11}c_A = 10$.

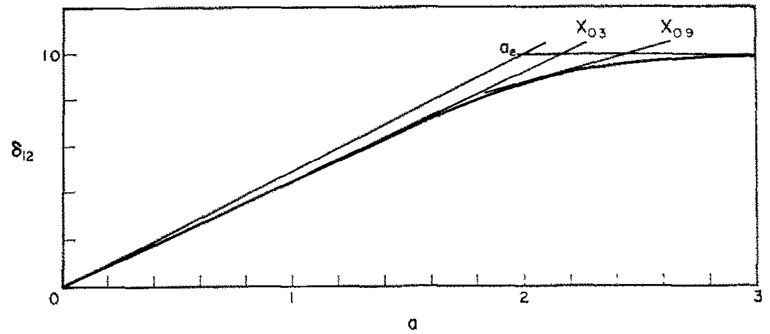

FIG. 2.—Dependence of the distribution factor upon the equivalent fraction for the formation of complex AB_2; $c_A\sqrt{K_{12}} = 10$.

Figure 2 shows the shape of the curve calculated for the formation of the AB_2, ($m = 1, n = 2$). It is linear up to $\delta_{12} = 0{\cdot}6$. The extrapolation of the tangent at $\delta_{12} = 0{\cdot}3$ intersects the horizontally extrapolated straight line at the point where the deviation from the equivalence point is $(\Delta a)_{0{\cdot}3} = 0{\cdot}175$. If the part about $\delta_{12} = 0{\cdot}9$

is used for extrapolation, a serious deviation results [$(\Delta a)_{0\cdot 9} = 0{\cdot}47$]. Thus, the extent of the systematic deviation increases, as the point used to draw the extrapolation tangent approaches the equivalence point. The general equation (8) allows the theoretical evaluation of the systematic error, if the type of the titration product and the values of the parameters δ_{mn}, K_{mn} and c_A are known.

The expressions log f_{mn} for individual types of titration products are summarized in Table I. To evaluate the extent of the end-point deviation for the more important types of titration products, the numerical values of the correction function f_{mn} given in Table II might be found useful.

TABLE I.—EXPRESSIONS OF THE CORRECTION FACTOR FOR THE MORE IMPORTANT TYPES OF TITRATION PRODUCTS

Type	$\log f_{mn}$
AB	$\log(1 + \delta_{11}) - \log(1 - \delta_{11})$
AB_2	$\log(1 + 2\delta_{12}) - \frac{1}{2}\log(1 - \delta_{12}) -$ $- \frac{1}{2}\log\delta_{12} - \log 2$
AB_4	$\log(1 + 4\delta_{14}) - \frac{1}{4}\log(1 - \delta_{14}) -$ $- \frac{3}{4}\log\delta_{14} - \log 4$
AB_6	$\log(1 + 6\delta_{16}) - \frac{1}{6}\log(1 - \delta_{16}) -$ $- \frac{5}{6}\log\delta_{16} - \log 6$
A_2B	$\log(1 + 2\delta_{21}) - 2\log(1 - \delta_{21}) - \log 2$

TABLE II.—VALUES OF THE CORRECTION FACTOR f_{mn} FOR VARIOUS TYPES OF TITRATION PRODUCTS

	Type				
	AB	AB_2	AB_4	AB_6	A_2B
δ_{mn}	f_{11}	f_{12}	f_{14}	f_{16}	f_{21}
0·05	1·105	2·524	2·875	2·653	0·609
0·10	1·222	2·000	2·021	1·849	0·741
0·20	1·500	1·750	1·591	1·455	1·094
0·30	1·857	1·746	1·483	1·351	1·633
0·40	2·333	1·837	1·468	1·324	2·500
0·50	3·000	2·000	1·500	1·333	4·000
0·60	4·000	2·245	1·568	1·367	6·875
0·70	5·667	2·619	1·677	1·426	13·33
0·80	9·000	3·250	1·856	1·523	32·50
0·90	19·00	4·667	2·213	1·709	140·0
0·95	39·00	6·653	2·640	1·922	580·0

In Fig. 3 there is a quite interesting dependence of the correction function values upon the position of the tangential point for individual types of the titration product A_mB_n. Apparently, the greater the ratio B:A, the greater the range of the linear part of the titration curve. The extrapolation tangents merge with the linear segment of the titration curve and the systematic error due to the extrapolated end-point remains constant up to the value of δ_{mn}, where the bend of the curve begins to occur. In the range of δ_{mn} from 0·2 to 0·4 the values of the function f_{mn} are fairly close within the range 1·1 to 1·80. Thus, in many cases an average value of f_{mn} may be used irrespective of the type of the complex.

Even in the case when the initial part of the curve (δ_{mn} approaching zero) is used to extrapolate the end-point, the evaluated consumption of the titrant does not correspond to the theoretical value. With the complex AB, for example, it is higher

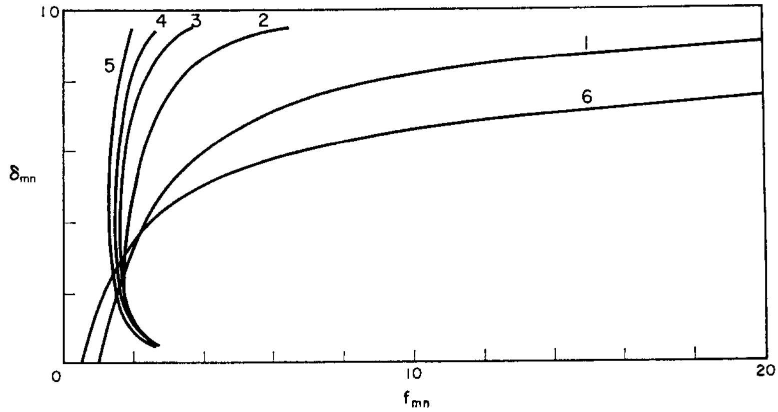

FIG. 3.—Dependence of correction factor f_{mn} upon the values of distribution factors for various types of titration products: (1) AB; (2) AB_2; (3) AB_3; (4) AB_4; (5) AB_6; (6) A_2B.

by the value $1/(K_{11}c_A)$. This systematic error becomes negligible only with low values of the term $(K_{mn}c_A^{(m+n-1)})^{-1/n}$, and depends thus upon the stability of the titration product.

The relative error, which is due to linear extrapolation of the end-point, can be readily expressed from equation (9)

$$\text{Error, \%} = \Delta a \frac{m}{n} 100 \tag{10}$$

If equation (10) is evaluated for the case of the complex AB, the solution obtained resembles the expression which was derived by Ringbom [*cf.* equation (34) in his monograph[5]] by another approach.

Equation (10) can also be taken as a relationship between a permissible relative error in the titration of the substance A, the stability constant and the position of the extrapolation straight line on the titration curve being given by the value of the correction term f_{mn}

$$\log \Delta a \frac{m}{n} = \log \frac{m}{n} + \log f_{mn} - \frac{m+n-1}{n} \log c_A - \frac{1}{n} \log K_{mn}. \tag{11}$$

The numerical values for the last two terms in equation (11) are given in Table III on the suppositions that the part of the curve at $\delta_{mn} = 0{\cdot}2$ is taken for the end-point extrapolation and that an accuracy of 0·1% is required. If the concentration of the substance to be titrated is known (*e.g.*, $10^{-4}M$), the minimum value of $\log K_{mn}$ necessary to achieve the required level of accuracy can be obtained.

End-point evaluation by the method of fan-traced tangents

To apply the proposed procedure for end-point evaluation, the stoichiometry of the titration product and the position of the horizontal asymptote corresponding to the maximum attainable value of the measured physical quantity must be known. As shown in Fig. 4, the tangents are laid off from the points chosen on a plot of the experimental titration curve, for instance at δ_{mn} equal to 0·2, 0·4, 0·6 and 0·8.

TABLE III.—PERMISSIBLE VALUES OF SOME PARAMETERS FOR A SUPPOSED 0·1% RELATIVE ERROR AND USING THE TANGENTIAL POINT AT $\delta_{mn} = 0{\cdot}2$

Type	AB	AB_2	AB_3	AB_4	AB_5	AB_6	A_2B
$\log K_{mn}$	6·8	14·1	21·7	29·6	37·6	45·7	10·7
$\frac{m+n-1}{n} \log c_A + \frac{1}{n} \log K_{mn}$	2·82	3·06	3·25	3·40	3·52	3·63	2·66

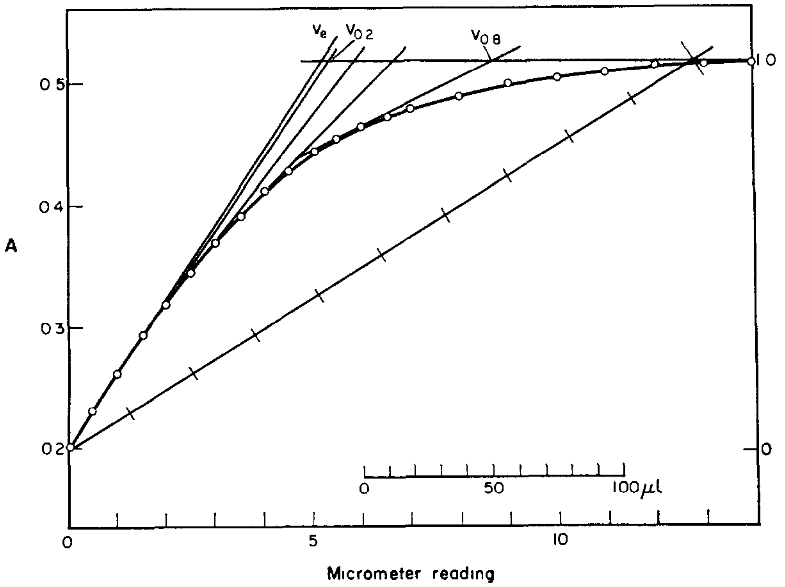

FIG. 4.—End-point evaluation by the method of fan-traced tangents.

The relative values of the distribution coefficient, δ, are evaluated either arithmetically or geometrically. A convenient method is to circumscribe a circle of convenient radius (*e.g.*, 100 mm) from the beginning of the curve. A line is drawn from the centre of this circle to the intersection point with the horizontal asymptote and this serves as a scale to draw a system of lines parallel to the abscissa, which cut the ordinate at suitable values of δ.

General methods for tangent construction to plane curves are known, but they are rather complicated. Any simple method may be used and if the titration curve is fairly symmetrical in the vicinity of the tangential point, the secant cutting equal parts of the curve on both sides of the point is suitable for orientation of the tangent. If the tangent is led through a longer linear segment of the titration curve, the tangential point is identified with the middle of this section.

Further, the intersects of the individual tangents with the upper asymptote are evaluated. Since the consumption of the titrant is directly proportional to the values of a, equation (9) can be used to evaluate the distance between the two intersection points:

$$v_c - v_d = k(f_c - f_d). \tag{12}$$

The values of the correction factors are read from Table II. The systematic deviation is calculated by multiplying the constant k by the relevant correction factor, *e.g.*,

$$\Delta v_c = kf_c. \tag{13}$$

The proposed procedure would be applicable even in case of an unknown composition of the titration product. Since the ratio of the differences in subsequently evaluated volumes is equal to the ratio of differences in corresponding correction factors, we obtain, for instance,

$$\frac{v_3 - v_1}{v_2 - v_1} = \frac{f_3 - f_1}{f_2 - f_1}. \tag{14}$$

Then the stoichiometry of the titration product could be solved by comparing the tabulated values. However, this approach can hardly yield unambiguous information since the volume differences are to a great extent influenced by inaccurate construction of the tangents.

EXPERIMENTAL

An aliquot of an ethanolic solution containing 57·8 μg of commercial diphenylthiocarbazone (dithizone) was transferred to the titration cuvette (length 30 mm) and 1 ml of hexamethylenetetramine buffer solution of pH 5·0 was added. The solution was diluted with a further amount of ethanol and water in order to produce 20 ml of 50% (by volume) alcoholic solution. For the photometric microtitration[14] 0·001*M* lead nitrate was dispensed with a syringe microburette.

As may be seen in Fig. 4, the bend of the experimental titration curve obtained is so great that the end-point evaluation seems to be quite difficult. Following the proposed procedure, a series of tangents was drawn and the following volumes (expressed as micrometer readings) were found: $v_{0·2} = 5·30$; $v_{0·4} = 5·78$; $v_{0·6} = 6.64$; $v_{0·5} = 8·65$.

Lead ion forms a chelate $\mathrm{Pb(HDz)_2}$ with dithizone, and since a dithizone solution is titrated with a lead salt (titrant B), the titration product is of the type $\mathrm{A_2B}$. For the evaluation of the constant k the two extreme volume readings may be used. Thus, we obtain

$$k = \frac{8·65 - 5·30}{32·50 - 1·094} = 0·1067$$

From equation (13) the correction values are found and used to express the end-point consumption v_e

$$\begin{array}{ll} (\text{for } \delta_{0·2}) & v_e = 5·30 - 0·1067 \times 1·094 = 5·30 - 0·12 = 5·18 \\ (\text{for } \delta_{0·8}) & v_e = 8·65 - 0·1067 \times 35·5 \ \ = 8·65 - 3·47 = 5·18 \end{array}$$

The agreement obtained is fairly good.

Zusammenfassung—Es wird zur Ermittlung eines systematischen Titrationsfehlers ein Verfahren angegeben, das sich durch lineare Extrapolation hyperbolischer Titrationskurven bei amperometrischen, photometrischen und anderen instrumentellen Titrationen ergibt. Es wird angenommen, daß die Titration auf einer einstufigen Ionenassoziation $m\mathrm{A} + n\mathrm{B} \rightleftharpoons \mathrm{A}_m\mathrm{B}_n$ beruht und die gemessene physikalische Eigenschaft zwischen bekannten unteren und oberen Grenzwerten liegt. Das Verfahren eignet sich zur Endpunktsbestimmung, auch wenn die Titrationskurven stark gekrümmt sind, und zur Voraussage der besten experimentellen Bedingungen für eine gegebene Titration.

Résumé—On décrit une méthode pour l'estimation d'une erreur de titrage systématique qui est introduite par extrapolation linéaire de courbes de titrage hyperboliques dans les titrages ampérométriques, photométriques et autres titrages instrumentaux. Il est admis que le titrage est basé sur une réaction d'association ionique en un seul stade, $m\mathrm{A} + n\mathrm{B} \rightleftharpoons \mathrm{A}_m\mathrm{B}_n$ et que la propriété physique mesurée se situe entre des valeurs minimale et maximale connues. La technique convient pour la détermination de la fin de réaction, même quand les courbes de titrage ont une courbure accentuée, et pour prédire le choix des conditions expérimentales optimales pour un titrage donné.

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SHORT COMMUNICATIONS

α-(Phenylazo)-4-nitrobenzyl cyanide, a new acid-base indicator

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THERE are few acid-base indicators applicable in strongly alkaline medium. In an earlier paper[1] was recommended the use of the 4-nitro- and 2,4-dinitrophenylhydrazones of *p*-nitroacetophenone as new acid-base indicators for the titration of weak acids. In this paper a further new indicator is described, α-(phenylazo)-4-nitrobenzyl cyanide. This compound can be prepared from benzyl cyanide by means of nitration and coupling with diazotized aniline. Indicator constants in mixtures of organic solvent and water have been determined on the basis of absorption spectra, according to the method used for the determination of the dissociation constants of Methyl Red in a mixture of alcohol and water[2] and according to our earlier method.[3]

EXPERIMENTAL

Preparation of α-(phenylazo)-4-nitrobenzyl cyanide

4-*Nitrobenzyl cyanide.* To 2·9 g of benzyl cyanide add 2·5 ml of 94–98% nitric acid dropwise with stirring, at below 30°, then stir for 30 min more. Pour the mixture into 50 ml of water and neutralize with alkali. Filter off the separated product and recrystallize it from alcohol. Yield 1·4 g, m.p. 116° (literature value 116–7°).

α-(*Phenylazo*)-4-*nitrobenzyl cyanide.* Dissolve 0·93 g of aniline in a mixture of 25 ml of 1*M* hydrochloric acid and 5 ml of water and add 0·69 g of sodium nitrite. Filter the diazonium salt solution and add it to 1·62 g of nitrobenzyl cyanide dissolved in 110 ml of ethanol, then neutralize the solution with 1*M* sodium hydroxide. Filter off the separated product and dry it at 100°. Yield 0·6 g, m.p. 201°. The substance is used as a 0·1% solution in 96% ethanol.

Determination of the dissociation constant

To a glycocol and sodium hydroxide buffer solution of known pH add enough organic solvent to give the required amount in a volume of 10 ml, and then 10 drops of 0·1% solution of indicator. Record the absorption spectrum. From the absorption spectra for various solvent media and pH values the dissociation constants of the indicator can be calculated according to our earlier work.[3]

Titration of weak acids

Dissolve about 1 mequiv of the weak acid in 50 ml of ethanol or acetone, or aqueous ethanol or acetone, add 10 drops of indicator solution and titrate with 0·1*M* aqueous sodium hydroxide (magnetic stirring).

DISCUSSION

Indicator constants

Figures 1 and 2 show the absorption spectra of the indicator dissolved in water and 75% ethanol and the method of calculation of the p*K* values therefrom. Table I lists the dissociation constants, absorption maxima and isosbestic points of the indicator.

Functioning of the indicator

p-Nitrobenzyl cyanide is also an acid-base indicator. This behaviour is due to the presence of the cyanide group. In consequence of the strongly electron-attracting cyanide group, an active methylene group comes into being, which easily dissociates a proton to form a nitronic acid. A more advantageous indicator property is gained, if *p*-nitrobenzyl cyanide is coupled with diazotized aniline. The acid colour of α-(phenylazo)-4-nitrobenzyl cyanide is yellow, the alkaline colour violet. The violet

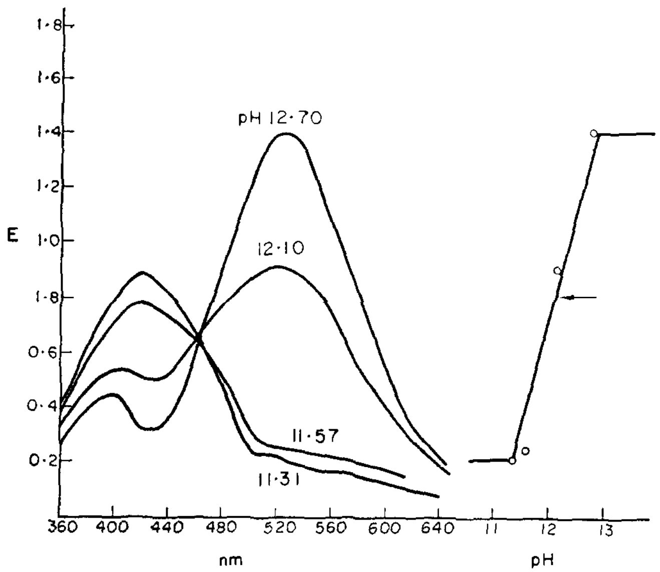


FIG. 1.—Absorption spectra of indicator in aqueous solution at various pH values, and plot of absorbance (*E*) at 520 nm *vs.* pH.

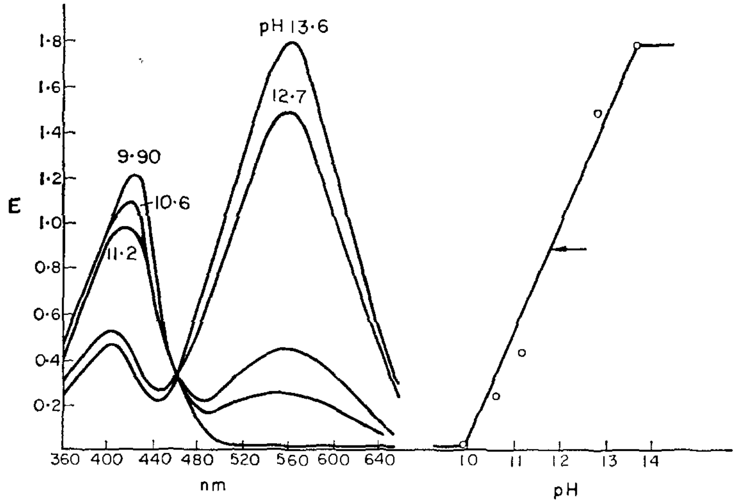
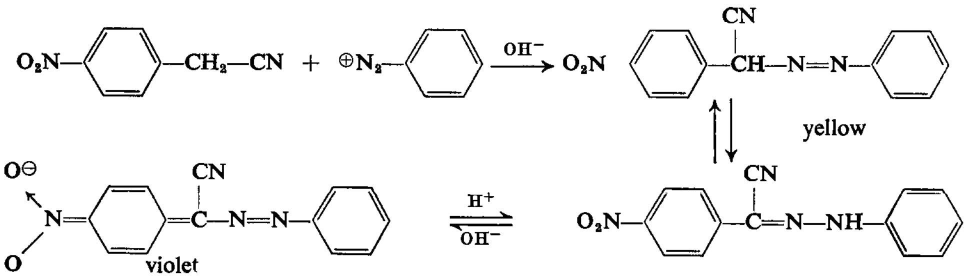


FIG. 2.—Absorption spectra of ethanolic indicator solution at various pH values, and plot of absorbance (*E*) at 560 nm *vs.* pH.

TABLE I.—INDICATOR CONSTANTS IN MIXTURES OF ORGANIC SOLVENT AND WATER

Solvent	λ_{max}, *nm*	Isosbestic point, *nm*	Apparent p*K*
water	520	460	12·10
25% ethanol	540	460	11·10
50% ethanol	560	460	11·35
75% ethanol	560	460	11·75
25% acetone	540	460	11·20
50% acetone	560	464	10·80
75% acetone	560	465	10·30

colour in alkaline medium is due to the nitronic acid structure:



The indicator constants of α-(phenylazo)-4-nitrobenzyl cyanide are markedly altered when the indicator is dissolved in an organic solvent. The absorption maximum of the indicator shifts 40 nm to longer wavelengths in acetone or in ethanol. This change may be explained by the fact that the indicator is less soluble and dissociated in water than in organic solvents.

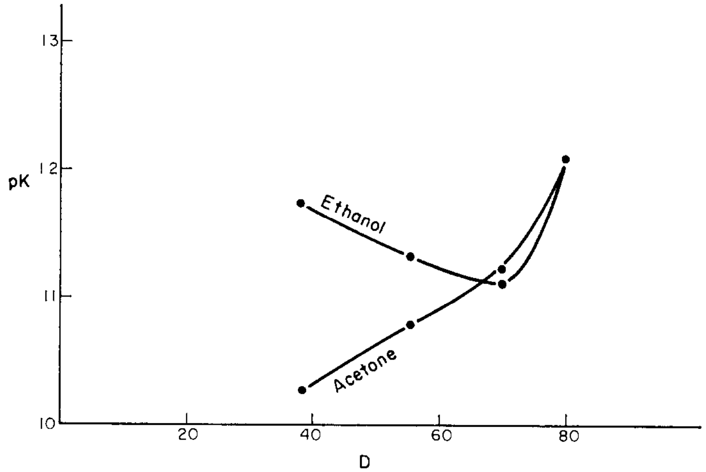


FIG. 3.—Variation of p*K* with dielectric constant of solvent medium.

When a weak acid carries no charge or is negatively charged, the value of p*K* increases in ethanolic or acetone medium.[4] The case is reversed with a positively charged weak acid. In other words, in ethanol or in acetone, weak acids carrying no charge or a negative charge become still weaker, while positively charged weak acids become stronger. The weak acids in Table II and α-(phenylazo)-4-nitrobenzyl cyanide indicator belong to the first group. In Fig. 3 the p*K* values of the indicator are plotted as a function of the dielectric constant of the solvent. This figure shows that in acetone the p*K* value of α-(phenylazo)-4-nitrobenzyl cyanide decreases with decrease of the dielectric constant of the medium, and in ethanol the value first decreases then increases slightly, but the pK value is always smaller in ethanol than in water. This property of α-(phenylazo)-4-nitrobenzyl cyanide is irregular and opposite to that of carboxylic acids. According to our earlier investigations[1] the pK value of phthalein indicators in acetone and ethanolic medium increases to a high degree, whereas that of nitronic acids is almost unchanged by variation of the dielectric constant of the medium. Though this irregular behaviour of α-(phenylazo)-4-nitrobenzyl cyanide is disadvantageous in titration of weak acids, nevertheless it becomes possible to titrate weak acids, using this indicator over a wide pK interval. The relatively strong trichloroacetic acid can also be titrated, with this indicator being used in acetone medium, as in this medium the pK value of weak carboxylic acids increases, while that of the indicator decreases. The weaker acids are to be titrated in ethanol or aqueous ethanol, where the pK values of the acids and the indicator are only slightly changed.

Results

Table II shows results obtained with the indicator used in titrations with 0·1M sodium hydroxide, in aqueous ethanol and acetone media. All three protons of citric acid can be titrated.

TABLE II.—TITRATION OF WEAK ACIDS (100% PURE)

Acid	Medium	Colour change	Error in titration, %
Tartaric	ethanol	yellow → violet-red	+0·6
Trichloroacetic	acetone	yellow → violet	−0·2
Citric	20% ethanol	yellow → pink	0
Salicyclic	acetone	yellow → violet	−0·8
Monochloroacetic	acetone	yellow → violet	+0·6
Nicotinic	20% ethanol	yellow → pink	−0·5
Anthranilic	ethanol	yellow → violet-red	0
4,6-Dinitro-*o*-cresol	ethanol	yellow → pink	+0·6

When 1 mequiv of sodium tartrate was dissolved in a mixture of 20 ml of water and 30 ml of ethanol and 10 drops of 0·1% indicator solution were added, the addition of 0·06 ml of 0·1M sodium hydroxide produced the transition colour. This 0·06 ml is the indicator error, and should be deducted from the result of the titration.

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Summary—A new acid-base indicator, α-(phenylazo)-4-nitrobenzyl cyanide, is proposed. The indicator changes colour from yellow to violet in the presence of alkali owing to the formation of a nitronic acid structure. This indicator is applicable for the titration of weak acids in acetone and ethanol media or in a mixture of these organic solvents and water, with 0·1M aqueous sodium hydroxide as titrant. The absorption spectra have been recorded for the indicator in 25%, 50% and 75% aqueous ethanol and acetone. By means of the spectra the dissociation constants in these media have been determined. The pK value of α-(phenylazo)-4-nitrobenzyl cyanide is 12·10 in water, and is decreased considerably in acetone but only slightly in ethanol. This behaviour is similar to that of positively charged weak acids and irregular for a weak acid carrying no charge or a negative charge.

Zusammenfassung—Ein neuer Säure-Base-Indikator, α-(Phenylazo)-4-nitrobenzylcyanid, wird vorgeschlagen. Der Indikator ändert seine Farbe in Gegenwart von Alkali von Gelb nach Violett, wobei sich eine Nitronsäuregruppierung bildet. Er ist zur Titration schwacher Säuren in Aceton- und Äthanolmedien oder einem Gemisch dieser organischen Lösungsmittel mit Wasser geeignet, wobei 0,1M wäßriges Natriumhydroxid als Titrant dient. Die Absorptionsspektren des Indikators wurden in 25%, 50% und 75% wäßrigem Äthanol und Aceton registriert. Mit Hilfe der Spektren wurden die Dissoziationskonstanten in diesen Medien bestimmt. Der p*K*-Wert von α-(Phenylazo)-4-nitrobenzylcyanid beträgt 12,10 in Wasser und sinkt in Aceton beträchtlich, in Äthanol nur schwach. Dieses Verhalten entspricht dem von positiv gelandenen schwachen Säuren; für eine schwache Säure ohne Ladung oder mit negativer Ladung ist es ungewöhnlich.

Résumé—On propose un nouvel indicateur acide-base, l'α-(phénylazo) 4-nitrobenzyl cyanure. La coloration de l'indicateur passe du jaune au violet en la présence d'alcali par suite de la formation d'une structure acide nitronique. Cet indicateur est applicable au titrage d'acides faibles en milieux acétone et éthanol ou dans un mélange de ces solvants organiques et d'eau, avec comme agent de dosage la soude aqueuse 0,1*M*. On a enregistré les spectres d'absorption de l'indicateur en éthanol et acétone aqueux à 25%, 50% et 75%. Au moyen des spectres, on a déterminé les constantes de dissociation dans ces milieux. La valeur du p*K* de l'α-(phénylazo) 4-nitrobenzyl cyanure est de 12,10 dans l'eau et décroît considérablement en acétone mais seulement légèrement en éthanol. Ce comportement est semblable à celui d'acides faibles chargés positivement et irrégulier pour un acide faible ne portant pas de charge ou portant une charge négative.

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Gas-chromatographic determination of ultramicro amounts of selenium in pure sulphuric acid

(*Received* 12 *April* 1969. *Accepted* 1 *September* 1969)

SPECTROPHOTOMETRIC,[1,2] fluorimetric[3,4] and catalytic[5] methods for the determination of selenium are based on the formation of piaselenols which are quantitatively made from selenium(IV) and aromatic *o*-diamines such as 3,3'-diaminobenzidine or 2,3-diaminoaphthalene. Tanaka and Kawashima[6] have presented a critical study of some 4-substituted *o*-phenylenediamines as spectrophotometric reagents for selenium. Nakashima and Tôei[7] have recently proposed a very sensitive gas-chromatographic procedure for selenium by electron-capture detection of 5-chloropiaselenol. The present paper describes the gas chromatographic determination of selenium in pure sulphuric acid.

Lovelock[8] has shown that the nitro group in an organic substance is more sensitive than the chlorine group to electron-capture detection. Hence 4-nitro-*o*-phenylenediamine is used as reagent in the gas chromatographic determination of selenium. As the oxidation number of selenium in pure sulphuric acid is not four but zero because of the reducibility by trace amounts of sulphurous acid, a bromine–bromide redox buffer is used for the conversion of elemental selenium into selenous acid.

EXPERIMENTAL

Reagents

*4-Nitro-*o*-phenylenediamine hydrochloride solution.* A 1% acidic solution is stable at room temperature for at least a week.

Stock selenium solution, 1 *mg/ml.* Selenium dioxide (351·3 mg) dissolved in 250 ml of distilled water. Diluted to provide working solutions.

Stock bromine–bromide redox buffer solution (0·1*M* bromine—0·2*M* bromide). Bromine water (saturated, 45·7 g) and potassium bromide (2·38 g), diluted to 100 ml with distilled water. Diluted to provide working solutions.

in diesen Medien bestimmt. Der pK-Wert von α-(Phenylazo)-4-nitrobenzylcyanid beträgt 12,10 in Wasser und sinkt in Aceton beträchtlich, in Äthanol nur schwach. Dieses Verhalten entspricht dem von positiv gelandenen schwachen Säuren; für eine schwache Säure ohne Ladung oder mit negativer Ladung ist es ungewöhnlich.

Résumé—On propose un nouvel indicateur acide-base, l'α-(phénylazo) 4-nitrobenzyl cyanure. La coloration de l'indicateur passe du jaune au violet en la présence d'alcali par suite de la formation d'une structure acide nitronique. Cet indicateur est applicable au titrage d'acides faibles en milieux acétone et éthanol ou dans un mélange de ces solvants organiques et d'eau, avec comme agent de dosage la soude aqueuse 0,1M. On a enregistré les spectres d'absorption de l'indicateur en éthanol et acétone aqueux à 25%, 50% et 75%. Au moyen des spectres, on a déterminé les constantes de dissociation dans ces milieux. La valeur du pK de l'α-(phénylazo) 4-nitrobenzyl cyanure est de 12,10 dans l'eau et décroît considérablement en acétone mais seulement légèrement en éthanol. Ce comportement est semblable à celui d'acides faibles chargés positivement et irrégulier pour un acide faible ne portant pas de charge ou portant une charge négative.

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EXPERIMENTAL

Reagents

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Stock selenium solution, 1 mg/ml. Selenium dioxide (351·3 mg) dissolved in 250 ml of distilled water. Diluted to provide working solutions.

Stock bromine–bromide redox buffer solution (0·1M bromine—0·2M bromide). Bromine water (saturated, 45·7 g) and potassium bromide (2·38 g), diluted to 100 ml with distilled water. Diluted to provide working solutions.

Selenium-free concentrated sulphuric acid. Dilute 100 ml of concentrated sulphuric acid with an equal volume of water, add 20 ml of 48% hydrobromic acid and heat strongly till dense white fumes appear.

Apparatus

A Shimazu Model GC-3AE gas chromatograph (Kyoto, Japan) equipped with an electron-capture detector was used. The glass column (1 m long, 4 mm bore) was packed with 15% S E-30 on 60–80 mesh Chromosorb W. The column and detector temperature was maintained at 200°. The nitrogen flow-rate was 44 ml/min.

Procedure

Put 1 ml (1·8 g) of sulphuric acid into a 100-ml beaker containing 10 ml of water and 3 ml of $10^{-3}M$ bromine–bromide redox buffer, and heat the solution in a hot water-bath for 20 min. Cool the solution and transfer it to a 100-ml separatory funnel, using 10 ml of distilled water for rinsing. Add 2 ml of 1% 4-nitro-*o*-phenylenediamine solution and let stand for 2 hr. Extract the 5-nitropiaselenol into 1 ml of toluene by shaking for 5 min. Inject 5 μl of the extract into the gas chromatograph column and measure the height of the peak with 3·7-min retention time (Fig. 1).

Prepare a calibration curve by adding known amounts of selenous acid to selenium-free sulphuric acid, or from guaranteed purity sulphuric acid without using the oxidation procedure.

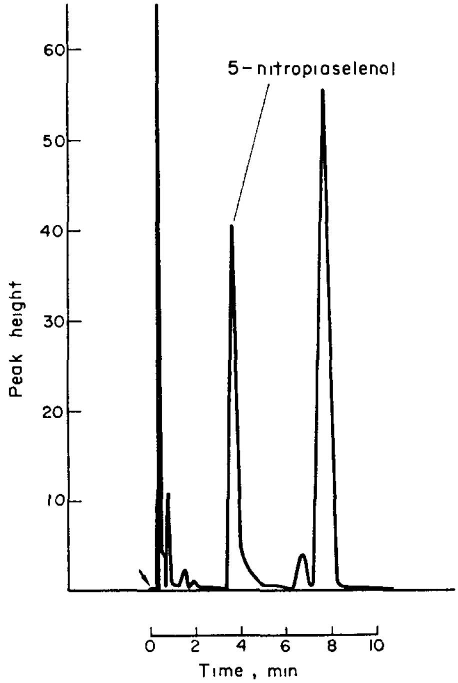

FIG. 1.—Gas chromatogram of 5-initropiaselenol.
Column 15% SE30/Chromosorb W in 1 m × 4 mm glass column.
Carrier gas nitrogen, flow-rate 44 ml/min. Sample 5 μl (0·12 μg Se/ml).

RESULTS AND DISCUSSION

It was found that selenium(IV) reacts quantitatively with the reagent to form 5-nitropiaselenol, if there is a 50000-fold molar excess of reagent; 2 ml of the reagent solution were therefore used. It was shown earlier[8] that 4-nitro-*o*-phenylenediamine does not react quantitatively with selenium(IV) at pH above 2. The reaction time at room temperature was measured at pH 0 and 1 and it was found that the reaction was complete in 1 hr. As expected, heating hastened the reaction and 5 min at 100° are sufficient for complete reaction. It was found that with 1 ml of toluene the volume of aqueous phase could be varied from 20 to 50 ml without effect on the efficiency of extraction.

As selenium in sulphuric acid is present as selenium(0) because of reduction by sulphurous acid, the selenium must be oxidized to selenous acid. The bromine–bromide redox buffer used has a standard potential of +1·09 V, and selenous acid is stable between +0·74 and +1·15 V at pH 0. Oxidation was shown to be complete by recovery experiments with 0·053 μg of amorphous selenium treated with 2 ml of $10^{-3}M$ bromine–bromide solution in a hot water-bath (about 90°) for 20 min. The recovery of the selenium was between 96 and 106%.

The minimum molar excess of buffer needed was found to be 1500-fold relative to selenium, but at room temperature must not exceed 7500-fold, or turbidity appears and affects the extraction; 7 ml of $10^{-3}M$ redox buffer is the maximum permissible.

The oxidation is complete in 10 min at the temperature of a hot water-bath (~90°) and in 20 min at room temperature.

The determination of selenic acid by this method was not successful, because selenium(VI) was not reduced to selenous acid by the redox buffer and selenium(VI) did not react with 4-nitro-*o*-phenylenediamine. Selenium in commercial pure sulphuric acid was determined and the result checked for accuracy by spiking the sample with 0·030 μg of selenium(IV). The results are shown in Table I.

TABLE I.—SELENIUM CONTENT OF SULPHURIC ACID

Supply company	Se, 10^{-6}%	
	Analytical grade reagent	Extra pure reagent
A	1·8	9·4
B	1·9	2·5
C	5·3	2·4
D	5·0	1·3
E	2·6	3·2

As the sensitivity of an electron-capture detector tends to vary during operation, the gas chromatograms should be run successively and an unknown content of selenium should be determined along with standard samples which contain similar amounts of selenium. The proposed procedure should find wide application where ultramicro amounts of selenium are to be determined. Its outstanding features are that it is simple, highly sensitive and rapid, and no special skill is necessary.

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Summary—Ultramicro amounts of selenium in pure sulphuric acid are converted into selenous acid with a bromine–bromide redox buffer solution. The selenous acid reacts quantitatively with 4-nitro-*o*-phenylenediamine to form 5-nitropiaselenol which can be extracted into toluene. The extract is very sensitive to electron-capture detection in gas chromatography, and the sensitivity is higher than that of 5-chloro- or 4,5-dichloro-piaselenol. The calibration curve (peak heights) is linear up to 0·15 μg of selenium in 1 ml of toluene. Pure sulphuric acid, commercially available, contains $10^{-6} \sim 10^{-5}$% selenium.

Zusammenfassung—Ultramikromengen Selen in reiner Schwefelsäure werden mit einer Brom–Bromid-Redoxpufferlösung in selenige Säure übergeführt. Die selenige Säure reagiert mit 4-Nitro-*o*-phenylendiamin quantitativ zu 5-Nitropiaselenol, das in Toluol extrahiert werden kann. Der Extrakt ist durch Gaschromatographie mit Elektroneneinfangdetektor sehr empfindlich nachzuweisen; die Empfindlichkeit ist höher als bei 5-Chlor- oder 4,5-Dichlorpiaselenol. Die Eichkurve (in Peakhöhen) ist linear bis 0,15 μg Selen in 1 ml Toluol. Handelsübliche reine Schwefelsäure ehthält 10^{-6} bis 10^{-5}%

Résumé—On convertit des ultra-microquantités de sélénium dans l'acide sulfurique pur en acide sélénieux par une solution tampon redox brome-bromure. L'acide sélénieux réagit quantitativement avec la 4-nitro *o*-phénylènediamine pour former le 5-nitropiasélénol qui peut être extrait en toluène. L'extrait est très sensible à la détection par capture d'électrons en chromatographie en phase galeuse, et la sensibilité est plus élevée que celle du 5-chloroou du 4,5-dichloropiasélénol. La courbe d'étalonnage (hauteurs de pic) est linéaire jusqu'à 0,15 μg de sélénium dans 1 ml de toluène. L'acide sulfurique pur, commercialement accessible, contient $10^{-6} \sim 10^{-5}\%$ de sélénium.

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Stability constants of lanthanide complexes with salicylhydroxamic acid

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SALICYLHYDROXAMIC ACID (SHA) forms lanthanide complexes which may be of analytical value. The present paper describes the determination of their stability constants in 3:1 v/v acetone–water medium. They have limited solubility in water but are soluble in the mixed solvent medium.

EXPERIMENTAL

Reagents

Lanthanide perchlorates. The corresponding oxides (99%, Johnson Matthey) were digested in perchloric acid and the excess of perchloric acid was removed by evaporation. The solutions were diluted to the desired concentration and were standardized by conventional methods.

Salicylhydroxamic acid. Prepared by the method of Ray and Bhaduri.[1]

The other chemicals used were of reagent grade.

Procedures

The general procedure consists of the titration with standard sodium hydroxide solution of 50 ml of acetone–water mixture (3:1 v/v) having metal ion concentration $\sim 2 \times 10^{-3}M$, reagent concentration $\sim 1 \times 10^{-2}M$, and sodium perchlorate in sufficient amount to maintain an ionic strength of 0·1. After each addition of a definite amount of alkali and stirring, the pH values were recorded with a Cambridge pH-meter with glass and calomel electrodes. Stirring was effected with a magnetic stirrer. The pH-meter was calibrated with aqueous buffers (pH 4·00 and 9·18) before and after titration. All titrations were carried out at 25 ± 0·5°. The acid dissociation constant of the ligand was determined by the same procedure but with the omission of the metal ion.

Calculations

Standard procedures were followed and the formation constants of the first two stages of reaction, K_1 and K_2, were evaluated graphically by using the equation

$$\frac{\bar{n}}{(1-\bar{n})[\mathrm{R}^-]} = \frac{(2-\bar{n})[\mathrm{R}^-]}{(1-\bar{n})} \cdot K_1K_2 + K_1$$

Résumé—On convertit des ultra-microquantités de sélénium dans l'acide sulfurique pur en acide sélénieux par une solution tampon redox brome-bromure. L'acide sélénieux réagit quantitativement avec la 4-nitro *o*-phénylènediamine pour former le 5-nitropiasélénol qui peut être extrait en toluène. L'extrait est très sensible à la détection par capture d'électrons en chromatographie en phase galeuse, et la sensibilité est plus élevée que celle du 5-chloroou du 4,5-dichloropiasélénol. La courbe d'étalonnage (hauteurs de pic) est linéaire jusqu'à 0,15 μg de sélénium dans 1 ml de toluène. L'acide sulfurique pur, commercialement accessible, contient $10^{-6} \sim 10^{-5}$% de sélénium.

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and the last two stages, K_2 and K_3, were evaluated by using the equation

$$\frac{(1 - \bar{n})}{(2 - \bar{n})[\mathrm{R}^-]} = \frac{(3 - \bar{n})[\mathrm{R}^-]}{(2 - \bar{n})} \, . \, K_2K_3 + K_2$$

where $\bar{n}$ is the average ligand number, R^- is the ligand and $K_n = [\mathrm{LnR}_n]/[\mathrm{LnR}_{n-1}][\mathrm{R}^-]$, Ln denoting a lanthanide(III) ion.

The significance of pH in acetone–water mixtures in which formation constants of rare earth complexes have been previously evaluated has been discussed.[3]

DISCUSSION

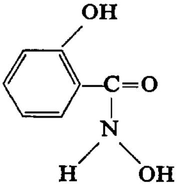
The value of the acid dissociation constant of the reagent and formation constants of rare earth–salicylhydroxamic acid complexes are given in Table I.

TABLE I.—FORMATION CONSTANTS OF RARE EARTH–SALICYLHYDROXAMIC ACID COMPLEXES

Metal ion	Log K_1	Log K_2	Log K_3	Log β_3
La^{3+}	6·30	5·96	4·90	17·16
Pr^{3+}	6·94	6·50	4·98	18·42
Nd^{3+}	7·03	6·64	5·10	18·77
Sm^{3+}	7·20	6·77	5·01	18·98
Eu^{3+}	7·40	6·84	5·04	19·28
Gd^{3+}	7·35	6·80	4·60	18·75
Dy^{3+}	7·72	7·00	5·06	19·78
Er^{3+}	7·82	7·03	5·10	19·93
Yb^{3+}	8·13	7·25	*	
Y^{3+}	7·24	6·50	*	

Temperature 25 + 0·5°C; ionic strength 0·1, pK_a, 8·86.
* Precipitation occurs.

Salicylhydroxamic acid (I) can behave as a monobasic and dibasic acid:



Consequently, the complexes of praseodymium, neodymium and samarium have been prepared and analysed. The composition is MR_3 as shown by the typical analysis: found, $\mathrm{Sm_2O_3}$, 28·8%; C, 41·6%; H, 3·0%; N, 7·9%; calculated, $\mathrm{Sm_2O_3}$, 29·07%; C, 41·05%; H, 3·01%; N, 7·82%.

However, for a dibasic acid where p$K_2 \gg$ pK_1 the highest complex species is formed well before the second stage of ionization of the acid begins, and the formation function may be derived by assuming the ligand to be monobasic. In fact, the maximum $\bar{n}$ values reached in our present experiments are ~2·5 which also supports our assumption of 1:3 complex formation.

The formation constants increase fairly regularly with decrease in ionic radius, with the gadolinium complex being less stable than predicted from simple ionic considerations.

In general log $K_1 >$ log $K_2 >$ log K_3 for a given metal ion. However, the differences in the values between the three constants are not much, indicating that there is almost equal tendency for the formation of neutral complex species LnR_3 as for LnR^{2+}.

The overall stability constants, β_3, of rare earth salicylhydroxamates are comparable with those of complexes of oxygen-donating ligands such as benzoylacetone and benzoylphenylhydroxylamine complexes, measured in the same solvent mixture. The dissociation constants (pK_a) of salicylhydroxamic acid, benzoylacetone[2] and benzoylphenylhydroxylamine[3] are 8·86, 9·58 and 10·26 respectively. It is expected that the rare earth complexes derived from salicylhydroxamic acid would be weaker than complexes derived from the other two. In fact, the average values of log β_3 of rare earth benzoylacetonates and benzoylphenylhydroxylamines are ~20 and 21 respectively, which are greater than those of the salicylhydroxamic acid complexes, ~19. It was not possible to determine log K_3 for ytterbium and yttrium because of precipitation of their complexes even when their $\bar{n}$ values reached ~2.

From the stability constants it can be deduced that if the physical characteristics of the precipitate are satisfactory, salicylhydroxamic acid might be as successful as benzoyl phenylhydroxylamine[4] for the gravimetric determination of the lanthanides.

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Summary—The stability constants of La, Pr, Nd, Sm, Eu, Gd, Dy, Er, Yb and Y complexes of salicylhydroxamic acid have been determined potentiometrically in 3:1 v/v acetone–water medium at 25 ± 0·5° and at an ionic strength of 0·1 with respect to sodium perchlorate. The stability constants are comparable with those of other lanthanide complexes with oxygen-donating ligands such as benzoylacetone and benzoylphenylhydroxylamine.

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Résumé—On a déterminé potentiométriquement les constantes de stabilité des complexes de La, Pr, Nd, Sm, Eu, Gd, Dy, Er, Yb et Y avec l'acide salicylhydroxamique en milieu acétone-eau 3:1 (v/v) à 25° ± 0,5° et pour une force ionique de 0,1 en ce qui concerne le perchlorate de sodium. Les constantes de stabilité sont comparables à celles d'autres complexes de lanthanides avec des ligands donateurs d'oxygène tels que la benzoylacétone et la benzoylphénylhydroxylamine.

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Complexometric determination of molybdenum(VI)

(*Received* 23 *June* 1969. *Accepted* 28 *August* 1969)

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Yaguchi and Kajiwara[9] studied the reaction of molybdenum with hydroxylamine hydrochloride and found that a 1:1 complex is formed, but wrongly assumed that on addition of EDTA a Mo(V)-complex is formed. Lassner and Schedle[10] in a critical paper stated that when molybdate solution is boiled with hydroxylamine (HyOH) hydrochloride no reduction takes place and that a 1:1:1 ternary complex Mo(VI)–HyOH–EDTA is formed. This ternary complex is more stable than the simple Mo(VI)–EDTA complex. Molybdenum cannot be displaced from it by copper at pH 4·5 and is only slowly displaced by bismuth at pH 2.

A complexometric method based on the formation of this 1:1:1 complex should be superior to all previous ones, because twice as much EDTA is required per mole of molybdenum. However, the authors[10] mentioned as disadvantages the poor selectivity, the need to use an empirical factor, and the unsuitability of the method in the presence of tungsten.

Recently, Lassner *et al.*[11] mentioned that similar complexes are formed by DCTA and NTA, but made no attempt to exploit them for determination of molybdenum. We can expect that use of DCTA would be superior to use of EDTA because DCTA forms more stable complexes, and displacement reactions (which might interfere in back-titrations) proceed slowly or not at all.

We have found that a very stable Mo–HyOH–DCTA complex is formed on prolonged boiling of molybdenum solutions with hydroxylamine. The excess of DCTA can easily be titrated with zinc chloride at pH 5 (hexamine buffer) or even with thorium nitrate at pH 3–4, Xylenol Orange being used as indicator in both cases. The displacement of molybdenum with zinc proceeds so slowly, that at the end-point the red colour of the zinc-Xylenol Orange lasts for at least 3 min. In addition we have found that phosphate, up to a 1:1 concentration ratio relative to molybdenum, does not interfere and that the displacement is then even slower than in its absence. Larger amounts of phosphate (*e.g.*, 10:1 ratio) obscure the end-point. We have also found very simple conditions for reliable determination of molybdenum in the presence of large amounts of tungstate.

A similar reaction with TTHA (triethylenetetraminehexa-acetic acid) leads to the formation of a 2:1 complex. Back-titration with zinc gives a less sharp end-point, however, making this reaction inconvenient for analytical purposes. DTPA, which forms a 1:1:1 complex in acidic medium, is also unsuitable.

EXPERIMENTAL

Reagents

Ammonium molybdate, 0·05*M*. Standardized gravimetrically with 8-hydroxyquinoline.

Other reagents include 0·05*M* solutions of zinc chloride, thorium nitrate, EDTA and DCTA; 10% hexamine solution and 0·5% Xylenol Orange solution. Solid hydroxylamine hydrochloride is used (a solution is unsuitable).

Determination of molybdenum

Procedure. To the nearly natural solution of molybdenum (containing 5–40 mg of Mo) add

TABLE I.—DETERMINATION OF MOLYBDENUM

		Back-titration			
Mo taken, *mg*	0·05*M* DCTA added, *ml*	0·05*M* Zn, *ml*	0·05*M* Th, *ml*	Mo found, *mg*	Error, *mg*
2·06	2·87	2·58	—	1·3$_9$	−0·6$_7$
2·06	4·79	4·40	—	1·8$_7$	−0·1$_8$
4·12	1·91	1·05	—	4·1$_3$	+0·0$_1$
4·12	2·87	—	1·82	4·0$_8$	−0·0$_4$
4·12*	4·79	3·95	—	4·0$_3$	−0·0$_9$
20·61	9·80	3·95	—	20·6$_3$	+0·0$_2$
20·61†	6·70	‡	—	—	—
41·21	11·76	3·17	—	41·2$_1$	0
41·21	11·76	—	3·22	40·9$_7$	−0·2$_4$
61·82	23·93	—	10·77	63·1$_3$	+1·3$_1$
61·82	23·93	10·55	—	64·1$_8$	+2·3$_6$
82·42	23·93	6·40	—	84·0$_9$	+1·6$_7$

* Added 50 mg Na_2HPO_4.
† Added 500 mg Na_2HPO_4.
‡ Bad end-point.

1–2 g of hydroxylamine hydrochloride, dilute to 150–200 ml and heat to boiling. The solution becomes yellow or slightly blue-green, depending on the molybdenum concentration. Add excess of DCTA and boil the solution (pH 4·5) for a further 15 min. The solution turns yellow or yellow-green. Cool, add hexamine solution to adjust the pH to 5–5·5, add a few drops of Xylenol Orange and titrate with 0·05*M* zinc to a red-violet colour which lasts at least 3 min.

Results. Good results were obtained for 5–40 mg of molybdenum (Table I). For smaller amounts than 5 mg the results are low, for higher amounts than 40 mg the results are high. The back-titration can also be carried out with thorium nitrate at pH 3–4. At pH <3 a slightly red colour appears before the end-point and makes the end-point more difficult to discern.

Determination of molybdenum in the presence of tungsten

We have found that this method can also be used in the presence of tungsten, provided that sufficient hydroxylamine hydrochloride (10 g) is used for formation of the Mo–HyOH–DCTA complex. The procedure is the same as described above. Table II shows the influence of hydroxylamine hydrochloride, Table III summarizes results for molybdenum determination in the presence of up to 276 mg of tungsten. It can be seen that EDTA is a less satisfactory reagent.

TABLE II.—EFFECT OF HYDROXYLAMINE HYDROCHLORIDE ON THE DETERMINATION OF Mo IN THE PRESENCE OF W

HyOH added, *g*	Mo taken, *mg*	W added, *mg*	0·05*M* DCTA, *ml*	Back-titration 0·05*M* Zn, *ml*	Mo found, *mg*	Error, *mg*
1	12·36	184	4·79	4·75	0·1$_{9}$	—12·1$_{7}$
2	12·36	184	4·79	3·50	6·1$_{9}$	−6·1$_{7}$
3	12·36	184	4·79	2·80	9·5$_{5}$	−2·7$_{9}$
4	12·36	184	4·79	2·30	11·9$_{4}$	−0·4$_{2}$
5	12·36	184	4·79	2·25	12·1$_{9}$	−0·1$_{7}$
5	12·36	276	4·79	3·60	5·7$_{1}$	−6·6$_{5}$
7	12·36	276	4·79	2·33	11·8$_{0}$	−0·5$_{6}$
10	12·36	276	4·79	2·20	12·4$_{2}$	+0·0$_{6}$
10	12·36	368	4·79	2·30	11·9$_{4}$	−0·4$_{2}$

Boiling solutions containing only molybdenum, tungsten and hydroxylamine are highly coloured (yellow to intense yellow-green). After addition of DCTA the resulting colour is green or blue-green depending on the amount of tungsten present. For this reason the amount of tungsten is limited to

TABLE III.—DETERMINATION OF Mo IN THE PRESENCE OF W

Mo taken, *mg*	W taken, *mg*	0·05*M* DCTA, *ml*	0·05*M* EDTA, *ml*	Back-titrn. Zn, *ml*	Back-titrn. Th, *ml*	Mo found, *mg*	Error, *mg*
4·12	9·2	4·79	—	3·95	—	4·0$_{3}$	−0·0$_{9}$
4·12	27·5	4·79	—	3·95	—	4·0$_{8}$	+0·0$_{9}$
4·12	92·0	4·79	—	3·93	—	4·1$_{3}$	+0·0$_{1}$
4·12	230·0	2·87	—	2·03	—	4·0$_{3}$	−0·0$_{9}$
4·12	276·0	4·79	—	4·00	—	3·7$_{9}$	−0·3$_{3}$
12·36	92·0	—	9·71	6·80	—	13·9$_{6}$*	+1·6$_{0}$
12·36	9·2	—	4·86	—	2·64	10·6$_{4}$	−1·7$_{2}$
4·12	276·0	—	4·86	3·85	—	4·8$_{4}$*†	+0·7$_{2}$
20·61	46·0	—	9·71	4·90	—	23·0$_{7}$*	+1·4$_{6}$
20·61	46·0	9·57	—	5·25	—	20·7$_{2}$	+0·1$_{1}$
41·21	92·0	16·27	—	7·70	—	41·2$_{5}$‡	+0·0$_{4}$
8·24	276·0	4·79	—	—	3·17	7·7$_{7}$	−0·4$_{7}$
20·61	9·2	9·57	—	—	5·22	20·8$_{6}$	+0·2$_{5}$
41·21	184·0	14·35	—	—	5·82	40·9$_{2}$	−0·2$_{9}$

* Fast displacement.

† Unsharp end-point.

‡ Average of three determinations.

300 mg/500 ml. Dilution to 500 ml is without effect on the Mo determination. Back-titration with thorium nitrate is less reliable at higher concentrations of tungsten and is recommended only for smaller amounts of tungsten. Generally the solutions have to be boiled at pH 4·5–5. At lower pH the formation of the Mo–HyOH–DCTA complex is not quantitative, probably on account of formation of Mo–W polycations (see ref. 10).

That a very large excess of hydroxylamine is needed may be due to catalysis by molybdenum(VI) of the decomposition of hydroxylamine,[12] besides the decomposition occurring on boiling.

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Summary—In acidic medium molybdenum(VI) forms a stable complex on boiling with excess of DCTA and hydroxylamine hydrochloride. Molybdenum can then be determined by back-titration of the excess of DCTA either with zinc chloride at pH 5–5·5 or with thorium nitrate at pH 3–4·5, Xylenol Orange being used as indicator in both cases. A simple method for the determination of molybdenum in the presence of moderate amounts of tungsten is also described.

Zusammenfassung—In saurem Medium bildet Molybdän(VI) beim Kochen mit überschüssiger DCTA und Hydroxylaminhydrochlorid einen stabilen Komplex. Molybdän kann dann durch Rücktitration der überschüssigen DCTA mit Zinkchlorid bei pH 5–5,5 oder mit Thoriumnitrat bei pH 3–4,5 bestimmt werden, wobei beidesmal Xylenolorange als Indikator dient. Ein einfaches Verfahren zur Bestimmung von Molybdän in Gegenwart mäßiger Mengen Wolfram wird ebenfalls angegeben.

Résumé—En milieu acide, le molybdène(VI) forme un complexe stable par ébullition avec un excès de DCTA et de chlorhydrate d'hydroxylamine. On peut alors doser le molybdène par titrage en retour de l'excès de DCTA soit avec le chlorure de zinc à pH 5–5,5, soit avec le nitrate de thorium à pH 3–4,5, l'Orangé Xylénol étant utilisé comme indicateur dans les deux cas. On dércit aussi une méthode simple pour le dosage du molybdène en la présence de quantités peu élevées de tungstène.

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The dissociation constants of alizarin fluorine blue

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SINCE the introduction of the method by Belcher, Leonard and West in 1958,[1] the formation of a blue complex between alizarin fluorine blue (3-aminomethylalizarin-*N*,*N*-diacetic acid), cerium(III)

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EXPERIMENTAL

Reagents

Alizarin fluorine blue. Thin-layer chromatography showed traces of alizarin, which were removed as far as possible by dissolving 1 g of alizarin fluorine blue in the minimum quantity of 0·5*M* sodium hydroxide (10–15 ml), diluting to 100 ml, adjusting the pH to 6·5–7·0 (the solution went deep wine-red) with hydrochloric acid and extracting with five 20-ml portions of methylene dichloride. The aqueous phase was then cooled in an ice-bath, and hydrochloric acid added dropwise until a heavy orange precipitate formed. After 2 hr the alizarin fluorine blue was filtered off, washed with ice-cold water, and dried in a vacuum desiccator at 50° over phosphorus pentoxide.

Alizarin fluorine blue disodium salt. Purified alizarin fluorine blue was weighed and suspended in water, under a nitrogen atmosphere, and the volume of sodium hydroxide required for half-neutralization was added from a micrometer syringe. The mixture was shaken till homogeneous, then water was removed by evaporation under vacuum. The damp solid remaining was dried at 50° over phosphorus pentoxide. The sodium content was checked by emission spectroscopy.

Potassium hydroxide solution. Analytical grade potassium hydroxide pellets in excess of the required weight were quickly washed with demineralized water, dried, and dissolved in demineralized water boiled free from air, about half the final volume being used. The solution was passed through a freshly regenerated column of IRA 400 ion-exchange resin (hydroxide form) into a polythene vessel, and washed through with demineralized water until the desired total volume was obtained. The solution was standardized potentiometrically with potassium hydrogen phthalate, and stored under nitrogen free from carbon dioxide.

Hydrochloric acid. Prepared by dilution of analytical grade acid and standardized potentiometrically with sodium carbonate.

Other reagents were analytical grade.

Apparatus

An Electronic Instruments Ltd. Model 39A Vibron vibrating capacitor pH meter, fitted with an E.I.L. type GHS 23 general purpose glass electrode, and a saturated calomel reference electrode. The cell used was

$$\mathrm{Hg^\circ}\ |\mathrm{Hg_2Cl_2}|\ \text{Satd. KCl}\ \|\text{Satd. KCl}\|\ \text{Test solution in } 0.1M\ \mathrm{KNO_3}\ |\ \text{Glass electrode}$$

Procedure

The test solution was maintained at 25 ± 0·1° in a double-walled vessel, by circulating water from a thermostat, and stirred by a small glass paddle. To minimize electrical interference the titration vessel and stirrer motor were surrounded by earthed brass gauze screens, and the metal of the apparatus stand was earthed. Samples of test substance were weighed individually on a microbalance and titrated (micrometer syringe burette) at ionic strength 0·1 (potassium nitrate).

RESULTS AND DISCUSSION

Bjerrum defined the degree of formation $\bar{n}$ of proton complexes, where $\bar{n}$ gives the average number of protons attached. In dealing with dissociation of acids, it is more convenient to use a quantity $R = n - \bar{n}$, where n is the total number of dissociable protons; R then represents the average number of protons dissociated and it can be shown[5] that

$$R = \frac{aC_a + [\mathrm{H^+}] - [\mathrm{OH^-}]}{C_a}$$

where C_a is the analytical concentration of the acid and a = equivs. of base per mol.

Then, by applying the conditions of mass balance and electroneutrality to the solution, it eventually follows that

$$\sum_{i=0}^{n} (R - i)\lambda_i[\mathrm{H^+}]^{n-i} = 0$$

where λ_i is the overall proton dissociation constant for the ith dissociation, defined by

$$\lambda_i = k_1 k_2 \ldots k_i$$

This equation gives the relation between $[H^+]$ and the degree of neutralization for any polyprotic acid.

Alizarin fluorine blue has four ionizable protons, and so the equation contains four unknowns. However, since k_1 and k_2 are well separated from k_3 and k_4 the simplifying assumption can be made that alizarin fluorine blue behaves as a mixture of two dibasic acids, and values of k_1 and k_2, and k_3 and k_4, can be obtained by considering separately the appropriate regions of the titration curve.

For a dibasic acid the general equation becomes

$$R[H^+]^2 + (R-1)k_1[H^+] + (R-2)k_1k_2 = 0$$

or

$$\frac{(R-1)}{Rk_2[H^+]} + \frac{1}{k_1k_2} = \frac{(2-R)}{R[H^+]^2}$$

Values of k_1 and k_2 can be obtained from the slope and intercept of the resulting linear plot. For accurate calculation, pairs of values were chosen from the titration curve, and the k values obtained by solving the resulting equations simultaneously.

The nitrogen atom of the iminodiacetic acid group can be protonated, but the protonation constant was not determined. If it is sufficiently different from k_1, the result for the latter will not be affected.

The main problem was the low solubility (approx. $5 \times 10^{-4}M$) of alizarin fluorine blue in water, and its slowness to dissolve. Mixed solvents do not improve the solubility sufficiently to justify their use with subsequent extrapolation to obtain a value for the dissociation constants in water. Since alizarin fluorine blue is readily soluble in alkali, the determination was carried out in two stages. Constants k_1 and k_2 were determined by dissolving the weighed sample in a known amount of potassium hydroxide solution and back-titrating with hydrochloric acid. To determine k_3 and k_4 the disodium salt of alizarin fluorine blue was titrated with potassium hydroxide. The higher solubility of the salt enabled a higher concentration to be used, with consequent improvement in the precision. The mean values and standard deviations of the constants found are $k_1 = 1{\cdot}28 \pm 0{\cdot}30 \times 10^{-5}$; $k_2 = 2{\cdot}82 \pm 0{\cdot}24 \times 10^{-8}$; $k_3 = 3{\cdot}72 \pm 0{\cdot}19 \times 10^{-11}$; $k_4 = 6{\cdot}39 \pm 0{\cdot}12 \times 10^{-12}$. A distribution diagram, showing the proportion of alizarin fluorine blue present in each ionized form at different

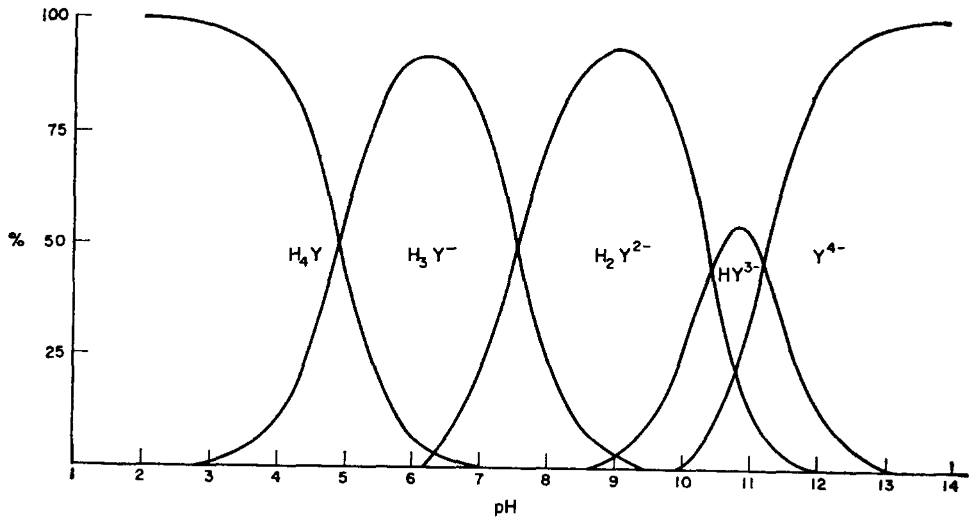
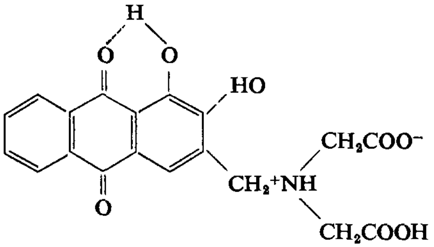


FIG. 1

pH values, is given in Fig. 1, where H_4Y represents the undissociated alizarin fluorine blue molecule.



Alizarin fluorine blue

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Summary—Dissociation constants for the analytical reagent alizarin fluorine blue (3-aminomethylalizarin-*N*,*N*-diacetic acid) have been determined by potentiometric titration at ionic strength 0·1, and are $k_1 = 1{\cdot}28 \pm 0{\cdot}30 \times 10^{-5}$; $k_2 = 2{\cdot}82 \pm 0{\cdot}24 \times 10^{-8}$; $k_3 = 3{\cdot}72 \pm 0{\cdot}19 \times 10^{-11}$; $k_4 = 6{\cdot}39 \pm 0{\cdot}12 \times 10^{-12}$.

Zusammenfassung—Die Dissoziationskonstanten des analytischen Reagens Alizarinfluorinblau (3-Aminomethylalizarin-*N*,*N*-diessigsäure) wurden durch potentiometrische Titration bei der Ionenstärke 0,1 ermittelt. Sie betragen $k_1 = 1{,}28 \pm 0{,}30 \cdot 10^{-5}$; $k_2 = 2{,}82 \pm 0{,}24 \cdot 10^{-8}$; $k_3 = 3{,}72 \pm 0{,}19 \cdot 10^{-11}$; $k_4 = 6{,}39 \pm 0{,}12 \cdot 10^{-12}$.

Résumé—On a déterminé les constantes de dissociation pour le réactif analytique alizarine fluorine bleue (acide 3-aminométhylalizarine *N*,*N*-diacétique) par titrage potentiométrique à la force ionique 0,1, et elles sont $k_1 = 1{,}28 \pm 0{,}30 \times 10^{-5}$; $k_2 = 2{,}82 \pm 0{,}24 \times 10^{-8}$; $k_3 = 3{,}72 \pm 0{,}19 \times 10^{-11}$; $k_4 = 6{,}39 \pm 0{,}12 \times 10^{-12}$.

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Complexometric titration of total iron with *o*-mercaptobenzoic acid as indicator

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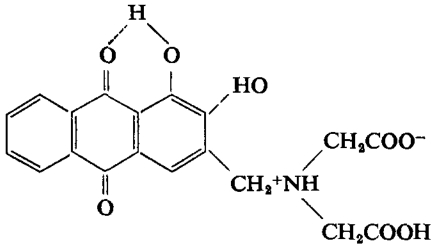
Various methods have been reported in the literature for the EDTA titration of iron(III) and iron(II). For the use of EDTA to determine total iron in a system containing both iron(III) and iron(II), the iron(II) has to be oxidized. Iron(III) can be titrated with EDTA, with ammonium thiocyanate,[1] salicylic acid,[2] sulphosalicylic acid,[3] Tiron[4,5] *etc* as indicator. These direct complexometric titrations have, however, poor end-points. Further, the formation of the iron(III) EDTA complex is slow at room temperature and a higher temperature (up to 60°) is advisable, but the increased risk of hydrolysis necessitates the use of a pH in the region of 1.

o-Mercaptobenzoic acid (MBA) is proposed in the present investigation as an indicator for the determination of iron. Arutyunov and Bakalyan[6] have reported the estimation of iron in food products by titration of the red precipitate formed between iron and MBA. However, the titration pH values, is given in Fig. 1, where H_4Y represents the undissociated alizarin fluorine blue molecule.



Alizarin fluorine blue

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Summary—Dissociation constants for the analytical reagent alizarin fluorine blue (3-aminomethylalizarin-*N*,*N*-diacetic acid) have been determined by potentiometric titration at ionic strength 0·1, and are $k_1 = 1·28 \pm 0·30 \times 10^{-5}$; $k_2 = 2·82 \pm 0·24 \times 10^{-8}$; $k_3 = 3·72 \pm 0·19 \times 10^{-11}$; $k_4 = 6·39 \pm 0·12 \times 10^{-12}$.

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Various methods have been reported in the literature for the EDTA titration of iron(III) and iron(II). For the use of EDTA to determine total iron in a system containing both iron(III) and iron(II), the iron(II) has to be oxidized. Iron(III) can be titrated with EDTA, with ammonium thiocyanate,[1] salicylic acid,[2] sulphosalicylic acid,[3] Tiron[4,5] *etc* as indicator. These direct complexometric titrations have, however, poor end-points. Further, the formation of the iron(III) EDTA complex is slow at room temperature and a higher temperature (up to 60°) is advisable, but the increased risk of hydrolysis necessitates the use of a pH in the region of 1.

o-Mercaptobenzoic acid (MBA) is proposed in the present investigation as an indicator for the determination of iron. Arutyunov and Bakalyan[6] have reported the estimation of iron in food products by titration of the red precipitate formed between iron and MBA. However, the titration is very slow, the end-point is not sharp, and the titration has to be carried out with a precipitate present. The precipitation can be avoided by the use of a pyridine–sulphuric acid buffer system. MBA forms a soluble deep blue complex with iron(II) in this medium (pH 6·4–7·4) and this can be titrated against EDTA, giving a very sharp colour change from blue to light yellow at room temperature (25–30°).

Iron(III) can also be determined conveniently because it is reduced by MBA to iron(II). Iron(III) forms a transient blue colour which soon disappears and then with excess of the reagent the deep blue iron(II) complex is formed. The reduction can be hastened by addition of ascorbic acid or hydroquinone before the reagent. The blue iron(II) complex is susceptible to oxidation but this can be prevented by addition of ascorbic acid or hydroquinone. Further, iron can be determined even in the presence of a large excess of copper if the latter is masked with sodium thiosulphate or ascorbic acid.

EXPERIMENTAL

Reagents

All solutions were prepared from analytical grade materials.

Iron(II), 0·01*M*. Prepared by dissolving the requisite amount of $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$ in a litre of water containing 5 ml of concentrated sulphuric acid, and standardized against potassium dichromate, *N*-phenylanthranilic acid[7] being used as indicator.

Iron(III), 0·01*M*. Prepared by dissolving the requisite amount of $Fe(NH_4)(SO_4)_2 \cdot 12H_2O$ in a litre of water containing 5 ml of concentrated sulphuric acid, and standardized by the tin(II) chloride method.[7]

o-*Mercaptobenzoic acid.* A 1% w/v solution in redistilled ethanol; stored in the refrigerator.

Pyridine, redistilled.

EDTA, 0·01*M*. Standardized against calcium, with Murexide[8] as indicator.

Determination of iron

To 5 ml of solution containing up to 5 mg of iron, add 15–20 mg of ascorbic acid or hydroquinone, let stand for 2 min, then add pyridine to adjust the pH to 6·4–7·4, followed by 3–4 ml of indicator solution, and titrate immediately with EDTA till the colour changes from blue to light yellow.

Determination of iron in presence of copper

To 5 ml of solution containing up to 5 mg of iron and 12 mg of copper add 15–20 mg of ascorbic acid, 2 ml of pyridine, 6–7 ml of 10% sodium thiosulphate solution and 3–5 ml of indicator solution and titrate immediately with EDTA till the colour changes from red to light yellow. If more copper is present, add the amount of sodium thiosulphate solution calculated to mask the copper completely; 5 ml of 10% sodium thiosulphate solution masks 0·25 mmole of copper (15·9 mg).

RESULTS

Typical titration results are shown in Tables I–IV.

TABLE I.—TITRATION OF IRON(II)

Fe(II) taken, *mg*	Fe(II) found, *mg*	Error, *mg*	Fe(II) taken, *mg*	Fe(II) found, *mg*	Error, *mg*
0·558	0·558	—	2·233	2·241	+0·008
1·168	1·160	−0·008	2·792	2·800	+0·008
1·675	1·680	+0·005	5·584	5·579	−0·005

TABLE II.—TITRATION OF IRON(III)

Fe(III) taken, *mg*	Fe(III) found, *mg*	Error, *mg*	Fe(III) taken, *mg*	Fe(III) found, *mg*	Error *mg*
0·558	0·558	—	2·233	2·241	+0·008
1·168	1·168	—	2·792	2·800	+0·008
1·675	1·670	−0·005	5·584	5·580	−0·004

TABLE III.—TITRATION OF TOTAL IRON

Fe(II) taken, *mg*	Fe(III) taken, *mg*	Total Fe, *mg*	Total Fe, found, *mg*	Error, *mg*
0·558	2·792	3·350	3·345	−0·005
1·168	2·332	2·400	3·995	−0·005
2·792	1·675	4·467	4·459	−0·008
5·584	0·558	6·142	6·138	−0·004

TABLE IV.—TITRATION OF IRON IN THE PRESENCE OF COPPER, WITH SODIUM THIOSULPHATE AS MASKING AGENT

Taken, *mg*		Fe found, *mg*	Error, *mg*
Fe	Cu		
0·558	6·354	0·558	—
2·792	6·354	2·800	+0·008
0·558	12·71	0·556	−0·002
2·792	12·71	2·785	−0·007

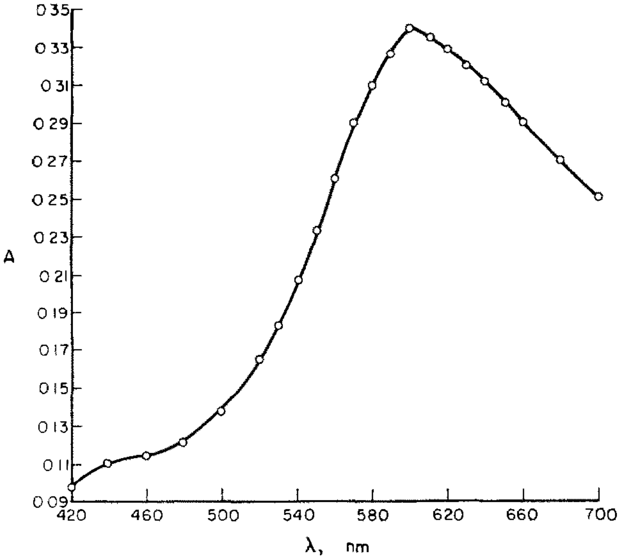

FIG. 1.—Absorption spectrum of the iron(II) complex with MBA at pH 6·4. 1 ml of 0·0025*M* iron(II) + 2 ml of pyridine + 1 ml of 1% MBA, diluted to 10 ml.

The absorption spectrum of the complex is shown in Fig. 1. Continuous variation[9] and mole ratio[10] plots showed that a 1:2 Fe–MBA complex is formed. The complex has maximum absorption over the pH range 6·4–7·4.

The stability constant, calculated by Harvey and Manning's method,[11] was found to be $\log K = 7{\cdot}7$ at 25°, at ionic strength 0·1.

Effect of diverse ions

Co(II), Ni, Mn(II) and Cu(II) interfere seriously in the titration and also form coloured complexes. Cu(II) can, however, be masked with sodium thiosulphate. There was no interference by anions such as chloride, fluoride, tartrate, phosphate, oxalate, citrate and acetate in amounts up to 250 mg.

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Summary—The soluble deep blue complex of iron(II) with *o*-mercaptobenzoic acid in aqueous pyridine medium (pH 6·4–7·4) can be titrated with EDTA at room temperature with a sharp colour change from blue to light yellow. *o*-Mercaptobenzoic acid forms a 2:1 complex with iron(II), maximum absorption at 600 nm. Its stability constant was found to be $\log K = 7{\cdot}7$. With iron(III), a transient blue colour is first formed which soon becomes colourless and then on the addition of excess of reagent, the deep blue complex is formed on reduction of the iron(III). Iron can be titrated in the presence of copper, if the latter is masked with sodium thiosulphate. Cobalt and nickel interfere. Common anions such as chloride, tartrate, phosphate, oxalate, citrate and acetate have no interference.

Zusammenfassung—Der lösliche tiefblaue Komplex von Eisen(II) mit *o*-Mercaptobenzoesäure in wäßrigem Pyridinmedium (pH 6,4–7,4) kann bei Raumtemperatur mit EDTA bis zu einem scharfen Farbumschlag von blau nach lichtgelb titriert werden. *o*-Mercaptobenzoesäure bildet mit Eisen(II) einen 2:1-Komplex mit Absorptionsmaximum bei 600 nm. Für seine Stabilitätskonstante wurde $\log K = 7{,}7$ gefunden. Mit Eisen(III) erscheint vorübergehend eine blaue Färbung, dann wird die Lösung farblos und bei Zugabe von überschüssigem Reagens bildet sich der tiefblaue Komplex nach Reduktion des Eisen(III). Eisen kann in Gegenwart von Kupfer titriert werden, wenn dieses mit Natriumthiosulfat maskiert wird. Kobalt und Nickel stören, häufiger vorkommende Anionen wie Chlorid, Tartrat, Phosphat, Oxalat, Citrat und Acetat stören nicht.

Résumé—On peut titrer le complexe soluble bleu foncé du fer(II) avec l'acide *o*-mercaptobenzoïque en milieu pyridine aqueuse (pH 6,4–7,4) au moyen d'EDTA à température ordinaire, avec un changement de coloration net du bleu au jaune clair. L'acide *o*-mercaptobenzoïque forme un complexe 2:1 avec le fer(II), maximum d'absorption à 600 nm. On a trouvé que sa constante de stabilité est $\log K = 7{,}7$. Avec le fer(III) il se forme d'abord une coloration bleue fugace qui bientôt disparaît puis, par addition d'un excès de réactif, il se forme le complexe bleu foncé par réduction du fer(III). On peut doser le fer en la présence de cuivre, si ce dernier est dissimulé au moyen de thiosulfate de sodium. Le cobalt et le nickel gênent. Les anions communs tels que chlorure, tartrate, phosphate, oxalate, citrate et acétate ne gênent pas.

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Hydrolysis of substituted 8-acetoxyquinolines

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IN this study, the hydrolysis of 2-methyl-8-acetoxyquinoline, an ester of analytical interest for the precipitation of metal ions from homogeneous solution (PFHS),[1] and of 5-chloro-8-acetoxyquinoline are compared and contrasted with the hydrolysis of the parent ester 8-acetoxyquinoline, in the presence and absence of metal ions.

EXPERIMENTAL

Reagents

8-Acetoxyquinoline. PFHS grade, stored over phosphorus pentoxide.

2-Methyl-8-acetoxyquinoline. Synthesized by the method of Büchi *et al.*[2] from 2-methyl-8-hydroxyquinoline, and stored over phosphorus pentoxide.

5-Chloro-8-acetoxyquinoline. Prepared by refluxing 10 g of 5-chloro-8-hydroxyquinoline, 10 ml of pyridine and 50 ml of acetic anhydride for 7 hr; the excess of reagents was then removed by heating under reduced pressure on a steam-bath, and the residue distilled (162–164°, 8 mbar). The product was recrystallized from benzene–petroleum ether to yield white platelets m.p. 82–84°.

Metal ion solutions. Prepared from the perchlorate salts. The copper(II) solution was standardized iodometrically.

The water used was distilled and demineralized.

Procedure

*p*K*$_a$* *Values.* About 60 mg of ester were weighed into the titration vessel, then dissolved in 1·0 ml of absolute ethanol, and diluted with 100.0 ml of 0·05*M* perchloric acid which was 0·10*M* in sodium perchlorate, and then titrated potentiometrically at 25·0 ± 0·1°, under nitrogen, with a standard carbonate-free solution of sodium hydroxide. The pK_a values were calculated in the manner of Takamoto *et al.*[3] Calculations showed that the hydrolysis that occurred during a potentiometric titration was negligible.

Hydrolyses of esters. Solutions made by adding 1·0 ml of a freshly prepared ethanolic solution of ester to 99 ml of perchloric acid (for pH values <3) or of a buffer solution (acetate for pH 3–6, phosphate for pH 6–7, borate for pH > 8) were adjusted to an ionic strength of 0·1, where necessary, with sodium perchlorate. The solutions, usually $2 \times 10^{-5}M$ in ester, were kept at 25·0 ± 0·1°, and samples withdrawn at appropriate intervals for measurement of absorbance (with 8-acetoxyquinoline, at 251·5 nm for pH <5 and at 240 nm for pH >5; with the 2-methyl ester, generally at 255 nm; with the 5-chloro ester, at 257 nm for pH <3·9 and at 235 nm for pH >3·9).

Values of log $(A_\infty - A_t)$, where A_∞ and A_t are the absorbances at the completion of the hydrolysis and at time t, when plotted against t yielded straight lines extending over several half-lives, indicating that the reactions were first-order with respect to ester.

Some rate constants for the 2-methyl ester, for the same conditions of temperature and ionic strength but with the ester at higher concentration (0·01–0·02*M*), were determined by a bromometric method[4] for the determination of 2-methyl-8-hydroxyquinoline. These constants were consistent with those determined spectrophotometrically.

RESULTS AND DISCUSSION

For the hydrolysis of 8-acetoxyquinoline, Wasmuth and Freiser[5] showed that the variation of the observed first-order rate constant with pH could be accounted for by assuming it to be a consequence of several hydrolysis reactions: that of the protonated ester catalysed by H$^+$, that of the free ester catalysed by H$^+$, a hydrolysis of the free ester without catalysis by H$^+$ or OH$^-$ (but possibly involving intramolecular catalysis by the quinoline nitrogen), and hydrolysis of the free ester catalysed by OH$^-$. This leads to the following expression for the observed rate constant:

$$k_{\text{obs}} = \frac{[\text{H}^+]}{K_a + [\text{H}^+]}\{k_1[\text{H}^+]\} + \frac{K_a}{K_a + [\text{H}^+]}\{k_2[\text{H}^+] + k_3 + k_4[\text{OH}^-]\}$$

in which k_1, k_2, k_3 and k_4 are the rate constants for the four hydrolysis reactions in the order mentioned above, and K_a is the acid dissociation constant of the protonated ester.

The results we obtained for the hydrolysis of both 2-methyl-8-acetoxyquinoline and 5-chloro-8-acetoxyquinoline can be described by this equation as shown in Fig. 1, the curves of which were plotted from the data of Table I. The curve for 8-acetoxyquinoline is based on the work of Barca and

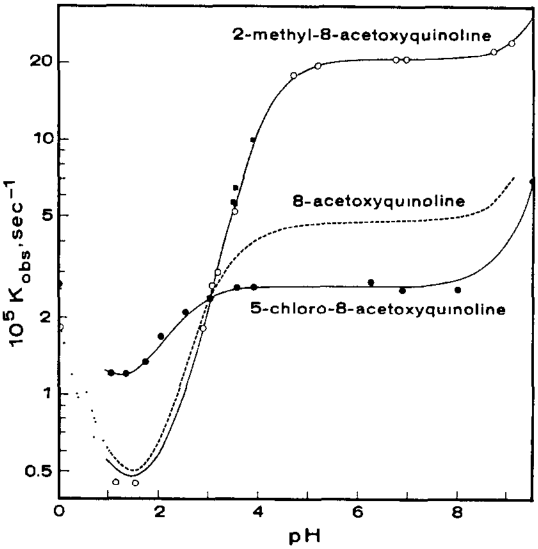

FIG. 1.—Variation, with pH, of observed first-order rate constants for hydrolysis of 8-acetoxyquinolines. (The curves below pH 1 are dotted because the ionic strength is greater than 0·1.) The points plotted as squares are for the hydrolysis of 2-methyl-8-acetoxyquinoline in the presence of 0·01–0·06*M* copper(II).

Freiser;[6] for this ester we obtained similar hydrolysis data over a narrower pH range. The similarities in the pH–rate constant relationships of the three esters suggests that they have the same hydrolysis mechanism.

The hypothesis[5,6] that the pH-independent hydrolysis of the neutral ester is due to intramolecular nucleophilic catalysis by the nitrogen atom is supported by our finding that k_3 for 2-methyl-8-acetoxyquinoline is higher, and for 5-chloro-8-acetoxyquinoline is lower, that that for 8-acetoxyquinoline: this accords with the order of basicity of the nitrogen atom in the three esters.

Freiser *et al.*[5,6] observed that the hydrolysis of 8-acetoxyquinoline is catalysed by several metal ions, the effect (with bivalent ions) on k_{obs} being given by $\dfrac{K_a k_m[M^{+2}][OH^-]}{K_a + [H^+]}$ as an additional factor in the equation cited earlier.

We confirmed catalysis of the hydrolysis of 8-acetoxyquinoline by both copper(II) and nickel ions, with very good agreement: k_m for Cu^{2+}, $8{\cdot}5 \times 10^7\, l^2.\text{mole}^{-2}.\text{sec}^{-1}$ (compared with $9{\cdot}1 \times 10^7$);[6] k_m for Ni^{2+}, $\sim 1{\cdot}6 \times 10^4\, l^2.\text{mole}^{-2}.\text{sec}^{-1}$ (compared with $\sim 1{\cdot}5 \times 10^4$).[6] In contrast, though, we detected no catalysis of the hydrolysis of 2-methyl-8-acetoxyquinoline by either copper(II) (0·01–0·06*M*, at pH 3·5–3·9) or nickel (0·01*M*, at pH 6·1–6·5). With 5-chloro-8-acetoxyquinoline, catalysis by copper(II) was observed, k_m being $\sim 10^8\, l^2.\text{mole}^{-2}.\text{sec}^{-1}$ (from experiments at pH 2·5–3·5 with $[Cu^{2+}] = 0{\cdot}01M$).

Our observation that the hydrolysis of 2-methyl-8-acetoxyquinoline appears uncatalysed by metal ions, whereas the hydrolysis of both the parent ester and the 5-chloro derivative is catalysed, supports the view[6] that the catalysis involves co-ordination of the metal ion to both the nitrogen and

TABLE I.—RATE CONSTANTS FOR HYDROLYSIS OF 8-ACETOXYQUINOLINES AND pK_a VALUES (25·0°C; ionic strength = 0·1)

Rate constant	2-methyl- 8-acetoxyquinoline	5-chloro- 8-acetoxyquinoline	8-acetoxyquinoline[6]
k_1, *l.mole^{-1}.sec^{-1}* × 10^5	1·5	1·8	2·55
k_2, *l.mole^{-1}.sec^{-1}* × 10^3	36	2·1	3·7
k_3, *sec^{-1}* × 10^5	20·7	2·68	4·7
k_4, *l.mole^{-1}.sec^{-1}*	1·8	0·8	1·14
pK_a of the conjugate acid:	3·99 ± 0·03	2·33 ± 0·02*	3·08 ± 0·01

* A spectrophotometric determination, at 245·5 nm, yielded the value 2·31 ± 0·04.

the carbonyl oxygen of the ester, to form a 7-membered ring. Models show that such co-ordination is prevented by a methyl group in the 2-position but is unhindered in the other two compounds. If chelation involved the ether oxygen, the 2-methyl group would exert no appreciable steric effect.

The fact that the hydrolysis of 2-methyl-8-acetoxyquinoline is much less affected by metal ions gives an advantage to this ester, in comparison to 8-acetoxyquinoline, as a reagent for the homogeneous precipitation of metal ions. With the parent ester, the rate of hydrolysis depends, *inter alia*, on the nature and concentration of the metal ion being precipitated, and may be several times the rate in the absence of the latter; with the 2-methyl compound, prediction of the rate of hydrolysis, and hence control of the precipitation, is more readily achieved.

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Summary—In the absence of metal ions, the hydrolysis of 2-methyl-8-acetoxyquinoline and of 5-chloro-8-acetoxyquinoline follow the same reaction paths as those of the parent ester 8-acetoxyquinoline, including an intramolecular catalysis by the quinoline nitrogen. Unlike the hydrolysis of the other esters, that of the 2-methyl compound appears not to be catalysed by metal ions, and this is consistent with the view that catalysis by a metal ion involves the formation of a 7-membered chelate structure.

Zusammenfassung—In Abwesenheit von Metallionen verläuft die Hydrolyse von 2-Methyl-8-acetoxychinolin und von 5-Chlor-8-acetoxychinolin ebenso wie die des zugrundeliegenden Esters 8-Acetoxychinolin über eine intramolekulare Katalyse durch den Chinolinstickstoff. Anders als die Hydrolyse der übrigen Ester wird die des 2-Methylderivats offenbar nicht durch Metallionen katalysiert. Dies stimmt mit der Auffassung überein, daß die Metallionenkatalyse die Bildung einer 7-gliedrigen Chelatstruktur einschließt.

Résumé—En l'absence d'ions métalliques, l'hydrolyse de la 2-méthyl 8-acétoxyquinoléine et de la 5-chloro 8-acétoxyquinoléine suit le même processus réactionnel que l'ester apparenté 8-acétoxyquinoléine, incluant une catalyse intramoléculaire par l'azote quinoléique. A l'opposé de l'hydrolyse des autres esters, celle du composé 2-méthylé apparaît ne pas être catalysée par les ions métalliques, et ceci est en accord avec la conception que la catalyse par un ion métallique implique la formation d'une structure chélatée heptagonale.

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Acid dissociation and metal chelate formation equilibria of some halogenated diphenylthiocarbazones

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IN THE course of an investigation of the effect of ligand substitution on the rate of formation of zinc, nickel and cobalt dithizonates[1,2] it was found that both electron-releasing and -withdrawing substituents resulted in ligands which reacted more rapidly with the metal ions than did the parent the carbonyl oxygen of the ester, to form a 7-membered ring. Models show that such co-ordination is prevented by a methyl group in the 2-position but is unhindered in the other two compounds. If chelation involved the ether oxygen, the 2-methyl group would exert no appreciable steric effect.

The fact that the hydrolysis of 2-methyl-8-acetoxyquinoline is much less affected by metal ions gives an advantage to this ester, in comparison to 8-acetoxyquinoline, as a reagent for the homogeneous precipitation of metal ions. With the parent ester, the rate of hydrolysis depends, *inter alia*, on the nature and concentration of the metal ion being precipitated, and may be several times the rate in the absence of the latter; with the 2-methyl compound, prediction of the rate of hydrolysis, and hence control of the precipitation, is more readily achieved.

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IN THE course of an investigation of the effect of ligand substitution on the rate of formation of zinc, nickel and cobalt dithizonates[1,2] it was found that both electron-releasing and -withdrawing substituents resulted in ligands which reacted more rapidly with the metal ions than did the parent compounds. This substituent effect is markedly different from that generally observed in equilibrium parameters such as the pK_a of the ligand or the formation constant of the chelate. Change of charge density at the site of chelation is generally reflected in a corresponding change of pK_a and log K_{f_1} in a given series. This study of the pK_a values for the ligands and of log K_{f_1} values for the Co(II), Ni and Zn chelates was undertaken to learn whether the unusual kinetic behaviour would be observed in the acid dissociation and/or the metal chelate formation equilibria.

EXPERIMENTAL

Materials

The di-*p*-fluoro, di-*p*-chloro-, di-*p*-bromo-, di-*p*-iodo-, and di-*m*-trifluoromethyl-phenylthiocarbazones were synthesized[3-5] by coupling two molecules of the diazonium compound with sodionitromethane in an alkaline ethanolic medium, giving the nitroformazyl compound which was then reduced by ethanolic ammonium sulphide solution to give the thiocarbazide product. The latter, in turn, was oxidized to the corresponding diphenylthiocarbazone. These synthesized dithizones as well as diphenylthiocarbazone were purified by precipitation with absolute ethanol from solutions of freshly distilled chloroform that had been treated with hydroxylamine hydrochloride.[6,7]

The melting points were found to be: di-*p*-fluoro 149–50°(lit.[8] 146–8°), di-*p*-chloro 72–3° (lit.[9] 173–4°), di-*p*-bromo 150–1°(lit.[9] 151–2°), di-*p*-iodo 159–60°(lit.[9] 160–1°) and di-*m*-trifluoromethyl 130–1°(lit.[9] 128–9°).

The absorption spectra in the region 320–760 nm as well as the peak ratios of these compounds in chloroform solutions were compared with those previously reported (Table I).

TABLE I.—ABSORPTIVITY DATA FOR DITHIZONES IN $CHCl_3$ AT 25°C

Diarylthiocarbazone	λ_1 min, *nm*	λ_1 max, *nm*	λ_2 min, *nm*	λ_2 max, *nm*	λ_3 min, *nm*	ε_1 max/ε_2 max
Diphenyl	700	605	507	443	364	2·4
($C_{13}H_{12}N_4S$)	*a*	605	505	445	—	2·5
Di-*p*-fluorophenyl	707	606	507	447	365	2·5
($C_{13}H_{10}F_2N_4S$)	*a*	607	507	447	—	2·5
Di-*p*-chlorophenyl	717	622	515	458	373	2·5
($C_{13}H_{10}Cl_2N_4S$)	*a*	621	515	458	—	2·6
Di-*p*-bromophenyl	718	626	522	458	373	2·5
($C_{13}H_{10}Br_2N_4S$)	*a*	626	522	458	—	2·5
Di-*p*-iodophenyl	718	635	530	466	384	2·6
($C_{13}H_{10}I_2N_4S$)	*a*	635	530	464	—	2·6
Di-*m*-trifluoro-methylphenyl	718	610	508	443	357	1·4
($C_{15}H_{10}F_6N_4S$)	*a*	610	510	445	—	1·4

a Reported values.[8]

Buffer solutions were prepared from reagent grade chemicals and demineralized water. At pH values below 7 they were freed from heavy metal ions by extraction with dithizone solution in carbon tetrachloride,[10] and were made up to 0·30*M* ionic strength by adjustment with sodium perchlorate solution.

The aqueous solutions of zinc, cobalt(II) and nickel perchlorates were standardized by titration with EDTA solution.[11] 1,4-Dioxan was purified by refluxing with metallic sodium[12] and redistilled daily. A 50% v/v aqueous dioxan solution was the medium for all absorbance measurements made in the determination of equilibrium constants. The stabilities of the dioxan solutions of the halogen substituted dithizones toward oxidation were found to decrease in the order F > Cl > Br > I, a behaviour similar to that found for their chloroform solutions.[1] To prevent the oxidation of the solutions of these dithizones the freshly distilled dioxan was vigorously shaken with a few crystals of hydroxylamine hydrochloride for about 10 min, followed by filtration before use.

Apparatus

A Cary 14 spectrophotometer was employed for all the spectrophotometric measurements made in this study.

A Beckman Research pH meter with a glass–calomel electrode pair was used for pH measurements. Standardization against Beckman buffers of pH 4.00 and 6.86 was carried out before each set of measurements. For measurements in 50% v/v aqueous dioxan solutions appropriate corrections were made for converting the pH meter readings into the corresponding hydrogen ion concentrations.

An ultrasonic disintegrator Model T-40Cl (Ultrasonic Industries, Inc., Albertson, L.I., N.Y.) was very useful for ensuring quick and complete dissolution of the ligands in dioxan.

Determination of acid dissociation constants

In each experiment, a series of 10–12 or more different solutions was prepared, each containing a mixture of buffer solution of 0·30*M* ionic strength, demineralized water and dioxan. That volume of ligand solution which on dilution would give an ionic strength of 0·10*M* and a final composition of 50% v/v aqueous dioxan, was added by pipette to each mixture just before the absorbance at the appropriate wavelength was recorded (Table II). Although in previous studies[14] a small change of absorbance with time had been observed, arising from slight oxidative decomposition of the ligand, it was found in this study that solutions prepared with the freshly distilled and hydroxylamine-treated dioxan were entirely stable for a number of hours.

TABLE II.—ABSORPTIVITY DATA FOR DITHIZONES IN DIOXAN (A) AND IN 50% V/V AQUEOUS DIOXAN MEDIUM (B) IN THE REGION 320–760 *nm* AT 25°C

Diarylthiocarbazone		λ_1 min, *nm*	λ_1 max, *nm*	λ_2 min, *nm*	λ_2 max, *nm*	λ_3 min, *nm*	ε_1 max/ε_2 max
Diphenyl	(A)	710	618	512	447	363	1·5
	(B)	700	598	505	435	360	
Di-*p*-F-phenyl	(A)	710	615	516	450	367	1·5
	(B)	700	596	506	424	350	
Di-*p*-Cl-phenyl	(A)	720	627	523	458	370	1·5
	(B)	700	596	506	424	350	
Di-*p*-Br-phenyl	(A)	723	632	525	456	370	1·4
	(B)	706	616	516	448	362	
Di-*p*-I-phenyl	(A)	726	638	530	465	380	1·6
	(B)	720	625	526	458	376	
Di-*m*-CF_3-phenyl	(A)	725	620	510	440	358	0·95
	(B)	715	600	510	420	348	

A plot of the absorbance values of the series of solutions against pH gave the characteristic sigmoid-shaped curves with inflection points corresponding to the pK_a values of the ligands. A more reliable graphical method from which the acid dissociation constants were calculated (Table III) is the one based on the equation,[14]

$$\mathrm{pH} = \mathrm{p}K_a + \log\frac{l\varepsilon_{HL}T_L - A}{A - l\varepsilon_L T_L} \tag{1}$$

or

$$\mathrm{pH} = \mathrm{p}K_a + \log f(A) \tag{2}$$

and

$$\mathrm{pH} = \mathrm{p}K_a \text{ at } \log f(A) = 0$$

TABLE III.—ACID DISSOCIATION CONSTANTS OF DITHIZONES AND FORMATION CONSTANTS OF THEIR 1:1 METAL CHELATES IN 50% V/V AQUEOUS DIOXAN SOLUTIONS OF 0·10*M* IONIC STRENGTH AT 25°C

Diarylthiocarbazone	pK_a(λ*)	Log K_{f1}(λ*)		
		Co(II)	Ni(II)	Zn(II)
Diphenyl	5·77(600)	6·43(520)	5·69(600)	6·16(500)
From Ref. 14	5·80		5·83	6·18
Di-*p*-F-phenyl	4·99(596)	5·94(440)	5·14(480)	5·75(500)
Di-*p*-Cl-phenyl	4·63(610)	5·63(440)	4·90(610)	5·37(510)
Di-*p*-Br-phenyl	4·40(616)	5·39(520)	4·72(430)	5·35(510)
Di-*p*-I-phenyl	4·03(625)	4·84(440)	4·66(625)	5·02(510)
Di-*m*-CF_3-phenyl	2·57(600)	3·48(580)	3·33(490)	3·83(495)
Di-*o*-CH_3-phenyl[14]	6·23		5·90	4·50
Di-*p*-CH_3-phenyl[14]	6·40		6·60	6·45

* Wavelength used for absorbance measurements, *nm*.

where ε_{HL} and ε_L are the molar absorptivities of the neutral and anionic forms of the ligand, A the absorbance, all at the same pH value, l is the path-length, and T_L is the total ligand concentration (in mole. l^{-1}). A plot of pH *vs.* log $f(A)$ gave a straight line of unit slope with an intercept [at log $f(A) = 0$] equal to the pK_a of the acid.

Determination of formation constants of 1:1 *metal complexes*

The solutions were prepared as for the pK_a determination except that each mixture contained a definite amount of the metal ion added as standard perchlorate solution. Just before the absorbance was recorded an aliquot of the ligand solution was added to the mixture to give a solution of 0·10M ionic strength in 50% v/v aqueous dioxan medium, with a metal-ligand concentration ratio (T_M/T_L) of 100 or more in order to prevent the formation of the 1:2 chelate complex. In the case of nickel, chelate precipitation could be avoided only when T_M was under 5 × $10^{-4}M$.

Absorbance measurements at the wavelength maximum of the metal complex were made at various time intervals. Extrapolation of absorbance to zero time was necessary since in the presence of metal ions, a slow change due to ligand oxidation was observed.

The variation of absorbance with pH provided the basis of the graphical method for the calculation of the formation constant.[14]

$$K_{f_1} = \frac{[\mathrm{H}^+]}{K_a T_M} \frac{(A - \varepsilon_{HL} T_L l)}{(\varepsilon_{ML} T_L l - A)} \tag{3}$$

$$\log K_{f_1} = \mathrm{p}K_a - \log T_M - \mathrm{pH} + \log \frac{(A - \varepsilon_{HL} T_L l)}{(\varepsilon_{ML} T_L l - A)} \tag{4}$$

where K_{f_1} is the formation constant of the 1:1 complex and A is the extrapolated absorbance. The value of log K_{f_1} for each metal complex was determined from a plot of log $f(A)$ *vs.* pH; this gave a straight line of unit slope with an intercept [at log $f(A) = 0$] equal to log $T_M K_a K_{f_1}$. The precision of log pK_a and log K_{f_1} was ±0.05.

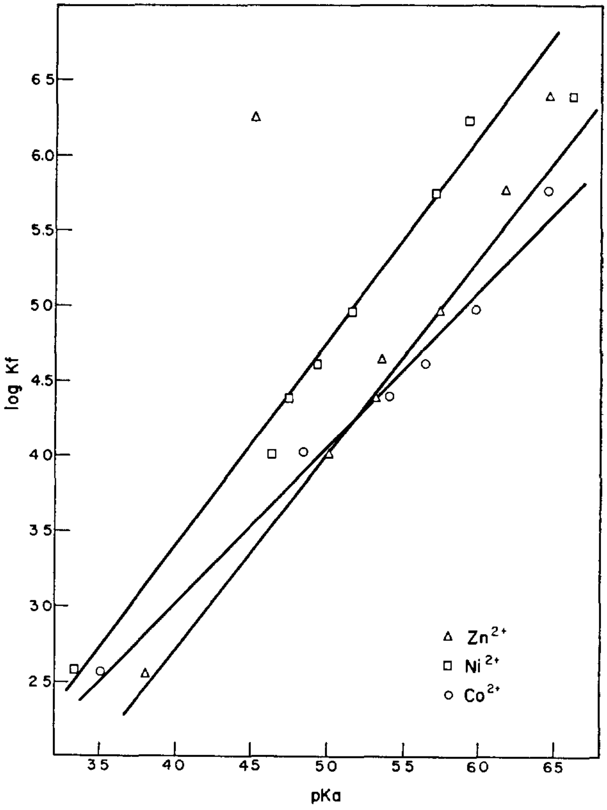

FIG. 1.—Variation of dithizonate chelate stabilities with reagent basicity (log K_{f_1} *vs.* pK_a) in 50% v/v aqueous dioxan at 25°C.

DISCUSSION

The effect of the substituents on the acid dissociation constants of the ligands is in reasonable accord with what could be expected from their electronic influence. There is a roughly linear correlation of the pK_a values of the ligands with the value of the Hammett σ constants of the substituents. Furthermore, as can be seen from Fig. 1, the variation of chelate stability with ligand basicity is in complete accord with the conventional $pK_a - \log K_f$ relationships. The explanation for the unusual kinetics of chelate formation with these substituted dithizones must be sought elsewhere.

Although of the reagents studied the *m*-trifluoromethyl analogue forms the weakest chelates, it is important to note that its complexes have proton displacement constants ($K_{f_1}K_a$) that are the highest in the series so that its chelates will form in significantly more acidic media than will those of dithizone. This property, plus a greater stability of the compound towards oxidative degradation, should make it quite a useful analytical reagent.

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Summary—The acid dissociation constants (K_a) of di-*p*-fluoro-, di-*p*-chloro-, di-*p*-bromo-, di-*p*-iodo- and di-*m*-trifluoromethylphenylthiocarbazones and the equilibrium formation constants (K_{f_1}) of their 1:1 complexes with Co(II), Ni and Zn have been determined at 25° in 50% v/v aqueous dioxan at 0.10 *M* ionic strength. Each of the electron-withdrawing substituents gives a reduction in pK_a roughly proportional to its Hammett σ value, and $\log K_{f_1}$ increases linearly with pK_a.

Zusammenfassung—Die Säuredissoziationskonstanten (K_a) der Di-*p*-fluoro-, Di-*p*-chloro-, Di-*p*-bromo-, Di-*p*-jodo- und Di-*m*-trifluormethyl-phenylthiocarbazone und die Bildungskonstanten (K_{f_1}) ihrer 1:1-Komplexe mit Co(II), Ni und Zn wurden bei 25° in 50% (V/V) wäßrigem Dioxan bei der Ionenstärke 0,1*M* bestimmt. Jeder der elektronenabziehenden Substituenten vermindert pK_a um einen Wert, der etwa seinem σ-Wert nach Hammett proportional ist; $\log K_{f_1}$ steigt linear mit pK_a.

Résumé—On a déterminé, à 25° en dioxane aqueux à 50% v/v et avec une force ionique 0,10*M*, les constantes de dissociation acide (K_a) des di-*p*-fluoro-, di-*p*-chloro-, di-*p*-bromo-, di-*p*-iodo- et di-*m*-trifluorométhylphénylthiocarbazones et les constantes de formation d'équilibre (K_{f_1}) de leurs complexes 1:1 avec Co(II), Ni et Zn. Chacun des substituants attracteur d'électrons donne une réduction du pK_a approximativement proportionnelle à sa valeur σ de Hammett, et $\log K_{f_1}$ croît linéairement avec pK_a.

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USE OF TETRACYANOPLATINATE(II) FOR THE LUMINESCENT DETECTION OF METAL IONS*

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Summary—The tetracyanoplatinate(II) (TCP) ion forms insoluble fluorescent compounds with many metal ions. This property has not hitherto been exploited for analytical use. The soluble sodium TCP salt has been applied as a reagent for metal ion detection. Fluorescent precipitates useful for detection of the metal ions were obtained with Y(III), Zr(IV), Ag(I), Zn(II), Cd(II), Hg(I), Hg(II), Al(III), Pb(II), La(III) and Th(IV). Limits of detection ranged from 5 to 200 ppm. With ammonium acetate as a masking agent, selective detection of 10 ppm of silver was achieved in the presence of the other metal ions. As little as 20 ppm of zirconium can be detected in the presence of hafnium, which yields a non-fluorescent precipitate.

THE DETECTION and/or determination of metal ions by luminescent methods constitutes an important and growing topic of present-day analytical research. The reagents used are mainly organic chelating molecules, producing characteristic fluorescent solutions with particular metal ions. Some inorganic compounds also possess luminescent properties. Of these, the tetracyanoplatinate(II) (TCP) ion is an unusual example since it is not a metal chelate. The physical properties of the TCP salts have been examined in some detail since the mid-19th century, yet their chemical reactions have received little attention. As far as could be ascertained from the literature the TCP salts have not been previously investigated as analytical reagents.

Many of the crystalline soluble TCP salts are fluorescent in the solid state, or in the frozen state in solution under ultraviolet excitation, and have been studied in some detail in radiation investigations. Apart from this, the applicability of metal–TCP compounds, in particular the insoluble compounds, does not appear to have been studied for metal ion detection. It seemed therefore of interest to study whether the luminescence of the insoluble metal TCP compounds could be exploited to detect metal ions in solution. The results of this study as they apply to detection are reported in this communication. The chemical and physical chemical aspects of the investigation will be reported elsewhere.

As a result of our investigation methods have been developed for the detection of certain metal ions. For example, silver, which is normally difficult to detect directly in the presence of such elements as lead, mercury and noble metals, is easily detected by means of the luminescent precipitate formed; zirconium, virtually indistinguishable chemically from hafnium, is readily detected in the presence of the latter because the zirconium TCP precipitate is luminescent and the hafnium one is not.

This communication describes the preparation and use of the pure barium and sodium TCP salts; the sodium salt is the preferred reagent. Use of sodium TCP as a

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reagent for the gravimetric and titrimetric determination of silver will be described in a later communication.

EXPERIMENTAL

Preparation of the tetracyanoplatinate(II) reagents

The barium and sodium TCP salts were prepared. The first recorded preparation of tetracyanoplatinate(II) compounds was by Gmelin[1] in 1822 for the potassium salt. Quadrat[2] in 1847 made the insoluble copper TCP from which he obtained the soluble barium salt, while Schertel[3] made the latter by the fusion of platinum disulphide with barium cyanide. None of these methods appeared to give good yields. Bergsøe[4] in 1899 synthesized the barium salt by a route involving the formation of an intermediate double salt of $PtSO_3 \cdot 3BaSO_3$, formed according to the reaction:

$$H_2PtCl_6 + 7Ba(OH)_2 + 5SO_2 \rightarrow PtSO_3 \cdot 3BaSO_3 + BaSO_4 + 3BaCl_2 + 8H_2O \quad (1)$$

The double salt was then digested with barium cyanide solution at 50° to yield barium TCP as follows:

$$PtSO_3 \cdot 3BaSO_3 + 2Ba(CN)_2 \rightarrow BaPt(CN)_4 + 3BaSO_4 \quad (2)$$

This method was reported to give good yields of the TCP salt, but it was not clear to what extent the yield was governed by the amount of barium cyanide in excess, the reaction temperature, and the digestion time.

Our first attempts to produce the barium TCP salt by Bergsøe's method, with a moderate excess of barium cyanide, produced rather poor yields. This was finally overcome by using a large excess of barium cyanide (about 5 times the stoichiometric requirements) and digestion for 4 hr at 50°; ~95% yields of pure material were then obtained.

The cyanide digestion temperature was found to be critical. At temperatures above 60° the double sulphite tends to decompose, depositing platinum black in the reaction mixture.

Poor yields were also obtained if in reaction (1) nitrate ion or nitric acid remained in the hexachloroplatinic acid solution, whether this was obtained as a commercial preparation or from dissolution of platinum sponge in *aqua regia*. The chloroplatinic acid solution must be repeatedly evaporated to dryness with hydrochloric acid in order to drive off all the nitric acid.

In the case of the alkali metal TCP salts, Quadrat[2] described some methods based on the reaction of the insoluble copper TCP with the metal hydroxides, and by treating tetrachloroplatinate salts with the appropriate alkali metal cyanide. These methods were considered too cumbersome as a means of obtaining the pure sodium TCP salt. In recent times Bergsøe *et al.*[5] (1962) described an ion-exchange method for the preparation of alkali metal TCP salts; a solution of the barium TCP salt was passed down a column of cation-exchange resin to convert the salt into the free tetracyanoplatinic acid, which was then neutralized with the appropriate alkali, or alkaline earth metal oxide or carbonate.

It was considered that the ion-exchange method would provide a purer sample of the sodium TCP, and it was modified by using a cation-exchanger in the sodium form.

Preparation of barium tetracyanoplatinate(II). Platinum sponge of 99·999% purity (2 g) was dissolved in *aqua regia* (20 ml) and the solution of hexachloroplatinic acid reduced to small bulk on a boiling water-bath. The residue was taken up in conc. hydrochloric acid (10 ml, MAR) and the volume of liquid reduced once more by evaporation. This hydrochloric acid treatment was repeated until no more nitric acid was present in the residue.

The residue was taken up in distilled water (10 ml) and transferred to a 500-ml round-bottomed flask with distilled water. The solution was adjusted to pH 9–10 with 0·5*M* barium hydroxide, and diluted to about 200 ml with distilled water; barium hydroxide (23 g) was then added. The orange mixture was stirred to dissolve most of the barium hydroxide and the flask was placed in a water-bath maintained at 70°. The vessel was provided with a gas-delivery tube and exit, and when the mixture was at about 70° sulphur dioxide was passed slowly through the reaction mixture until the latter was colourless, indicating that all the barium hexachloroplatinate(IV) had been reduced, and was then passed for a further 15 min to ensure complete reduction. The contents of the flask, a mixture of the double sulphite and barium sulphate, were adjusted to pH 9–10 with 0·5*M* barium hydroxide and then filtered.

The reaction product was collected on a Whatman No. 542 paper in a Büchner funnel and washed with hot distilled water. The precipitate was very fine and difficult to collect, and decantation was impracticable since the precipitate did not settle. The product was sucked dry on the filter, transferred to a 250-ml beaker, and treated with a suspension of barium cyanide (20 g in 50 ml of water). The mixture was heated to 50° and stirred constantly for 4 hr. The precipitate decreased in bulk as reaction (2) proceeded. Carbon dioxide was then passed through the suspension in order to destroy the excess of barium cyanide. The mixture was filtered and the solution of the barium TCP salt obtained was evaporated to small bulk. Green crystals of the barium TCP tetrahydrate were obtained on cooling the concentrate.

The yield was 4·87 g: 92·6% of the theoretical from the platinum taken. Analysis: found, C 9·3, 9·3%; H 1·6, 1·7%; Ba 26·6, 26·6%; $[Pt(CN)_4]^{2-}$58·6, 58·6%: calculated for $BaPt(CN)_4 \cdot 4H_2O$, C 9·43%; H 1·59%; Ba 27·0%; $[Pt(CN)_4]^{2-}$ 58·8%.

Notes. 1. Determination of the water content of the product by drying to constant weight was found to be impracticable. The dried salt was extremely hygroscopic.

2. Further purification of the product was attempted by recrystallization from water, the solution being saturated with carbon dioxide. Yellow crystals of barium TCP tetrahydrate were obtained, and did not differ in analytical composition from the green material. This is consistent with the observations of Levy.[6] Both tetrahydrates gave a green fluorescence under ultraviolet excitation, but the yellow form was much less fluorescent.

Preparation of sodium tetracyanoplatinate(II). A column of Amberlite IR-120 cation-exchange resin, 250 mm long and 20 mm in diameter, was changed into the sodium form by passage of a saturated solution of sodium bromide through it, and then washed free from bromide ions with demineralized water. A solution of the pure barium TCP tetrahydrate (1 g in 25 ml of water) was placed on the column, which was then washed with demineralized water until the effluent no longer gave a precipitate with silver nitrate solution, *i.e.*, all the TCP ion was washed from the resin.

The solution collected from the column was evaporated to small bulk and colourless crystals of the sodium TCP trihydrate were obtained on cooling the concentrate. The product gave a bright blue fluorescence under the ultraviolet lamp. Yield 0·76 g; 96·8% of theoretical. Analysis: found, $[Pt(CN)_4]^{2-}$ 74·7, 74·8%; H_2O 13·4, 13·4%; calculated for $Na_2Pt(CN)_4$ $[Pt(CN)_4]^{2-}$ 74·9%; H_2O 13·5%.

Note. The $[Pt(CN)_4{}^{2-}$ ion was determined by the argentometric potentiometric titration used for the analysis of the barium TCP. The water of crystallization was determined by heating the weighed samples to constant weight at 160°. The anhydrous salt was not hygroscopic.

The reaction of tetracyanoplatinate(II) with metal ions

Quadrat[2] described the preparation and analysis of some insoluble TCP compounds, and Stokes[7] in 1853 stated that the precipitates obtained from the heavy metal ions and soluble TCP salts were usually non-fluorescent, but that mercury(II) gave a strongly fluorescent precipitate and silver a very weakly fluorescent precipitate. Since then no other investigators have reported fluorescence of insoluble TCP compounds. Müller,[8] for example, in 1903 reported the production of coloured precipitates from the addition of a 3% solution of potassium TCP to certain metal salts in solution; no mention was made that any of the precipitates exhibited fluorescence.

A large number of soluble metal tetracyanoplatinate(II) salts have been prepared, mainly because of the interest shown in their fluorescent characteristics in the solid state and their possible use as scintillation materials. Pringsheim[9] lists a number of soluble TCP salts prepared by various investigators before 1949. Later Tolstoi *et al.*[10] prepared the alkali, alkaline earth and rare earth metal TCP salts in order to measure their fluorescence lifetimes.

In the present investigation, preliminary tests showed which of the metals selected and available gave precipitates with the sodium tetracyanoplatinate(II) reagent. The metals listed in Table I, as 5% w/v aqueous solutions of their nitrates or other soluble metal salts where the nitrates were not available, were treated with an excess of 5% w/v aqueous solution of the reagent.

Since several of the metal ion solutions were naturally acidic, the pH was raised, after the addition of TCP, by addition of 0·1*M* or 2·5*M* ammonium solution, the former being used for fine control. A greatly extended range of precipitates was thus obtained but some of these precipitates were evidently the metal hydroxides. However, when a fluorescent precipitate was produced only on addition of the ammonia it was concluded that at least some of the TCP ion had been brought out of solution, and further that either these metal-TCP compounds were soluble in acid and precipitated by ammonia, or that fluorescence was caused by adsorption of the TCP ion onto the metal hydroxide precipitate.

A more detailed study of the precipitation was then carried out under carefully controlled pH conditions. In this series of experiments the usual buffer solutions could not be used to control the pH, because they contained anions which would have given precipitates with some of the metal ions.

Each metal ion solution (0·1 ml) was treated with the sodium TCP reagent 0·1 ml), then adjusted to different pH values with the aid of narrow-range indicator papers and dropwise addition of 0·1*M* ammonia hydroxide or 0·1*M* nitric acid. The information obtained narrowed our interest (*i*) to those precipitates which formed in solutions of pH 6 or less, irrespective of whether they were fluorescent or not; and (*ii*) those precipitates that were fluorescent and which formed in solutions of pH above 6. The precipitates which formed in alkaline solutions were no longer of particular interest unless they were fluorescent, as some might well have been metal hydroxides.

The results are tabulated in Table I and discussed below.

DISCUSSION

Our investigation of the effect of pH on the formation of insoluble metal TCP precipitates revealed the conditions under which they were obtained. Certain of these precipitates, however, were non-fluorescent (see Table I), particularly those formed in solutions of pH 2, and it was not known whether they were indeed tetracyanoplatinates. It is known that the crystalline alkali and alkaline earth metal TCP compounds are fluorescent in the solid state[9,10] Hence it seemed reasonable to expect any metal TCP precipitate to fluoresce. Many of the precipitates formed at pH 6–10 were fluorescent, as shown in Table I. Those that did not fluoresce and produced precipitates only in alkaline solution warranted further investigation, but were not of importance in this study of the TCP compounds. It was considered desirable to check that all the precipitates of interest did contain the metal tetracyanoplatinates.

TABLE I.—REACTION OF METAL IONS WITH TETRACYANOPLATINATE(II)

No precipitate	Non-fluorescent precipitate			Fluorescent precipitate	
	From aqueous solution	After addition of NH_3		From aqueous solution (pH)	After addition of NH_3 (pH)
Ba	Co(II)	Au	Mn(VII)	Ag (1–9)	Al (4–6)
Ca	Cr(III)	Be	Nd	Hg(II)(1–5)	Cd (6–9)
Cr(VI)	Cu(II)	Bi(V)	Ni$^+$		La (10–12)
Cs	Fe(II)	Ce(III)	Pr		Pb (7–9)
K	Fe(III)	Ce(IV)	Pt		Th (7–9)
Li	Hg(I)	Co(II)†	Sb(III)		Y (10)
Mo	Ni	Cr(III)*	Sb(V)		Zn (6–9)
Na	Sb(III)	Cu(II)†	Sc		Zr (4–7)
Pd	V	Er	Sn(II)		
Rb		Eu	Sn(IV)		
Re(IV)		Fe(II)*	Tb		
Sr		Fe(III)*	Ti(III)		
Tl(III)		Hf	Ti(IV)		
		Hg(I)‡	Tl(I)		
		Ho	U(IV)		
		In	U(VI)		
		Mg	V		
		Mn(II)			

* Precipitation, pH 1–12.
† Precipitation, pH 1–6.
‡ Precipitation, pH 1–5.

The amounts available were too small for full analysis so we relied on ultraviolet examination, after dissolution of the samples in suitable media, for the peaks at 256 and 280 nm, attributable to the $[Pt(CN)_4]^{2-}$ ion.[11] In all cases the presence of the TCP ion in the precipitates was confirmed.

From the results and consideration of the conditions of precipitation, we believe that those compounds precipitated in acid solution are simple TCP compounds, *e.g.*, $NiPt(CN)_4$, whereas those obtained from an alkaline solution are probably basic salts, *e.g.*, $Pb(OH)_2 \cdot xPbPt(CN)_4$.

The silver, mercury and lead precipitates were found to have certain differences as follows:

Silver TCP. A white precipitate was obtained over the pH range 1–9, but none at pH 9–12, presumably because of ammine formation. The product had a brilliant bluish-green fluorescence which became less intense on standing, and finally disappeared. Stokes[7] found that only a weakly fluorescent precipitate was obtained.

Three factors were found to affect the decay time of the fluorescence: the decay time was shortened if the silver concentration was decreased, the excess of sodium TCP increased, or the degree of agitation increased.

When 0·5 ml of silver nitrate solution was treated with one drop of 1% sodium TCP reagent, the times needed for disappearance of the fluorescence were 2700, 600 and 15 sec for 1000, 100 and 10 ppm of silver respectively. The pH of the solutions did not seem to affect these times. The time factor must therefore be taken into account when applying the TCP test for detection of silver. The decay of the fluorescence, which occurs only with silver TCP, may be caused by photodecomposition, especially in ultraviolet light. Stoke's observation of weak fluorescence could have been due to delay in examination.

Mercury(I) TCP. At the mercury(I) concentration used a dark blue non-fluorescent precipitate was obtained over the pH range 1–5. At higher pH values elemental mercury was deposited in the reaction mixture.

When mercury(I) was examined at different dilution levels extremely anomalous results were obtained. At concentrations from 1 part in 10 down to 1 part of Hg(I) in 100, sodium TCP reagent gave a dark blue-non-fluorescent precipitate. From 1 part in 100 down to 1 part of Hg(I) in 200, a pale blue non-fluorescent precipitate was obtained. From 1 part in 200 down to 1 part in 10000 of Hg(I), a yellow precipitate was obtained which gave a blue fluorescence on standing for about 2 min.

With a concentrated solution of mercury(I) acetate dissolved in dilute sulphuric acid, sodium TCP gave a bright yellow precipitate having a blue fluorescence.

Quadrat[2] reported an analysis of the blue mercury(I) precipitate he had obtained and indicated that it may have contained nitrate ion. This fact was confirmed by us during an infrared study of these different precipitates. The dark blue precipitate gave the characteristic absorption lines of the nitrate ion on the spectrum. Mercury(I) therefore appears to yield under certain conditions a complex TCP nitrate which constitutes a positive interference in the test for the Hg(I) ion.

The test can be applied to detect Hg(I) at pH 1–5 provided the concentration of the metal does not exceed 1000 ppm. At this concentration, nitrate does not interfere with the performance of the test, which relies on the production of the yellow form of precipitate having a blue fluorescence.

The mercury(II) ion, as nitrate, does not yield anomalous precipitates at any concentration.

Lead TCP. Over the pH range 7–9 a white precipitate with a bluish-green fluorescence was obtained. At pH 1–4 there was no precipitation. With excess of ammonia a white non-fluorescent precipitate was obtained. It was found that lead also can form TCP nitrate complexes.

Three distinct varieties of lead TCP were produced: a non-fluorescent pink variety, an orange variety which had a yellow fluorescence, and white variety with a bluish-green fluorescence. The pink and orange forms showed the characteristic absorption lines of the nitrate when subjected to infrared analysis. The pink and orange complexes only occurred when the lead nitrate concentration was extremely high. Concentrations of up to 5% as lead nitrate gave a white variety with the bluish-green fluorescence.

Determination of the limits of identification

Solutions of the metal nitrates were prepared, containing 1000 ppm of the metal ion. A measured volume of the metal solution (0·5 ml) was taken in a micro test-tube, a drop of 1% sodium TCP reagent was added, and the pH of the mixture adjusted as indicated in Table II. The precipitate was examined *in situ*, under ultraviolet light. The metal ion solution was then diluted stepwise and treated as above until the dilution was so high that fluorescence under ultraviolet lamp was no longer visible. The concentration at which fluorescence was just visible on the precipitate was noted as the limit of detection for the metal ion.

TABLE II.—LIMITS OF DETECTION

Metal ion	pH for Precipitation	Colour of precipitate	Colour of fluorescence	Limit of detection *ppm*
Y(III)	10	White	Bluish-green	100
Zr(IV)	4–7	White	Green	20
Cr(III)	1–12	Blue	None	—
Fe(II)	1–12	White	None	—
Fe(III)	1–12	Brown	None	—
Co(II)	1–6	Pink	None	—
Ni(II)	1–6	Pale-green	None	—
Cu(II)	1–6	Pale-blue	None	—
Ag(I)	1–9	White	Bluish-green	10
Zn(II)	6–9	White	Green	50
Cd(II)	6–9	White	Green	200
Hg(I)	1–5	Blue*	None	—
		Yellow†	Blue	100
Hg(II)	1–5	White	Blue	5
Al(III)	4–6	White	Green	200
Pb(II)	7–9	White	Bluish-green	100
La(III)	10–12	White	Green	10
Th(IV)	7–9	White	Green	20

* Above 1000 ppm [Hg(II)].
† Below 1000 ppm [Hg(II)].

Of the metal ions forming insoluble TCP compounds at pH 2, only silver, mercury(I) and mercury(II) yielded fluorescent precipitates. This difference provided a possible way of detecting these metal ions in the presence of the others, and in the presence of those metals which form non-fluorescent TCP compounds. However, those metals forming non-fluorescent precipitates are of some importance because they constitute a possible cause of interference by masking the fluorescent TCP to be detected.

The detection of the silver ion was explored first, because the methods for the chemical detection of silver in silver groups (Group I) of the classical qualitative analysis scheme and in metallurgical and geological specimens are laborious and require separation of silver from the other metals. A simple direct test would offer some advantage.

In application of the TCP test for silver in the silver group, lead does not interfere, because it does not give a TCP precipitate at pH 2, but mercury(I) and mercury(II) both yield fluorescent precipitates at pH 2 and do interfere. Metal ions yielding non-fluorescent TCP precipitates at pH 2 may also interfere.

Tests on solutions containing 10 ppm of silver showed that observation of the fluorescence of the silver compound became impossible in the presence of 2 ppm of mercury(I), 200 ppm of chromium(III), 200 ppm of iron(II), 1 ppm of iron(III), 800 ppm of cobalt(II), 200 ppm of nickel(II) or 40 ppm of copper(II).

Further tests with various silver concentrations showed there was a linear relationship between silver ion concentration and the maximum tolerable interfering metal ion concentration.

Attempts to prevent the interference of other metal ions by addition of conventional masking agents such as EDTA, DCTA and other complexing substances were unsuccessful. These masking agents require buffering of the solution, and, the usual buffer solutions contain anions which themselves give precipitates with many metal ions. The silver ion was also complexed. It was found, however, that only the silver ion gave a fluorescent precipitate in ammonium acetate solution (used to produce a solution buffered at pH 7). The ammonium acetate acted as a complexing agent as well as a buffer.

The blue copper TCP compound dissolved in the ammonium acetate buffer to yield a deep blue solution, indicating that complexing had occurred, although free ammonia could not have been present to form the copper ammine complex.

Investigation showed that in order to detect 10 ppm of silver a final concentration of 10% of ammonium acetate in the precipitation solution was the maximum permissible. The more concentrated the ammonium acetate the more masking effect it would have, but later work on the gravimetric determination of silver as its TCP showed that extremely high concentrations of ammonium acetate dissolved some of the silver TCP precipitate.

The addition of ammonium acetate (1000-fold w/w ratio to silver) was found to raise the interference levels of mercury(I) to 10 ppm, iron(III) to 10 ppm and copper(II) to 250 ppm. The other interfering metal ions were unaffected, and the interference levels were again in linear relationship with the silver concentration, as in the absence of masking agent. As much as 1000 ppm of mercury(II) was masked with ammonium acetate.

Metals yielding precipitates only at pH values well above 2 did not interfere, whether the precipitation was fluorescent or not.

SOME ANALYTICAL APPLICATIONS OF SODIUM TCP REAGENT

The investigation has yielded a direct selective test for silver with many applications. Some of these are given below together with methods for other metal ions.

Reagents

Analytical-grade reagents and demineralized water were used throughout.

Ammonia solution, 0·1*M*. Prepared by dilution of concentrated ammonia solution.

Nitric acid, 0·1*M*.

Ammonium acetate solution, 10% w/v.

Sodium tetracyanoplatinate(II) solution, 1% w/v.

Silver in the presence of all metal ions

Place a drop of test solution* containing not less that 10 ppm of silver in a micro test-tube.† Add a drop each of the ammonium acetate and sodium TCP reagent. Flick the tube to mix the contents and place it immediately under an ultraviolet lamp (preferably enclosed in a box with its base and inside walls blackened). A white precipitate, having a bluish-green fluorescence and fading within minutes, indicates the presence of silver.

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* Of the nitrates. If halides are present they must be removed by heating with sulphuric acid. Silver halides (except the fluoride) do not react with TCP.

† The preferred vessel. The depressions in a spot-tile are not deep enough for the fluorescence to be seen.

Silver in galena

Heat 0·1 g of powdered sample with conc. sulphuric acid until fumes of sulphur trioxide are evolved, and repeat this process to remove any chloride present in the ore. Heat the residue to red heat, cool it, add a few drops of conc. nitric acid, warm, cool, centrifuge, separate the supernatant liquid, evaporate it to dryness, and take up the residue in 0·2 ml of 2·5*M* nitric acid. Treat one drop of the solution with 1 drop each of the ammonium acetate and sodium TCP reagents.

An ore analysed by emission spectroscopy and found to contain the elements Pb, As, Sb, Al, sI, Ca, Fe, Cu, Sn, Ni and Ag, was tested and a faintly green fluorescent precipitate was obtained.

Lead in the presence of mercury(II)

Take a drop of test solution containing about 100 ppm of lead in a micro test-tube, adjust the pH to 9 with 0·1*M* ammonia solution and add a drop of TCP reagent. A white precipitate having a bluish-green fluorescence indicates the presence of lead. Lead is distinguishable from silver by the fact that the fluorescence of the silver TCP fades within minutes, whereas that of lead TCP is quite stable. Up to 1000 ppm of mercury(II) can be tolerated in the test solution.

Lead in the presence of silver and mercury(II)

To a drop of test solution containing about 100 ppm of lead add a drop of 5% sodium chloride and warm to coagulate the silver chloride. Cool the mixture, adjust the pH to 9 with solution of ammonia and add a drop of sodium TCP reagent. A bluish-green fluorescent precipitate indicates the presence of lead. Up to 1000 ppm of silver and mercury(II) can be tolerated in the test solution.

Mercury(II) in the presence of lead

Adjust a drop of test solution [containing not less than 5 ppm of mercury(II)] to pH 2, in the micro-tube. Add a drop of sodium TCP reagent. A blue fluorescent precipitate indicates the presence of mercury(II).

Zirconium in the presence of hafnium

Take a drop of the test solution, containing not less than 20 ppm of zirconium, preferably as the nitrate, in the tube and adjust the pH to 6. Add a drop of the sodium TCP reagent. A green fluorescent precipitate indicates the presence of zirconium. Up to 100 ppm of hafnium can be tolerated in the solution.

Thorium in the presence of cerium

Adjust a drop of the test solution, containing not less than 20 ppm of thorium, to pH 9 and add a drop of the TCP reagent. A green fluorescent precipitate indicates the presence of thorium.

CONCLUSIONS

The tetracyanoplatinate(II) ion in the form of its sodium salt has proved a useful and versatile reagent for the detection of silver and some other metal ions, and for the determination of silver. Its application in the detection of zirconium in the presence of hafnium is of some interest because of the lack of suitable direct chemical methods for detecting zirconium. We have reported only on the preliminary work in this study of the zirconium–hafnium system, which is being continued to establish methods for the analysis of zirconium-containing materials. Systems involving other metal ions which yield fluorescent precipitates are also being examined.

The original aim of the investigation to produce a fluorescent titrimetric reagent based on a square planar complex ion of platinum is still being considered. It is felt that there may exist a complex of this metal with π-acceptor ligands which does exhibit strong fluorescence in solution. The possibility of this aspect is being explored.

The possibility of determination of metal ions by means of fluorescence of their TCP compounds has not been overlooked. It is considered that analysis by means of a modified spectrofluorophotometric technique may prove more fruitful than either gravimetric or titrimetric methods.

Zusammenfassung—Das Tetracyanoplatination (TCP) bildet unlösliche fluoreszierende Verbindungen mit vielen Metallionen. Diese Eigenschaft wurde bisher analytisch noch nicht ausgenützt. Das lösliche Natrium-TCP-Salz wurde als Reagens zum Metallionen-Nachweis verwendet. Zum Nachweis geeignete fluoreszierende Nie-, derschläge wurden mit Y(III), Zr(IV), Ag(I), Zn(II), Cd(II), Hg(I)-Hg(II), Al(III), Pb(II), La(III) und Th(IV) erhalten. Die Nachweisgrenzen lagen bei 5–200 ppm. Mit Ammoniumacetat als Maskierungsmittel wurde ein selektiver Nachweis von 10 ppm Silber in Gegenwart anderer Metallionen erzielt. 20 ppm Zirkonium können in Gegenwart von Hafnium nachgewiesen werden; Hafnium gibt eine nicht fluorreszierende Fällung.

Résumé—L'ion tétracyanoplatinate(II) (TCP) forme des composés fluorescents insolubles avec de nombreaux ions métalliques. Cette propriété n'a pas été exploitée jusqu'ici à des fins analytiques. Le sel de sodium soluble du TCP a été appliqué comme réactif pour la détection d'ions métalliques. On a obtenu des précipités fluorescents utiles pour la détection d'ions métalliques avec Y(III), Zr(IV), Ag(I), Zn(II), Cd(II), Hg(I), Hg(II), Al(III), Pb(II), La(III) et Th(IV). Les limites de détection se sont situées entre 5 et 200 ppm. Avec l'acétate d'ammonium comme agent de dissimulation on a réalisé la détection sélective de 10 ppm d'argent en la présence des autres ions métalliques. Des quantités aussi faibles que 20 ppm de zirconium peuvent être détectées en la présence de hafnium qui donne un précipité non fluorescent.

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L'AUTOMATISATION EN ANALYSE PAR ACTIVATION NEUTRONIQUE ET SES APPLICATIONS A LA PRODUCTION INDUSTRIELLE

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Résumé—On tente d'expliquer pour quelles raisons l'analyse par activation n'a pratiquement pas encore réussi à sortir du domaine du laboratoire. On donne les conditions pour qu'une méthode analytique puisse être appliquée en cours de production industrielle et on étudie comment l'analyse par activation pourrait s'adapter à ces conditions. On présente enfin un cas de réussite d'une telle adaptation: l'analyse automatique de l'oxygène dans les aciers.

LA DÉCOUVERTE de ce procédé d'analyse élémentaire date de plus de trente ans. On connaît bien ses divers avantages: grande sensibilité, bonne précision, utilisation d'étalons primaires, bonne représentativité (gros échantillons, analyse dans la masse), conservation souvent possible de l'échantillon.[1,2] Et pourtant la radio-activation n'est encore pratiquement utilisée que par les laboratoires très spécialisés de l'energie atomique, des universités ou de quelques rares industries.

Cette diffusion, qui semble limitée à la recherche, tient principalement à deux caractères propres à l'analyse par activation.

(*a*) Il faut d'abord irradier l'échantillon à analyser au moyen de neutrons dont la principale source est constituée par la réaction de fission. C'est pourquoi l'analyse par activation s'est primitivement développée à proximité des centres nucléaires équipés de réacteurs.

(*b*) Le résultat du comptage de la radio-activité induite dans l'échantillon par l'irradiation se traduit le plus souvent par des histogrammes donnant l'intensité du rayonnement gamma en fonction de son énergie. Or, ces spectres sont en général très complexes; leur dépouillement est long et nécessite un personnel très qualifié.

Si les qualités de précision et de représentativité sont particulièrement appréciables pour les industriels, il n'en demeure pas moins que l'activation ne pourra s'imposer comme méthode d'analyse en cours de production que si elle répond à trois autres impératifs dont l'importance est primordiale: un temps de réponse assez bref, un grand débit de dosages et un coût rendant son utilisation rentable. Ceci a été longtemps impossible, du fait de la dépendance vis-à-vis des réacteurs et du dépouillement manuel des résultats; le développement récent des générateurs de neutrons et des petites calculatrices a changé les données du problème.

C'est ce qui explique que, en dehors des recherches sur le dosage des traces ultimes, il existe maintenant une nouvelle tendance très dynamique de l'analyse par activation dont le but est de rendre cette méthode applicable dans l'industrie.

ADAPTATION DE L'ANALYSE PAR ACTIVATION A L'INDUSTRIE

Développement des générateurs de neutrons

Le premier point était de s'affranchir des réacteurs. Cela a été rendu possible par le développement des petits accélérateurs de particules peu coûteux qui, équipés de cibles tritiées, permettent d'obtenir des débits de l'ordre de 10^{11} à 10^{12} neutrons par seconde.[3] Il s'agit de neutrons de 14 MeV et des études[4,5] ont montré qu'on pouvait ainsi, avec ou sans thermalisation, doser plusieurs dizaines d'éléments avec une sensibilité qui atteint souvent la partie par million.

De plus, de nombreux dispositifs ont été imaginés[6,7] pour obtenir des irradiations uniformes malgré la grande hétérogénéité des flux produits.[8] Il en résulte une reproductibilité proche de la limite théorique et un écart-type relatif individuel inférieur à 2% est courant.

Automatisation du dépouillement

Le second point était de rendre automatique le dépouillement des comptages. L'utilisation d'une petite calculatrice électronique dans ce but n'est pas nouvelle.[9] Mais il est, par contre, très rare de voir cette calculatrice montée en ligne, directement à la sortie de l'ensemble de spectrométrie.

En fait, le problème se pose différemment suivant la complexité du spectre gamma obtenu.[2]

(*a*) Si l'irradiation de l'échantillon ne donne naissance qu'à un seul radio-isotope ou bien si le radio-isotope choisi pour le dosage émet un rayonnement plus énergétique que ceux émis par les autres, il suffit d'utiliser un sélecteur à un seul canal que l'on centre sur le photopic gamma à mesurer. Le résultat du comptage se lit alors directement sur une échelle après une simple soustraction du bruit de fond.

(*b*) Si, par contre, le radio-isotope choisi pour le dosage ne produit pas le photopic le plus énergétique du spectre ou bien si on veut doser simultanément plusieurs éléments, on a le choix entre deux solutions.

1. On peut faire autant de comptages avec un sélecteur monocanal qu'il y a d'éléments à doser, en laissant l'échantillon refroidir entre chaque comptage de façon à faire disparaître les activités gênantes ou bien, au contraire, à obtenir certaines activités par différence. Le temps de réponse est alors relativement long mais il est possible d'augmenter le débit d'analyses par l'imbrication des séquences successives et par leur commande automatique au moyen d'un programmateur.

2 On peut utiliser un sélecteur multicanal qui permet d'enregistrer l'ensemble du spectre gamma. Ces informations sont ensuite traitées par une calculatrice qui, au moyen d'un programme appliquant la méthode des moindres carrés,[10,11] reconstitue le spectre de l'échantillon à partir des spectres de ses éléments constitutifs. Les quantités de ces derniers se déduisent alors des coefficients de pondération.

Dans tous les cas, il faut évidemment rapporter les activités mesurées à un poids d'échantillon donné et à un flux de neutrons bien déterminé.[12]

Les petites calculatrices électroniques permettent d'envisager maintenant une automatisation complète de tous ces calculs, d'où une grande rapidité d'analyse accompagnée d'une économie de personnel.

CAS DU DOSAGE DE L'OXYGENE DANS LES ACIERS

Le dosage de l'oxygène est très important dans de nombreuses industries, surtout en métallurgie. Plusieurs procédés tels que la fusion réductrice sous vide ou sous gaz inerte peuvent fournir rapidement des résultats précis mais les masses ainsi analysées sont très faibles par rapport à la méthode par activation; de plus, lorsqu'un grand nombre de dosages doit être effectué, l'activation ajoute l'avantage d'être économique grâce à la possibilité qu'elle offre de rendre l'analyse entièrement automatique.

Principe

On utilise une réaction qui ne se produit d'ailleurs qu'avec les neutrons très rapides donnés par les petits accélérateurs:

$$^{16}_{8}\mathrm{O} + \mathrm{n}(14\ \mathrm{MeV}) \rightarrow {}^{16}_{7}\mathrm{N} + \mathrm{p}$$

L'azote-16 ainsi formé décroît avec une période de 7,4 s, ce qui permet une mesure rapide, et il émet principalement des rayons gamma de 6,1 MeV. Or, ce radio-isotope est pratiquement le seul à émettre un rayonnement aussi énergétique. Il est donc facile d'automatiser le comptage en utilisant un sélecteur monocanal dont la fenêtre est réglée entre 4,5 et 6,5 MeV.[13]

Appareillage

L'équipement décrit ici a été mis au point par le Professeur Hoste à l'Université de Gand;[14,15] il est à présent commercialisé par la S.A.M.E.S. à Grenoble. Il comprend trois parties.[16]

Un générateur de neutrons du type D (150 kV, 1,5 mA) peut fournir, avec les cibles tritiées actuelles, un débit constant de neutrons de $2\cdot10^{10}$ n/s pendant 10 heures environ. Une irradiation de 5 s étant suffisante, il est possible de faire 5000 dosages par cible, ce qui est donc très économique. Les irradiations sont commandées par le mouvement d'un écran escamotable en tantale. Ce générateur est entièrement blindé, ce qui permet de l'installer dans une salle de 3 m^2 seulement. Il est cependant nécessaire de l'entourer de protections importantes contre les neutrons rapides,[17] de l'ordre de 1,20 à 1,50 m de béton.

Le système de transfert présente la particularité d'être constitué d'un double pneumatique de façon à pouvoir irradier ensemble, l'un derrière l'autre et pendant le même temps, l'échantillon et un étalon d'oxygène.[18,19] Ainsi, même s'il y a des variations du débit de neutrons pendant l'irradiation, l'échantillon et l'étalon reçoivent des flux qui restent toujours proportionnels. Ce double pneumatique relie la double station d'irradiation, placée contre la cible, aux deux stations départ-arrivée, l'une étant pour l'étalon et l'autre pour l'échantillon. Cette dernière est équipée d'une glissière pour récupérer l'échantillon ou en introduire un nouveau. Par contre, le même étalon peut servir indéfiniment. Un chronoscope à temps fixes de 5, 10 et 15 s permet de sélectionner le temps d'irradiation en fonction de la teneur à déterminer et de l'usure de la cible. Un second chronoscope à temps fixe de 30 s donne le temps de comptage. Deux paires de cellules photo-résistantes n'autorisent l'une le déclenchement de l'irradiation et l'autre le démarrage du comptage que si échantillon et étalon sont tous les deux en place. Le programmateur assure automatiquement le va-et-vient des échantillons et des étalons par la commande de vannes à air comprimé. Il permet un fonctionnement manuel "coup par coup" ou bien automatique, les échantillons stockés dans le magasin étant alors analysés l'un après l'autre, une, deux ou trois fois chacun (ce qui est possible puisque l'analyse est non-destructive).

La spectrométrie gamma est faite au moyen de deux chaînes identiques comprenant chacune un détecteur à iodure de sodium, un sélecteur monocanal et une échelle qui a la particularité d'être remise à zéro sur le complément du bruit de fond lors de l'introduction d'un nouvel échantillon; un muret en plomb sépare les deux détecteurs.

Echantillon et étalon sont ainsi comptés séparément mais simultanément. A la fin du comptage, les nombres d'impulsions obtenus avec chacune des deux chaînes sont envoyés dans une petite calculatrice. Celle-ci fait le rapport entre ces deux nombres puis affecte ce rapport d'un coefficient tenant compte de la quantité d'oxygène contenue dans l'étalon, du poids de l'échantillon et d'un facteur k dû aux différences entre les conditions opératoires pour l'échantillon et pour l'étalon. Ces différences proviennent des efficacités de comptage, qui peuvent être différentes pour les deux chaînes, et du fait que l'étalon est irradié derrière l'échantillon; il est facile de déterminer ce facteur k en utilisant un échantillon identique à l'étalon. Le résultat du dosage est imprimé directement en nombre de ppm d'oxygène.

Résultats

Une telle installation est en fonctionnement depuis décembre 1966 dans une aciérie de la Société Cockerill-Ougree-Providence, juste au pied des convertisseurs

L.D.[20] Les résultats obtenus en exploitation de routine peuvent être résumés par le tableau suivant.[21,22]

poids de l'échantillon	37 g
sensibilité limite	environ 5 ppm
précision au niveau de 50 ppm	10 %
au niveau de 500 ppm	4 %
au niveau de 1000 ppm	2 %
temps de réponse sans tenir compte du prélèvement	45 s
compte-tenu du prélèvement	3 mn
nombre de dosages actuellement effectués (3 par échantillon)	75000/an
prix de revient du dosage (amortissement sur 5 ans)	3,20 F

Cette installation répond donc parfaitement aux besoins des aciéristes qui doivent connaître très rapidement l'état d'oxydation des bains de métal à affiner.

DOSAGE AUTOMATIQUE DES AUTRES ELEMENTS

Le cas des autres éléments se présente de façon généralement beaucoup plus complexe. Cependant, comme on l'a signalé plus haut, le dosage automatique peut être possible par décroissance sélective ou par la méthode des moindres carrés, à condition bien entendu que l'élément à doser se transmute en un radio-isotope émettant un rayonnement gamma suffisamment intense.[5] On peut citer quelques exemples d'applications dont certaines sont en cours de réalisation:

dosage du silicium dans les aciers[23]
dosage de Fe, Si et Al dans les minerais de fer[24]
dosage de l'azote dans les engrais
dosage du phosphore dans les scories Thomas
dosage du hafnium dans les produits nucléaires
dosage du baryum dans les huiles.

Nous n'avons jusqu'à présent envisagé que les analyses séquentielles par prélèvement mais il est évident que la prochaine étape du développement industriel de l'analyse par activation sera constituée par le dosage en continu qui permettra de contrôler la production directement sur bande transporteuse ou sur tuyauterie.[25,26,27]

Summary—Reasons are given for the applications of activation analysis being generally confined to laboratory use. Conditions are given for application of analytical methods to industrial process control, in particular for automatic determination of oxygen in steels.

Zusammenfassung—Es werden Gründe dafür angegeben, daß die Anwendung der Aktivierungsanalyse im allgemeinen auf das Laboratorium beschränkt ist. Es werden die Bedingungen dafür angegeben, daß analytische Methoden auf die industrielle Prozeßüberwachung angewandt werden können, speziell auf die automatische Sauerstoffbestimmung in Stählen.

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A STUDY OF SOME MATRIX EFFECTS IN THE DETERMINATION OF BERYLLIUM BY ATOMIC-ABSORPTION SPECTROSCOPY IN THE NITROUS OXIDE–ACETYLENE FLAME

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Summary—A study has been made of a number of interferences observed in the trace determination of beryllium by atomic-absorption in the nitrous oxide–acetylene flame. The major negative interference caused by the presence of excess of aluminium salts may be overcome by the use of 8-hydroxyquinoline. Magnesium and silicon also depress the Be signal, but most other metals cause enhancement. In most instances the enhancements may be made uniform by the addition of potassium ions to the sample solution.

In continuation of previous work in this laboratory on the determination of trace elements in a matrix of alumina or in the presence of large amounts of aluminium salts,[1,2] it was decided to investigate the behaviour of beryllium atoms in the long-path (50 mm) nitrous oxide–acetylene flame when nebulized from solutions containing high concentrations of aluminium and various other elements.

Beryllium, being an element capable of forming highly refractory compounds, cannot be atomized efficiently in low-temperature flames, *e.g.*, a sensitivity of 300 ppm for 1% absorption has been quoted for 120-mm long air–acetylene flame,[3] but the introduction of the high-temperature, highly reducing, nitrous oxide–acetylene flame enabled Amos and Willis[4] to determine trace levels of beryllium by atomic-absorption spectroscopy (AAS). These authors reported a 10% depression of sensitivity caused by 500 ppm of aluminium, but observed no interference from 2·5*N* (*ca.* 12% w/v) sulphuric acid, though 1000 ppm of phosphorus (as phosphoric acid) caused a 2% enhancement. In the same paper it was shown that 1000 ppm of aluminium caused 10–20% enhancement in magnesium absorption. These and subsequent workers[5,6] have investigated the effects of potassium as an ionization suppressant on calcium, barium, *etc*, and several other significant interference effects in the nitrous oxide–acetylene flame have since been reported. In this work, the enhancement or depressant effects of many metal ions, acids and other compounds on the AAS determination of beryllium have been studied with special reference to aluminium interference.

EXPERIMENTAL

Apparatus

Techtron AA4 atomic-absorption spectrophotometer, with an A.S.L. beryllium hollow-cathode lamp and detector modulated at 285 Hz, fitted with an R213 photomultiplier and a 50-mm slot burner head for premixed nitrous oxide–acetylene. The wavelength was set at the most sensitive beryllium absorption line at 234·86 nm; the lamp current was 6 mA, slitwidth 100 nm (0·33-nm optical slit-width), nitrous oxide pressure 110 kN/m^2, acetylene pressure sufficient to give a red-zone of *ca.* 20 mm height; position of measurement in the flame usually 10–15 mm above the burner head.

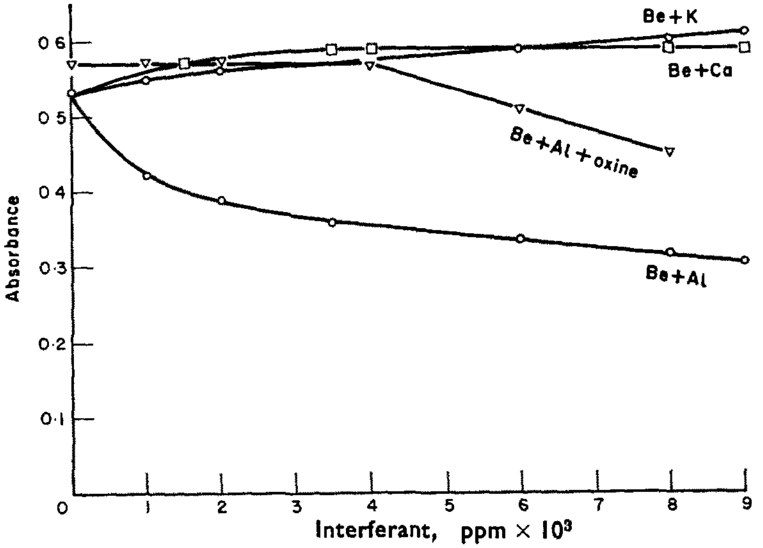

Fig. 1.—Effect of various interferants on 4 ppm of beryllium atomic absorption.

Reagents

Stock beryllium solution, 100 ppm. Prepared by dissolving 1·9656 g of analytical-grade $BeSO_4 \cdot 4H_2O$ in water and diluting to 1 litre. Test solutions were prepared by dilution from this stock solution.

Aluminium chloride solution, 50000 ppm. Prepared by dissolving 50 g of aluminium foil in excess of hydrochloric acid (1 + 1) and diluting to 1 litre.

8-*Hydroxyquinoline solution*, 10% w/v. Prepared by dissolving 100 g of 8-hydroxyquinoline in hydrochloric acid (1 + 1) and diluting to 1 litre with water.

Potassium solution, 100000 ppm. Prepared by dissolving 25·9 g of potassium nitrate in water and diluting to 100 ml.

All solutions used were prepared from analytical-grade reagents except where stated.

Experiments on solutions containing high concentrations of aluminium and other metals

The direct determination of trace amounts of beryllium in aluminium alloys or alumina by atomic absorption in the nitrous oxide–acetylene flame, after simple dissolution in hydrochloric acid, would be desirable, but previous work[4] suggested that considerable interference would be caused by as little as 500 ppm of aluminium. On continued addition of aluminium chloride to solutions containing 4 ppm of beryllium, a continuously increasing depression of signal was noticed and above about 5000 ppm of aluminium the depression became approximately linear with respect to aluminium concentration (see Fig. 1). At the 4000- and 9000-ppm aluminium levels depressions of 32% and 42·5% respectively were observed. It is clear that this is a very serious effect, the rapid variation of signal with aluminium concentration in the region 0–2500 ppm of the interferent obviously being the source of considerable error in the determination of traces of beryllium. It is well known that aluminium salts can cause major negative interferences in the atomic-absorption determination of many elements in the cooler air–propane and air–acetylene flames, owing to the formation of refractory alumina clotlets which are not readily dissociated, thereby entrapping the trace elements present.

In the nitrous oxide–acetylene flame, however, both enhancement and depression of sensitivity have been observed, *e.g.*, aluminium has been shown to enhance the AAS signal for magnesium,[4] titanium[6,7] and vanadium,[8] whereas there is a depression in the AAS signal for beryllium,[4] strontium[6] and cobalt.[3] It is clear, therefore, that several factors are involved (see Discussion), one of which may still be the formation of refractory clotlets which are not dissociated completely.

Previously it has been reported that the addition of 5% of oxine (8-hydroxyquinoline) to solutions containing magnesium and 200 ppm of aluminium could overcome their depressant effects in a low-temperature flame[9]. The reduction of interference is presumed to be caused by more efficient dissociation of the aluminium-containing clotlets in the presence of the organic compound. In this respect the atomization of beryllium in the flame would also be expected to be improved by the presence of oxine. A study of the effect of increasing oxine concentration in the AAS signal for 4 ppm of beryllium showed that up to 2% of oxine gave maximal enhancement of *ca.* 8%, but if the

TABLE I.—THE EFFECT OF HIGH CONCENTRATIONS OF VARIOUS METAL IONS ON THE ATOMIC-ABSORPTION SENSITIVITY OF BERYLLIUM*

Ion	Compound added	Concentration *ppm*	Effect on Be signal %
K	KNO_3	10000	+17·0
Pb	$Pb(NO_3)_2$		+17·0
Sn(II)	$SnCl_2$		+17·0
Mo(VI)	$(NH_4)_6Mo_7O_{24}$		+17·0
Sr	$Sr(NO_3)_2$		+15·1
Cd	$CdSO_4$		+15·1
Zr	$ZrCl_4$		+15·1
Hg(II)	$Hg(NO_3)_2$		+13·2
Co(II)	$CoCl_2$		+13·2
U(VI)	$UO_2(NO_3)_2$		+13·2
Ca	$Ca(NO_3)_2$		+11·3
Cu(II)	$CuSO_4$		+11·3
Th	$Th(NO_3)_4$		+9·4
V(V)	NH_4VO_3	4000	+9·4
Na	$NaNO_3$	10000	+7·5
Bi	$Bi(NO_3)_3$		+7·5
Fe(III)	$FeCl_3$		+7·5
Cr(III)	$CrCl_3$		+7·5
Se(IV)	H_2SeO_3		+6·6
Zn	$ZnSO_4$		+5·7
Mn(II)	$MnSO_4$		+5·7
Te(IV)	Te in HNO_3/HCl		+1·9
Nb(V)	Nb in HF	4000	+1·9
Ti(IV)	Ti in HF	10000	+1·0
Ni	$NiSO_4$		0·0
Mg	$Mg(NO_3)_2$		−3·8
Si	H_2SiF_6		−18·9
Al	$AlCl_3$		−43·4

* All solutious contained 4 ppm beryllium, which in pure aqueous solution gave an absorbance of 0·53.

concentration was increased above *ca.* 6% of oxine, the absorption fell off again, presumably because of increased viscosity and reduction of nebulizer efficiency. The effect of adding 2·5% of oxine to solutions containing up to 4000 ppm of aluminium and from 1 to 4 ppm of beryllium, was to overcome the depression completely and to obtain a linear calibration curve exactly similar to that of a pure aqueous beryllium solution containing 2·5% of oxine (see Fig. 1). It was necessary to acidify the solutions with hydrochloric acid in order to obtain complete dissolution of the oxine and to prevent precipitation of the $Al(C_9H_6ON)_3$ complex. Unfortunately the "masking" of aluminium by oxine falls off steadily if concentrations of the metal are increased to above 4000 ppm, and a corresponding increase in oxine concentration to, say, 5% could not offset this.

Although beryllium atoms have been reported to be completely un-ionized in the nitrous oxide–acetylene flame,[4] it was decided to test the effect of ionization suppressants and it was found that the presence of 9000 ppm of potassium and calcium produced enhancements of 15% and 11·3% respectively (Fig. 1). Subsequent investigations showed that many other metals, when added in large amounts, could cause significant enhancements of sensitivity for beryllium (see Table I).

From Table I it can be seen that the maximal enhancement of 17% was caused by the presence of 10000 ppm of potassium, lead, tin(II) or molybdenum (VI) whilst the other metal ions tested produced a steadily decreasing series of enhancements down to titanium(IV) and nickel, which exhibited little or no enhancement. Apart from magnesium which caused a depression of 3·8%, the only depressants encountered were silicon and aluminium.

It was found that linear calibration curves could be constructed for 0·5–4 ppm beryllium in the presence of excess of potassium, uranium, copper, *etc* and virtually no further enhancement of sensitivity was achieved by changing from 10000 to 20000 ppm of potassium. For all these minor enhancement interferences, it is clearly undesirable to have to construct a different calibration curve to account for the presence of each individual element, or group of elements, and it was discovered that if the metal ions of Sr, Cd, Zr(IV), Hg(II), Co(II), U(VI), Ca, Cu(II), Th, V(V), Na, Bi, Fe(III),

TABLE II.—THE EFFECT OF ORGANIC SOLVENTS ON THE ABSORPTION OF 4 ppm OF BERYLLIUM

Solvent added, 20% v/v	Interference, %
Methanol	+11·3
Ethanol	+13·2
Propan-2-ol	+20·8
Glycerol	−17·0
Acetone	+15·1
Acetic acid	+15·1

Cr(III), Se(IV), Zn, Mn(II), Te(IV), Nb(V), Ti(IV) and Ni were present in concentrations up to 4000 ppm the enhancement could be raised to the maximum produced by potassium, simply by making the solutions 10000 ppm in potassium by addition of 25·9% w/v potassium nitrate solution (equivalent to 100000 ppm of potassium). This procedure was also effective for masking up to 4000 ppm of magnesium. At concentrations greater than *ca.* 5000 ppm of the original interferent the addition of excess of potassium nitrate could not always be relied upon to bring the enhancement up to the required level, but for many of the elements producing enhancement as great or nearly as great as that by potassium [*e.g.*, U(VI), Mo(VI)], up to 10000 ppm of the original interferent plus 10000 ppm of potassium could be tolerated.

A 4000-ppm concentration of aluminium caused a 32% depression for 4 ppm of beryllium and this was reduced to a 21% depression by the addition of 10000 ppm of potassium; this may be considered as an enhancement effect on the absorption of the free beryllium atoms existing in the presence of aluminium, in which case it would represent a 17% enhancement—the same value produced by potassium for pure beryllium. A similar effect was predicted for silicon, but the precipitation of K_2SiF_6 prevented further investigation.

A study of the effect of position of measurement in the flame for a solution containing 4 ppm of beryllium, 4000 ppm of aluminium and 10000 ppm of potassium showed that optimal absorption occurred at a height of *ca.* 10 mm above the burner head, *i.e.*, the same as for pure solutions of beryllium.

Experiments on solutions containing acids, ammonium salts and organic compounds

Because some of the solutions previously described contained free hydrochloric acid, it was decided initially to test the effect of this acid on beryllium absorption, but no interference was noticed when solutions were made 1*M* with respect to hydrochloric acid. Subsequently 4-ppm beryllium solutions were prepared which contained orthophosphoric, sulphuric, hydrochloric and nitric acids at the 10000-ppm level with respect to Cl, S, N and P (*i.e.*, 3·16, 3·06, 1·03 and 4·50 w/v, respectively, of the pure acids).

Sulphuric acid caused a 5·7% enhancement, but the other acids showed no interference, nor did hydrofluoric acid at the 2 and 4% w/v levels. A systematic study of the enhancement casued by sulphuric acid revealed a steady increase in signal up to *ca.* 2·75% w/v sulphuric acid (7·5% enhancement) followed by a gradual decline until no effect at all was observed when the test solution contained *ca.* 9·2% w/v sulphuric acid. A similar reduction in the enhancement was noticed when solutions containing beryllium and aluminium were made more than *ca.* 6% w/v in oxine, and this could be caused by reduction of nebulizer efficiency in more viscous solutions. An attempt to verify the viscosity effect was made by making gradual additions of sucrose to solutions, the results being closely similar to those obtained with sulphuric acid, *i.e.*, a maximal enhancement of *ca.* 7% was observed at 2–3% w/v of sucrose, followed by a gradual decline. Ammonium chloride and ammonium nitrate, when added in the range 1–10% w/v, caused enhancements very similar to those obtained with potassium in the range 1000–10000 ppm and the ammonium radical may therefore, be grouped in Table I, with the metals causing optimal enhancement.

The effect of organic solvents can be seen in Table II; the results are predictable with the possible exception of acetic acid, where such a large enhancement was not expected. In each case the fuel flow-rate was adjusted to give the best flame conditions.

Finally the effect of a powerful surface active agent was investigated. The addition of 0·5% cetyltrimethylammonium bromide caused no interference.

DISCUSSION

Of the interference effects observed in AAS in the nitrous oxide–acetylene flame some may be explained by direct extension of the theories available to account for the interferences in lower temperature flames, *e.g.*, organic solvent enhancement, which is primarily due to increased efficiency of nebulization.

In the high-temperature flame, ionization assumes greater importance and in many cases the addition of an ionization suppressant is valuable. In other cases, the ability of this flame to dissociate and reduce refractory oxides may cause a complete reversal of an interference effect, *e.g.*, in the air–propane flame the presence of aluminium severely depresses absorption sensitivity for magnesium whereas the opposite effect is observed in the nitrous oxide–acetylene flame. The presence of aluminium and titanium has been shown to give a maximal enhancement of *ca.* 25 % in the AAS determination of vanadium[8,10] and similar results were obtained for molybdenum.[11] In these cases, it has been proposed that a competition mechanism has been operating by which aluminium and titanium atoms preferentially remove atomic oxygen from the flame plasma, allowing a higher concentration of the test element in its atomic form, this process being favoured by a large excess of the interferent. It has also been reported that a number of refractory elements, especially aluminium, have a major enhancement effect in the determination of titanium.[6,7] However, aluminium depresses the absorption of strontium[6] and experiments on the AAS of calcium in the nitrous oxide–acetylene flame (in connection with the present work) showed that the presence of excess of aluminium could almost completely eliminate the calcium absorption signal.

For beryllium, it has been shown that the major depression caused by aluminium could be overcome by the addition of oxine. This would tend to indicate that the formation of refractory particles in the base of the flame is still of major importance even in a high-temperature reducing flame, and if this is the case, it becomes difficult to explain the enhancements previously noted. That the formation of refractory clotlets is not a generally valid assumption to account for depression of sensitivities in this flame medium is further suggested by the observation that other elements potentially capable of forming such high melting point oxides (*e.g.*, Mo, Zr, U, Th, Nb) cause *enhancement* of beryllium absorption. Bearing this in mind, it was noted that the only three elements, of those investigated, to cause negative interference were magnesium, aluminium and silicon, of which magnesium could scarcely be considered as capable of forming refractory particles in the flame. Furthermore in the periodic table magnesium and silicon flank aluminium, being elements of atomic number 12, 14 and 13 respectively. It is well known that beryllium and aluminium present what is probably the best example of the "diagonal relationship", there being many chemical similarities; there are also certain chemical similarities between beryllium and silicon (*e.g.*, see F. A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry*, Interscience, New York, 1962, pp. 168–177). In addition the ability of aluminium to replace silicon in silicate lattices to form the important group of aluminosilicate minerals illustrates further the close relationship of these elements. It is pertinent here to note that the major source of beryllium is the mineral beryl, $3BeO \cdot Al_2O_3 \cdot 6SiO_2$, and considering these facts it is clear that a special case of refractory compound formation in the flame may well be responsible for the major depressant effects of aluminium and silicon, while the minor depression due to magnesium may also be the result of a chemical interaction causing reduction in atomic population. There are other examples of specific chemical interference in atomic absorption in the nitrous oxide–acetylene flame, *e.g.*, the enhancement caused by hydrofluoric acid and iron on titanium, zirconium, hafnium and tantalum[4,7] and the recently reported enhancement effect of nitrogen-containing compounds on the atomic absorption of zirconium, which has been utilized in the indirect determination of these substances.[12]

Before commenting further on the table of enhancement interferences, it is necessary to consider the possibility of ionization. From the very high first ionization potential of the beryllium atom (9·32 eV) it is evident that even in the nitrous oxide–acetylene flame the degree of ionization of beryllium will be very low and the magnitude of the effect will not be significant in this work.

The problem of explaining the majority of the enhancements is very complex. In work reported to date the effect of added sulphuric acid has been to cause enhancements for absorption of calcium, aluminium and zinc,[13] and titanium[6] but at the 5% v/v level sulphuric acid causes a 25% depression of the molybdenum signal.[11] Orthophosphoric acid has been shown to give enhancement of sensitivity for a number of elements; in the cases of calcium and barium the increases in signal caused by 10000 ppm of phosphorus (as phosphoric acid) were attributed to an improvement in dissociation rate.[5] Koirtyohann and Pickett[13] have recently reported 10% enhancements of calcium and barium atomic emissions from a nitrous oxide–acetylene slot flame upon making the samples 0·3*M* (*ca.* 2·9% w/v) with respect to phosphoric acid, also a 15% enhancement was observed for the AAS of 1 ppm of Aluminium. Similar results were obtained with sulphuric and perchloric acids (0·3–1*M*), ammonium orthophosphate and sodium chloride (1–2%) and a theory was developed involving the spatial distribution of the sample within the flame. According to this explanation, the particles, after they have dried in the base of the flame, will be heavier in the presence of an involatile salt or high-boiling acid and will therefore diffuse more slowly towards the edges of the flame, giving a higher concentration in the centre of the flame (*i.e.*, along the axis of the burner slot).

In the present work it was found that orthophosphoric acid (4·5% w/v) produced no enhancement of beryllium absorption and, when considered with the marked depression of molybdenum sensitivity by sulphuric acid, this theory does not appear to be generally satisfactory. Similarly, organic materials, including sucrose, were stated to produce no effect on the atomic emission of Ca, Sr, Ba, Li, Na, K, Al, and Ga or atomic absorption of Ca, Al and Zn, whereas it has been observed here that there are major interferences from organic compounds in the AAS of beryllium, sucrose behaving in a very similar fashion to sulphuric acid (over a similar % w/v range). Beryllium absorption is also enhanced by the presence of 1–2% of ammonium compounds and sodium chloride, but it is not thought valid to refer to sodium chloride as an involatile salt at the temperatures encountered in the nitrous oxide–acetylene flame. Further, a comparison of the interference effects on the absorption of beryllium produced by the same weight concentrations of different metal ions, leads inevitably to the conclusion that spatial distribution is only one of a number of important factors involved.

It is not easy to apply the "oxygen competition" theory developed by Sachdev, Robinson and West[8] to such a wide range of metal ion interferents. Moreover, the two elements, aluminium and titanium, which enhance sensitivity for vanadium and molybdenum do not have this effect on beryllium. The major depression by aluminium may be explained by compound formation, but this seems unlikely to be an important cause of interference between titanium and beryllium. The refractory elements which, in large excess, would be expected to cause significant reduction in atomic oxygen concentration, occur in various positions in the table of enhancements from Mo (maximal enhancement of 17 %) to Ti (minimal enhancement of 0·95 %), and it is difficult to consider these effects as being in any way separate from the similar effects of the other metals in the table.

Because no simple coherent theory can be invoked to explain all the observed effects, it is necessary to consider most of the metallic interferents individually; however, certain factors do appear to be common to a number of determinations, *e.g.*, the addition of hydrochloric or nitric acid usually produces no significant variation of signal, and the expected organic solvent effects are usually observed. In the determination of beryllium the gradual building up of the enhancement with increasing concentration of interferant material, followed by a steady decline, is probably the result of the enhancement effect being gradually overcome by reduction of nebulizer efficiency as the solutions become denser and more viscous.

For some of the interferences noted it is possible to postulate a specific chemical action which could improve atomization in the flame (*e.g.*, the formation of the $[Be(H_2O)_4]^{2+}$ ion from oxy- or hydroxy-species as sulphuric acid is added), but in most instances it is not easy to conceive of simple explanations for these "releasing" effects.

CONCLUSION

The enhancement effects observed cannot be accounted for by ionization suppression or ascribed to any other *single* phenomenon. In all cases both physical and chemical interactions occur which may be additive or subtractive. The theories of chemical releasing and complexation reactions, of oxygen competition and chemical change of the flame conditions, of spatial distribution in the flame and nebulization effects must all be considered and it is, therefore, extremely difficult, if not impossible, to attempt accurate prediction of an interference effect.

However, for the interference of aluminium and silicon in beryllium AAS, it has been suggested that a strong chemical action is the predominant cause, and in the case of aluminium, accurate analyses may be performed after addition of 8-hydroxyquinoline reagent.

For many metallic enhancements it has been shown that their interferences are not additive, with certain limitations, and accurate analyses may therefore be performed by making addition of excess of potassium nitrate in order to give maximal enhancement.

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Zusammenfassung—Es wurde eine Untersuchung einer Anzahl Interferenzen vorgenommen, die in der Spurenermittlung von Beryll bei atomischer Absorption in der Nitrooxyd-Azetylenflamme beobachtet wurden. Die grössere, negative Interferenz, die durch Vorhandensein von übermässigen Aluminiumsalzen verursacht wird, kann durch Verwendung von 8-Hydroxyquinoline vermieden werden. Magnesium und Silizium drücken auch das Be Signal herab, aber die meisten anderen Metalle verursachen Verstärkung. In den meisten Fällen kann die Verstärkung durch Zufügen von Kalium Ionen zu der Musterlösung gleichförmig gemacht werden.

Résumé—On a effectué une étude sur un certain nombre d'interférences observées dans la détermination de traces de béryllium par absorption atomique dans la flamme protoxyde d'azote–acétylène. L'interférence négative majeure causée par la présence d'excès de sels d'aluminium peut être surmontée par l'emploi de 8-hydroxyquinoléine. Le magnésium et le silicium abaissent aussi le signal de Be mais la plupart des autres métaux causent une exaltation. Dans la plupart des cas, les exaltations peuvent être rendues uniformes par l'addition d'ions potassium à la solution échantillon.

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DETERMINATION OF MICROGRAM AMOUNTS OF METALS BY CHRONOMETRIC ANALYSIS

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Summary—The reaction between peroxidisulphate and iodide, modified by the addition of thiosulphate to show the Landolt effect, has been used for the determination of copper and iron in the range 1–100 μg/ml, based on the catalytic effect of these ions. The procedure is rapid and simple, and the errors are less than 10%. The interference from iron in the determination of copper may be overcome by the addition of a masking reagent such as fluoride.

LANDOLT reactions were first used for catalytic microdeterminations by Erdey and Svehla[1–3] who used the slow reaction between hydrogen peroxide and iodide, accelerated by molybdate ions. Ascorbic acid was used to change the reaction to one showing the Landolt effect, since it reduces instantaneously the free iodine formed by oxidation by the peroxide. Free iodine is then only detectable in solution after all the ascorbic acid has been consumed. Variamine Blue was added as an indicator for free iodine.

Erdey and Svehla later suggested that the peroxidisulphate–iodide–ascorbic acid system might be used for the determination of some metal ions.[4]

The reaction between peroxidisulphate and iodide proceeds in two steps, as follows:[5]

$$S_2O_8^{2-} + I^- = S_2O_8I^{3-} \qquad (1)$$

$$S_2O_8I^{3-} + I^- = 2SO_4^{3-} + I_2 \qquad (2)$$

The second step is fast, but the first is slow and is accelerated in the presence of copper and iron ions, the former having the greater effect.

Sodium thiosulphate was used to change the reaction to one with the Landolt effect, as it reacts with the free iodine:

$$I_2 + 2S_2O_3^{2-} = 2I^- + S_4O_6^{2-}$$

Free iodine occurring after consumption of the thiosulphate was indicated by the appearance of the blue colour in the presence of starch.

EXPERIMENTAL

Reagent solutions

(1) *Oxidizing solution*, containing 7 g of potassium peroxidisulphate and 10 ml of 1*M* sulphuric acid in 500 ml.

(2)–(7) *Reducing solutions*: see Table I.

All reducing solutions contained 6·8 g of sodium acetate, 10 ml of 1*M* sulphuric acid and 5 g of starch, and were diluted to 500 ml with distilled water.

(8) *Copper(II) stock solution* contained 3·93 g of copper sulphate pentahydrate in 1 l. (copper concentration = 1 mg/ml).

(9) *Iron(II) stock solution* contained 1·404 g of ammonium iron(II) sulphate and 10 drops of concentrated sulphuric acid, in 1 l. (iron concentration = 0·2 mg/ml).

TABLE I.—REDUCING SOLUTIONS

No.	Purpose	Potassium iodide, *g*	Sodium thiosulphate, *g*	Copper sulphate, *g*
(2)	Investigation	1·65	0·13	—
(3)	Investigation with copper	1·65	0·63	0·0589
(4)	Determination of 1–10 μg/ml of copper	1·65	0·4	—
(5)	Determination of 10–100 μg/ml of copper	1·3	1·2	—
(6)	Determination of 1–10 μg/ml of iron	1·3	0·08	—
(7)	Determination of 10–1000 μg/ml of iron	1·65	0·2	—

Procedure

Test-tubes were thoroughly cleaned with chromic acid, washed with distilled water, and dried before use. Known, and equal, quantities of one of the solutions (2)–(7) were transferred to a number of test-tubes to each of which were added equal quantities of water and of solutions containing different concentrations of catalyst. Into each test-tube was put a glass rod with a flattened end (for stirring) and the test-tubes were put in a water-bath controlled at 25 ± 0·5°. The oxidizing solution (1) was also put into the water-bath, and all solutions were left for 2 hr to reach constant temperature. A known volume of solution (1) was added to the first test-tube, the stop-watch was started, the solution stirred, and the time taken for the blue colour to appear was recorded. This procedure was repeated for each test-tube.

The uncatalysed reaction between peroxidisulphate and iodide is second-order. This was checked experimentally both for the uncatalysed and the catalysed reaction. Equal portions (2 ml) of reducing solution (2) were transferred to a series of test-tubes containing increasing amounts of water. The procedure as described was then followed, with the same volume of oxidizing solution (1) in each test-tube. In a second series of experiments, reducing solution (3) was used, which contained 75 μg of copper per ml. For each series, a plot of recorded reaction time against total volume gave a straight line passing through the origin, verifying that the reaction was in each case second-order. From the known concentrations of the reacting species, the rate constants were calculated, and found to be, at 25°, $2{\cdot}32 \times 10^{-1}$ $\text{l.mole}^{-1}.\text{min}^{-1}$ uncatalysed, and $1{\cdot}79 \times 10^{3}$ $\text{l.mole}^{-1}.\text{min}^{-1}$ when catalysed by copper(II).

Procedure for the determination of copper or iron

Determination of copper in the range 1–10 *μg/ml.* Into each of 36 test-tubes transfer 5 ml of reducing solution (4) then add 5 ml of distilled water to each of the first three, 5 ml of solution containing 1 μg of copper per ml to each of the next three, 5 ml of 2 μg/ml copper solution to the next three, and so on up to 10 μg/ml of copper. Then to each of the last three add 5 ml of the unknown solution, and follow the described procedure for each test-tube, calculating the average of the three time measurements obtained for each concentration. The reciprocal time values are proportional to the concentration of catalyst.

We have found that results obtained from plots of reciprocal time are not as reliable as those obtained from plots of t_0/t values (where t_0 is the time measured in the absence of catalyst), and hence the latter are to be preferred.

Other concentrations, and determination of iron. For the determination of copper in the range 10–100 μg/ml and of iron in the ranges 1–10 and 10–100 μg/ml, the reducing solutions (5)–(7) are used, respectively, and the concentrations of the standard catalyst solutions are chosen suitably. The data for the calibration graphs as obtained are reproduced in Table II. The error of the determinations was within the limits ±10% for both ions.

TABLE II.—DATA FOR CALIBRATION CURVES

Element	Range of concentration *μg/ml*	Graph of t_0/t *vs.* concentration		Std. devn. of t_0/t
		Intercept	Slope	
Copper	1–10	1·206	0·524	0·46
	10–100	1·208	0·696	1·64
Iron	1–10	0·962	0·157	0·06
	10–100	0·967	0·079	0·08

The effect of other ions on the reaction was also investigated. Since the reproducibility of the measurements is about 10%, the interference due to a given ion may be neglected at a given catalyst concentration if the t_0/t value is within 10% of the value in the absence of that ion. Expressed in these terms, it was found that lithium, sodium, potassium, calcium, zinc and molybdate do not interfere at concentrations below 0·1M, strontium, barium, silver, chromium(III), manganese(II), cobalt, nickel and vanadate at concentrations below $10^{-2}M$, aluminium and lead in concentrations below $10^{-3}M$, and arsenic, antimony, cerium and mercury in concentrations below $10^{-4}M$. Of the last-mentioned, As(III), Sb(III) and Hg(I) give rise to negative errors because they are themselves oxidized.

The possibility of masking iron in solution, and hence of determining copper in its presence, was investigated, using fluoride as masking reagent.

Three series of solutions were prepared, containing, in the first, increasing amounts of copper(II), and sodium fluoride (5 g/l); in the second, the same concentrations of copper and fluoride and also iron(II) ($10^{-3}M$); and in the third series, copper, fluoride and iron(III) (also $10^{-3}M$). The concentration of iron was therefore from 5 to 50 times that of the copper. The calibration graphs, prepared as described under *Procedure* were the same within experimental error, supporting the use of fluoride as masking reagent, and making possible the determination of copper in the presence of iron.

The chronometric method described has been successfully applied to the determination of traces of copper present as an activator in zinc sulphide luminescent powder.

Zusammenfassung—Bei der Reaktion zwischen Peroxydisulfat und Jodid wurde Thiosulfat zugegeben, um den Landolteffekt zu erzielen. Diese Reaktion wurde zur Bestimmung von Kupfer und Eisen im Bereich 1–100 μg/ml auf Grund ihrer katalytischen Wirkung verwendet. Das Verfahren geht schnell und einfach und die Fehler sind kleiner als 10%. Die Störung durch Eisen bei der Bestimmung von Kupfer kann durch Zugabe eines Maskierungsmittels wie Fluorid beseitigt werden.

Résumé—On a utilisé la réaction entre le peroxydisulfate et l'iodure, modifiée par l'addition d'hyposulfite pour montrer l'effet Landolt, pour la détermination du cuivre et du fer dans le domaine 1–100 μg/ml, en se basant sur l'influence catalytique de ces ions. La technique est rapide et simple, et les erreurs sont inférieures à 10%. L'interférence du fer dans le dosage du cuivre peut être éliminée par l'addition d'un agent de dissimulation comme le fluorure.

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VERWENDUNG MÄßIG DISSOZIIERTER KOMPLEXE BEI SPEKTRALPHOTOMETRISCHEN BESTIMMUNGEN—II.

REAKTIONEN VON ARSENAZO III MIT URANYL UND THORIUM(IV)

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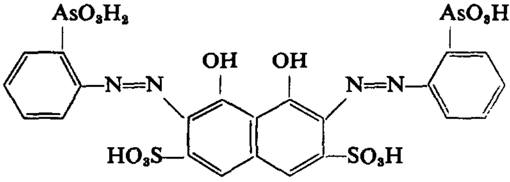
Zusammenfassung—Bei Reaktion von Uranylionen mit Arsenazo III entstehen in sauren Lösungen zwei dissoziierte Komplexe des Typus ML. Ihr Konzentrationsverhältnis in der Lösung ist von der Acidität abhängig. Die Werte der differentiellen molaren Extinktionskoeffizienten dieser Komplexe beim Absorptionsmaximum 565 nm betragen $5{,}3 \cdot 10^3$ bzw. $8{,}8 \cdot 10^3$ l.mole^{-1}.mm^{-1}. Auf Grund der festgelegten Beständigkeitskonstanten wurden die bisherigen empirischen Kenntnisse über die Empfindlichkeit der Reaktion erklärt. Thorium(IV) bildet mit Arsenazo III in sauren Lösungen M_2L-, ML_2- und zwei ML-Komplexe. Der in analytischer Praxis verwendete mäßig dissoziierte Komplex ML_2 entsteht vorwiegend in stark sauren Lösungen bei einem hohen Reagensüberschuß. Der differentielle molare Extinktionskoeffizient des Komplexes ML_2 im Absorptionsmaximum 658 nm beträgt $12{,}8 \cdot 10^3$ l.mole^{-1}.mm^{-1}.

Arsenazo III (2,7-Bis[azo-2-arsonphenyl]chromotropsäure) ist das meist benutzte Reagens aus der Reihe der symmetrischen Bisazoderivaten der Chromotropsäure. Es wurde erstmals im Jahre 1959 für die Bestimmung einer Reihe von Elementen durch Savvin[1] vorgeschlagen. Eine breite Anwendung fand das Reagens insbesondere bei Uran-[2–9] und Thoriumbestimmungen.[10–19] Weitere Verwendungsmöglichkeiten wurden in der Monographie[20] von Savvin angegeben.



Arsenazo III

Trotz der großen Bedeutung von Arsenazo III in der analytischen Chemie wurden bisher die grundlegenden Fragen der Komplexbildung nicht befriedigend erklärt. In der Mehrzahl der Veröffentlichungen[1–9,20] wurde bei der Reaktionen von Uranylionen mit Arsenazo III die Bildung eines ML-Komplexes nachgewiesen. Nach Buděšínský[21] entsteht ein Komplex des Typus M_2L_2. Auch die Möglichkeit der Bildung eines ML_2-Komplexes ist erwähnt[22] worden. Für die Extinktionskoeffizienten bei Absorptionsmaximum wurden folgende Werte angegeben: $5{,}3 \cdot 10^3$ l.mole^{-1}.mm^{-1} bei pH 2,[23] $6{,}0 \cdot 10^3$ in $6M$ Salpetersäure[6] und $7{,}5 \cdot 10^3$ in $5{,}6M$ Perchlorsäure.[9] Auch bei der Anwendung des Reagens bei Thoriumbestimmungen[10–19] wurden die Fragen der

Komplexbildung bisher nicht eindeutig gelöst. Arsenazo III–Thorium(IV)-Komplexe folgender Typen wurden beschrieben: ML, ML_2, ML_3 und sogar ML_4.[16,20,24] Nach Buděšínský[21] entsteht ein M_2L_2-Komplex.

Es kann erwartet werden, daß die Komplexe von Arsenazo III bei einer hohen Acidität zu bedeutendem Teil dissoziieren werden. Darauf zeigt die Abhängigkeit der molaren Extinktionskoeffizienten von der Ligandkonzentration[6] sowie der publizierte Wert der Beständigkeitskonstante eines Arsenazo III–Uranyl-Komplexes ($K = 1 \cdot 10^4$ in $6M$ Salpetersäure). In der ersten Mitteilung dieser Reihe[25] wurde gezeigt, daß die Bestimmung der Beständigkeitskonstanten der Komplexe und somit auch ihrer Zusammensetzung für die Auswertung einer für die spektralphotometrische Analyse dienenden Reaktion unerläßlich sind.

Im Weiteren geben wir einen Überblick über die Komplexbildung von Arsenazo III mit Uranylionen und Thorium(IV) bei Bedingungen der analytischen Verwendung, d.h. in mäßig und stark sauren Lösungen. Die grundlegende Methode der Untersuchung war die Auswertung photometrischer Titrationskurven. Bei der Bildung von dissoziierten Komplexen wurden die Titrationskurven nach den von uns beschriebenen Methoden analysiert.[26]

Verwendete Symbole und Bezeichnungen

c_M; c_L	totale Metall- bzw. Ligandkonzentration, molar
$[M_aL_b]$	Gleichgewichtskonzentration des Komplexes M_aL_b
K	Beständigkeitskonstante;
	$K_{M_aL_b} = \frac{[M_aL_b]}{(c_M - a \cdot [M_aL_b])^a \cdot (c_L - b \cdot [M_aL_b])^b}$
ΔA	Extinktionsmodul, gemessen gegen gleiche c_L
ΔA_0	Extinktionsmodul bei einem großen Titrantüberschuß (horizontaler Ast einer photometrischen Titrationskurve)
ε_L; ε_{ML}	molarer Extinktionskoeffizient des Liganden bzw. Komplexes ML (gegen Wasser)
$\Delta\varepsilon_{ML}$	differentieller molarer Extinktionskoeffizient des Komplexes ML[26]
$\Delta\varepsilon_{ML,\mathrm{eff}}$	effektiver differentieller molarer Extinktionskoeffizient des Komplexes ML (Steigung des Anfangsteiles einer photometrischen Titrationskurve)[26]
H_0	Acidität nach Hammettscher Funktion; die H_0-Werte für HNO_3 und $HClO_4$ aus[27,28] entnommen.

EXPERIMENTELLER TEIL

Lösungen

Uranylnitrat-Stammlösung, $1{,}45 \cdot 10^{-3}M$. Der UO_2^{2+}-Gehalt wurde gravimetrisch bestimmt.

Thorium(IV)-Nitrat-Lösung, $1{,}00 \cdot 10^{-3}M$. Die Thorium(IV)-Konzentration wurde chelatometrisch[29] bestimmt.

Die Acidität der Lösungen wurde durch konz. Perchlorsäure *p.a.* bzw. Salpetersäure *p.a.* eingestellt. Jeweils 100 ml der konz Salpetersäure wurden zwecks Beseitigung der salpetrigen Säure 1 g Harnstoff zugesetzt.[16]

Zur Herstellung der Ligandenstammlösung wurden 90–100 mg chromatographisch reines Arsenazo III in 10 ml Wasser gelöst. Die Lösung wurde durch eine kleine Säule mit Dowex 50 × 8 (H^+-Form) laufen gelassen und schließlich auf 100 ml aufgefüllt. Die Konzentration der Stammlösung wurde coulometrisch[30] bestimmt. Die Arsenazo III-Lösungen waren mindestens 2 Monate beständig.

Reinigung von Arsenazo III

Es wurden 1–2 g des Ausgangsproduktes (Spolana Neratovice) in 15–25 ml 5%-iges Ammoniumhydroxid gelöst. Nach Filtration der Lösung wurde das Arsenazo III durch eine Zugabe von 10 ml Salzsäure (1:1) ausgefällt. Die Umfällung wurde noch einmal wiederholt, und 0,5 g des auf diese Weise vorgereinigten Präparates wurde in 7 ml eines Gemisches n-Propanol–NH_4OH konz.–H_2O (1:1:1, Volumenverhältnis) bei 50° aufgelöst. Nach dem Erkalten wurde filtriert und das Filtrat auf eine Säule (ϕ 25 mm, Höhe 120 mm) von mikrokristallinischer Zellulose (Lachema, Brno) gegeben. Die Säule wurde vorher mit dem Laufmittel, bestehend aus n-Propanol–NH_4OH konz.–H_2O (Volumenverhältnis 3:1:1), durchgespült. Die Elutionsgeschwindigkeit betrug 1,5 ml/Min. Nachdem die blau gefärbte Zone von Arsenazo III die Mündung der Kolonne erreicht hatte, wurden 10 ml-Fraktionen des Eluats entnommen. Die Reinheit der einzelnen Fraktionen wurde chromatographisch am Papier Whatman 4 mit 1*M* Salzsäure als Laufmittel kontrolliert. Als Verunreinigung des Ausgangsproduktes wurden auf dem Papierchromatogramm ein roter (Arsenazo I, $R_f \sim 0{,}35$) und ein brauner Fleck ($R_f \sim 0{,}05$) sichtbar. Arsenazo III ergab einen langgezogenen rotvioletten Fleck ($R_f \sim 0{,}25$).

Die chromatographisch einheitlichen Fraktionen wurden vereinigt und bei maximal 80° auf 10–15 ml eingedampft. Dann wurde das Arsenazo III mit 10 ml konz. Salzsäure und schließlich mit wenig Äthanol gewaschen. Das Präparat wurde an der Luft bei Zimmertemperatur getrocknet.

Bei der papierchromatographischen Reinheitskontrolle wurde nur ein einziger Fleck von Arsenazo III erhalten.

Die Spektren der Lösungen von reinem Arsenazo III und der maximale Wert von $\varepsilon_L = 3{,}6 \cdot 10^3$ $\text{l.mole}^{-1}.\text{mm}^{-1}$ bei 540 nm sind in guter Übereinstimmung mit den meisten publizierten Arbeiten, mit Ausnahme von B. Buděšínský.[21] Im Absorptionsspektrum von Arsenazo III treten im Bereich der Wellenlängen 400–700 nm in Abhängigkeit von der Acidität der Lösung (von pH 2,8 bis H_0 −2,5) praktisch keine Änderungen auf. Bei einer größeren Acidität als H_0 −3 macht sich die Protonisierung von Azogruppen[20] in den Absorptionskurven deutlich bemerkbar.

Photometrische Titrationen

Die Titrationen wurden unmittelbar in den Meßküvetten mit Hilfe einer Agla-Mikrodosierungsspritze durchgeführt. Das Volumen der titrierten Lösung blieb während der Titration praktisch unverändert und betrug in der 10-mm Küvette 2,5 ml und in der 20-mm Küvette 5,0 ml. Das maximal zugesetzte Volumen der Titerlösung betrug weniger als 1–2% des Gesamtvolumens. Nach jeder Zugabe von 0,001–0,005 ml der Titerlösung wurde die Lösung in der Küvette mit einem Teflon-Stäbchen durchgemischt. Anschließend wurden entweder die Absorptionsspektren im Wellenbereich 580–720 nm registriert oder es wurde nur bei der Wellenlänge des Absorptionsmaximums gemessen. Bei dem Studium der Reaktionen von Thorium(IV) mit Arsenazo III wurden zwei Arten von Titrationskurven aufgenommen:

(*a*) Titration des Liganden mit dem Kation. ΔA wurde direkt gemessen.

(*b*) Titration des Kations mit dem Liganden. In diesem Fall wurde als Vergleichslösung Wasser benutzt. Vom Meßwert wurde die Extinktion einer reinen Arsenazo III-Lösung gleicher Konzentration abgezogen.

Bei der Untersuchung der Reaktion von Arsenazo III mit Uranyl wurden nur Titrationen mit Kation ausgeführt.

MEßERGEBNISSE

Reaktionen von Uranyl

Photometrische Titrationskurven von Arsenazo III-Lösungen mit Uranyl bei pH 2,8 (0,1*M* Essigsäure) weisen einen scharfen Knick auf, der einem Molverhältnis Arsenazo III:UO_2^{2+} = 1:1 genau entspricht. Die Steigungen der Anfangsteile der Kurven sind c_L-unabhängig ($\Delta\varepsilon_{ML,\text{eff}} \equiv \Delta\varepsilon_{ML} = 5{,}3 \cdot 10^3$ $\text{l.mole}^{-1}.\text{mm}^{-1}$ bei $\lambda_{\max}$ 656 nm).

Bei höheren Aciditäten (ab pH 1) wurde eine c_L-Abhängigkeit der $\Delta\varepsilon_{\text{eff}}$-Werte festgestellt. Eine Übersicht der Ergebnisse ($\Delta\varepsilon_{\text{eff}}$ bei $\lambda = 656$ nm) und der gewählten experimentellen Bedingungen (c_L, H_0) ist in Tab. I gegeben. Nach jeder Titration wurde noch der Extinktionsmodul ΔA_0 bei einem großen UO_2^{2+}-Überschuß durch Zugabe kleiner Kriställchen von Uranylnitrat bzw. Uranylperchlorat in die Meßküvette ermittelt.

TABELLE I.—AUSWERTUNG PHOTOMETRISCHER TITRATIONSKURVEN VON ARSENAZO III MIT URANYL

Acidität	$c_L \cdot 10^5 M$	$\Delta\varepsilon_{eff} \cdot 10^{-3}$ l.mole.$^{-1}$mm^{-1}	$\Delta\varepsilon_{ML} \cdot 10^{-3}$ l.mole.$^{-1}$mm^{-1} (a)	(b)	$K \cdot 10^{-4}$ (a)	(c)
0,5M HNO_3	1,37	0,75				
pH 0,2	2,74	1,39				
	6,85	2,55	6,1	6,0	1,04	1,07
	13,7	3,58				
	22,1	4,45				
1,0M HNO_3	1,37	0,39				
H_0 −0,2	2,74	0,75	6,5	6,4	0,49	0,48
	6,85	1,52				
	13,7	2,56				
1,12M $HClO_4$	1,52	0,70				
H_0 −0,3	4,36	1,65	7,1	7,1	0,71	0,81
	10,9	3,10				
5,8M HNO_3	2,74	1,20				
H_0 −1,75	6,85	2,48	8,3	8,15	0,63	0,66
	13,7	3,85				
5,5M $HClO_4$	1,52	4,80				
H_0 −2,6	4,36	6,60	8,2	8,3	10,0	10,5
	10,9	7,40				
11,5M HNO_3	2,74	0,72				
H_0 −3,0	5,48	1,26	9,0	8,9	0,32	0,32
	10,9	2,33				

(*a*) aus der c_L-Abhängigkeit der $\Delta\varepsilon_{eff}$-Werte bestimmt
(*b*) aus ΔA_0 bestimmt
(*c*) bei der logarithmischen Analyse der Titrationskurven ermittelt

Reaktionen von Thorium(IV)

Eine Titrationskurve von Arsenazo III durch Thoriumnitratlösung in 0,1*M* Essigsäure (pH 2,8) bei 662 nm ist in Abb. 1 dargestellt. Die Steigung der Kurve ist c_L-unabhängig und wird durch die Zahl 4,6 · 10^3 l.mole^{-1}.mm^{-1} ($\equiv \Delta\varepsilon$) charakterisiert. Bei der Titration des Kations mit Arsenazo III bei den gleichen Bedingungen bei 672 nm ($= \lambda_{max}$) wurde keine Abhängigkeit der Steigungen der Anfangsteile der Titrationskurven von c_M festgestellt. Die Steigung ($\equiv \Delta\varepsilon$) beträgt 2,6 · 10^3 l.mole$^{-1}\cdot$ mm^{-1}. Die Titrationskurven von Thorium(IV) mit dem Liganden weisen einen S-förmigen Verlauf auf.

Meßergebnisse und gewählte experimentelle Bedingungen (c_L, H_0) für die Titrationen von Arsenazo III mit Thorium(IV) in stark sauren Lösungen sind in Tab. II zusammengestellt. Tabelle III enthält die Meßergebnisse und die gewählten experimentellen Bedingungen für Titrationen von Thorium(IV) mit Arsenazo III in stark sauren Lösungen.

AUSWERTUNG UND DISKUSSION

Die Komplexbildung wurde aus dem Gesichtspunkt der analytischen Verwendung der Reaktionen untersucht. Bei der Bildung von wenig dissoziierten Komplexen wurde deshalb lediglich das Verhältnis M:L aus der Form der Titrationskurve ermittelt. Die für die spektralphotometrische Anwendung wichtige Konstante $\Delta\varepsilon_{M_aL_b}$ ist in diesem Fall unmittelbar durch die Steigung der Eichkurve gegeben.

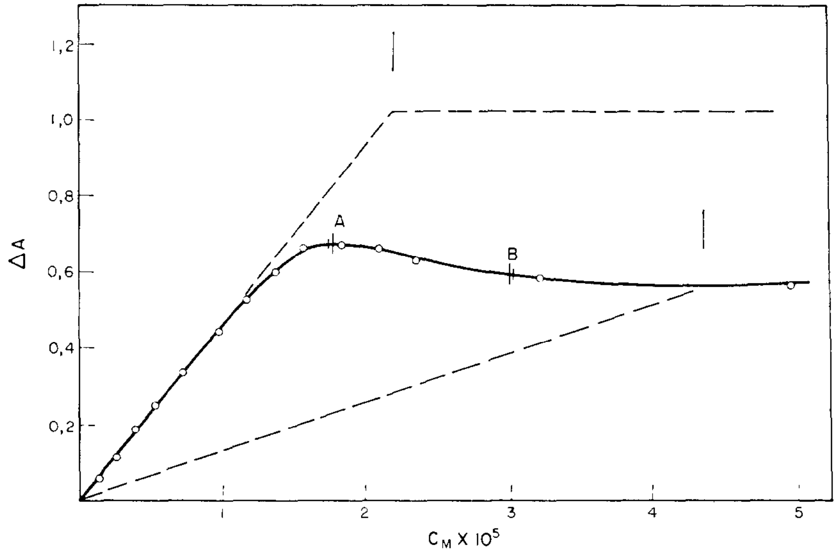


Abb. 1.—Photometrische Titration von Arsenazo III mit Thorium(IV). 0,1*M* Essigsäure, pH 2,8; $c_L = 2{,}21 \cdot 10^{-5} M$; $\lambda = 662$ nm.

TABELLE II.—AUSWERTUNG PHOTOMETRISCHER TITRATIONSKURVEN VON ARSENAZO III MIT THORIUM(IV)

Acidität	$c_L \cdot 10^5 M$	$\Delta\varepsilon_{eff} \cdot 10^{-3}$ *l.mole.*$^{-1}$*mm*$^{-1}$	$\Delta\varepsilon_{ML_2} \cdot 10^{-3}$ *l.mole.*$^{-1}$*mm*$^{-1}$ (*a*)	$K \cdot 10^{-9}$ (*a*)	(*b*)
2,8*M* HNO_3	1,20	9,50			
H_0 −1,0	2,40	11,0	12,8	10,0	
	4,80	12,0			
	7,20	12,6			
5,6*M* HNO_3	0,44	1,31			
H_0 −1,75	1,50	8,37			
	2,21	9,97	12,8	8,6	8,9
	11,05	12,4			
	15,05	12,4			
	22,1	12,7			
11,3*M* HNO_3	3,96	4,54			
H_0 −3,05	7,92	7,84	12,7	0,26	0,34
	19,8	11,4			

(*a*) aus der c_L-Abhängigkeit der $\Delta\varepsilon_{eff}$-Werte bestimmt
(*b*) bei der logarithmischen Analyse der Titrationskurven ermittelt

Die Grundlagen der Auswertung von photometrischen Titrationskurven bei der Bildung von dissoziierten Komplexen wurden früher abgeleitet:[26]

1. Trägt man die für gleiche Reaktionsbedingungen (Acidität) gewonnenen $\Delta\varepsilon_{eff}$-Werte bei Bildung eines einkernigen Komplexes (ML_b oder M_aL) in geeigneten Koordinaten auf, so erhält man Geraden, deren Steigung den differentiellen molaren Extinktionskoeffizienten ($\Delta\varepsilon_{ML_b}$ bzw. $\Delta\varepsilon_{M_aL}$) angibt. Die Wahl der richtigen Koordinaten hängt vom vermuteten Komplextyp ab. Aus derselben Beziehung läßt sich der Wert der Beständigkeitskonstante *K* ermitteln. Aus den Werten von $\Delta\varepsilon$ der Komplexe kann man die ΔA_0-Werte berechnen. Das hat besondere Bedeutung für

TABELLE III.—AUSWERTUNG PHOTOMETRISCHER TITRATIONSKURVEN VON THORIUM(IV) MIT ARSENAZO III

Acidität	$c_M \cdot 10^5 M$	$\Delta\varepsilon_{eff} \cdot 10^{-3}$ *l.mole.$^{-1}$mm^{-1}*	$\Delta\varepsilon_{ML} \cdot 10^{-3}$ *l.mole.$^{-1}$mm^{-1}* (*a*)	$K \cdot 10^{-4}$ (*a*)	$K \cdot 10^{-4}$ (*b*)
$2{,}8M$ HNO$_3$	2,0	4,8			
H_0 −1,0	4,0	5,5	6,7	14	
	10,0	6,1			
	50,0	6,6			
$5{,}6M$ HNO$_3$	0,99	3,3			
H_0 −1,75	1,98	4,6			
	4,95	6,1	8,1	6,8	8,0
	9,90	7,0			
	99,0	7,8			
$11{,}3M$ HNO$_3$	0,99	0,9			
H_0 −3,05	1,98	1,45			
	3,96	1,65	7,3	1,2	1,4
	9,90	3,9			
	19,8	5,05			
	99,0	6,6			

(*a*) aus der c_M-Abhängigkeit der $\Delta\varepsilon_{eff}$-Werte bestimmt
(*b*) bei der logarithmischen Analyse der Titrationskurven ermittelt

die logarithmische Analyse, wenn sich die ΔA_0-Werte experimentell nicht bestimmen lassen.

2. Die bei gleichen Reaktionsbedingungen (Acidität) experimentell erhaltenen Titrationskurven lassen sich bei bekannten ΔA_0-Werten innerhalb bestimmter, vom Komplextyp abhängiger Koordinaten, in eine Gerade transformieren. Zur Ermittlung der Zusammensetzung des in der Lösung vorliegenden Komplexes sind diejenigen Koordinaten zu wählen, bei denen die transformierten Titrationskurven, die bei verschiedenen Konzentrationen der titrierten Lösung erhalten wurden, in *einer* Geraden zusammenfallen ("logarithmische Analyse der Titrationskurven"). Außerdem muß die Steigung dieser Geraden mit der theoretisch berechneten Steigung übereinstimmen. Die Koordinaten für die einzelnen Komplextypen (M_aL_b) für die photometrischen Titrationen von Kation durch Ligand und umgekehrt sowie die theoretischen Steigungen der resultierenden Geraden folgen aus Gl. (1) und (2):

$$\log \frac{1}{b \cdot \dfrac{c_M}{c_L} \Delta A_0 - a \cdot \Delta A} = -\frac{1}{a} \cdot \log \frac{\Delta A}{(\Delta A_0 - \Delta A)^b} + \frac{1}{a} \cdot \log \frac{K \cdot b^b}{\Delta\varepsilon_{M_aL_b}^{a+b-1}} \tag{1}$$

für c_L = Konst.

$$\log \frac{1}{a \cdot \dfrac{c_L}{c_M} \cdot \Delta A_0 - b \cdot \Delta A} = -\frac{1}{b} \cdot \log \frac{\Delta A}{(\Delta A_0 - \Delta A)^a} + \frac{1}{b} \cdot \log \frac{K \cdot a^a}{\Delta\varepsilon_{M_aL_b}^{a+b-1}} \tag{2}$$

für c_M = Konst.

Diese Gleichungen wurden analog wie bereits für den ML-Komplex angegeben[26] berechnet. Aus dem Ordinatenabschnitt bei einem bekannten $\Delta\varepsilon_{M_aL_b}$-Wert läßt sich die Beständigkeitskonstante berechnen. Man setzt bei diesem Verfahren nach Möglichkeit immer die experimentell ermittelten ΔA_0-Werte und die daraus berechneten $\Delta\varepsilon_{M_aL_b}$ ein. Nur wenn die ΔA_0-Werte experimentell nicht zugänglich sind (z.B.

wegen Bildung eines anderen Komplexes bei größeren Titrantüberschüssen), müssen die bei der Auswertung der Konzentrationsabhängigkeiten von $\Delta\varepsilon_{\text{eff}}$ erhaltenen differentiellen molaren Extinktionskoeffizienten und die daraus berechneten (Ref. 26, Gl. (5)) ΔA_0-Werte eingesetzt werden.

Reaktion von Arsenazo III mit Uranylionen

In mäßig saurer Lösung (pH 2,8) wird ein fester Komplex des Typus ML gebildet. Der ermittelte $\Delta\varepsilon_{\text{ML}}$-Wert bei λ_{max} 656 nm, $5{,}3 \cdot 10^3$ l.mole^{-1}.mm^{-1}, stimmt mit der Literaturangabe überein.[23]

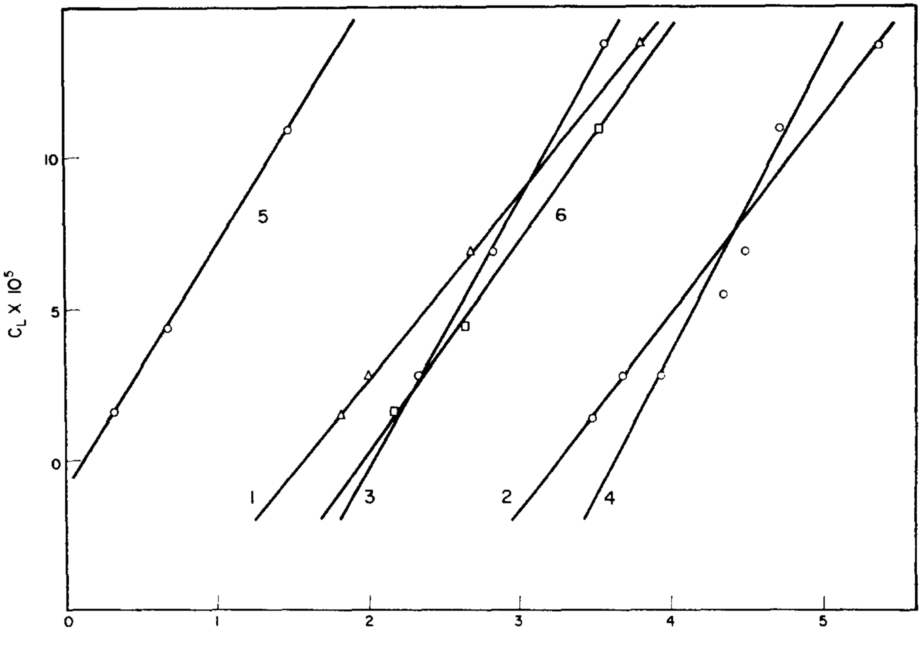


ABB. 2.—Auswertung der c_L-Abhängigkeit von $\Delta\varepsilon_{\text{eff}}$ bei Titration von Arsenazo III mit Uranyl.
1 0,5*M* HNO_3; *2* 1,0*M* HNO_3; *3* 5,6*M* HNO_3; *4* 11,6*M* HNO_3; *5* 1,1*M* $HClO_4$; *6* 5,6*M* $HClO_4$.

In sauren Lösungen werden dissoziierte Komplexe gebildet. Abbildung 2 zeigt die Auswertung der Konzentrationsabhängigkeit der $\Delta\varepsilon_{\text{eff}}$-Werte für einen vermuteten Typ ML. Die hieraus ermittelten $\Delta\varepsilon_{\text{ML}}$-Werte stimmen gut mit jenen $\Delta\varepsilon_{\text{ML}}$-Werten überein, die aus den experimentell ermittelten ΔA_0-Werten bei einem großen Uranylüberschuß berechnet wurden (Tab. 1).

Abbildung 3 zeigt die transformierten Titrationskurven. Alle Geraden besitzen innerhalb der für einen ML-Komplex gültigen Koordinaten die Steigung $-1{,}00 \pm 0{,}03$. Damit ist das Vorliegen eines 1:1 Komplexes eindeutig bewiesen. Die aus dem Ordinatenabschnitt ermittelten *K*-Werte sind in guter Übereinstimmung mit jenen, die bei der Auswertung der Konzentrationsabhängigkeit der $\Delta\varepsilon_{\text{ML,eff}}$-Werte festgestellt wurden (Tab. 1).

Mit Hilfe der transformierten Titrationskurven läßt sich auch zeigen, daß in sauren Lösungen bei keinen Konzentrationsverhältnis c_M/c_L Komplexe des Typus

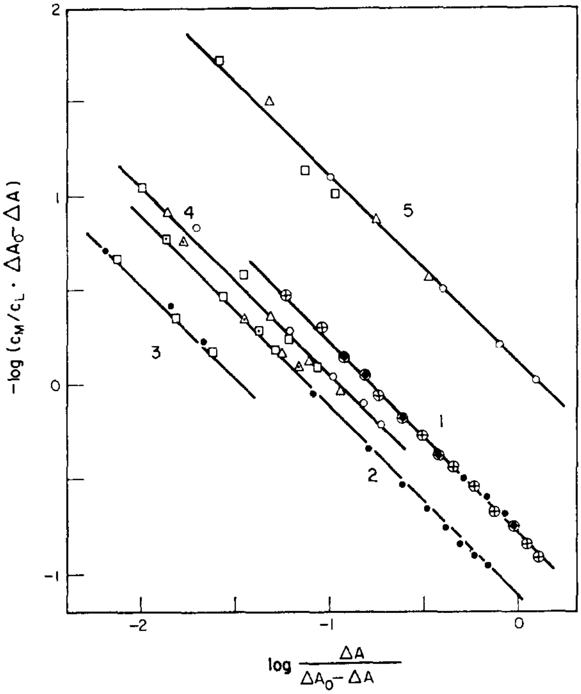


Abb. 3.—Logarithmische Analyse der Titrationskurven von Arsenazo III mit Uranyl (vorausgesetzter Komplex ML).

1. 0,5M HNO_3; $c_L = 2{,}65 \cdot 10^{-5}M$ ● und $2{,}21 \cdot 10^{-4}M$ ⊕
2. 5,8M HNO_3; $c_L = 2{,}74 \cdot 10^{-5}M$ ●, $6{,}85 \cdot 10^{-5}M$ △ und $13{,}7 \cdot 10^{-5}M$ ⊡
3. 11,6M HNO_3; $c_L = 5{,}48 \cdot 10^{-5}M$ □ und $10{,}96 \cdot 10^{-5}M$ ●
4. 1,1M $HClO_4$; $c_L = 1{,}52 \cdot 10^{-5}M$ ○, $4{,}36 \cdot 10^{-5}M$ △ und $10{,}9 \cdot 10^{-5}M$ □
5. 5,6M $HClO_4$; c_L und Bezeichnungen wie bei *4*.

M_2L_2 entstehen. Abbildung 4 zeigt die Transformation von zwei bei gleicher Acidität, jedoch verschiedenen c_L gewonnenen Titrationskurven innerhalb der für einen M_2L_2-Komplex gültigen Koordinaten. Die Steigungen der beiden *getrennten* Linien (etwa —0,75) weichen erheblich von der geforderten Steigung —0,5, vgl. Gl. (1), ab.

Die Abhängigkeit der $\Delta\varepsilon_{ML}$-Werte der Uranyl–Arsenazo III-Komplexe von der Acidität der Lösung (H_0) wird in Abb. 5 dargestellt. Es ist ersichtlich, daß bei gleicher Acidität dieselben Ergebnisse ($\Delta\varepsilon_{ML}$) erzielt werden, unabhängig von der Art der benutzten Säure. Auch das Verhältnis von ΔA-Werten bei verschiedenen Wellenlängen ist bei gleicher Acidität von dem Charakter der Säure unabhängig. Aus dem Verlauf der in Abb. 5 dargestellten Kurve, mit Rücksicht auf die Ergebnisse der logarithmischen Analyse, folgt, daß in dem System zwei (oder mindestens zwei) ML-Komplexe entstehen. Ihr Konzentrationsverhältnis in der Lösung hängt von der Acidität ab. Die Wellenlängen der Absorptionsmaxima beider Komplexe sind im Rahmen der Meßgenauigkeit identisch (656 ± 2 nm). Bei kleineren Aciditäten als pH 1 entsteht überwiegend ein ML-Komplex mit einem $\Delta\varepsilon_{ML}$-Wert von $5{,}3 \cdot 10^3$ $l.mole^{-1}.mm^{-1}$ bei 656 nm. Bei höheren Aciditäten als H_0-2 kann praktisch die ausschließliche Bildung eines weiteren ML-Komplexes (Bezeichnung ML*) mit $\Delta\varepsilon_{ML*} = 8{,}8 \cdot 10^3$ bei 656 nm vorausgesetzt werden. Eine vollständige Beschreibung des Gleichgewichtes zwischen den beiden Komplexen, d.h. die Erklärung ihrer

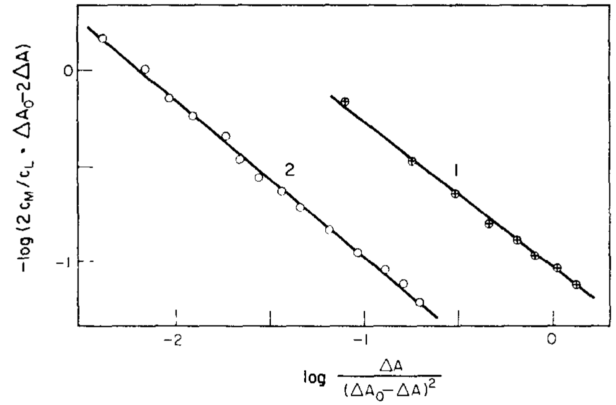


ABB. 4.—Logarithmische Analyse der Titrationskurven von Arsenazo III mit Uranyl (vorausgesetzter Komplex M_2L_2).
0,5M HNO_3; *1.* $c_L = 2{,}65 \cdot 10^{-5}M$; *2.* $c_L = 2{,}21 \cdot 10^{-4}M$.

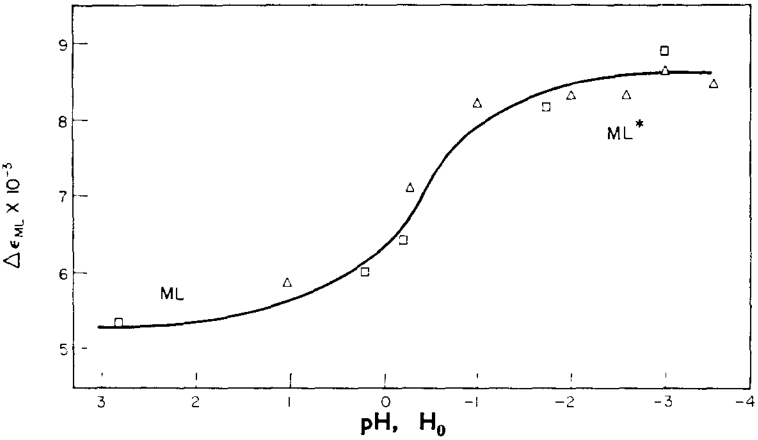


ABB. 5.—Differentielle Extinktionskoeffizienten der Komplexe von Arsenazo III mit Uranyl in Abhängigkeit von der Acidität.
△ bestimmt bei Anwesenheit von HNO_3
□ bestimmt bei Anwesenheit von $HClO_4$
⊡ bestimmt bei Anwensenheit von CH_3COOH.

Struktur, übersteigt den Rahmen dieser Arbeit. Die Spektren beider Komplexe (umgerechnet auf $\Delta\varepsilon_{ML}$ bzw. $\Delta\varepsilon_{ML^*}$) sind in Abb. 6 dargestellt.

Die früher veröffentlichten unterschiedlichen Beziehungen zwischen den ΔA-Werten der Uranyl-Arsenazo III-Komplexe und der Säurekonzentration[6,9] lassen sich somit leicht erklären. Die Autoren haben lediglich die $\Delta\varepsilon_{ML,\text{eff}}$-Werte gemessen. Die Abhängigkeit dieser Werte weist mit Aciditätserhöhung ein Minimum auf, bedingt einerseits durch die wachsende Dissoziation des ML-Komplexes ($\Delta\varepsilon_{ML} = 5{,}3 \cdot 10^3$) und anderseits durch Erhöhung der $\Delta\varepsilon_{ML,\text{eff}}$-Werte ab bestimmten Säurekonzentrationen in Zusammenhang mit der bevorzugten Bildung des Komplexes ML* ($\Delta\varepsilon_{ML^*} = 8{,}8 \cdot 10^3$).

Aus einem Vergleich der $\Delta\varepsilon_{ML,\text{eff}}$-Werte bei entsprechenden c_L-Werten und gleicher Acidität (eingestellt durch Salpetersäure bzw. Perchlorsäure) wird für die

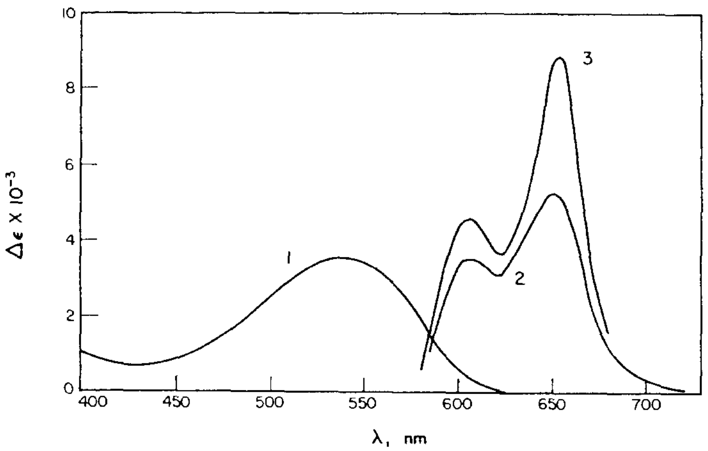


ABB. 6.—Spektren von Arsenazo III (als ε_L) und von Arsenazo III-Uranylkomplexen (als $\Delta\varepsilon_{ML}$ und $\Delta\varepsilon_{ML^*}$).
1. Arsenazo III, pH 2,8; *2.* Komplex ML (pH 2,8); *3.* Komplex ML* (11M HNO_3).

analytische Praxis die große Bedeutung für die richtige Auswahl der Säure ersichtlich. Bei Verwendung von Salpetersäure wurden stets niedrigere K-Werte und somit[26] auch $\Delta\varepsilon_{ML,eff}$-Werte gefunden als bei Anwesenheit von Perchlorsäure (vgl. Tab. 1). Es muß angenommen werden, daß bei Anwesenheit von Salpetersäure neben der Komplexbildung Arsenazo III-Uranyl (Komplexe ML und ML*) noch eine Konkurrenzreaktion der Salpetersäure mit Uranyl verläuft. Daher ist zwar das Konzentrationsverhältnis der Komplexe ML und ML* bei gleicher Acidität von der Art der Säure unabhängig, die Gleichgewichtskonzentrationen dieser Komplexe sind jedoch bei Anwesenheit von Salpetersäure wesentlich kleiner als in einem Reaktionsmedium mit Perchlorsäure. Die Existenz von Komplexen des Uranyls mit Nitrationen ist bekannt.[31]

Reaktionen von Arsenazo III mit Thorium(IV)

Bei höheren Aciditäten (H_0 — 1; 2,8M Salpetersäure) wurde bei Titrationen von Arsenazo III mit Thorium eine merkliche c_L-Abhängigkeit ($c_L = 10^{-5}$ bis $10^{-4}M$) der effektiven Extinktionskoeffizienten festgestellt (Tab. 2). Die graphische Auswertung der gemessenen $\Delta\varepsilon_{eff}$-Werte in den Koordinaten $c_L{}^2$ gegen $c_L{}^2/\Delta\varepsilon_{eff}$ deutete auf die Anwesenheit eines dissoziierten ML_2-Komplexes. Der Wert von $\Delta\varepsilon_{ML_2} = 12{,}8 \cdot 10^3$ l.mole^{-1}.mm^{-1} bei 658 nm ist im Bereich $-1 > H_0 > -3$ von der Acidität der Lösung unabhängig. Für die transformierten Titrationskurven (Abb. 7) wurden die benötigten ΔA_0-Werte mit Hilfe dieser Zahl ($12{,}8 \cdot 10^3$) berechnet. Unmittelbar experimentell lassen sich die ΔA_0-Werte nicht bestimmen, da bei großen Überschüssen von c_M andere Komplexe entstehen (vgl. unten). Die Geraden *1* und *2* in Abb. 7 bestätigen das Vorliegen eines ML_2-Komplexes. Dagegen wird durch die Geraden *2′* und *2″* der Abb. 7 das Nichtvorhandensein eines ML-Komplexes bei diesen Reaktionsbedingungen eindeutig bewiesen.

Bei Titrationen von Thorium(IV) mit Arsenazo III, also bei Bedingungen eines c_M-Überschusses, ist die Beziehung zwischen c_M und $c_M/\Delta\varepsilon_{eff}$ linear—es kann die Bildung von ML-Komplexen vorausgesetzt werden. Die aus den Steigungen

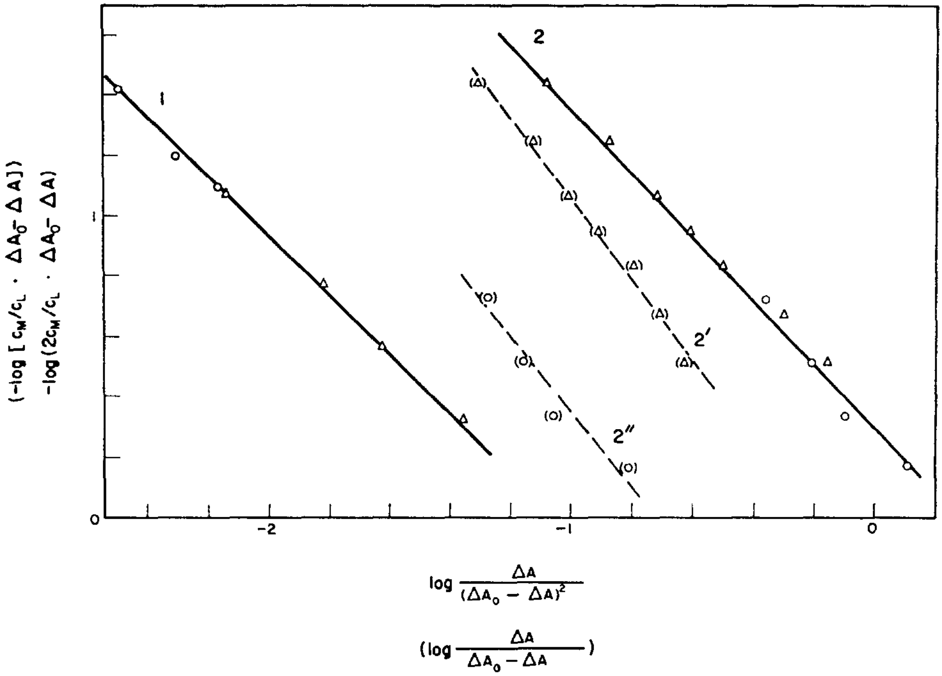


Abb. 7.—Logarithmische Analyse der Titrationskurven von Arsenazo III mit Thorium(IV). Vorausgesetzter Komplex ML_2 (*1* und *2*) oder ML (*2′* und *2″*).
1. $11{,}6M$ HNO_3; $c_L = 7{,}92 \cdot 10^{-5}M$ △ und $19{,}8 \cdot 10^{-5}M$ ○
2. $5{,}8M$ HNO_3; $c_L = 0{,}44 \cdot 10^{-5}M$ ○ und $2{,}21 \cdot 10^{-5}M$ △
2′ wie *2*, $c_L = 2{,}21 \cdot 10^{-5}M$; *2″* wie *2*, $c_L = 0{,}44 \cdot 10^{-5}M$.

ermittelten $\Delta\varepsilon_{ML}$-Werte sind wie bei den Uranylkomplexen von der Acidität der Lösung abhängig. Deshalb nehmen wir an, daß mindestens zwei Thorium(IV)–Arsenazo III-Komplexe des Typs ML gebildet werden, weiter ML und ML* bezeichnet. Die transformierten Titrationskurven (Geraden *1* und *2* in Abb. 8) bestätigen die Bildung von ML-Komplexen. Die benötigten ΔA_0-Werte wurden aus den Werten von $\Delta\varepsilon_{ML}$ berechnet. Durch die Geraden *1′* und *1″* wird das Nichtvorhandensein eines M_2L-Komplexes bei diesen Reaktionsbedingungen bewiesen.

Die Abweichung eines Teiles der Kurve *2* (Abb. 8) von der theoretischen Steigung kann durch gleichzeitige Anwesenheit des ML_2-Komplexes bei einem kleineren Überschuß von c_M erklärt werden. Ähnliche Abweichungen wurden auch bei der Bildung des ML_2-Komplexes bei kleineren $c_L(c_L \leqslant 2 \cdot 10^{-5}M)$ und einer höheren Acidität (H_0 —3,05) beobachtet während der Titration von Arsenazo III mit Thorium(IV). Sie lassen sich durch Bildung von ML-Komplexen erklären. Aus den angeführten Ergebnissen geht aber hervor, daß in stark sauren Lösungen bei einem genügenden Reagensüberschuß vorwiegend der ML_2-Komplex, bei einem großen Thorium(IV)-Überschuß praktisch nur die ML- und ML*-Komplexe entstehen.

Die Zusammensetzung der Thorium–Arsenazo III-Komplexe, die bei kleinen Säurekonzentrationen entstehen, kann nicht mit Hilfe der oben erwähnten Methoden bestimmt werden, da es keine Konzentrationsabhängigkeit der Steigungen der Anfangsteile von photometrischen Titrationskurven gibt. Man kann jedoch auf sie schließen aus dem Verlauf der photometrischen Titrationskurven, sowie aus einem

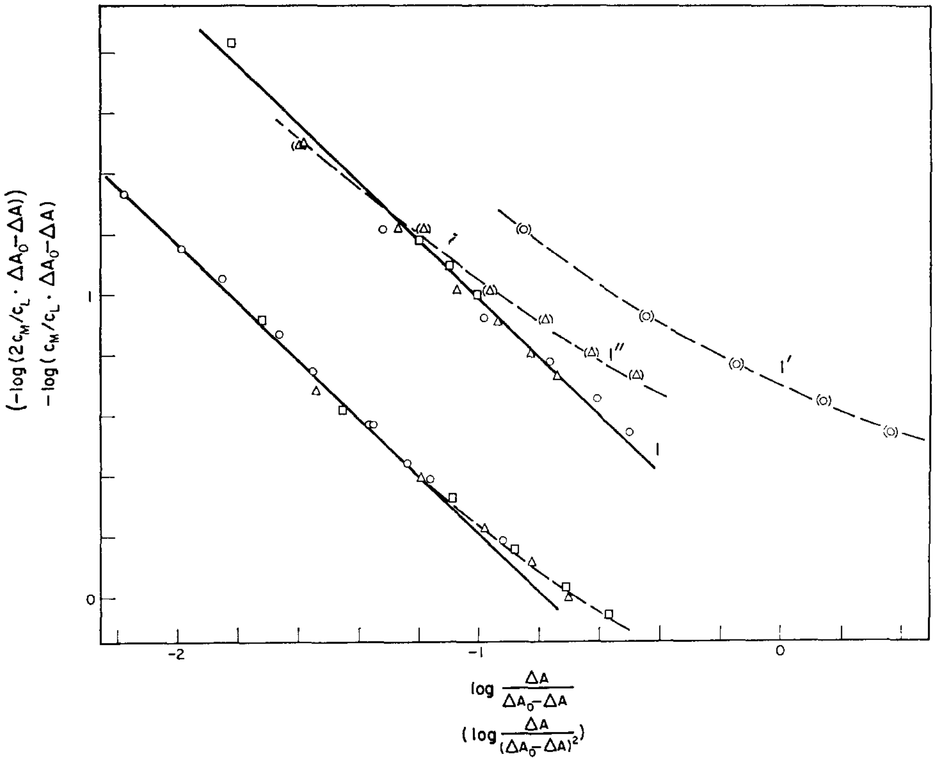


Abb. 8.—Logarithmische Analyse der Titrationskurven von Thorium(IV) mit Arsenazo III. Vorausgesetzter Komplex ML (*1* und *2*) oder M_2L (*1′* und *1″*).
1. $5{,}8M\ HNO_3$; $c_M = 1{,}98 \cdot 10^{-5}M$ ○, $4{,}95 \cdot 10^{-5}M$ △ und $9{,}9 \cdot 10^{-5}M$ □
2. $11{,}6M\ HNO_3$; $c_M = 1{,}98 \cdot 10^{-5}M$ ○, $3{,}96 \cdot 10^{-5}M$ ○, $9{,}9 \cdot 10^{-5}M$ △ und $19{,}8 \cdot 10^{-5}M$ □
1′ wie *1*; $c_L = 1{,}98 \cdot 10^{-5}M$; *1″* wie *1*; $c_L = 4{,}95 \cdot 10^{-5}M$.

Spektrenvergleich mit Komplexen, deren Zusammensetzung bei einer höheren Acidität eindeutig festgestellt wurde. Aus Abb. 1 ist ersichtlich, daß bei der Titration von Arsenazo III mit Thorium(IV) bei pH 2,8 nacheinander zwei Komplexe entstehen. Der gefundene Wert des differentiellen Extinktionskoeffizienten bei großen Reagensüberschüssen (Steigung des Anfangsteiles der Titrationskurve, $4{,}6 \cdot 10^3$ l.mole^{-1}.mm^{-1} bei λ_{max} 662 nm) sowie das ganze Spektrum sind mit dem Wert $\Delta\varepsilon_{ML}$ und dem Absorptionsspektrum des ML-Komplexes identisch, der bei größeren Säurekonzentrationen (H_0 —0,1) bei einem Metallüberschuß entsteht.

Bei Titrationen von Thorium(IV) mit Arsenazo III bei pH 2,8 wird bei λ_{max} 672 nm eine c_M-unabhängige Steigung der Anfangsteile der Titrationskurven, die einem differentiellen Extinktionskoeffizienten $2{,}6 \cdot 10^3$ entspricht, beobachtet. Diese Zahl entspricht dem bei 662 nm gefundenen Wert von $2{,}5 \cdot 10^3$, der durch den horizontalen Ast der Titrationskurve (Abb. 1) gegeben wird. Die erwähnte S-förmige Form der Titrationskurve von Thorium(IV)-Lösungen mit Arsenazo III läßt sich durch gleichzeitige Bildung des ML-Komplexes bei kleiner werdenden Metallüberschüssen erklären.

Die beschriebenen Tatsachen, die bei Titrationen bei pH 2,8 festgestellt wurden, können nicht durch gleichzeitige Bildung von zwei Komplexen eines gleichen Typs, z.B. ML, erklärt werden, da ihr Konzentrationsverhältnis in der Lösung von dem Verhältnis der reagierenden Komponenten ($c_L:c_M$) unabhängig sein müßte. Eine schrittweise Bildung von Komplexen ML und M_2L_2 ist durch die Form beider Titrationskurven ebenfalls ausgeschlossen. Deshalb muß man neben dem ML-Komplex mit $\Delta\varepsilon_{ML}$ 4,6 · 10^3, der bei einem Ligandenüberschuß bei pH 2,8 entsteht, noch die Existenz eines M_2L-Komplexes bei Bedingungen eines Metallüberschusses annehmen ($\Delta\varepsilon M_2L = 2{,}6 \cdot 10^3$ bei λ_{max} 672 nm). Bei der schrittweisen Bildung der wenig dissoziierten Komplexen ML und M_2L bei der photometrischen Titration von Arsenazo III mit Thorium(IV) (Abb. 1) entspricht dem Punkt *A* die Zusammensetzung 86,5 % mol. ML und 13,5 % mol. M_2L, und dem Punkt *B* 9 % mol. ML und 91 % M_2L.

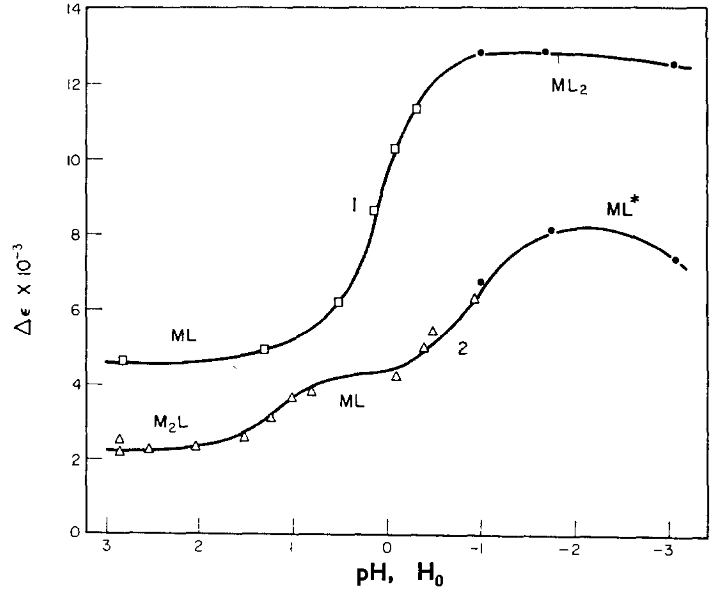


Abb. 9.—Differentielle Extinktionskoeffizienten der Komplexe von Arsenazo III mit Thorium(IV) in Abhängigkeit von der Acidität.—*1* bei $c_L \gg c_M$; *2* bei $c_M \gg c_L$; ● extrapolierte Werte aus den Konzentrationsabhängigkeiten von $\Delta\varepsilon_{eff}$.

In Abb. 9 sind Abhängigkeiten der differentiellen molaren Extinktionskoeffizienten von der Acidität der Lösung bei einem solchen c_L-oder c_M-Überschuß dargestellt, bei welchem praktisch keine Konzentrationsabhängigkeit der $\Delta\varepsilon_{eff}$-Werte bemerkbar ist. Die Werte sind stets für das Maximum bei längeren Wellenlängen (vgl. Abb. 10) angegeben. Kurve *1* (Abb. 9) charakterisiert die Komplexe ML und ML_2, die bei Bedingungen eines Arsenazo III-Überschusses gebildet werden. Die Komplexe M_2L, ML und ML* werden in Abhängigkeit von der Acidität der Lösung bei großen Metallüberschüssen vorwiegend gebildet, Kurve *2*, Abb. 9. Differentielle Absorptionsspektren (als $\Delta\varepsilon$) der vier Arsenazo III–Thorium(IV)-Komplexe sind in Abb. 10 angeführt. Es ist beachtlich, daß die λ_{max} der beiden 1:1-Komplexe (ML, $\Delta\varepsilon_{ML}$ 4,6 · 10^3 und ML*, $\Delta\varepsilon_{ML^*}$ 8,1 · 10^3) gleich wie im Fall der Uranylkomplexe im Rahmen der Meßgenauigkeit identisch sind (662 ± 2 nm).

Bei den untersuchten Bedingungen (c_M, c_L, Acidität) entstehen keine Komplexverbindungen anderer Typen (M_2L_2,[21] ML_3 und ML_4[16]).

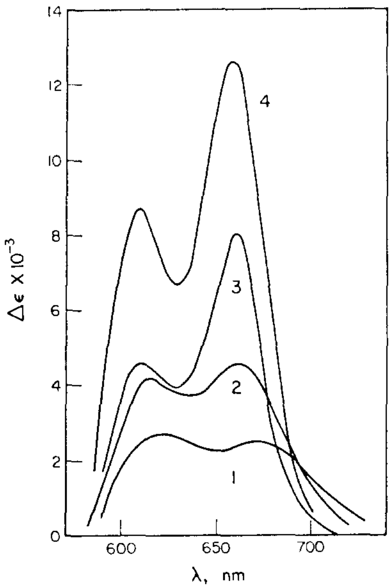


Abb. 10.—Spektren von Arsenazo III-Thorium(IV)-Komplexen (als $\Delta\varepsilon_{M_aL_b}$). *1* Komplex M_2L; *2* Komplex ML; *3* Komplex ML*; *4* Komplex ML_2.

FOLGERUNGEN FÜR DIE ANALYTISCHE PRAXIS

Bei der spektralphotometrischen Uranylbestimmung mit Arsenazo III ist es günstig, die bevorzugte Bildung des ML*-Komplexes mit $\Delta\varepsilon_{ML^*} = 8{,}8 \cdot 10^3$ (656 nm) in stark sauren Lösungen bei $H_0 < -1$ auszunutzen. Als Reaktionsmedium bewährte sich Perchlorsäure besser als Salpetersäure. Bei $c_L \geqslant 1 \cdot 10^{-4}M$ und $-1 > H_0 > -2{,}5$ ist es dann möglich, die Bestimmung bei Bedingungen, die einer vollständigen Komplexbildung nahe kommen, zu verwirklichen weil $\Delta\varepsilon_{ML^*,\text{eff}}$ ändert sich kaum mit c_L und nähert sich dem Wert von $\Delta\varepsilon_{ML^*}$.

Die Bestimmung von Thorium(IV) in stark salpetersauren Lösungen beruht auf der Bildung eines ML_2-Komplexes. Bei einem genügenden Ligandenüberschuß ($c_L \geqslant 1 \cdot 10^{-4}M$) sind die Steigungen der Eichkurven praktisch c_L-unabhängig und sie nähern sich dem Wert von $\Delta\varepsilon_{ML_2} = 12{,}8 \cdot 10^3$.

SCHLUßBETRACHTUNG

Die Ergebnisse des Studiums der Komplexbildung von Arsenazo III mit Uranyl und Thorium(IV) weisen darauf hin, daß die vollständige Analyse der photometrischen Titrationskurven eindeutige Resultate auch in komplizierten Fällen bei Entstehung von mehreren dissoziierten Komplexen liefern kann. Die allgemeinen Fragen der Auswertung von photometrischen Titrationskurven beim Studium der Gleichgewichte (Komplextyp, *K*) und Eigenschaften ($\Delta\varepsilon_{M_aL_b}$) dissoziierter Komplexe wollen wir noch einmal später ausführlich behandeln.

Für die erwiesene Interesse und Unterstützung sind wir Herrn Prof. Dr. Lumír Sommer, Dr.Sc., aus der Universität UJEP Brno zu Dank verpflichtet.

Summary—The reaction of uranyl ion with Arsenazo III in acid solution gives rise to the formation of two complexes of the type ML, the proportions of these two being dependent on the acidity. The molar absorptivities of the complexes at 565 nm are $5{\cdot}3 \times 10^3$ and $8{\cdot}8 \times 10^3$ $\text{l.mole}^{-1}.\text{mm}^{-1}$. The formation constants have been determined, and the apparent variation in the sensitivity of the reaction is explained. In acid solution thorium forms complexes with Arsenazo III of the types M_2L, ML (two), and ML_2, the last of which is analytically useful, although partially dissociated. It predominates in strongly acid solution containing a large excess of reagent, and has a molar absorptivity at 658 nm of $12{\cdot}8 \times 10^3$ $\text{l.mole}^{-1}.\text{mm}^{-1}$.

Résumé—La réaction de l'ion uranyle avec l'Arsenazo III en solution acide engendre la formation de deux complexes du type ML, leurs proportions dépendant de l'acidité. Les coefficients d'absorption moléculaire des complexes à 565 nm sont $5{,}3 \times 10^3$ et $8{,}8 \times 10^3$ $\text{l. mole}^{-1}.\text{mm}^{-1}$. On a déterminé les constantes de formation, et l'on explique la variation apparente dans la sensibilité de la réaction. En solution acide, le thorium forme avec l'Arsenazo III des complexes des types M_2L, ML (deux) et ML_2, ce dernier étant analytiquement utile, quoique partiellement dissocié. Il prédomine en solution fortement acide contenant un grand excès de réactif, et a un coefficient d'absorption moléculaire à 658 nm de $12{,}8 \times 10^3$ $\text{l.mole}^{-1}.\text{mm}^{-1}$.

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SHORT COMMUNICATIONS

2,4-Bis(4-nitrobenzazo)resorcinol-6-sulphonic acid as a new acid–base indicator

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In research on 2,4-bis(nitrobenzazo)resorcinol-6-sulphonic acid (BRS) as a selective qualitative reagent for magnesium, the substance was found suitable as an acid-base indicator, capable of filling a gap in the series of alkaline region indicators.

The substance was prepared according to Podstata and Allan,[1] and purified by a two-stage reprecipitation. The purity at each step was checked by paper chromatography, and the final purity was verified by means of elementary analysis.

Two colour transitions were found, at pH 6·8–8·2 (yellow → red), and at pH 10·5–13 (red → blue-violet). The dissociation constant values pK_1 7·64 and pK_2 11·64 correspond to these transitions, and were obtained as described elsewhere.[2]

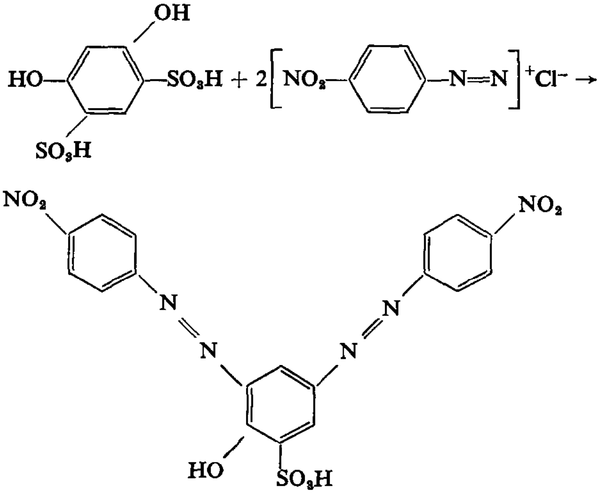
The polarographic behaviour of the substance was investigated and the problem of its possible structures discussed. The use of BRS as a new acid-base indicator was tested by a series of determinations of weak and strong acids. It proved very suitable for the determination of *p*-hydroxybenzoic acid, permitting, in contrast to the commonly used indicators, the carboxyl group to be titrated without simultaneous titration of the labile proton of the hydroxyl group.

The literature shows that the use of resorcinol azo dyes as acid-base indicators is rare (Tropaeolin O and Azo Violet[3,4]); no mention has been made of bisazo dyes derived from resorcinol.

EXPERIMENTAL

Preparation

Heat resorcinol with conc. sulphuric acid for about 90 min at 140–160°.[5] Cool the mixture, and quickly collect the precipitate on a sintered porcelain dish by suction. Moisten the product with a little conc. sulphuric acid and subject it to suction for 30 min.



Treat *p*-nitroaniline (2·76 g) with 5 ml of 2*M* hydrochloric acid and quickly add (all at once, in order to prevent formation of amino-azo dye)[6] the theoretical quantity of solid sodium nitrite (1·38 g) cooled with ice. Then dissolve resorcinol-4,6-disulphonic acid (9 g) in boiling water (about 200 ml) and add sodium acetate (30 g). Cool with ice (100 g), and then add the 0·02 mole of diazonium salt. As the coupling is slow, heat the reaction mixture to 30° after an hour. Collect the precipitated dye rapidly under suction and wash it with a small quantity of water.

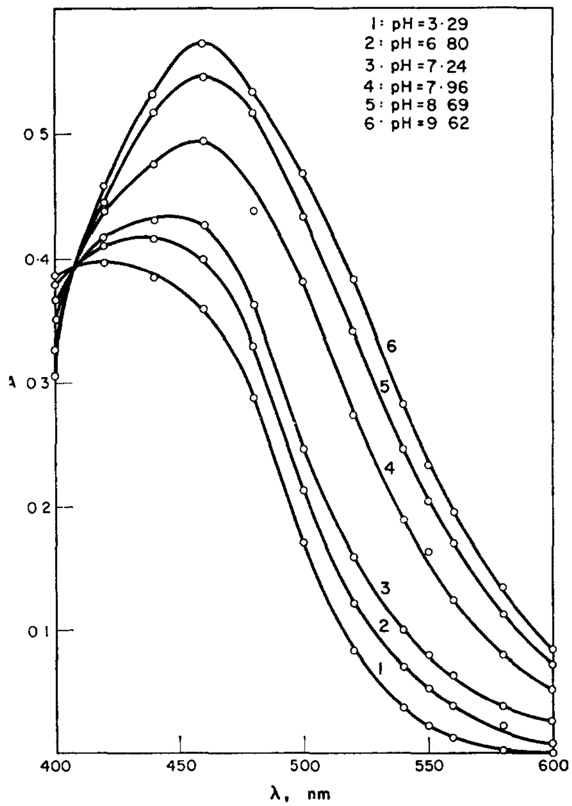


FIG. 1.—Absorption spectra of 2·4 × $10^{-5}M$ indicator solution, pH 3·29–9·62.

Dissolve the purified substance in boiling water (200 ml) and add sodium carbonate (about 10 g) till alkaline. Salt out the sodium salt by adding about 5% w/v of solid sodium chloride, cool, dilute the solution to twice its volume and collect the brown-red precipitate by suction. In the second stage of purification dissolve the precipitate in 400 ml of water, filter hot, and add 2*M* hydrochloric acid to the hot filtrate till it is acid to Congo Red, collect, wash and dry the amorphous red precipitate. Test the product chromatographically, with Whatman No. 4 paper and (*a*) 20% ammonia-isopentanol-pyridine, (1:1:1), (*b*) 20% ammonia, and by elementary analysis. (The R_f value of the product is 0·6, and of the impurities, 0·07.)

For use as an indicator the purified product is precipitated again as the sodium salt.

Spectrophotometric studies

Measurements were made of the absorption spectra of 2·4 × $10^{-5}M$ indicator solutions buffered at pH values from 3·29 to 13·30, and (except for the pH 13·3 solution) kept at constant ionic strength with sodium perchlorate (Figs. 1 and 2). The dissociation constants of the indicator were calculated from the equation

$$\log \frac{\alpha_1}{1 - \alpha_1} = \mathrm{pH} - \mathrm{p}K_1 \qquad (1)$$

where α_1 is the degree of dissociation, and were verified by a graphical method[2] (from the dependence of the absorbance on pH) and by a linear regression method,[3] and were found to be $\mathrm{p}K_1 = 7{\cdot}64$; $\mathrm{p}K_2 = 11{\cdot}64$.

Applications

The indicator was found suitable for most acid-base titrations (*e.g.*, benzoic and phthalic acids dissolved in 70% ethanol, malonic, tartaric, acetic acids in water, mineral acids, *p*-hydroxybenzoic acid, titrated with sodium hydroxide) but not for phosphoric acid because of the mismatch of p*K* values for the acid and the indicator. Some results are given in Table I.

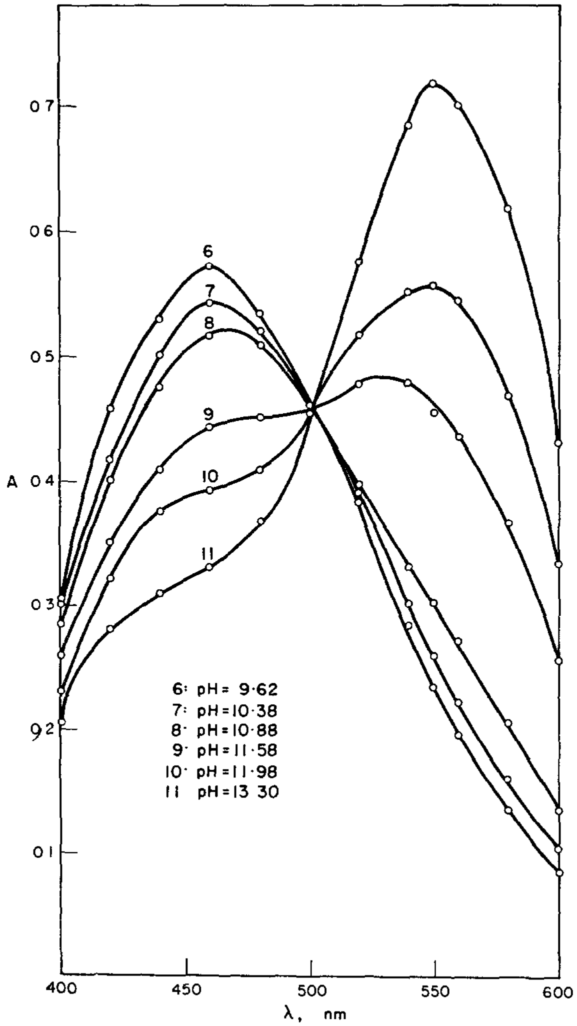


Fig. 2.—Adsorption spectra of 2·4 × $10^{-5}M$ indicator solution, pH 9·62–13·30.

TABLE I.—ACID–BASE TITRATIONS WITH THE NEW INDICATOR

Acid	0·02*M* NaOH, *ml*		Acid	0·02*M* NaOH, *ml*	
	theory	found		theory	found
Hydrochloric	7·46	7·46 7·48 7·46	Malonic	8·40	8·40 8·40 8·38
Tartaric	6·72	6·70 6·70 6·70	*p*-Hydroxybenzoic	5·66	5·68 5·68 5·66
Benzoic	4·80	4·84 4·80 4·80	Acetic	7·36	7·34 7·36 7·34
Phthalic	8·22	8·22 8·22 8·22			

In non-aqueous media, *e.g.*, acetic acid, pyridine, acetone and methanol, the indicator gave no distinct colour transition.

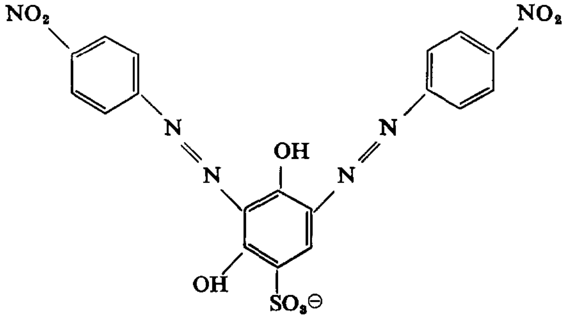
It was found experimentally that the most suitable quantity of indicator for visual titrations is 0·01–0·05 ml of 0·1% indicator solution (*i.e.*, a saturated solution) in 25 ml of titration solution.

DISCUSSION

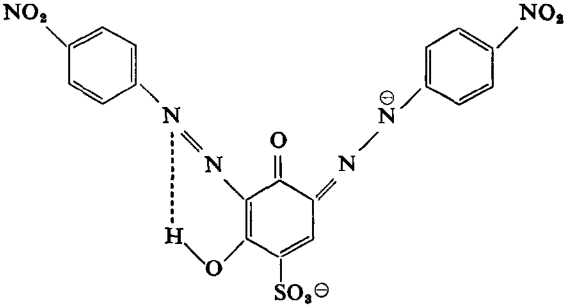
The indicator is polarographically active, giving an anodic wave, most probably because it forms a complex with mercury (a more detailed explanation will be given elsewhere), and a cathodic reduction wave, common in azo-substances.

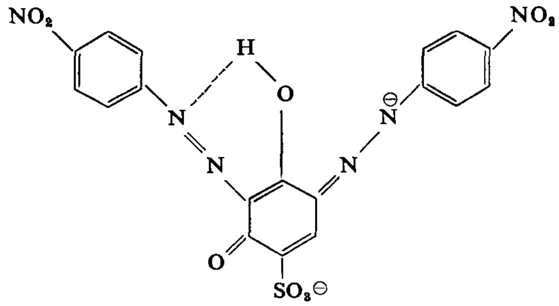
The most probable cause of the strong bathochromic shift with increasing pH is associated with the quinonoid groups. As the indicator is derived from resorcinol, the orthoquinone structure is energetically most suitable, and therefore most likely to be produced in the first dissociation, with quinone formation between the second hydroxy group and the second azo group in the second dissociation. However, the paraquinone structure cannot be completely left out of account.

An attempt to determine the structures by means of infrared spectra was unsuccessful. On the basis of common structural relationships in organic chemistry it can be supposed that in acid medium (yellow form of the indicator) the structure is:

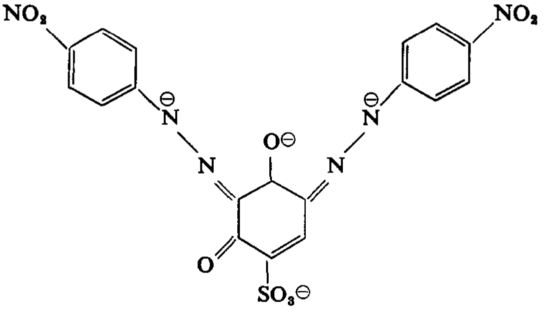


with dissociation of one proton to give the red forms:

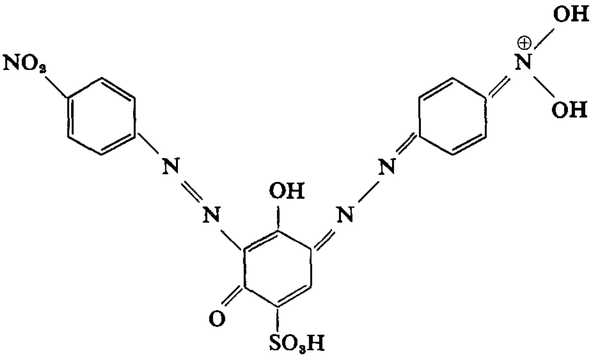




and loss of another proton in strongly alkaline medium to give the violet-red form:



In strongly acidic medium (70% sulphuric acid), a red form is produced:



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Summary—2,4-Bis(4-nitrobenzazo)resorcinol-6-sulphonic acid is suggested as a new visual acid-base indicator, which because of its colour sharpness and other qualities is useful in titrations of weak acids. There are two colour transitions, one from yellow to red at pH 6·8–8·2, the other from red to blue-violet at 10·5–13·0. The corresponding dissociation constants are pK_1 7·64, and pK_2 11·64.

Zusammenfassung—2,4 - Bis(4 - nitrobenzazo)resorcinol - 6 - sulphonic Säure wird als neue sichtbare Anzeige auf Säurengrundlage vorgeschlagen, welches wegen der Farbschärfe und anderer Eigenschaften nützlich bei Titrierung schwacher Säuren ist. Es gibt zwei Farbübergänge, einer von gelb auf rot bei pH 6,8–8,2, der andere von rot auf blau-violett bei 10,5–13,0. Die entsprechenden Dissoziationskonstanten sind pK_1 7,64, und pK_2 11,64.

Résumé—On suggère l'acide 2,4-bis(4-nitrobenzazo) résorcinol 6-sulfonique comme un nouvel indicateur visuel acide–base qui, par suite de sa netteté de coloration et d'autres qualités, est utile dans les titrages d'acides faibles. Il y a deux transitions de coloration, l'une du jaune au rouge à pH 6,8–8,2 l'autre du rouge au bleu-violet à pH 10,5–13,0. Les constantes de dissociation correspondantes sont $pK_1 = 7,64$ et $pK_2 = 11,64$.

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Silver (III) as an oxidative titrant

Determination of some sugars, carboxylic acids and inorganic ions

(*Received* 22 *May* 1969. *Accepted* 16 *October* 1969)

THE EVIDENCE for the existence of silver(III) was obtained by Jirsa[1] who made a mixed oxide of silver(II) and silver(III) by the anodic oxidation of silver(I) salts. A pure variety of silver(III) was obtained by Carmon[2] by the oxidation of silver(I) with ammonium persulphate. Subsequently stable compounds of silver(III) were obtained by complexation. Malaprade[3] complexed silver(III) with periodate and the sparingly soluble sodium diperiodatoargentate(III) $Na_7[Ag(IO_6)_2]$ was prepared. Malatesta[4] used tellurate as complexing agent for preparing a ditelluratoargentate(III) compound $Na_6H_3[Ag(TeO_6)_2]\cdot 18H_2O$. Ray[5] isolated a number of 4-co-ordinated silver(III) ethylenebiguianide (enbg) salts of the type $[Ag^{III}(enbg)_2]\cdot X_3$ where X is $\frac{1}{2}SO_4^{2-}$, NO_3^-, ClO_4^- or OH^-. In spite of the interesting behaviour of silver(III) compounds, no attempts appear to have been made for their use as oxidizing titrants and the present work is directed towards this end.

EXPERIMENTAL

Materials

All the chemicals used were of reagent grade.

Silver(III) solution. Malatesta's procedure[4] was employed with some modification for the preparation of silver(III) solution. Silver nitrate (1·36 g), potassium tellurite (3·8 g), potassium persulphate (6·5 g) and potassium hydroxide (9 g) were added to about 250 ml of water. The order of addition was not important. The mixture was shaken thoroughly and heated on a hot-plate for about 30 min. It became greenish and finally a light red solution mixed with black oxides of silver was obtained. After cooling, the black precipitate was filtered off on a porosity-4 sintered-glass crucible.

The persulphate used is just sufficient to oxidize silver(I) and tellurite to silver(III) and tellurate respectively and is therefore completely removed during boiling. If an excess of persulphate is used, boiling for a longer time is necessary for its complete decomposition. The removal of persulphate is necessary because of its interference in the oxidation of substrate compounds and in the estimation of silver(III) by the iodimetric method. The absence of persulphate in the prepared solution can be ascertained by acidifying about 1 ml of solution with dilute sulphuric acid till the red colour is completely discharged [silver(III) is then reduced to silver(I)], adding 5 ml of 0·5*M* sodium bicarbonate and 1 ml of 10% potassium iodide solution, letting stand for 2 min, then adding starch. Absence of a blue colour shows the absence of persulphate.

The prepared solution was diluted to 250 ml. The silver(III) concentration was found to be $\sim 1{\cdot}26 \times 10^{-2}M$. From the amount of silver(I) taken, the silver(III) solution should have been $3{\cdot}2 \times 10^{-2}M$. The divergence may be due to loss of silver by precipitation as oxide. The final concentration of potassium hydroxide in the prepared solution was ~0·5*M*. The solution obtained was fairly stable (for at least 3 months).

Procedure

For standardization of silver(III) solution, treat 5 ml of it with 10 ml of 0·02*M* arsenite solution, let stand for 1 min and then acidify with ~1*N* sulphuric acid till the colour disappears. Then add 5 ml of 0·5*M* sodium bicarbonate and 1 ml of 10% potassium iodide solution. Back-titrate the unconsumed arsenite with standard iodine solution (0·006*N*), using starch as indicator. Run a blank.

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The prepared solution was diluted to 250 ml. The silver(III) concentration was found to be $\sim 1{\cdot}26 \times 10^{-2}M$. From the amount of silver(I) taken, the silver(III) solution should have been $3{\cdot}2 \times 10^{-2}M$. The divergence may be due to loss of silver by precipitation as oxide. The final concentration of potassium hydroxide in the prepared solution was $\sim 0{\cdot}5M$. The solution obtained was fairly stable (for at least 3 months).

Procedure

For standardization of silver(III) solution, treat 5 ml of it with 10 ml of $0{\cdot}02M$ arsenite solution, let stand for 1 min and then acidify with $\sim 1N$ sulphuric acid till the colour disappears. Then add 5 ml of $0{\cdot}5M$ sodium bicarbonate and 1 ml of 10% potassium iodide solution. Back-titrate the unconsumed arsenite with standard iodine solution ($0{\cdot}006N$), using starch as indicator. Run a blank.

For determinations, to 25 ml of silver(III) solution add an amount of sample that will reduce less than half the silver(III) and keep it at 75–80° for the time shown in Table I. Determine the excess of silver(III) as described for standardization. If the temperature is >80° erratic results are obtained. Run a blank.

TABLE I

Sample	Amount *μmole*	Ag(III) consumed, *equiv/mole of sample*	Duration, *hr*
Glucose	1·55	23·90	4
Fructose	2·51	24·05	4
Sucrose	1·24	47·90	4
Xylose	2·26	20·13	4
Maltose	0·825	48·23	4
Lactose	1·16	48·20	4
Arabinose	1·86	20·08	4
Mannose	1·82	24·10	4
Potassium tellurite	16·1	2·01	4
Thiosulphate	5·33	8·05	½
Sulphite	14·9	2·01	1
Hydrogen peroxide	24·3	1·99	1
Chromium(III)	3·80	3·01	1
Potassium ferrocyanide	7·25	1·005	½
Sulphide	1·33	7·98	3
Tartaric acid	6·78	10·05	1
Citric acid	1·61	18·10	1
Salicylic acid	0·692	28·10	1
Ascorbic acid	1·41	20·02	1
Formic acid	16·5	2·01	1

DISCUSSION

From the results (which were reproducible within 0·5%), it is clear that the sugars and organic acids are oxidized to carbon dioxide and water by heating at 80° for an appropriate time with an excess of silver(III) solution. Arabinose and xylose, which are pentoses, require 20 equivalents of Ag(III) for complete oxidation. The hexoses such as glucose, fructose, mannose, consume 24 equivalents, whereas sucrose, maltose, and lactose require 48 equivalents. Organic acids, *viz.*, formic, tartaric, citric, ascorbic and salicylic, take 2, 10, 18, 20, 28 equivalents respectively. Inorganic compounds such as potassium hexacyanoferrate(II), sodium sulphite, hydrogen peroxide, chromium sulphate, sodium sulphide, and sodium thiosulphate require 1, 2, 2, 3, 8, 8 equivalents respectively. It shows that thiosulphate, sulphite and sulphide ions are converted into sulphate, hydrogen peroxide into water and oxygen, chromium(III) to chromium(VI) and $Fe(CN)_6^{4-}$ to $Fe(CN)_6^{3-}$. If the amount of silver(III) added is less than twice that required, complete oxidation is uncertain; this may be due to the fact that in such cases solid silver(II) oxide formed in the system oxidizes the substrate very slowly. This was found to happen with potassium tellurite, glucose, fructose, sucrose, xylose, maltose, lactose, arabinose, mannose, sodium sulphide, tartaric acid, citric acid and salicylic acid, but not with the other compounds tested. Tellurate does not interfere as an oxidant, since silver(III), being a stronger oxidant, reoxidizes any tellurite that may be formed in the reaction mixture.

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Summary—Silver(III) has been stabilized as its tellurato complex and used for the oxidation of sugars, organic acids, ferrocyanide, sulphide, peroxide and thiosulphate, the excess of oxidant being measured by reducing it with an excess of arsenite and then titrating the surplus arsenite with iodine.

Zusammenfassung—Silber(III) wurde als Telluratkomplex stabilisiert und zur Oxidation von Zuckern, organischen Säuren, Ferrocyanid, Sulfid, Peroxid und Thiosulfat verwendet. Der Überschuß an Oxidationsmittel wird mit überschüssigem Arsenit reduziert und dessen Überschuß mit Jod titriert.

Résumé—L'argent(III) a été stabilisé sous forme de son complexe tellurique et utilisé pour l'oxydation de sucres, acides organiques, ferrocyanure, sulfure, peroxyde et thiosulfate, l'excès d'oxydant étant mesuré en le réduisant avec un excès d'arsénite puis en titrant l'excès de celui-ci à l'iode.

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The volumetric determination of nitrite with chloramine T

(*Received* 1 *September* 1969. *Accepted* 15 *September* 1969)

THE METHOD most frequently used for the volumetric determination of nitrite seems to be the titration with permanganate. Disadvantages of the method are the low reaction-rate, and the decomposition and air-oxidation of the nitrous acid during the titration. As a consequence complicated procedures are often given, and the results obtained are not satisfactory.[1]

The application of chloramine T (sodium salt of *p*-toluenesulphochloramide, $CH_3C_6H_4SO_2$-NClNa . $3H_2O$) as an oxidimetric reagent has been described frequently in the literature. It is cheap, may be obtained in a rather pure state, and its solution is rather stable. Literature surveys are given by Bishop and Jennings,[2] Kolthoff and Belcher[3] and Berka, Vulterin and Zýka.[4]

The direct titration of nitrite with chloramine T has been described, but does not give satisfactory results.[4] An indirect method is possible,[3] but no detailed information seems available on the scope and limitations of the method. In this paper some information on this point is therefore given. In the procedure used, a modification of the earlier procedure,[3] the sample is oxidized to nitrate with chloramine T, then iodide is added and oxidized to iodine by the excess of the reagent, and the iodine is titrated with thiosulphate solution.

EXPERIMENTAL

Reagents

A chloramine T solution, about 0·05*M*, was prepared by dissolving as far as possible about 25 g of the reagent, filtering into a 2-litre volumetric flask, and diluting to the mark. The solution was stored in an amber bottle. A cation-exchanger, 20–50 mesh, dry capacity 4·8 mequiv/g was used.

Procedure

In a 500-ml stoppered conical flask take 25 ml of chloramine T solution (or 50 ml if more than 30 mg of nitrite are present), add the sample, dilute to about 150 ml, add 10 ml of 9*M* acetic acid and after 2 min add 10 ml of 10% potassium iodide solution. Place the flask in the dark for 5 min and titrate in the usual way with thiosulphate solution and starch indicator.

Perform a blank in the same way. From the difference in the quantities of thiosulphate added, calculate the nitrite content of the sample.

RESULTS AND DISCUSSION

Stock solutions were prepared with the products of two different manufacturers. The pH of both solutions was about 10, in agreement with Berka *et al.*[4] Bishop gives the value 7·7 however.[2] The titre of one solution decreased 0·3% in 5 weeks and 0·7% in 10 weeks, the other solution had a

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RESULTS AND DISCUSSION

Stock solutions were prepared with the products of two different manufacturers. The pH of both solutions was about 10, in agreement with Berka *et al.*[4] Bishop gives the value 7·7 however.[2] The titre of one solution decreased 0·3% in 5 weeks and 0·7% in 10 weeks, the other solution had a constant titre for 3 weeks. More stable solutions have been described in the literature.[2,4] The purities of the two chloramine T, samples, (calculated from the thiosulphate titre, standardized against iodate) were 98 and 98·5% respectively. This is in agreement with Bishop.[2]

The repeatability of the method was checked in two series of five experiments with 25 mg of nitrite. In both cases the relative standard deviation was about 0·1%.

Interferences were investigated by adding the foreign compound immediately after the sample had been added and then completing the procedure described above. The foreign compounds were added in quantities of 1,2,5,10,25,50 and 125 mg. The maximum permissible amount (error below 0·3% when 25 mg of nitrate were present) was found to be less than 1 mg for S^{2-}, NH_4^+ and SCN,$^-$ 1 mg for $Fe(CN)_6^{4-}$ 5 mg for Cu^{2+}, 50 mg for I^-, and 125 mg (or more) for Br^-, $Fe(CN)_6^{3-}$, Hg^{2+}, Pb^{2+}, and ClO_3^-.

Iodide interferes if present in too large amounts because it consumes too much chloramine T, and not enough is left for the oxidation of nitrite. Theoretically, bromide should not interfere, because the bromine formed also oxidizes nitrate.

Cu^{2+} reacts slowly with iodide $Fe(CN)_6^{4-}$, S^{2-}, NH_4^+ and SCN^- react about quantitatively with chloramine T; the reaction products do not react appreciably with iodide under the experimental conditions. Hg^{2+} and Pb^{2+} react with part of the I^-, but presumably this does not interfere with the reaction with chloramine T. ClO_3^- probably has no oxidizing properties under the experimental conditions. $Fe(CN)_6^{3-}$ possibly oxidizes nitrite to some extent, but the $Fe(CN)_6^{4-}$ formed in this way consumes an equivalent amount of chloramine T, and no error results.

It should be noted that the interfering compounds investigated had not been in contact with nitrite for a long time before the analysis was performed. If the contact had taken place for a longer time, some interfering reaction might have taken place in some cases, before the analysis itself was started. Investigations of this point have not been performed because the prevailing conditions during storage (such as pH and concentration) may considerably influence the extent to which the interfering reaction takes place.

Several attempts have been made to eliminate some of the interferences. Solutions containing NH_4^+ were boiled at high pH, but high results were obtained probably because of incomplete removal of ammonia, which consumes more reagent than nitrite does. Sodium tetraphenylborate forms an insoluble salt with NH_4^+, but the interference could not be prevented by this reaction because the reagent was found to react with chloramine T. EDTA also reacts with chloramine T and therefore the interference of copper could not be eliminated by the addition of this complexing agent.

Application of a cation-exchange column gave satisfactory results; 35 ml of a solution containing 25 mg of nitrite and variable amounts of Cu^{2+} and NH_4^+ were passed through the column (about 50 × 10 mm) into the titration flask, the column was rinsed with about 50 ml of water, and the resulting solution was diluted to 150 ml and treated as described under *Procedure*. Results of 13 experiments with 25 mg of nitrite and 10 mg of Cu^{2+} (3 experiments), 10 mg of NH^{4+} (3), 125 mg of Cu^{2+} (2), 125 mg of NH_4^+ (2), and no foreign compound (3) all gave results about 0·10 mg of nitrate low, an error of 0·4%. The error is probably caused by oxidation of nitrite by air, during the run through the column (45 min). The error was not considered serious but possibly may be further reduced if a smaller column is used.

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Summary—Nitrite may be determined by oxidation with chloramine T, reaction of the excess of chloramine T with excess KI, and titration of I_2 formed, with thiosulphate. The reproducibility and some interferences are discussed.

Zusammenfassung—Nitrit kann bestimmt werden durch Oxidation mit Chloramin T, Reaktion des überschüssigen Chloramin T mit überschüssigem KI und Titration des gebildeten I_2 mit Thiosulfat. Die Reproduzierbarkeit und einige Störungen werden diskutiert.

Résumé—On peut déterminer le nitrite par oxydation avec la chloramine T, réaction de l'excès de chloramine T avec un excès de KI et titrage de I_2 formé avec le thiosulfate. On discute de la reproductibilité et de quelques interférences.

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Exchange reactions of ternary ion-association complexes directly in the organic phase

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A NEW approach has been developed that combines the advantages of solvent extraction with the inherently high sensitivities afforded through the incorporation of large organic dye cations into ternary ion-association complexes containing the metal ion of interest. Basically, the new technique involves the formation of a complex, $[ML_x^-]R^+$, where R^+ initially is either a non-coloured or a non-fluorescent organic cation. Following extraction of $[ML_x^-]R^+$ a second cation, R_1^+, which is capable of exchanging with the first R^+ group, is added directly to the organic phase. In this instance, however, R_1^+ is purposely selected to be highly coloured or fluorescent, thereby yielding the highly coloured or fluorescent complex $[ML_x^-]R_1^+$. Unreacted R_1^+ is readily back-extracted, leaving only the dye-complex in the organic phase. In the present paper the determinations of gold and uranium are described to illustrate the advantages of the new technique.

EXPERIMENTAL

Reagents

A uranium stock solution (1·00 mg/ml) was prepared by dissolving 1·180 g of triuranium octa-oxide in 10 ml of concentrated nitric acid and diluting to 1 litre with distilled water.

A 1·00 mg/ml gold solution was prepared by dissolving 1·000 g of gold rod in 5 ml of *aqua regia*, evaporating to incipient dryness and diluting to 1 litre with 0·1*M* hydrochloric acid.

Working solutions were prepared by further dilution.

Dye solutions were prepared by dissolving 30 mg of Brilliant Green (C.I. No. 42040, bisulphate salt) or Rhodamine 6G (C.I. No. 45160, chloride salt) in 100 ml of absolute ethanol.

The following aqueous solutions were used: 1*M* ammonium thiocyanate, 0·1*M* sodium benzoate and 0·01*M* tetraphenylarsonium chloride.

Apparatus

Absorption spectra were obtained with a dual-beam recording spectrophotometer whereas measurements at a fixed wavelength were made on a single-beam instrument. Matched 10-mm absorption cells were used in all instances.

Fluorescence measurements were obtained with a single-beam, uncorrected spectrofluorometer.

Extractions were carried out in 60-ml separatory funnels equipped with all-Teflon fittings. A large, industrial-type centrifuge was used to hasten the separation of phases.

Procedures

Gold–thiocyanate system. The aqueous phase, containing ≤ 20 μg of gold(III), is made 0·02*M* in thiocyanate, 0·002*M* in tetraphenylarsonium chloride and 0·01*M* in hydrochloric acid. Following extraction with 5·00 ml of benzene for 1 min (vigorous shaking), the sample is centrifuged and the aqueous layer is discarded. Approximately 0·5 ml of alcoholic dye solution is added to the benzene fraction and mixed, and the resulting solution is back-washed with an equal volume of 0·01*N* hydrochloric acid to remove unreacted dye (30-sec shaking time is ample). The extract is then analysed either spectrophotometrically or spectrofluorometrically, depending on the choice of dye. Beer's law is obeyed over the range 1–20 μg of gold. For Brilliant Green, maximum absorbance is at 640 nm; for Rhodamine 6G the excitation maximum is 525 nm and the emission maximum is 550 nm.

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Exchange reactions of ternary ion-association complexes directly in the organic phase

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A NEW approach has been developed that combines the advantages of solvent extraction with the inherently high sensitivities afforded through the incorporation of large organic dye cations into ternary ion-association complexes containing the metal ion of interest. Basically, the new technique involves the formation of a complex, $[ML_x^-]R^+$, where R^+ initially is either a non-coloured or a non-fluorescent organic cation. Following extraction of $[ML_x^-]R^+$ a second cation, R_1^+, which is capable of exchanging with the first R^+ group, is added directly to the organic phase. In this instance, however, R_1^+ is purposely selected to be highly coloured or fluorescent, thereby yielding the highly coloured or fluorescent complex $[ML_x^-]R_1^+$. Unreacted R_1^+ is readily back-extracted, leaving only the dye-complex in the organic phase. In the present paper the determinations of gold and uranium are described to illustrate the advantages of the new technique.

EXPERIMENTAL

Reagents

A uranium stock solution (1·00 mg/ml) was prepared by dissolving 1·180 g of triuranium octaoxide in 10 ml of concentrated nitric acid and diluting to 1 litre with distilled water.

A 1·00 mg/ml gold solution was prepared by dissolving 1·000 g of gold rod in 5 ml of *aqua regia*, evaporating to incipient dryness and diluting to 1 litre with 0·1*M* hydrochloric acid.

Working solutions were prepared by further dilution.

Dye solutions were prepared by dissolving 30 mg of Brilliant Green (C.I. No. 42040, bisulphate salt) or Rhodamine 6G (C.I. No. 45160, chloride salt) in 100 ml of absolute ethanol.

The following aqueous solutions were used: 1*M* ammonium thiocyanate, 0·1*M* sodium benzoate and 0·01*M* tetraphenylarsonium chloride.

Apparatus

Absorption spectra were obtained with a dual-beam recording spectrophotometer whereas measurements at a fixed wavelength were made on a single-beam instrument. Matched 10-mm absorption cells were used in all instances.

Fluorescence measurements were obtained with a single-beam, uncorrected spectrofluorometer.

Extractions were carried out in 60-ml separatory funnels equipped with all-Teflon fittings. A large, industrial-type centrifuge was used to hasten the separation of phases.

Procedures

Gold–thiocyanate system. The aqueous phase, containing $\leq 20\ \mu g$ of gold(III), is made 0·02*M* in thiocyanate, 0·002*M* in tetraphenylarsonium chloride and 0·01*M* in hydrochloric acid. Following extraction with 5·00 ml of benzene for 1 min (vigorous shaking), the sample is centrifuged and the aqueous layer is discarded. Approximately 0·5 ml of alcoholic dye solution is added to the benzene fraction and mixed, and the resulting solution is back-washed with an equal volume of 0·01*N* hydrochloric acid to remove unreacted dye (30-sec shaking time is ample). The extract is then analysed either spectrophotometrically or spectrofluorometrically, depending on the choice of dye. Beer's law is obeyed over the range 1–20 μg of gold. For Brilliant Green, maximum absorbance is at 640 nm; for Rhodamine 6G the excitation maximum is 525 nm and the emission maximum is 550 nm.

Uranium(VI)*-benzoate system.* This is similar to the gold–thiocyanate system except that instead of being 0·02*M* in thiocyanate, the aqueous phase is 0·05*M* in sodium benzoate and has a pH in the range 2–5. There is one other significant difference. The complex, [Brilliant Green$^+$] [$UO_2(C_6H_5COO)_3^-$], decomposes with time but can be stabilized by the addition of acetone. At least 40% by volume is necessary. This composition is achieved most readily by diluting 2·00 ml of acetone, previously added to a dry 5-ml volumetric flask, to the mark with the benzene extract.

In the procedures above, the various reagent concentrations cited are not necessarily optimum values but are sufficient for demonstrating the advantages of the extraction–exchange approach. Preliminary pH studies, however, have shown that acidity definitely does not need to be closely controlled. In practice, any value in the range 2–9 is satisfactory. Above about pH 5 some difficulty may be encountered with emulsion formation.

DISCUSSION AND RESULTS

From a 0·01*M* thiocyanate solution at pH 2 thiocyanate ion can be quantitatively extracted into benzene as the binary complex [R^+] [CNS^-] with either Brilliant Green or Rhodamine 6G as the R^+ group. Consequently, in ternary complex reactions based on metal–thiocyanate–dye systems, the anion dye side-reaction can cause excessively high blank values since the R^+ group is solely responsible for the colour and/or fluorescence in both the binary and ternary complexes.

To investigate the possible advantages of the present approach in minimizing the [R^+] [CNS^-] side-reaction the gold–thiocyanate system was selected for initial study. The absorbances obtained for 10 μg of gold were 0·902, 0·884 and 0·887 for three independent determinations. Most important, however, the corresponding blank was only 0·003. If the same amount of Brilliant Green had been added directly to the 0·01*M* thiocyanate, the corresponding blank value would have been approximately 0·9, *i.e.*, approximately the same as the sample signal. Thus, instead of a sample-to-background ratio of 1:1, the exchange approach gave a ratio of about 300:1.

Attempts to extract microgram amounts of uranium(VI) as the complex, [ϕ_4As^+] [$UO_2(CNS)_3^-$,] were not as successful as the gold experiments. Although various thiocyanate concentrations up to 1*M* were investigated, the maximum net absorbance obtained for 100 μg of uranium was only about 0·3 with a corresponding blank that was also about 0·3 (for 1*M* thiocyanate), indicating that significant amounts of thiocyanate were being extracted as [ϕ_4As^+] [CNS^-] in the initial extraction and remaining in the benzene phase as [Brilliant Green$^+$] [CNS^-] following the exchange reaction. Attempts to lower the amount of binary-bound thiocyanate by back-extracting with iron(III) solutions (1 mg/ml; 10 ml taken for phase equilibration) met with moderate success. In this instance the blank was reduced from 0·3 to 0·09 with an average deviation of ±0·01 for four runs.

The formation and extraction of the red ternary complex, [Rhodamine B$^+$] [$UO_2(C_6H_5COO)_3^-$], was first reported by Feigl[1] and later used by Anderson and Hercules[2] for the quantitative determination of trace amounts of uranium. In the latter work complete extraction of uranium(VI) was obtained only when the aqueous:organic volume ratio was 1:10. In the exchange approach, however, uranium is completely extracted at aqueous:organic phase ratios of 2:1 and indications are that much larger ratios can be tolerated. As pointed out previously, the benzene extracts of the uranyl–benzoate–dye complexes are unstable and both their absorbance and fluorescence decrease rapidly with time. In the case of the Brilliant Green complex, the rate of decrease in absorbance was found to vary from about 8% per min at the 5-μg uranium level to approximately 3% per min at the 20-μg level. Stabilizing with a minimum of 40% v/v of acetone, however, yielded extracts with absorbances which were constant for several hours and decreased only about 2% overnight.

Although Růžička and Starý[3–5] have recently described the analytical implications of chelate exchange in the organic phase, apparently the present work is the first report of exchange reactions involving ternary ion-association complexes. Because much larger concentrations of intermediate ligand, L, can be utilized effectively when coupled with an exchange reaction a number of interesting and potentially useful analytical systems are now open for study. Futhermore, since the initial (tetraphenylarsonium) extraction can be carried out at a lower acidity than normally employed with the triphenylmethane and rhodamine dyes, the possibility of using masking agents to increase selectivity further is also greatly enhanced. Finally, dye purity and light-fastness appear to cause considerably fewer problems in the proposed technique and much smaller quantities of dye are needed.

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Summary—The analytical implications of exchanging a highly coloured or fluorescent group R for a non-coloured or non-fluorescent one directly in the organic phase are discussed for ternary ion association complexes of the type [ML$_x^-$]R$^+$. Several examples are given to illustrate the approach.

Zusammenfassung—Die analytischen Gesichtspunkte beim Austausch einer stark gefärbten oder fluoreszierenden Gruppe *R* in ternären Ionenassoziationskomplexen des Typs [ML_x^-]R^+ gegen eine farblose oder nicht fluoreszierende in der organischen Phase werden diskutiert. Mehrere Beispiele werden zur Erläuterung des Vorgehens angegeben.

Résumé—On discute des incidences analytiques de l'échange d'un groupe R hautement coloré ou fluorescent par un autre non coloré ou non fluorescent directement dans la phase organique pour les complexes d'association d'ions ternaires du type (ML$_x^-$]R$^+$. On donne plusieurs exemples pour illustrer cette voie.

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The structure of primary nickel dithizonate

(*Received* 18 *September* 1969. *Accepted* 18 *October* 1969)

ALTHOUGH a considerable volume of work has been published on the structure of diphenylthiocarbazone (dithizone, H_2Dz) complexes,[1,2] the crystal structures of only Hg(HDz)$_2$ and Cu(HDz)$_2$ have been determined.[3,4] Both these complexes were shown to co-ordinate through sulphur and nitrogen. Several authors have grouped the complexes according to various properties. All have concluded that the nickel, palladium and platinum compounds are unusual, and are characterized by multiple visible absorption bands,[5] a high formation constant[6] and a strong absorption band at 1220 cm^{-1} in the infrared.[7] On the basis of these results, Math, Fernando and Freiser[6] proposed that the dithizone ligand was bonded through two nitrogen atoms in the nickel complex. These workers seem to have assumed that they had a 1:1 complex; however, they used the term "octahedrally co-ordinated" in their discussion.

We have reacted nickel and dithizone at various pH values from 1 to 11 and with metal:ligand ratios from 1 to 100 without finding evidence of any complex other than Ni(HDz)$_2$, nor has a secondary complex been reported elsewhere. The visible and infrared spectra published by Math *et al.* are identical to those found for our Ni(HDz)$_2$. We have also prepared fourteen other dithizone complexes and the powder diffraction patterns of Ni(HDz)$_2$, Pd(HDz)$_2$ and Pt(HDz)$_2$ show that they are closely isostructural and, in fact, constitute the only group of isomorphs among the complexes investigated. Surprisingly it was found that Ni(HDz)$_2$ is paramagnetic, with a magnetic moment of 3·15 BM.

Recrystallization of Ni(HDz)$_2$ from chloroform yielded black needles which are triclinic, space group $P\bar{1}$; $a = 0{\cdot}462$ nm, $b = 1{\cdot}099$ nm, $c = 1{\cdot}250$ nm; $\alpha = 88{\cdot}8°$, $\beta = 97{\cdot}4°$, $\gamma = 99{\cdot}1°$; $Z = 1$, $D_0 = 1{\cdot}50$, $D_c = 1{\cdot}51$. The structure was determined from a Patterson projection down the *a* axis, and refined by observed and difference Fourier syntheses to yield $R = 0{\cdot}15$ for the 338 *0kl* data (250 observed with Ni-filtered Cu $K\alpha$ radiation).

The molecule is centrosymmetric with a planar configuration about the nickel that is essentially the same as that found for the copper complex (Fig. 1). The dithizone moiety is bonded to the nickel atom through one nitrogen and one sulphur atom and definitely not as suggested by Math *et al.*[6]

The unit cell dimensions of Ni(HDz)$_2$ are very similar to those of Cu(HDz)$_2$ but with the exception that *a* is longer (0·462 *vs.* 0·429 nm) and *c* is shorter (1·250 *vs.* 1·336 nm). This suggests that the Ni(HDz)$_2$ molecule is tilted further out of the basal plane of the unit cell than is Cu(HDz)$_2$, thus

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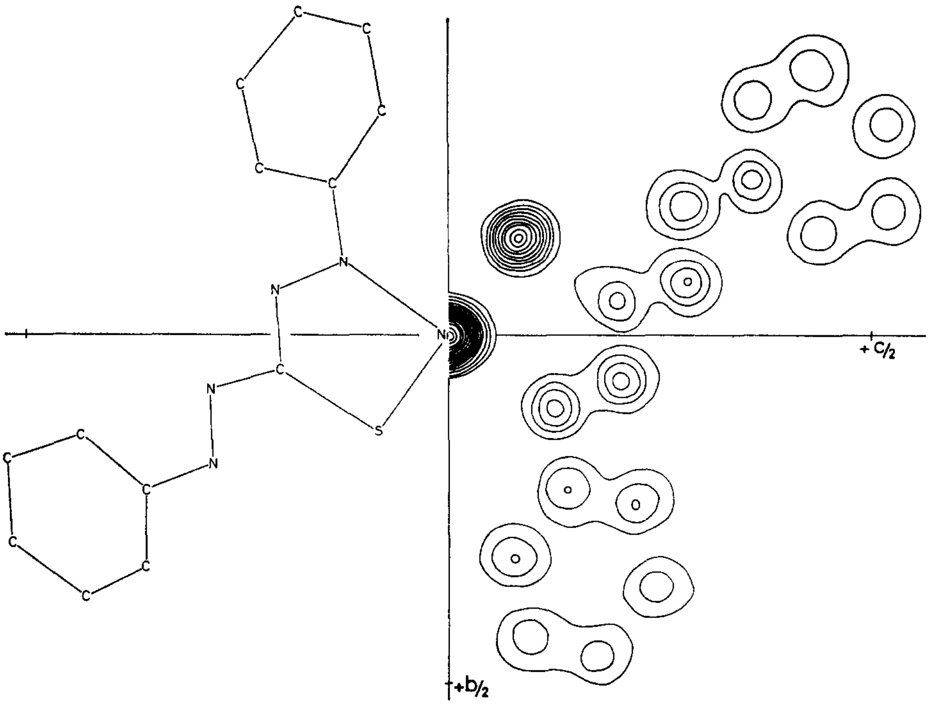

FIG. 1.—Structure of the nickel complex.

possibly allowing pseudo-octahedral co-ordination of the nickel atom with either sulphur or nitrogen atoms in the neighbouring molecules above and below it. Such a configuration would account for the paramagnetic susceptibility of the nickel complex, which cannot be explained by a simple planar arrangement.

A three-dimensional structure analysis is being done to determine in detail the co-ordination around the nickel atom. This will be reported later.

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Summary—Primary nickel dithizonate is found to be isostructural with the palladium and platinum complexes, and the nickel dithizonate molecule is shown to contain nickel in an approximately square planar configuration bonded to the organic ligand through both sulphur and nitrogen atoms.

Zusammenfassung—Primäres Nickel-Dithizonat ist isostrukturell mit den Palladium- und Platinkomplexen. Es wird gezeigt, daß das Nickeldithizonatmolekül Nickel in ungefähr quadratisch planarer Konfiguration enthält. Es ist sowohl über Schwefel als auch über Stickstoff an den organischen Liganden gebunden.

Résumé—On a trouvé que le dithizonate de nickel primaire est isostructural avec les complexes du palladium et du platine, et l'on montre que la molécule de dithizonate de nickel contient le nickel dans une configuration plane carrée approximativement, liée au coordinat organique par l'intermédiaire à la fois des atomes de soufre et d'azote.

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Determination of dicyclohexylamine in sodium cyclamate

(*Received* 8 *September* 1969. *Accepted* 26 *October* 1969)

For the past two years or so colorimetric methods for the determination of mono and dicyclohexylamine in cyclamates have been in regular use in Nobel Division of I.C.I. Ltd. That for the mono compound is the same as that of Bradford and Weston[1] except that benzene is used instead of chloroform as extractant, and considerable demand has been evident for the method used for the dicyclo compound. The method described here is a colorimetric procedure based on the use of Bromophenol Blue, but before it was chosen a number of possible techniques were explored.

The possibility of using a colorimetric procedure in which the amine is reacted with carbon disulphide to form a dithiocarbamate[2] was first examined. A yellow colour is obtained when the method is used for secondary amines, but lack of sensitivity in the microgram range precludes its use for dicyclohexylamine. Thin-layer chromatographic procedures,[3] although sensitive and useful for exploratory work, were not suitable for routine work. Likewise, gas chromatography, although useful for preparative work, is unsuitable for the many different users of cyclamate.

During a literature search for a colorimetric method appropriate for dicyclohexylamine, it was noted that Bromophenol Blue has been used as a complexing agent for the determination of cationic surfactants.[4] In the titration of sodium oleyl sulphate with cetyltrimethylammonium bromide solution, the end-point is detected by forming the complex of cetyltrimethylammonium bromide with Bromophenol Blue, which is soluble in chloroform, and it was considered that it might be possible that dicyclohexylamine would react in the same way, since dicyclohexylamine has itself been recommended as a cationic surfactant.[5] Moreover it is claimed[6] that complexes are formed by reaction of Methyl Orange with fatty amines, but the authors could not identify the complexes by infrared spectroscopy. However, the yellow colour of the complex indicated that the cationic form of the Methyl Orange predominated and hence the complex may be a salt of the cationic amine. Preliminary experiments with Methyl Orange gave inconsistent results so the Bromophenol Blue reaction was explored.

A 10-μg amount of dicyclohexylamine gave a measurable colour in the presence of excess of monocyclohexylamine in sodium cyclamate.

The method described is applicable to samples of sodium cyclamate for the determination of dicyclohexylamine down to the order of 1 ppm in the presence of as much as 600 ppm of monocyclohexylamine.

EXPERIMENTAL

Reagents

Bromophenol Blue solution. Add 0·075 g of solid Bromophenol Blue to 60 ml of water in a 100-ml beaker followed by 10 ml of 0·1*M* sodium bicarbonate and stir continuously for about 15 min until dissolution is complete. Add 0·2*M* hydrochloric acid and adjust the pH of the solution to 4·0 (pH meter). Transfer the solution to a 100-ml volumetric flask and make up to volume with water.

Acetic acid–hydrochloric acid reagent. Mix 200 ml of 1*M* hydrochloric acid with 166·6 ml of glacial acetic acid in a 1-litre volumetric flask and dilute to the mark with water.

Sodium hydroxide, 0·1*M*.

Standard dicyclohexylamine solution. Dissolve 0·5 g of dicyclohexylamine in 100 ml of chloroform. Dilute 1 ml of this solution to 200 ml with chloroform (1 ml contains 25 μg of dicyclohexylamine).

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Sodium hydroxide, 0·1*M*.

Standard dicyclohexylamine solution. Dissolve 0·5 g of dicyclohexylamine in 100 ml of chloroform. Dilute 1 ml of this solution to 200 ml with chloroform (1 ml contains 25 μg of dicyclohexylamine).

Procedure

Dissolve 10 g of the sodium cyclamate sample in 100 ml of water and transfer the solution to a separating-funnel. Add 10 ml of 0·1*M* sodium hydroxide and extract the mixture three times with 10-, 5- and 5-ml quantities of chloroform. Combine the chloroform extracts in a second separating-funnel, add 100 ml of water followed by 3 ± 0·2 ml of the acetic acid–hydrochloric acid reagent and 1 ml of the Bromophenol Blue reagent. Shake the mixture for 3 min and at the end of this time set it aside for 30 min, protecting it from sunlight.

Open the tap of the separating-funnel momentarily to disperse any entrapped water, dry the stem of the funnel with filter paper, run off the chloroform layer into a graduated flask and dilute it to 25 ml with chloroform. Entrapped water may also be removed by passing the chloroform solution through a dry filter paper. Prepare a blank in the same way, omitting only the sample. Measure the absorbance of the test solution and of the blank against chloroform in 40-mm cells at 410 nm.

Purify sodium cyclamate by making it just alkaline and then extracting with chloroform. Dissolve 10-g portions in water and add known amounts of up to 75 μg of dicyclohexylamine, dilute each solution in turn to 100 ml and carry out the test described, to obtain a calibration curve, which should be linear.

DISCUSSION

An absorbance of 0·110 was found to be equivalent to 1 ppm of dicyclohexylamine. Amounts of 3 or 6 mg of monocyclohexylamine in 10-g samples of sodium cyclamate did not interfere with the determination of 10–75 μg of dicyclohexylamine. Samples of sodium cyclamate taken from various sources were tested and found to contain from less than 1 up to 2·5 ppm of dicyclohexylamine.

Should some impurity other than dicyclohexylamine be present in the cyclamate and produce a small amount of yellow colour, the apparent amount of dicyclohexylamine found would be incorrect but it would be certain that not more than this amount of dicyclohexylamine was present.

The purity of the dicyclohexylamine used in this work was checked by testing fractions obtained by preparative gas chromatography. Traces of 5 other compounds, including monocyclohexylamine, were present but the yellow colour due to the Bromophenol Blue was only obtained from the fraction corresponding to the dicyclohexylamine peak.

The conditions for the preparation of the dicyclohexylamine fraction were as follows.

Column	6 m × 13 mm
Stationary phase	SE 30 (30% on Chromosorb W)
Column temperature	250°
Nitrogen flow-rate	300 ml/min
Amount of commercial dicyclohexylamine	50-μl portions injected at repeated intervals

Thin-layer chromatography (TLC) can be used as an alternative method for the separation and determination of small amounts of dicyclohexylamine. A known weight (about 10 g) of sodium cyclamate is dissolved in 100 ml of water and, after being made alkaline, the solution is extracted four times with 10-, 5-, 5- and 5-ml quantities of chloroform. The combined chloroform extracts are evaporated to 0·5 ml in a specially designed graduated tube, at room temperature, by means of a jet of air. With a Hamilton syringe 0·05 ml of the solution is applied as a single spot on a Kieselgel G thin-layer plate. Standards (0·05 ml of chloroform containing 2·5–10 μg of dicyclohexylamine) are put on the plate at the same time. The chromatogram was developed with a mixture of ammonia, acetone and petroleum ether (b.p. 40–60°) (17:833:400). After development, the plate is sprayed with a 1:1 mixture of 0·1*N* iodine and 10% sulphuric acid and the size of the spots compared. It is easy to differentiate between 25-, 50-, 75- and 100-μg amounts of dicyclohexylamine added to 10-g amounts of sodium cyclamate dissolved in 100 ml of water. Samples of sodium cyclamate, when tested by this method, gave results comparable to those obtained by the colorimetric procedure, but we would not recommend a TLC procedure for routine work, because it is more time-consuming and less suited to plant control work than the relatively simple colorimetric method.

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Summary—Dicyclohexylamine is determined in sodium cyclamate at levels of concentration down to the order of 1 ppm by measurement of the yellow colour of the chloroform extract of its Bromophenol Blue complex.

Zusammenfassung—Dicyclohexylamin wird in Mengen bis herunter zu 1 ppm in Natriumcyclamat durch Messung der gelben Farbe des Chloroformextraktes seines Komplexes mit Bromphenolblau bestimmt.

Résumé—On dose la dicyclohexylamine dans le cyclamate de sodium à des niveaux de concentration descendant jusqu'à l'ordre de 1 ppm par mesure de la coloration jaune de l'extrait chloroformique de son complexe avec le Bleu de Bromophénol.

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Coulometrische Titration von Hypochloriten und Chloraten

(*Eingegangen am* 14. *Oktober* 1968. *Revidiert am* 29. *September* 1969. *Angenommen am* 15. *Oktober* 1969)

HYPOCHLORIT und Chlorat wurden coulometrisch bei Generator-stromstärken von 0,2 bis 100 mA titriert. Die Messungen fanden in einer offenen "H-Zelle" statt. Der Meßraum hatte ein Volumen von 100 ml. Als Hilfselektrode diente ein Platinblech in 1*N* Natriumsulfatlösung. Die Elektrodenräume waren durch eine Salzbrücke aus Gelatine/1*N* Naturiumsulfatlösung getrennt. Die Endpunkte wurden biamperometrisch an einem Platin-Drahtpaar bzw. amperometrisch an einer rotierenden Platinelektrode indiziert. Der Meßraum wurde mit einem Magnetrührer gerührt.

Bestimmung von Hypochlorit

Elektrolyt. Eisen(III) sulfat, 0,1*M*; Natriumacetat, 1*M*; pH-Wert auf 4,3 bis 4,7 eingestellt.

Die Generatorkathode war eine Platindrahtspirale mit einer Oberfläche von *ca.* 600 mm^2. Die Potentialdifferenz zwischen den Indikatorelektroden für biamperometrische Indikation betrug 700 mV.

Die Elektrolytlösung (30 bis 50 ml) wird vor und während der Messung mit Stickstoff gespült. Nach Einschalten des Generatorstroms wird bei laufender Registrierung des Indikationsstroms die Probe zugegeben. Die biamperometrische Indikation ergibt am Endpunkt ein scharfes Minimum.

Sehr kleine Konzentrationen werden besser nach dem indirekten amperometrischen Verfahren von Christian[1] bestimmt. Die Probe wird zu überschüssigem Eisen(II) gegeben und der Gehalt aus dem Anstieg der Indikationskurve ermittelt.

Chlorverflüchtigung aus der Lösung ist vermeidbar, wenn vor Probezugabe bereits soviel Eisen(II) erzeugt wurde, daß nur ein kleiner Rest von Hypochlorit austitriert werden muß.

Chloride, Perchlorate, Chlorate und Sulfate in sehr hoher Konzentration sowie Nitrate in max. zehnfachem Überschuß stören die Bestimmung nicht. Chlorite werden mittitriert.

Probebestimmungen wurden mit Natriumhypochloritlösung[2] ausgeführt, deren Gehalt durch Titration mit Arsenit[3] kontrolliert wurde.

TABELLE I.—BESTIMMUNG VON HYPOCHLORIT

Einwaage, *μMol*	Durchschnittsergebnis von *n* Bestimmungen, *μMol*	Strom, *mA*	*n*	Fehler, %
93,6	93,2	28,66	4	−0,4
17,61	17,58	4,64	11	−0,2
9,084	9,093	2,50	11	+0,1
1,018	1,021	0,266	4	+0,3
0,2119	0,2119	0,265	5	0,0*
0,1033	0,1021	0,247	5	+1,2*

* Indirekte amperometrische Bestimmung.[1]

Zusammenfassung—Dicyclohexylamin wird in Mengen bis herunter zu 1 ppm in Natriumcyclamat durch Messung der gelben Farbe des Chloroformextraktes seines Komplexes mit Bromphenolblau bestimmt.

Résumé—On dose la dicyclohexylamine dans le cyclamate de sodium à des niveaux de concentration descendant jusqu'à l'ordre de 1 ppm par mesure de la coloration jaune de l'extrait chloroformique de son complexe avec le Bleu de Bromophénol.

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Die Generatorkathode war eine Platindrahtspirale mit einer Oberfläche von *ca.* 600 mm^2. Die Potentialdifferenz zwischen den Indikatorelektroden für biamperometrische Indikation betrug 700 mV.

Die Elektrolytlösung (30 bis 50 ml) wird vor und während der Messung mit Stickstoff gespült. Nach Einschalten des Generatorstroms wird bei laufender Registrierung des Indikationsstroms die Probe zugegeben. Die biamperometrische Indikation ergibt am Endpunkt ein scharfes Minimum.

Sehr kleine Konzentrationen werden besser nach dem indirekten amperometrischen Verfahren von Christian[1] bestimmt. Die Probe wird zu überschüssigem Eisen(II) gegeben und der Gehalt aus dem Anstieg der Indikationskurve ermittelt.

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Chloride, Perchlorate, Chlorate und Sulfate in sehr hoher Konzentration sowie Nitrate in max. zehnfachem Überschuß stören die Bestimmung nicht. Chlorite werden mittitriert.

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0,2119	0,2119	0,265	5	0,0*
0,1033	0,1021	0,247	5	+1,2*

* Indirekte amperometrische Bestimmung.[1]

Bestimmung von Chlorat

Elektrolyt. Titantetrachlorid, 0·1*M*; Kaliumrhodanid, 0·08*M*; Salzsäure, 2*M*. Die Generatorkathode war eine nach Slovák und Přibyl[4] präparierte Kupferamalgamelektrode mit einer Oberfläche um *ca.* 1400 mm^2. Zur Indikation diente eine auf +25 mV gegen SCE polarisierte rotierende Platinelektrode. Diese Elektrode bestand aus einem Platindraht, der in das Ende eines L-förmig gebogenen Glasrohrs eingeschmolzen war. Sie rotierte mit 1000 Umdrehungen pro Minute und diente gleichzeitig zum Rühren der Lösung.

Unter strömendem Stickstoff wird bei laufender Registrierung des Indikationsstroms Titan(III) erzeugt (Indikationsstrom steigt linear an), bis die Titan(III)- Konzentration mindestens äquivalent der zu erwartenden Probemenge an Chlorat ist. Danach wird die Probe ohne Stromunterbrechung zugegeben und weiter elektrolysiert, bis der Indikationsstrom erneut linear ansteigt, nachdem er zunächst stark abgesunken war. Die Zeitdifferenz der linearen Kurventeile ergibt den Gehalt an Chlorat. Das Absinken des Indikationsstromes rührt von der Bildung von Hypochlorit während der Messung her. Ammoniumsalze, Chloride, Perchlorate und Sulfate stören die Bestimmung nicht. Probebestimmungen wurden mit gereinigtem und getrocknetem Natriumchlorat ausgeführt.

TABELLE II.—BESTIMMUNG VON CHLORAT

Einwaage, *μMol*	Durchschnittsergebnis von *n* Bestimmungen, *μMol*	Strom, *mA*	*n*	Fehler, %
1243,0	1243,1	100,0	4	+0,09
235,4	235,6	28,9	6	+0,08
46,88	47,29	28,9	4	+0,85
11,453	11,453	11,1	4	0,0
1,395	1,385	1,43	4	+0,7

Zur Analyse von Gemischen kann in einer ersten Probe Hypochlorit bestimmt werden. In einer weiteren Probe wird Chlorat bestimmt, nachdem zuvor Hypochlorit durch Kochen mit Wasserstoff peroxid in alkalischer Lösung ausgetrieben worden ist. In einer dritten Probe können Verunreinigungen, die mit Titan(III) reduzierbar sind, bestimmt werden, indem man vorher alle oxydierenden Chlorverbindungen durch Kochen mit konz. HCl in Chlor umwandelt und mit Luft austreibt.

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Summary—Hypochlorite was determined by direct coulometric titration with iron(II) in an acetate buffered solution. Chlorate was titrated with titanium(III) in 2*M* hydrochloric acid. Amperometric indication with one and two electrodes, respectively, was used. Mixtures of hypochlorites and chlorates, *e.g.*, in industrial electrolytes, may be analysed.

Zusammenfassung—Hypochlorit wurde durch direkte coulometrische Titration mit Eisen(II) in acetathaltiger Lösung bestimmt. Chlorat kann mit Titan(III) in 2*M* salzsäure coulometrisch titriert werden. Die Äquivalenzpunkte wurden durch amperometrisch Indikation mit einer bzw. mit zwei polarisierten Elektroden angezeigt. Hypochlorit und Chlorat können in Mischungen z.B. in technischen Elektrolyselaugen, bestimmt werden.

Résumé—On a déterminé l'hypochlorite par titrage coulométrique direct avec le fer(II) dans une solution tamponnée à l'acétate. On a titré le chlorate avec le titane(III) en acide chlorhydrique 2*M*. On a utilisé l'indication ampérométrique une et deux électrodes respectivement. On peut analyser des mélanges d'hypochlorites et de chlorates, par exemple dans des électrolytes industriels.

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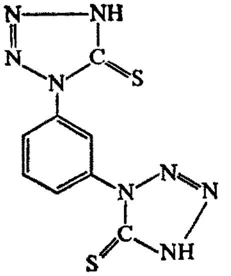
Analytical applications of *m*- and *p*-phenylene-di(1-tetrazoline-5-thione)

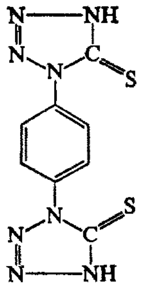
Gravimetric determination of ruthenium(III) in presence of large amounts of rhodium(III)

(*Received* 1 *July* 1969. *Accepted* 19 *September* 1969)

FOLLOWING the introduction of certain monofunctional 1-substituted tetrazoline-5-thiones as gravimetric reagents for metals,[1–3] a difunctional compound, *p*-phenylene-di(l-tetrazoline-5-thione) (PDT-5) was also successfully used in the determination of silver[4] and copper.[5] The present communication describes the use of PDT-5 and its isomer, *m*-phenylene-di(l-tetrazoline-5-thione) (MDT-5) in the gravimetric determination of ruthenium(III). Studies have indicated that both reagents can be applied to the determination of ruthenium in the presence of many cations and anions. Since there are few good weighing forms for ruthenium, the high sensitivity of its precipitation with PDT-5 and MDT-5 is promising. The novelty of the method lies in the fact that even large amounts of rhodium(III) do not interfere. The reagents, in acetone solution, when treated with solutions of ruthenium(III), give an intensely green precipitate (at pH 5·5–7·0), whereas no reaction is observed under identical conditions (or at low pH) with solutions of rhodium(III). The precipitates were found to contain a 1:1 mole ratio of ruthenium to PDT-5 or MDT-5 and can be easily dried at 110–115° or in a vacuum desiccator (after washing with acetone or alcohol).



MDT-5



PDT-5

EXPERIMENTAL

Reagents

Standard ruthenium(III) solution. A 0·25% w/v solution of hydrated ruthenium(III) chloride in water, standardized by the method of Gilchrist and Wichers.[6]

m- *and* p-*phenylene-di*(1-*tetrazoline-5-thione*). Prepared by the method described by Lieber and Slutkin,[7] and used as 2% w/v solutions in acetone.

Rhodium(III) chloride solutions. Standardized by the thionalide method.[8]

Qualitative tests

About 5 ml of the metal ion solution containing 0·5–5 mg of the metal ion were mixed with the acetone solution of the reagent. The reactions at room temperature and after heating for a few minutes on the water-bath were noted, the pH range used being 4–7. Ca, Sr, Ba, Zn, Mg, Co(II), Ni, Fe(II), Mn(II), Sn(II), Sn(IV), Be, Ce(III), Ce(IV), Rh(III), Ga(III), In(III), Sm(III), Eu(III), Yt, Al, As(III), Sb(III), Cr(III), Th, Ti(IV), Zr, Nb(V), Gd(V), V(IV), U(VI), MoO_4^{2-} WO_4^{2-} VO_3^- gave no reaction. Ag, Tl(I), Cd, Hg(I), Hg(II) and Pb gave white precipitates; Cu(II) green; Ru(III) intense green; Fe(III) brown; Pd(II) reddish-brown; Bi yellow; Ir(IV) violet. Au(III) (brown) and Pt(IV) (red) gave precipitates only after long heating (50–60 min) and cooling for a few hours. Thus the number of interfering ions in the determination of ruthenium is limited.

Procedure for the determination of ruthenium

A known volume (1–20 ml) of the ruthenium(III) chloride solution (containing 1–100 mg of Ru) was diluted with distilled water to 60–70 ml. The pH of the solution was adjusted to 5·0–6·5 (but not >7·0),* 2% acetone solution of PDT-5 or MDT-5 was added (2 ml for each mg of Ru). The mixture was stirred slowly, and heated at 90–95° on the water-bath for 3–5 min. An intensely green (appearing black) precipitate of the ruthenium(III) complex was obtained. (Precipitation does not ensue at room temperature, hence heating of the solution is essential.) The precipitate was allowed to settle at room temperature for 15 min, and then filtered off on a medium porosity sintered-glass crucible. It was washed first with distilled water and then with a little acetone or alcohol, and finally dried at 115° to constant weight (~45 min). The precipitate was weighed as $Ru(C_8H_4N_8S_2)Cl$. The gravimetric factor for ruthenium is 0·2444. The results are shown in Table I.

TABLE I.—DETERMINATION OF RUTHENIUM(III) WITH MDT-5 AND PDT-5 IN PRESENCE AND ABSENCE OF RHODIUM(III)

	MDT-5			PDT-5		
Ru taken, *mg*	Ru found, *mg*	Rh added, *mg*	Ru found, *mg*	Ru found, *mg*	Rh added, *mg*	Ru found, *mg*
0·50	0·50			0·51		
	0·49			0·50		
	0·50			0·50		
1·00	0·99	1·0	1·01			
	0·99		1·00			
	0·98		1·00			
5·00	5·00	10·0	5·00	5·01	25·0	5·00
	4·98		5·01	5·00		5·01
	4·98		5·01	5·00		5·00
10·01	$10{\cdot}0_8$					
	$10{\cdot}0_1$					
	$10{\cdot}0_6$					
25·02	$25{\cdot}1_0$	100·0	$25{\cdot}1_0$	$24{\cdot}9_5$	200·0	$25{\cdot}0_7$
	$25{\cdot}1_8$		$25{\cdot}1_8$	$24{\cdot}9_8$		$25{\cdot}1_2$
	$25{\cdot}1_1$		$25{\cdot}2_0$	$25{\cdot}0_1$		$25{\cdot}1_1$
50·05	49·9	200·0	50·3	50·0	500·0	50·1
	49·9		50·4	50·0		50·4
	50·0		50·6	50·0		50·5
75·1				75·6		
				75·3		
				76·0		
100·1	99·9			99·6		
	100·0			99·0		
	99·0			99·4		

Experimental conditions

No co-precipitation of reagent was found, even with 100-fold excess present. The complexes of ruthenium(III) with MDT-5 and PDT-5 are non-crystalline, and thermally stable up to 145°. Their solubility, at various levels of pH and temperature, was determined in the usual way, and the results are shown in Table II. Both complexes are practically insoluble in water, dilute acids and alkalis, and most organic solvents.

Extent of co-precipitation of rhodium

A part of the precipitates obtained in the presence of rhodium(III) was decomposed by heating to dryness with 10 ml of *aqua regia*, and the residue taken up in very dilute hydrochloric acid and tested for rhodium with *m*-phenylenediamine,[11] methylaniline,[11] and thioanalide.[12] A feeble positive test was obtained with the first reagent and negatives with the other two, showing that the amount

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* At low pH (< 4·0), a small amount of the water-insoluble acid form of the reagents may be precipitated, and admixed with the precipitate. At pH > 7·0, a partial decomposition of the ruthenium precipitates is likely to take place.

TABLE II.—SOLUBILITY OF RUTHENIUM(III) COMPLEXES IN WATER

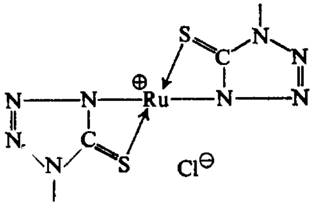
Temperature, °C	pH	Solubility, *mg/l.*	
		Ru(PDT-5)Cl	Ru(MDT-5)Cl
25	4·0	4·0	3·0
	5·5	2·0	1·0
	7·0	0·1	0·1
50	4·0	5·0	5·0
	5·5	2·0	3·0
	7·0	1·0	2·0
100	4·0	5·0	6·0
	5·5	4·0	5·0
	7·0	3·0	3·0

of rhodium co-precipitated with ruthenium is very small. The recovery of ruthenium in the presence of rhodium is shown in Table I.

Composition and structure of the ruthenium(III) precipitates

Microanalysis shows the metal:ligand ratio as 1:1; the complexes have the empirical formula $Ru(C_8H_4N_8S_2)Cl$. Found: Ru (MDT-5)Cl; Ru, 24·0%, C, 23·5%, H, 1·0%, N, 26·9%, Cl, 8·5%: Ru(PDT-5); Ru, 23·8%, C, 23·4%, H, 1·1%, N, 27·0%, Cl, 8·5%: required: Ru 24·4%, C 23·2%, H 0·9%, N 27·1%, Cl 8·6%.

The elemental analysis, infrared and reflectance data, and magnetic moment measurements have indicated[9,10] that the reaction of ruthenium with MDT-5 and PDT-5 results in the formation of polymeric internal complexes of the type.



Interferences

There is generally no interference by the common anions (Table III). Only a few cations interfere; these include Ag, Cu(II), Hg(I), Hg(II), Pb, Cd, Fe(III), Bi, Pd(II), Pt(IV), Au(III), and Ir(IV). In the precipitation of metal ions with MDT-5 and PDT-5, the control of pH of the solution was found to be an important factor. Below pH 4·0, the water-insoluble acid form of the reagents was

TABLE III.—RUTHENIUM(III) PRECIPITATION WITH PDT-5 AND MDT-5 IN PRESENCE OF CERTAIN COMMON ANIONS

Added, *mg*					Ruthenium, *mg*		
NO_3^-	SO_4^{2-}	PO_4^{3-}	Br^-	I^-	Added	Recovered (with PDT-5)	Recovered (with MDT-5)
10·0	10·0	—	—	—	5·0	5·0	5·0
50·0	50·0	—	—	—	5·0	5·0	5·0
—	—	10·0	—	—	5·0	5·0	5·0
—	—	50·0	—	—	25·0	25·0	25·1
—	—	—	10·0	10·0	25·0	25·0	25·1
—	—	—	100·0	100·0	25·0	25·0	25·1
10·0	10·0	10·0	10·0	10·0	25·0	25·1	25·1
50·0	50·0	50·0	50·0	50·0	25·0	25·1	25·1

partially regenerated, and in very basic solutions, an apparent decomposition of the reagents and the complexes took place, and in consequence, the precipitates were found to be mixed with a little sulphide.

DISCUSSION

The precision was fair, and the accuracy was generally within the permissible limits. The data given in Table I indicates that PDT-5 gave the best results. A single determination generally takes not more than 90 min. The favourable conversion factor is an advantage and gives high sensitivity.

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Summary—A simple and rapid method is described for the gravimetric determination of ruthenium(III) with two new isomeric reagents, *m*- and *p*-phenylene-di(1-tetrazoline-5-thione). Solutions containing milligram amounts of ruthenium(III) on treatment with the acetone or alcohol solutions of the reagents at pH 5·5–7·0 give a quantitative yield of an intensely green insoluble 1:1 complex which can be easily filtered off and dried at 110–115°. Amounts of ruthenium down to 0·5 mg can be determined with fairly good accuracy and precision. Even large amounts of rhodium do not cause any interference. The following cations interfere: Pd(II), Pt(IV), Au(III), Ir(IV), Bi, Fe(III), Cu(II), Hg(I), Hg(II), Pb, Cd, Tl(I) and Ag.

Zusammenfassung—Eine einfache und schnelle Methode zur gravimetrischen Bestimmung von Ruthenium(III) wird beschrieben. Sie bedient sich zweier neuer isomerer Reagentien, *m*- und *p*-Phenylendi (1-tetrazolin-5-thion). Milligrammengen Ruthenium(III) enthaltende Lösungen geben bei Zugabe der Reagentien in Aceton oder Alkohol bei pH 5,5–7,0 in quantitativer Ausbeute intensiv grünen unlöslichen 1:1-Komplex, der leicht abfiltriert und bei 110–115° getrocknet werden kann. Rutheniummengen bis herunter zu 0,5 mg können mit ziemlich guter Genauigkeit und Richtigkeit bestimmt werden. Selbst große Mengen Rhodium stören nicht. Folgende Kationen stören: Pd(II), Pt(IV), Au(III), Ir(IV), Bi, Fe(III), Cu(II), Hg(I), Hg(II), Pb, Cd, Tl(I) und Ag.

Résumé—On décrit une méthode simple et rapide pour la détermination gravimétrique du ruthénium(III) avec deux nouveaux réactifs isomères, les *m* et *p*-phénylène di(1-tétrazoline 5-thione). Des solutions contenant des quantités de ruthénium(III) de l'ordre du milligramme, par traitement avec les solutions acétoniques ou alcooliques des réactifs à pH 5,5–7,0 donnent un rendement quantitatif d'un complexe insoluble 1:1 intensément vert, que l'on peut aisément séparer par filtration et sécher à 110–115.° Des quantités de ruthénium descendant jusqu'à 0,5 mg peuvent être déterminées avec d'assez bonnes exactitude et précision. Même de grandes quantités de rhodium ne causent pas d'interférence. Les cations suivants interfèrent: Pd(II), Pt(IV), Au(III), Ir(IV), Bi, Fe(III), Cu(II), Hg(I), Hg(II), Pb, Cd, Tl(I) et Ag.

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LETTER TO THE EDITOR

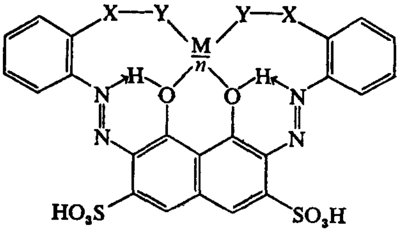
Trivial names of the most important derivatives of 3,6-bis(arylazo)-4,5-dihydroxy-2,7-naphthalenedisulphonic acid

SIR,

Recently[1] a nomenclature for reagents of the type of arsenazo III, *i.e.*, 3,6-bis(*o*-arsonophenylazo)-4,5-dihydroxy-2,7-naphthalenedisulphonic acid, was suggested. Unfortunately, this suggestion is not based on the international nomenclature. The first exception is the use of the name "arsenazo" for traditional reasons. Less understandable is the use of orthanilic S for 3,6-bis(*o*-sulphophenylazo)-4,6-dihydroxy-2,7-naphthalenedisulphonic acid, sulphochlorophenol S for 3,6-bis(5′-chloro-2′-hydroxy-3′-sulphophenylazo)-4,5-dihydroxy-2,7-naphthalenedisulphonic acid, orthanilic K for 3-(*o*-carboxyphenylazo)-6-(*o*-sulphophenylazo)-4,5-dihydroxy-2,7-naphthalenedisulphonic acid, and antipyrine M for 3-(2′-antipyrinylazo)-6-(*m*-sulphophenylazo)-4,5-dihydroxy-2,7-naphthalenedisulphonic acid.

One can agree with the author that it is not necessary to look for names for reagents which are less prominent in analytical chemistry. However, selection should be made more drastically.

It is well known that in the case of 3,6-bis(phenylazo)-4,5-dihydroxy-2,7-naphthalenedisulphonic acid the *ortho* substituent of the benzene rings is the most important carrier of selectivity and sensitivity of reagents. From this point of view, the reagents which are able to form complexes of the type *A* should be differentiated from all other azo derivatives of chromotropic acid. Undoubtedly they are reagents of unusual quality, for which the use of a trivial name is quite reasonable. The name "azo", either with or without the suffix III (I recommend III to prevent any confusion with existing names), should be kept for 3,6-bis(phenylazo)-4,5-dihydroxy-2,7-naphthalenedisulphonic acid because of tradition. The prefix of this name should contain the name of the benzene *ortho*-substituent, for reasons which are quite clear. Experience with reagents which are able to form complexes of type *A* shows very clearly that only the totally symmetric reagents are the most important. The names following from these conditions are listed in Table I.



$1 \leq n \leq 2$

A

TABLE I.—TRIVIAL NAMES OF SEVERAL REAGENTS

Name	phenyl substituents
sulphonazo III	*o*-sulpho
methylsulphonazo III	*p*-methyl-*o*-sulpho
phosphonazo III	*o*-phosphono
chlorophosphonazo III	*p*-chloro-*o*-phosphono
arsonazo III	*o*-arsono
aminomethylazo III*	*o*-[bis(carboxymethyl)aminomethyl]

* The use of the prefix "bis(carboxymethyl)" is not necessary because it is less important for complex formation.

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Editorial note. This system sometimes gives the same results as Savvin's, sometimes not. Once a name has been coined by the discoverer of a reagent, there is no excuse for inventing another name for it in subsequent work by others. It is this behaviour (made worse by development of trade-names) that leads to confusion. This correspondence is now closed.

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ATOMIC-FLUORESCENCE SPECTROSCOPY OF LEAD

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Summary—The fluorescence spectrum of lead excited with a high-intensity hollow-cathode lamp has been investigated and the probable mechanism of fluorescence transitions is suggested. It is confirmed experimentally that the most intense fluorescence line at 405·78 nm is mostly due to direct-line fluorescence. The premixed air–hydrogen flame, the separated air–acetylene flame, and the oxy-hydrogen flame diluted with argon have been used, the last mentioned giving a detection limit of 0·02 ppm with the line at 405·78 nm.

THE DETERMINATION of lead by atomic-fluorescence spectroscopy has already been reported by several authors, who have used either continuous excitation sources[1–3] or line excitation sources.[3–8] The best detection limit of 0·0035 ppm was obtained by Massmann,[6] who used a special hollow-cathode lamp as source, and evaporated the sample in an electrically heated graphite in an argon atmosphere.

In this study, a lead high-intensity hollow-cathode lamp of the Sullivan-Walsh design[9] was used as a fluorescence excitation source. This type of lamp has recently been used successfully for the atomic-fluorescence determination of silver,[10] beryllium,[11] arsenic,[5] copper,[5] magnesium,[12] iron,[5,13] cobalt[5,13] and nickel.[5,13,14] Atomic fluorescence of lead excited with a high-intensity hollow-cathode lamp was mentioned very briefly by Manning and Heneage.[5]

This paper reports the detailed investigation of the complete fluorescence spectrum of lead excited by a high-intensity hollow-cathode lamp and the determination of lead by atomic-fluorescence spectrophotometry in various premixed flames.

EXPERIMENTAL

Apparatus

A Techtron AA-4 atomic-absorption spectrophotometer equipped with a lead high-intensity hollow-cathode lamp and ultraviolet-sensitive HTV R 106 photomultiplier was coupled to a Hitachi Perkin–Elmer Model 165 recorder. The lamp and detector were square-wave modulated at 285 Hz. The instrument was adapted for fluorescence measurements in practically the same manner as described in our previous paper.[13] The optical arrangement is shown diagrammatically in Fig. 1. The mirror in the optical path of the exciting beam increased the fluorescence emission by 100%, but the mirror in the optical path of the fluorescence radiation enhanced the signal by only 70%, and also increased the background emission of the flame, and was not always found to be advantageous. The instrumental settings were adjusted to the maximum values:[13] primary lamp current, 15 mA; booster current, 300 mA; slit-width, 300 μm (band-width 0·99 nm).

Reagents

A stock lead solution was prepared by dissolving 1·000 g of spectrally pure metal in nitric acid (1 + 1) and diluting to 1000 ml with twice distilled water. More dilute solutions were prepared with the same concentration of nitric acid. All other solutions were prepared from reagent-grade chemicals.

Flame conditions

An air–hydrogen flame, an oxy-hydrogen flame diluted with argon, and a separated air–acetylene flame were used. The Techtron FE-1 emission burner head for the air–acetylene flame was fitted with a chamber with five concentric rows of holes and tangential nitrogen inlet to facilitate separation of the flame[15] (Fig. 2). For the air–hydrogen and hydrogen–oxygen–argon flames, a specially manufactured Meker-type brass burner head with 97 holes 0·5 mm diameter was also fitted with the chamber described.

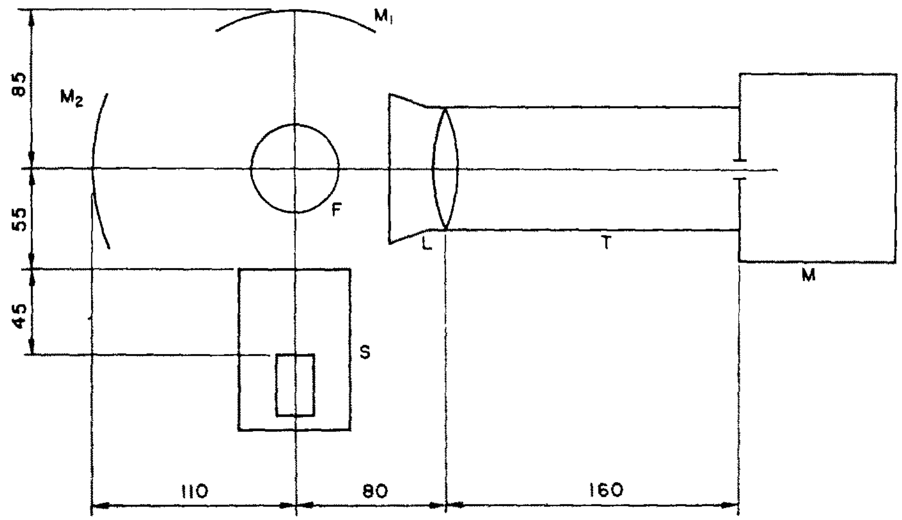

FIG. 1.—Optical arrangement for atomic-fluorescence measurements.
S—excitation source M_1, M_2—mirrors
F—flame T—selective radiation gathering tube
L—condensing lens M—monochromator

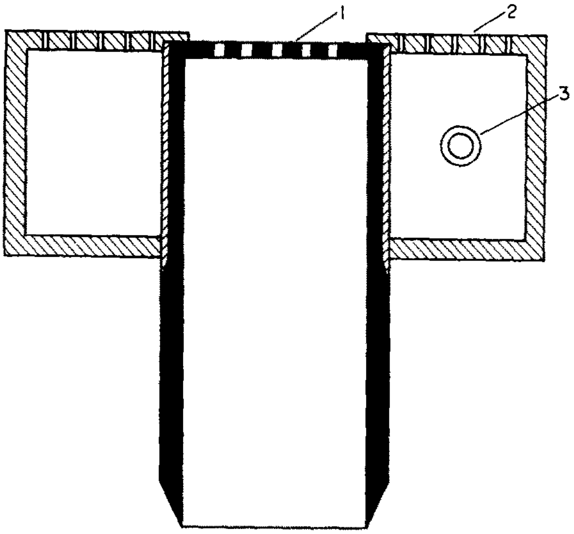

FIG. 2.—Burner for a nitrogen-separated air–acetylene flame.
(1) Burner head, (2) chamber, (3) nitrogen inlet

The dependence of background emission of the flames and of the fluorescence signal on the fuel to oxidant ratio was investigated to find the optimum gas flow-rates. From Fig. 3 it is apparent that the fluorescence signal in the hydrogen–oxygen–argon flame at a given oxygen flow-rate is strongly dependent on the hydrogen flow-rate, whereas the fluorescence signal in the air–hydrogen flame is practically independent of the hydrogen flow-rate. For the separated air–acetylene flame, the dependence of the fluorescence signal on the acetylene flow-rate exhibits a flat maximum. The resulting optimum gas flow-rates are listed in Table I.

The height of measurement in the flame was not critical, but to avoid emission from the primary reaction zone, the measurements on all flames were taken at 15–25 mm above the burner top.

The solution uptake rate was set to 4·7 ml/min for the air–hydrogen and hydrogen–oxygen–argon flame, and to 5·2 ml/min for the air–acetylene flame.

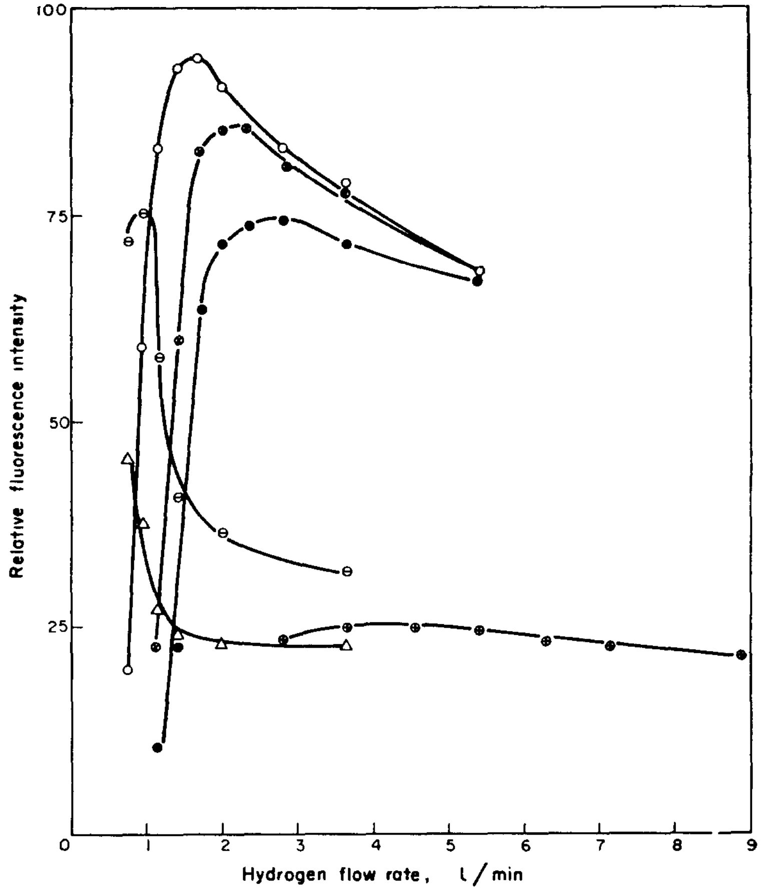

FIG. 3.—Variation of relative fluorescence intensity for lead at 405·78 nm in air-hydrogen, argon-hydrogen, and hydrogen-oxygen-argon flames.

⊕—air-hydrogen

△—argon-hydrogen

hydrogen-oxygen-argon, oxygen flow

⊖—0·10 l./min

○—0·35 l./min

⊗—0·65 l./min

●—0·75 l./min

TABLE I.—BURNER OPERATING CONDITIONS

Flame	Flow-rate, *l./min*				
	H_2	C_2H_2	Air	O_2	Ar
H_2-air	4·55	—	6·35	—	—
H_2-O_2-Ar	1·70	—	—	0·35	5·70
C_2H_2-air	—	0·95	6·25	—	—

Emission and fluorescence spectra of lead

To choose the most sensitive fluorescence lines, the relative intensities of lines emitted by the excitation spectral source and of corresponding fluorescence lines in all the flames were determined. In scanning the fluorescence spectrum, a 10-ppm solution of lead was sprayed into the flame under the optimum conditions and at a slit-width of 50 μm. The emission spectrum of the lamp was scanned at the maximum lamp operating currents and at a slit-width of 10 μm. The relative emission and fluorescence intensities measured were corrected for the detector response.

Atomic-absorption measurements

To compare the atomic fluorescence and atomic absorption of lead, the same equipment was used, but with a 100-mm long air–acetylene flame. The instrumental settings were: primary lamp current, 6 mA; booster current, 300 mA; slit-width, 50 μm. The gas flow-rates and solution uptake rate were the same as for the fluorescence measurements.

RESULTS AND DISCUSSION

Atomic-fluorescence lines

Spectral characteristics of lead lines which exhibit atomic fluorescence in the three flames studied are listed in Table II. All fluorescence lines correspond to the transition to the $6p^2\,{}^3P$ level. As expected from atomic-absorption measurements, both resonance lines at 217·00 and 283·31 nm give relatively high fluorescence signals due to resonance fluorescence; in the case of the line at 283·31 nm a contribution from stepwise-line fluorescence cannot be excluded. The additional intense signals at 261·37 and 261·42, 280·20, 363·96, 368·35 and 405·78 nm must be mostly due to direct-line fluorescence; for example, for the lines at 405·78 and 363·96 nm, excitation by the 283·31 nm line to the $7s\,{}^3P_1{}^0$ state followed by radiative transition to the metastable $6p^2\,{}^3P_2$ and $6p^2\,{}^3P_1$ states, respectively, seems to be the most probable. This was assumed because of the great energy difference between the ground state of the atom and the two other components of the triplet $6p^2\,{}^3P$ state, and also because of the weak atomic absorption of these lines (see Table III). The fluorescence emission at 368·35 nm is the result of stepwise fluorescence, with the lower term of the fluorescence transition not being the ground state of the atom, *i.e.*, excitation with the 283·31 nm line to the $7s\,{}^3P_1{}^0$ state followed by a radiationless transition to the $7s\,{}^3P_0{}^0$ state, and then fluorescence transition to the metastable $6p^2\,{}^3P_1$ state. The energy which the excited atom must lose by a radiationless transition to the $7s\,{}^3P_0{}^0$ state is very small. For the most intense fluorescence line at 405·78 nm and for the lines at 368·35 and 363·96 nm this mechanism was confirmed experimentally by filtering off both resonance lines with a glass filter. Contributions of only 5 and 34% of the resonance fluorescence were found for the 405·78 and 368·35 nm lines, respectively. The fluorescence emission at 363·96 nm is completely direct-line fluorescence.

TABLE II.—RELATIVE EMISSION AND FLUORESCENCE INTENSITIES OF LEAD LINES

Line,[16] *nm*	Oscillator strength	Energy levels, *eV*	Transition[17,18]	Relative lamp emission intensity,	Relative fluorescence intensity		
					Air–H_2	H_2–O_2–Ar	Air–C_2H_2
217·00	0·048	0–5·712	$6p^2\,{}^3P_0$–$6d\,{}^3D_1{}^0$	15	18	16	26
261·37*	0·19	0·969–5·712	$6p^2\,{}^3P_1$–$6d\,{}^3D_1{}^0$	49	15	13	22
261·42*	2·7	0·969–5·711	$6p^2\,{}^3P_1$–$6d\,{}^3D_2{}^0$				
280·20	5·1	1·320–5·744	$6p^2\,{}^3P_2$–$6d\,{}^3F_3{}^0$	55	8	5	10
283·31	0·22	0–4·375	$6p^2\,{}^3P_0$–$7s\,{}^3P_1{}^0$	79	76	68	69
363·96	0·26	0·969–4·375	$6p^2\,{}^3P_1$–$7s\,{}^3P_1{}^0$	47	42	33	35
368·35	0·64	0·969–4·334	$6p^2\,{}^3P_1$–$7s\,{}^3P_0{}^0$	65	19	25	11
405·78	2·3	1·320–4·375	$6p^2\,{}^3P_2$–$7s\,{}^3P_1{}^0$	100	100	100	100

* Lines unresolved in emission and fluorescence spectra.

TABLE III.—SENSITIVITIES OF LEAD DETERMINATION BY ATOMIC-FLUORESCENCE AND ATOMIC-ABSORPTION SPECTROSCOPY IN VARIOUS FLAMES

Line, *nm*	Detection limit, *ppm*			
	AFS			AAS
	H_2–O_2–Ar	Air–H_2	Air–C_2H_2 (separated)	Air–C_2H_2
405·78	0·02*	0·10	0·20	15†
283·31	0·05	0·12	0·15	0·12
363·96	0·05	0·15	0·40	15
217·00	0·06	0·20	0·12	0·08
368·35	0·07	0·30	1·5	12
261·37 261·42	0·15	0·45	0·30	6
280·20	0·30	0·80	1·0	>100

* Signal to noise ratio = 2.

† Values obtained with the same instrument and the same spectral source.

The same confirmation could be made for the unresolved 261·37 and 261·42 nm lines and the 280·20 nm line, by filtering off the radiation of the 217·00 nm resonance line. In the case of the 280·20 nm line, the upper energy level of which lies 0·032 eV higher than the energy level of the 217·00 nm resonance line, thermally assisted direct-line fluorescence, postulated by Dagnall and co-workers for the explanation of some fluorescence transitions of antimony[19] and bismuth[20] must be assumed.

Analytical working curves and detection limits

In Fig. 4, the analytical working curves for the most sensitive lead line at 405·78 nm in various flames are shown, and in Fig. 5 for all the lead fluorescence lines observed in the hydrogen–oxygen–argon flame. In Fig. 4 the 217·00 nm line, which exhibits the best detection limit in the separated air–acetylene flame, is also included. The dependence of the relative fluorescence intensity on the concentration of lead is linear over a range of up to three orders of magnitude. Despite the fact that there are a number of factors causing analytical curves to have shapes differing from the theoretical growth curves,[21] the shapes of the working curves for the resonance lines are in very good agreement with those derived by Hooymayers[22] for the case when the source-line half-width is narrow compared to the absorption line half-width.

From theoretical results[22] it can be concluded that differences in the shapes and positions of the analytical curves for the same line excited in various flames by the same spectral source and with use of the same optical arrangement, are caused by differences in the ground-state atom concentration, fluorescence yield factor and the *a*-parameter. For the 405·78 nm line (see Fig. 4), the fluorescence signal obtained from the separated air–acetylene flame is higher than that from the air–hydrogen flame for all lead concentrations. This is evidently due to a higher efficiency of atomization in the hotter air–acetylene flame. The highest signal was obtained in the oxy-hydrogen flame diluted with argon, as might be expected,[13,23,24] owing to the higher fluorescence yield factor than for the air–hydrogen flame because of the quenching cross-section of argon being smaller than that of nitrogen. A 4·0-fold increase in the fluorescence signal was observed. For the other fluorescence lines, 3·1, 3·7, 2·5, 3·4, 3·0 and 5·0-fold increases, resulting from using the hydrogen–oxygen–argon flame in place of the air–hydrogen flame were found for the 217·00, 261·37 and 261·42, 280·20, 283·31, 363·96 and 368·35 nm lines, respectively. Since the noise of measurement for both flames is practically the same, the higher signal in the hydrogen–oxygen–argon flame results in lower detection limits. The use of the nitrogen sheath makes both air–hydrogen and hydrogen–oxygen–argon flames steadier and produces a further improvement (approximately 2-fold) in the detection limits. In the case of the separated air–acetylene flame, the relatively high background, especially at longer wavelengths, causes a deterioration in the detection limits in most cases compared with the air–hydrogen flame. Therefore, the best signal-to-noise ratio in the separated air–acetylene flame was obtained for the line at 217·00 nm.

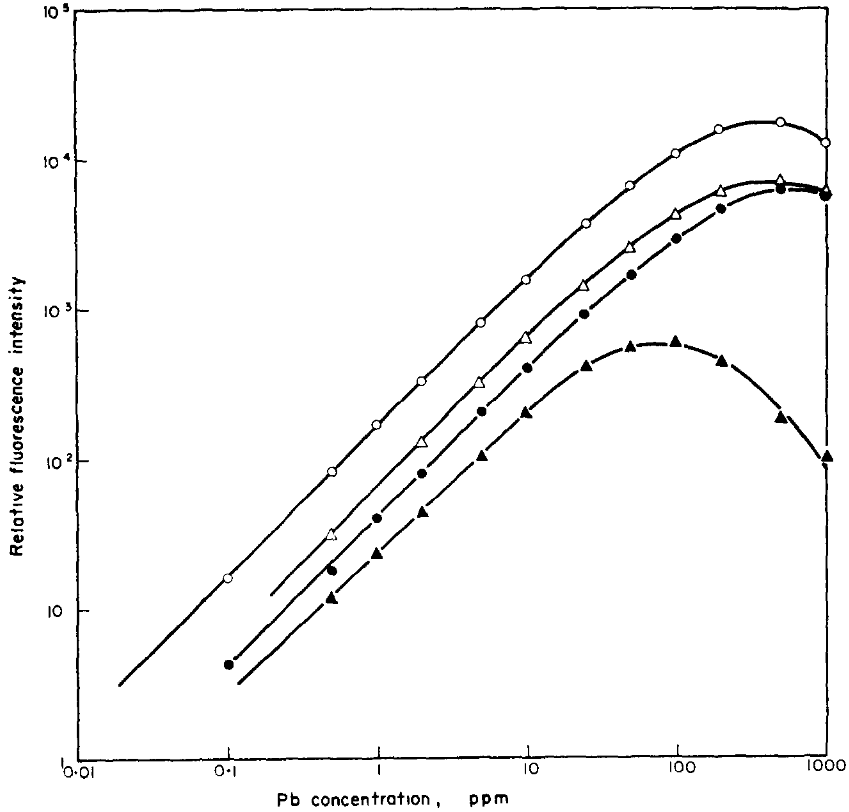

Fig. 4.—Analytical working curves for the Pb 405·78 nm line with various premixed flames.
●—air–hydrogen △—air–acetylene (separated)
○—hydrogen–oxygen–argon ▲—air–acetylene (separated, Pb 217·00 nm)

A comparison of detection limits for atomic fluorescence with various flames and atomic absorption, using the same instrument and the same spectral source, is made in Table III. In atomic fluorescence, there are seven sensitive analytical lines giving detection limits below 1 ppm. In atomic absorption only, two sensitive (resonance) lines are available while the absorption of the other lines which exhibit atomic fluorescence is considerably weaker. When the hydrogen–oxygen–argon flame is used, five fluorescence lines give better detection limits than the most sensitive atomic

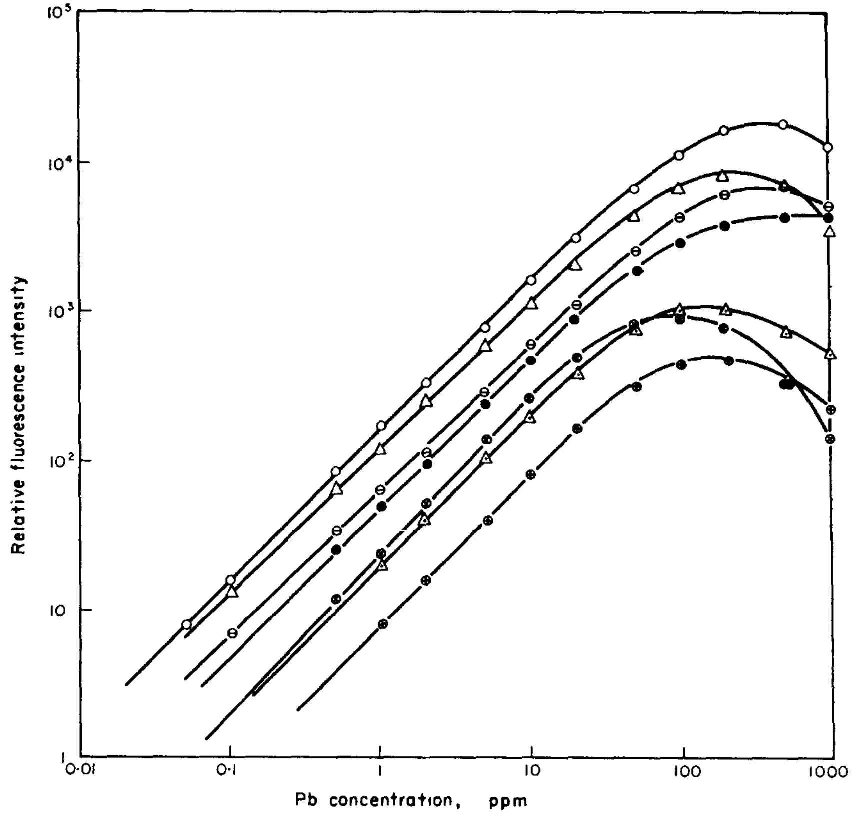

FIG. 5.—Analytical working curves for all fluorescence lines observed in the hydrogen–oxygen–argon flame.

○—405·78 nm ●—368·35 nm
△—283·31 nm ⊗—217·00 nm
⊖—363·96 nm ◬—261·37 and 261·42 nm
⊕—280·20 nm

absorption line at 217·00 nm (0·08 ppm). The best detection limit of 0·02 ppm was obtained for the 405·78 nm line.

Chemical interferences

The effect of hydrochloric, sulphuric, phosphoric, nitric, perchloric and hydrofluoric acids in concentrations of 0·01, 0·1 and 0·5M and of a 100-fold excess of Na, K, Cu, Mg, Ca, Zn, Al, V, Bi, Cr, Mo, W, Mn, Fe, Co and Ni on the fluorescence signal produced by a 5-ppm lead solution was investigated. In all the three flames studied, only 0·1 and 0·5M hydrofluoric acid and molybdate caused a significant interference (>50% decrease in fluorescence signal from a 5-ppm lead solution). Among the other ions, copper and tungsten slightly decrease the fluorescence signal (<10%) in the air–hydrogen flame, while aluminium shows the same effect in the hydrogen–oxygen–argon flame. The chemical interference of hydrofluoric acid was considerably lowered by the addition of EDTA (final concentration 0·005M). The effects of the interfering cations were eliminated in the same manner. Similar interferences from hydrofluoric acid and molybdate were found for lead determined by atomic absorption in a 100-mm air–acetylene flame, as would be expected.

Zusammenfassung—Das mit einer intensiven Hohlkathodenlampe angeregte Fluoreszenzspektrum von Blei wurde untersucht und der wahrscheinliche Mechanismus der Fluoreszenzübergänge angegeben. Es wird experimentell bestätigt, daß die intensivste Fluoreszenzlinie bei 405,78 nm hauptsächlich als Resonanzfluoreszenz zustande kommt. Verwendet wurden die vorgemischte Luft-Wasserstoff-Flame, die getrennte Luft-Acetylen-Flamme und die mit Argon verdünnte Sauerstoff-Wasserstoff-Flamme. Die zuletzt genannte gibt mit der Linie bei 405,78 nm eine Nachweisgrenze von 0,02 ppm.

Résumé—On a étudié le spectre de fluorescence du plomb excité avec une lampe à cathode creuse de haute intensité et l'on suggère le mécanisme probable des transitions de fluorescence. Il est confirmé expérimentalement que la raie de fluorescence la plus intense à 405,78 nm est principalement dûe à la fluorescence de raie directe. On a utilisé la flamme prémélangée air–hydrogène, la flamme séparée air–acétylène et la flamme oxy–hydrogène diluée à l'argon la, dernière mentionnée donnant une limite de détection de 0,02 ppm avec la raie à 405,78 nm.

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SUBSTOICHIOMETRIC DETERMINATION OF TRACES OF PALLADIUM BY NEUTRON-ACTIVATION ANALYSIS

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Summary—A highly selective, rapid one-step radiochemical separation procedure for palladium has been developed. It is based on the solvent extraction of palladium diethyldithiocarbamate from a 5*M* hydrochloric acid solution with a substoichiometric amount of copper diethyldithiocarbamate in chloroform. The separation has been applied to the determination of traces of palladium by neutron-activation analysis, in platinum, the rocks W-1 and PCC-1 and a biological material (kale). Amounts of palladium down to 10^{-8} g have been determined.

Neutron-activation analysis has been used to determine traces of palladium in rocks,[1,2] ores,[3] meteorites[4–6] and various metals.[7–10] Most of the previously reported methods of separation of palladium involve either precipitation or solvent extraction of the dimethylglyoximate, and, owing to the incompleteness of the process, involve many successive separation steps and therefore are complicated and time consuming. By use of the substoichiometric principle, the chemical separation has been greatly simplified and, because of the very high selectivity of this separation, a procedure has been developed which we would expect to be applicable to almost any type of matrix.

Table I.

Stable palladium isotope	Abundance %	Cross-section, *barn*	Product of (n, γ) reaction	Half-life	Major radiations
102	0·96	4·8	103	17 days	EC, Rh X-ray
106	27·33	0·29	107m	21·3 sec	IT, Pd X-ray
108	26·71	12	109	13·6 hr	β,⁻ Ag X-ray
108	26·71	0·2	109m	4·7 min	IT, Pd X-ray
110	11·81	0·2	111	22 min	$\beta,^- \gamma$
110	11·81	0·04	111m	5·5 hr	β,⁻ Pd X-ray

EC = electron capture; IT = internal transition.

The stable isotopes and the nuclear reactions resulting from thermal neutron irradiation of palladium are shown in Table I. The irradiation facilities available have thermal neutron fluxes of (1–6) × 10^{-10} n.mm^{-2}.sec.$^{-1}$ Under these conditions and from the data given in Table I, it can be shown that the most suitable isotope for the determination of palladium is palladium-109, which can be detected either by the beta or the gamma radiation and silver X-ray (22 keV) associated with the decay. It follows that under suitable conditions (irradiation in a flux of 10^{20} n.mm^{-2}.sec^{-1} to saturation activity followed by radiochemical separation) it is theoretically possible to determine down to 10^{-10} g of palladium.

For a substoichiometric separation by solvent extraction it is necessary to have a chelating agent which forms a very strong, readily extractable complex with the metal concerned. Diethyldithiocarbamic acid is known to form a strong complex with palladium. Exchange data, for carbon tetrachloride as solvent, have been reported to give the following order of decreasing extractability of metal diethyldithiocarbamates:[12] Hg(II), Pd(II), Ag, Cu, Tl(III), Ni, Bi, Pb, Co(III), Cd, Tl(I), Zn, In, Sb(III), Fe(III), Te(IV) and Mn. However, the order varies somewhat with the solvent used and the content of the aqueous phase. In a previous paper[13] the investigation of the extraction of palladium with a solution of copper diethyldithiocarbamate in chloroform was reported. This extractant was chosen because solutions of diethyldithiocarbamic acid and its sodium salt are not very stable, whereas a stock solution of the copper(II) complex in chloroform ($10^{-2}M$) keeps for months. The palladium complexes formed are more soluble in chloroform than carbon tetrachloride.

It was shown that under substoichiometric conditions two reactions occur:

$$Pd^{2+}_{(aq)} + Cu(DDC)_{2(org)} \rightleftharpoons Pd(DDC)_{2(org)} + Cu^{2+}_{(aq)} \tag{1}$$

$$Pd(DDC)_{2(org)} + Pd^{2+}_{(aq)} + 2Cl^{-}_{(aq)} \rightleftharpoons 2PdCl(DDC)_{(org)} \tag{2}$$

where DDC is the diethyldithiocarbamate ion and the subscripts "aq" and "org" indicate an aqueous and an immiscible organic phase respectively.

The extraction constant of the first complex, palladium diethyldithoicarbamate, into chloroform was found to be about 10^{70}, indicating that a substoichiometric determination using this complex is likely to be very selective. But at equilibrium the chloride complex (2) will be completely formed under substoichiometric conditions from solutions containing palladium chloride and hydrochloric acid only. However, the rates of the two reactions are affected by the hydrogen ion and chloride ion concentrations of the aqueous phase. Where both are high, *e.g.*, in $5M$ hydrochloric acid, palladium diethyldithiocarbamate is formed rapidly while the formation of palladium chloride diethyldithiocarbamate does not take place for several hours. Thus conditions can be chosen such that palladium diethyldithiocarbamate is formed on extraction with a substoichiometric amount of copper diethyldithiocarbamate.

EXPERIMENTAL

Reagents

All reagents were prepared from analytical reagent grade chemicals.

Copper diethyldithiocarbamate solution. Sodium diethyldithiocarbamate was recrystallized by dissolution in the minimum volume of ethanol and addition of a large excess of ether. After drying under vacuum, the crystals (0·45 g) were dissolved in distilled water, excess of copper sulphate solution was added and the resulting precipitate of copper diethyldithiocarbamate was extracted with several portions of chloroform. The extracts were combined and diluted to 100 ml with chloroform to give an approximately $10^{-2}M$ stock solution. This was diluted further with chloroform as required to give an approximately $5 \times 10^{-4}M$ solution. The exact concentration was determined by measuring the absorbance at 436 nm and assuming the molar absorptivity to be the same in chloroform as in carbon tetrachloride ($1{\cdot}3 \times 10^3$ mole.l^{-1}.mm^{-1}).[12]

Palladium carrier solution. Prepared by dissolving finely divided palladium metal in *aqua regia.* The resulting solution was evaporated to dryness with hydrochloric acid, several times, to remove oxides of nitrogen. The final solution in hydrochloric acid was diluted to approximately $10^{-2}M$ with distilled water.

Palladium-103 solution. Irradiated palladium metal was dissolved as above. The ^{111}Ag (active decay product of ^{111}Pd) was removed, before dilution, by the addition of inactive silver nitrate solution to the solution of palladium in hydrochloric acid, the resulting precipitate of silver chloride being centrifuged off. This procedure was repeated once and the final solution diluted to $10^{-2}M$ with distilled water as before. Because of the low specific activity of the palladium-103, this solution was used alone, *i.e.*, without the addition of palladium carrier solution.

Both the palladium carrier solution and the palladium-103 solution were standardized against $3 \times 10^{-3}M$ EDTA by the back-titration method developed by MacNevin and Kriege.[14]

Radiotracer solutions. Used for direct interference studies and prepared by irradiating the elements or their oxides in a flux of 10^{10} n.mm^{-2}sec^{-1} for 8 hr (Universities of Manchester and Liverpool Research Reactor).

Apparatus

Scintillation counter. The detector used was a 76 × 76 mm NaI(Tl) well-type crystal. For activity measurements this was associated with a single-channel gamma-ray spectrometer. For experiments using palladium-103 as a tracer, counting was carried out in a 10–50 keV channel; for experiments with palladium-109 (test analyses) counting was carried out in a 10–30 keV channel, and for the direct interference studies a discriminator voltage setting corresponding to 10 keV was used. Gamma-spectra were recorded by means of a 400-channel pulse-height analyser.

Chloroform solutions of palladium-103 and -109 had to be evaporated to dryness before counting, as the rhodium and silver X-rays used to detect these isotopes are strongly absorbed by solvents containing chlorine.

Filter paper. Dry Whatman No. 41 was used.

Irradiation

The test samples were weighed (see Table IV), sealed in quartz ampoules and irradiated in a reactor simultaneously with an appropriate amount of palladium chloride standard. Times of irradiation were 12 hr or 7 days at thermal neutron fluxes of 10^{10} or 6×10^{10} n.mm^{-2}.sec^{-1}. For irradiations the Harwell DIDO and the Universities of Manchester and Liverpool Research Reactor were used.

Development of method

All preliminary experiments were carried out with about $10^{-2}M$ palladium-103 and about $5 \times 10^{-4}M$ copper diethyldithiocarbamate in chloroform.

Extraction time. The time to reach the extraction equilibrium of palladium diethyldithiocarbamate from 5*M* hydrochloric acid was investigated by extraction of palladium for different times from 10 ml of 5 ± 1*M* hydrochloric acid containing 1·0 ml of palladium-103 solution, 5·0 ml of copper diethyldithiocarbamate solution being used as the extractant. The organic phase was filtered, a 3·0-ml aliquot was evaporated to dryness and the activity measured. From Fig. 1 where the activities of the organic phase are plotted *vs.* time of shaking, it can be seen that extraction equilibrium is reached in under 1 min and that the extract is unaffected by up to 2 hr shaking. This shows that the chloride complex is not formed. For all further experiments an extraction time of about 5 min was chosen.

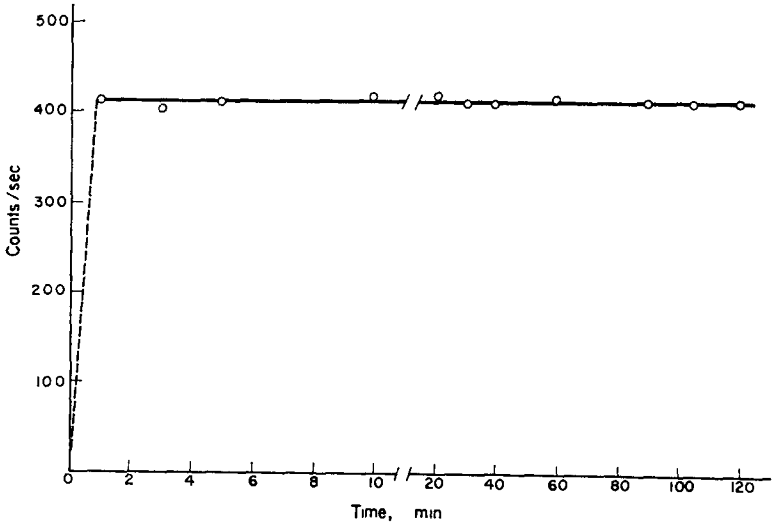

FIG. 1.—Extraction time of palladium from 5*M* hydrochloric acid with copper diethyldithiocarbamate ($10^{-2}M$ palladium-103; $5 \times 10^{-4}M$ copper diethyldithiocarbamate).

Reproducibility. To test that under the conditions above, exactly equal amounts of palladium could be extracted from solutions of varying palladium concentration, a series of solutions of 5 ± 1*M* hydrochloric acid containing increasing amounts of palladium-103 solution were extracted with 5·0 ml of copper diethyldithiocarbamate solution for about 5 min. The activity of the extracts was measured as before and plotted against the amount of palladium originally present in the aqueous phase. From the graph obtained (Fig. 2) it can be seen that after the equivalence point was reached, very good substoichiometric reproducibility was achieved.

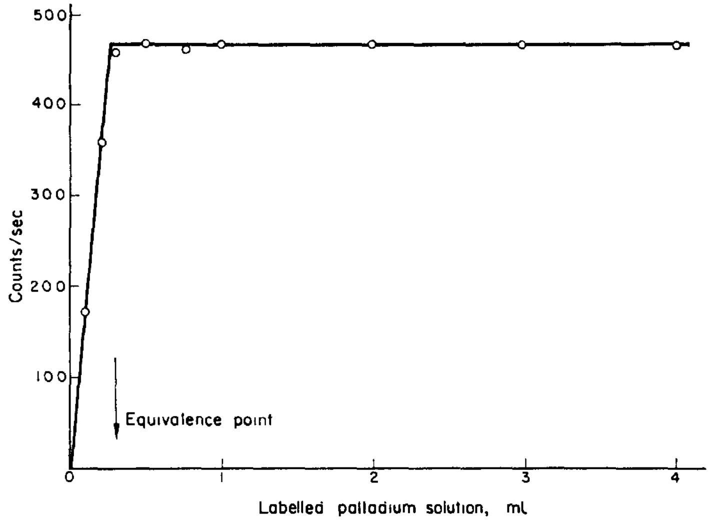

Fig. 2.—Substoichiometric reproducibility of the extraction of palladium from 5*M* hydrochloric acid with copper diethyldithiocarbamate ($10^{-2}M$ palladium-103; $5 \times 10^{-4}M$ copper diethyldithiocarbamate).

Selectivity

Indirect interference studies. These were based on the detection of any depression of the palladium activity extracted as the diethyldithiocarbamate, caused by the presence of various species in the original aqueous solution. Palladium-103 solution was mixed with the appropriate amounts of foreign species (Table II) in 5 ± 1*M* hydrochloric acid and the extraction carried out as before.

The species investigated in this way included most of the metals in the oxidation states most likely to be present after normal dissolution procedures, and the more common non-metal anionic species that are stable in fairly concentrated hydrochloric acid solution. Where groups of metals were known to be chemically similar, *e.g.*, lanthanides, alkali metals, alkaline earth metals, only a few members of the group were tested.

Where possible the aqueous solution contained the foreign species in 1000-fold molar excess over palladium. (This was based on the principle of the addition of mg amounts of palladium carrier to a matrix being analysed in gram quantities containing a high proportion of the species.) When the species being examined was only sparingly soluble in hydrochloric acid, a saturated solution was used.

From the results it can be seen that certain oxidizing substances significantly decrease the activity extracted. This is due to oxidation of the reagent and is prevented, except in the case of Se(IV) and Se(VI) by the addition of an excess of sodium sulphite (5 ml of a freshly prepared saturated solution). The continued interference of selenium is due to the reduction of Se(IV) and Se(VI) to selenium metal by the sulphite. This in turn reduces Pd(II) to the metal. Sulphite itself will reduce Pd(II) but the reduction is normally so slow as to be unimportant.

The only other interference with the extraction is that of Au(III) which appears to form a more readily extractable diethyldithiocarbamate than palladium.

Direct interference studies. The purpose of this investigation was to detect small quantities of highly radioactive species which might be extracted into the organic phase (possibly by some mechanism other than complexing with the diethyldithiocarbamate ion) without significantly depressing the palladium extraction. A labelled solution of the ion to be investigated was mixed with a non-active palladium carrier solution in 5 ± 1*M* hydrochloric acid and the substoichiometric extraction carried out as before. All the platinum metals (except rhodium, which produces only a very short-lived

TABLE II.

Foreign ion added	^{103}Pd extracted, % (compared with standard)	^{103}Pd extracted, in the presence of excess Na$_2$SO$_3$, %	Foreign ion added	^{103}Pd extracted, % (compared with standard)	^{103}Pd extracted, in the presence of excess Na$_2$SO$_3$, %
			Orthophosphate	98·8	
Aluminium	97·0		Platinum(IV)		
Antimony(III)	97·7		(10 mg)	98·1	
Antimony(V)	1·5	100·0	Potassium	100·0	
Arsenic(III)	97·3		Rhenium(VII)	—	101·0
Arsenic(V)	99·7		Rhodium(III)		
*Barium	98·6		(40 mg)	—	104·0
Beryllium	100·0		Ruthenium(IV)		
Bismuth	97·5		(10 mg)	—	98·5
Borate	98·5		Selenium(IV)	66·6	25·9
Bromide	99·4		Selenium(IV)		
Cadmium	97·8		(1 mg)	—	93·9
Calcium	101·9		Selenium(VI)	5·6	53·5
Cerium(III)	101·0		Selenium(VI)		
Cerium(IV)	0·5	101·5	(10 mg)	—	95·2
Perchlorate	99·0		*Silicate	95·0	
Chromium(III)	98·4		*Silver	99·5	
Cobalt(II)	99·4		Sodium	100·0	
Copper(II)	99·4		Strontium	104·5	
Gallium	98·4		Sulphate	101·5	
*Germanium	101·9		Sulphite	97·9	
Gold(III)			Tellurium(IV)	101·1	
(100 mg)	0·7	5·6	Tellurium(VI)	75·4	102·9
Indium(III)	99·7		*Thallium(I)	101·2	
Iodide	101·2		Thorium(IV)	99·4	
Iridium(IV)			Tin(II)	103·3	
(10 mg)	—	103·0	Tin(IV)	96·9	
Iron(II)	97·5		Titanium(IV)	96·9	
Iron(III)	25·5	97·2	*Tungsten(VI)	97·6	
Magnesium	101·2		Uranium(VI)	84·4	98·0
Manganese(II)	97·0		Vanadium(V)	55·2	100·6
*Mercury(I)	103·1		Vanadium(VI)	1·5	99·3
Mercury(II)	99·0		Zinc	103·0	
Molybdenum(VI)	65·8	99·5	*Zirconium(IV)	102·4	
Nickel	98·8		*Lead(II)	101·0	
*Niobium(V)	98·6		Hydrogen		
Nitrate	4·0	101·1	peroxide	1·6	99·0
Osmium(IV)			Ammonium	100·0	
(50 mg)	—	94·8	Acetate	97·4	

1 mg (10^{-5} mole) of palladium present in all cases.
10^{-3} mole of foreign ion present unless otherwise stated.
* Solution saturated with respect to this species.

isotope on thermal neutron irradiation) and those metals known to form fairly strong diethyldithiocarbamates were examined.

The results (Table III) show that a small amount of activity may appear in the organic phase, because of incomplete separation of the phases by filtration. This can be removed by washing the organic phase with 5*M* hydrochloric acid. The only isotopes extracted to a significant extent are ^{198}Au and ^{197}Pt. Gold(III), as in the indirect interference studies, completely replaces palladium from the diethyldithiocarbamic acid. Platinum(IV) also appears to form a more readily extractable diethyldithiocarbamate than palladium, but the reaction is so much slower than that with palladium that even with excess of platinum not enough is extracted to depress the palladium extraction significantly.

These experiments show that the separation is very selective for palladium. The only elements which interfere in any way are gold, selenium and platinum.

Elimination of interferences

Gold. As gold is likely to be present in trace quantities in most matrices, often in similar quantities to palladium, and its nuclear characteristics result in a considerably higher specific activity than that of palladium under the same irradiation conditions, it will nearly always be necessary to remove gold

TABLE III.

Foreign ion added		Labelling radioisotope	Total activity added, *cps*	Activity of substoichiometric extract, *cps*	Radioactivie ion extracted, %
Mercury(II)	2·0 g	^{203}Hg	7340	1·30	0·02
Cerium(IV)	0·14 g	^{144}Ce	3330	0·36	0·01
Silver*		^{111}Ag	1050	0·30	0·03
Cobalt(II)	0·6 g	^{60}Co	13070	0·38	0·003
Thallium(I)*		^{204}Tl	10460	0·003	3×10^{-5}
Iodine(−I)	1·3 g	^{131}I	18600	10·4	0·05
Copper(II)	0·6 g	^{64}Cu	29000	1·0	0·003
Gold(III)	0·02 g	^{198}Au	23390	166·3	0·7
Ruthenium(IV)	0·01 g	^{97}Ru	7780	1·4	0·02
Osmium(IV)	0·05 g	^{193}Os	5233	1·1	0·02
Iridium(IV)	0·01 g	^{194}Ir	72777	1·0	0·0014
Platinum(IV)	0·10 g	^{197}Pt	800000	16000	0·2

1 mg of palladium present in all cases.

* Solution saturated with respect to this species.

before the substoichiometric separation is carried out. This is achieved quickly and simply by extracting the gold as gold(III) chloride from the solution in $5 \pm 1M$ hydrochloric acid, with diethyl ether.

When 10 mg of gold (labelled with ^{198}Au) in 1·0 ml of palladium carrier solution in $5 \pm 1M$ hydrochloric acid, were extracted with three 50-ml portions of diethyl ether before the substoichiometric extraction of palladium, a decontamination factor of about 2000 resulted. This decreased somewhat on lowering of the gold concentration and, for a solution containing 0·01 mg of gold, the decontamination factor was only about 200. In the test analyses, where the sample contained only trace quantities of gold, three ether extractions with no addition of carrier were found to be quite sufficient. A few more extractions may be needed for a matrix containing a high proportion of gold. For the platinum sample however, where a large quantity of carrier free ^{199}Au is produced from the decay of the 30-min half-life ^{199}Pt, the concentration of gold was too low for the ether extraction to give a large enough decontamination factor and so the addition of gold carrier was necessary.

Selenium and platinum. The reduction by selenium is insignificant if it is present only in mg amounts, while the extraction of platinum is so slow that it will not extract significantly in a shaking time of 5 min unless it is present in high concentrations.

In the test analysis of the platinum sample it was found that a preliminary separation of palladium by dimethylglyoxime precipitation, reduced the platinum concentration sufficiently to prevent its interference. We would also expect this method to be suitable for high selenium content samples.

Dissolution procedures

The procedures detailed below were tested by adding 1·0 ml of palladium-103 solution to the non-irradiated matrix. After dissolution the palladium was extracted with a substoichiometric amount of copper diethyldithiocarbamate solution. No significant losses of palladium were observed.

Rocks. To the test matrix in a 50-ml Teflon beaker, 1·0 ml of palladium carrier solution was added and the matrix dissolved in a mixture of hydrofluoric (10 ml), hydrochloric (2 ml) and nitric (10 ml) acids. After the silicon had been fumed off, four evaporations to dryness were carried out with 5-ml portions of hydrochloric acid, to remove oxides of nitrogen. The final residue was dissolved in 5 ml of concentrated hydrochloric acid.

Biological material (kale). To the test matrix in a 150-ml beaker, 1·0 ml of palladium carrier solution was added. After dissolution in 5 ml of nitric acid, the solution was evaporated to dryness. This was repeated several times until all the carboniferous material had been oxidized. Four evaporations to dryness were carried out with 5-ml portions of hydrochloric acid, to remove oxides of nitrogen, before dissolution of the final residue in 5 ml of concentrated hydrochloric acid.

Platinum. To the test matrix in a 150-ml beaker, 1·0 ml of palladium carrier solution and 1·0 ml of gold carrier solution (1 mg/ml) were added. The matrix was dissolved in 10 ml of *aqua regia* and the resulting solution diluted to about 100 ml with distilled water before addition of 2 ml of a 1% solution of dimethylglyoxime in ethanol. The solution was warmed and stirred. The palladium dimethylglyoxime formed was filtered off and washed first with dilute hydrochloric acid and then with distilled water. This precipitate was then dissolved off the paper by the addition of hot, concentrated nitric acid. A further 1·0 ml of gold carrier solution was added, the resulting solution evaporated to dryness, and the residue dissolved in 5 ml of hydrochloric acid. Four evaporations to dryness were carried out with 5-ml portions of hydrochloric acid to remove oxides of nitrogen, and the final residue dissolved in 5 ml of concentrated hydrochloric acid.

Extraction procedures

The dissolved samples were diluted with 5 ml of distilled water and extracted with three 50-ml portions of diethyl ether for 1–2 min. The ether layers were discarded and the aqueous phase shaken with 20 ml of chloroform for 30 sec (to remove any chloroform soluble substances). The separated aqueous phase was warmed to remove final traces of the organic solvents. After addition of 5 ml of freshly prepared, saturated sodium sulphite solution and 5 ml of concentrated hydrochloric acid, extraction was carried out with 5·0 ml of copper diethyldithiocarbamate solution for about 5 min. The organic phase was washed with two 10-ml portions of 5*M* hydrochloric acid (to remove traces of highly active aqueous phase), filtered, and a 3·0-ml aliquot evaporated to dryness and counted. This extraction was repeated once as a check.

The irradiated palladium standard (weight of palladium y_s) was dissolved in 5 ml of concentrated hydrochloric acid after the addition of 1·0 ml of palladium carrier solution. Freshly prepared, saturated sodium sulphite solution (5 ml) was added to this solution and extraction with a substoichiometric amount of copper diethyldithiocarbamate solution carried out as for the test samples. Washing of the aqueous phase was omitted. The activities of equal aliquots of the organic extracts from the test (a) and standard (a_s) samples were measured and the amount of palladium present in the test sample (y) calculated from the equation:

$$y = y_s \, . \, a/a_s.$$

RESULTS AND DISCUSSION

The results of the test sample analyses are summarized in Table IV. It can be seen that in all cases the reproducibility is very good. The mean values are slightly

TABLE IV.

Sample	Sample weight, *g*	Palladium standard activity, *cps*	Palladium sample activity, *cps*	Palladium found, *μg*	Palladium found, *ppm*	Mean, *ppm*	Results of other authors, *ppm*
W-1*	1·0059	870	3·4	$3{\cdot}9 \times 10^{-2}$	$3{\cdot}9 \times 10^{-2}$		
	1·0006	1320	4·8	$3{\cdot}6 \times 10^{-2}$	$3{\cdot}6 \times 10^{-2}$	$3{\cdot}9 \times 10^{-2}$	$1{\cdot}9 \times 10^{-2}$
	0·5404	450	1·0	$2{\cdot}2 \times 10^{-2}$	$4{\cdot}1 \times 10^{-2}$		(ref. 15)
	0·6672	1950	5·4	$2{\cdot}8 \times 10^{-2}$	$4{\cdot}1 \times 10^{-2}$		$1{\cdot}4 \times 10^{-2}$
							(ref. 16)
PCC-1*	1·0052	870	2·8	$3{\cdot}2 \times 10^{-2}$	$3{\cdot}2 \times 10^{-2}$		
	1·0033	1320	3·2	$2{\cdot}4 \times 10^{-2}$	$2{\cdot}4 \times 10^{-2}$		
	0·5062	1130	1·7	$1{\cdot}5 \times 10^{-2}$	$2{\cdot}9 \times 10^{-2}$	$2{\cdot}9 \times 10^{-2}$	$0{\cdot}7 \times 10^{-2}$
	0·5687	1130	1·9	$1{\cdot}7 \times 10^{-2}$	$3{\cdot}0 \times 10^{-2}$		(ref. 16)
	0·6948	1950	4·0	$2{\cdot}1 \times 10^{-2}$	$2{\cdot}9 \times 10^{-2}$		
Kale†	1·0031	450	1·3	$2{\cdot}8 \times 10^{-2}$	$2{\cdot}8 \times 10^{-2}$		
	0·4919	1950	2·8	$1{\cdot}4 \times 10^{-2}$	$2{\cdot}9 \times 10^{-2}$	$2{\cdot}6 \times 10^{-2}$	
	0·4894	1950	2·1	$1{\cdot}1 \times 10^{-2}$	$2{\cdot}2 \times 10^{-2}$		
	0·4730	1950	2·5	$1{\cdot}3 \times 10^{-2}$	$2{\cdot}6 \times 10^{-2}$		
Pt§	0·2615	240	8·4	0·350	1·34		
	0·2510	240	7·1	0·296	1·18	1·29	2·13
	0·2541	940	35·0	0·373	1·46		(ref. 7)
	0·2514	940	28·2	0·300	1·20		

* Provided by U.S. Geological Survey, Washington D.C. U.S.A.

† Provided by H. J. M. Bowen, The University, Reading, England.

§ Sample Pt3 (Ref. 7) provided by D. F. C. Morris, Brunel University, London, England.

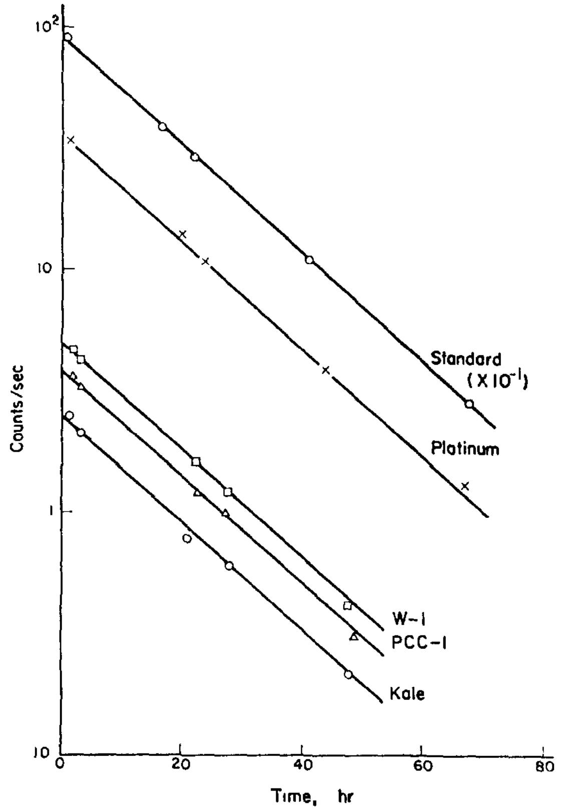

FIG. 3.—Decay curves of palladium diethyldithiocarbamate extracts.

higher than those obtained by other authors in the case of rocks[15–17] and slightly lower for the platinum.[7] Variation of sample size indicated that there were no self-shielding effects in the rocks or the kale. The radiochemical purity of the palladium diethyldithiocarbamate extracts was confirmed both by decay measurements, Fig. 3, and by comparison of their gamma-ray spectra with that of the standard, Fig. 4. It can be seen from the spectra that the extracts from the platinum sample contained a very small amount of ^{199}Au, but as only the 22-keV peak was counted, this would have very little effect on the results.

The standard rock W-1 contains trace amounts of some 40 elements and large amounts of 6 other elements, the main constituents being SiO_2 and Al_2O_3;[17] PCC-1 contains trace amounts of 10 elements and large amounts of 6 other elements with the main constituents being SiO_2 and MgO.[18] The platinum sample contains trace amounts of Se, Te, Os, Ir, Fe, Au, Ru, Co, As and Sb,[19] and the kale is a complicated organic matrix.[20] The fact that satisfactory results were obtained with all these materials, including the platinum matrix which must be one of the most difficult materials to analyse for trace palladium, shows the versatility of the method. The results of the preliminary experiments, together with the radiochemical purity of the palladium extracts from the test analyses, clearly indicate as predicted, that this substoichiometric copper diethyldithiocarbamate extraction is highly selective for palladium.

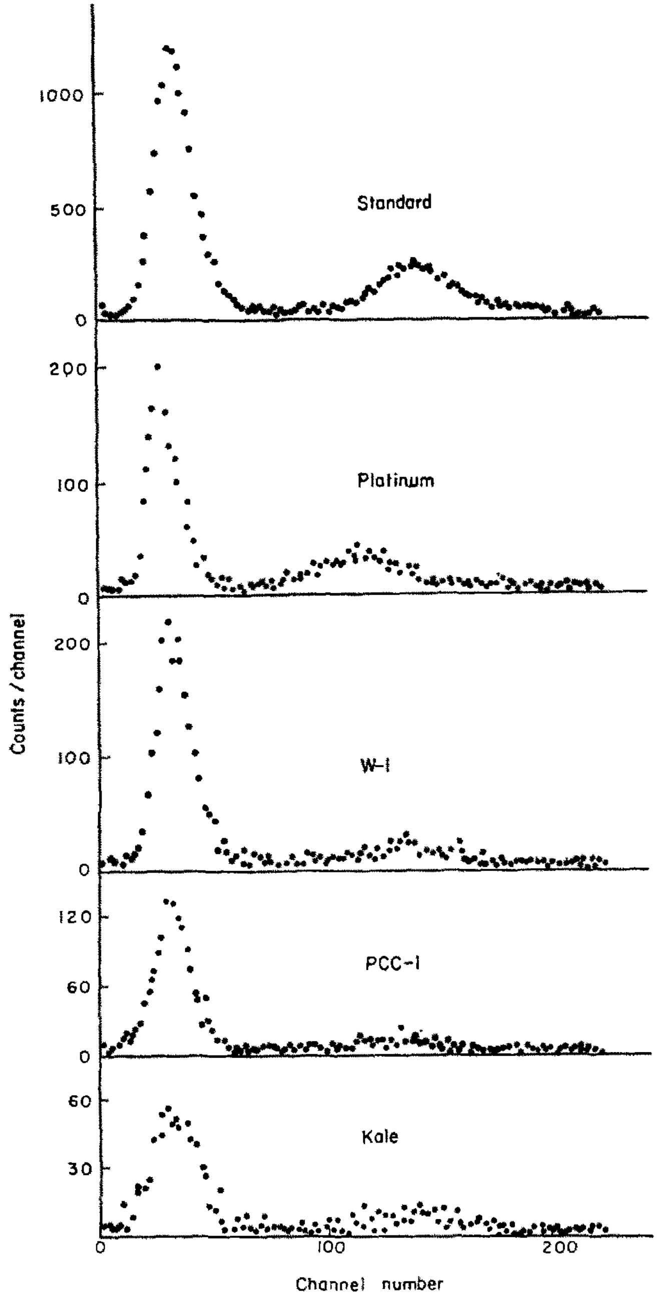

FIG. 4.—Gamma-ray spectra of palladium diethyldithiocarbamate extracts.

CONCLUSION

As has been shown before, metallic salts of diethyldithiocarbamic acid are very suitable for substoichiometric separations by solvent extraction. Methods for arsenic[21] and gold[22] have been developed, and now palladium. Although a few extraction constants have been determined, insufficient are known for prediction of the conditions for the substoichiometric separation of many metals and, as our kinetic studies have shown, this is not the only factor involved, especially with the so-called inert metals such as palladium and platinum.

Zusammenfassung—Ein hochselektives, schnelles, einstufiges radiochemisches Abtrennverfahren für Palladium wurde entwickelt. Es beruht auf der Extraktion von Palladium-diäthyldithiocarbamat aus 5M salzsaurer Lösung mit einer unterstöchiometrischen Menge Kupferdiäthyldithiocarbamat in Chloroform. Das Abtrennverfahren wurde auf die Bestimmung von Palladiumspuren durch Neutronenaktivierung in Platin, den Gesteinen W-1 und PCC-1 und einem biologischen Material (Kohl) angewandt. Bis herunter zu 10^{-8} g Palladium wurden bestimmt.

Résumé—On a élaboré, pour le palladium, une technique de séparation radiochimique hautement sélective, rapide et en un stade. Elle est basée sur l'extraction par solvant du diéthyldithiocarbamate de palladium d'une solution en acide chlorhydrique 5M avec une quantité substoechiométrique de diéthyldithiocarbamate de cuivre en chloroforme. On a appliqué la séparation à la détermination de traces de palladium par analyse par activation de neutrons dans le platine, les roches W-1 et PCC-1 et une substance biologique (chou vert). On a dosé des quantités de palladium descendant jusqu'à 10^{-8} g.

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FURTHER STUDY OF INDIVIDUAL ION ACTIVITIES IN PURE AQUEOUS SODIUM CHLORIDE SOLUTION

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Summary—The e.m.f. values between a chloride electrode and a reference electrode were measured in aqueous NaCl solutions between 10^{-5} and 6 m, saturated KCl and 1*M* KNO_3 bridges being used. The effect of the various liquid junctions is calculated and discussed. The consistency of the results is inspected, assuming either the MacInnes or the Guggenheim convention. The choice of different reference points for the standardization of the e.m.f.'s and for the activity coefficients is discussed. A comparison is made between the results obtained with an Ag/AgCl electrode of the second kind and a solid membrane chloride electrode.

IN A RECENT paper[1] the individual activities of Na^+ and Cl^- in pure aqueous solutions of sodium chloride were studied. The activity of Cl^- was calculated on the basis of measurements made with a standard calomel electrode and a saturated potassium chloride bridge against an Ag/AgCl electrode of the second kind. The range of concentrations studied was from 10^{-3} to 6 m. In the present paper the study has been extended by (*a*) lowering the concentrations of sodium chloride down to 10^{-5} m; (*b*) use of a potassium nitrate bridge in addition to the chloride bridge, and (*c*) use of a solid membrane chloride electrode. The implications of these extensions and the results obtained are discussed.

EXPERIMENTAL

The experimental details have already been described previously.[1] Additional particulars are as follows. In addition to the electrodes previously described, the Orion Analyzer Chloride Ion Activity Electrode Model 94-17 was employed. This electrode will be referred to as the solid membrane chloride electrode. In addition to the saturated potassium chloride bridge a 1*M* potassium nitrate bridge was employed. The bridges were connected with the test solutions through an asbestos fibre sealed in glass. The rate of diffusion is discussed below.

RESULTS AND DISCUSSION

The effect of the liquid junctions

A summary of the results obtained is given in Table I. The experimental e.m.f.'s tabulated in columns *b* and *c* include the problematic liquid junction potentials (E_j) between the bridge and the test solutions of sodium chloride.

The calculation of E_j for the sodium chloride junction with the saturated potassium chloride bridge (by using the Henderson equation) has already been discussed.[1] In a similar way the E_j between sodium chloride and the 1*M* potassium nitrate solution has been calculated. The results are plotted in Fig. 1.

It can be seen that the use of conductivities calculated for the real concentrations yields (in the case of the nitrate bridge) results significantly different from those obtained by using the limiting conductivities (unlike the case of the chloride bridge). In the following discussion E_j will be taken from the values obtained from the conductivities corresponding to the real concentrations.

TABLE I.—EXPERIMENTAL e.m.f.'s BETWEEN A SOLID MEMBRANE CHLORIDE ELECTRODE AND A SATURATED CALOMEL ELECTRODE

NaCl *mole/kg*	E_{Cl^-}, *mV* KCl bridge	E_{Cl^-}, *mV* KNO$_3$ bridge	ΔE_j, *mV* experimental	ΔE_j, *mV* from Fig. 1
a	*b*	*c*	*d*	*e*
10^{-5}	—	259·0		
2×10^{-5}	—	249·4		
5×10^{-5}	—	234·0		
10^{-4}	213·1	217·5	11·9	12·1
2×10^{-4}	199·1	202·1	10·5	11·2
3×10^{-4}	187·9	191·8	11·2	10·7
5×10^{-4}	177·1	176·6	10·0	10·0
7×10^{-4}	168·5	170·9	9·9	9·6
10^{-3}	157·5	161·4	11·4	9·1
3×10^{-3}	131·4	134·2	10·3	7·7
7×10^{-3}	111·4	113·3	9·4	6·7
10^{-2}	102·1	104·2	9·6	6·5
3×10^{-2}	76·3	77·2	8·4	5·5
8×10^{-2}	54·4	54·4	7·5	4·8
10^{-1}	49·4	49·4	7·5	4·7
2×10^{-1}	34·1	33·4	6·8	4·5
3×10^{-1}	25·3	24·3	6·5	4·5
5×10^{-1}	14·4	13·1	6·2	4·6
1	−0·5	−2·0	6·0	4·9
2	−16·7	−17·9	6·3	5·3
3	−26·6	−28·2	5·9	5·5
4	−34·7	−36·2	6·0	5·6
5	−41·9	−43·7	5·7	5·6
6	−49·1	−50·8	5·8	5·6

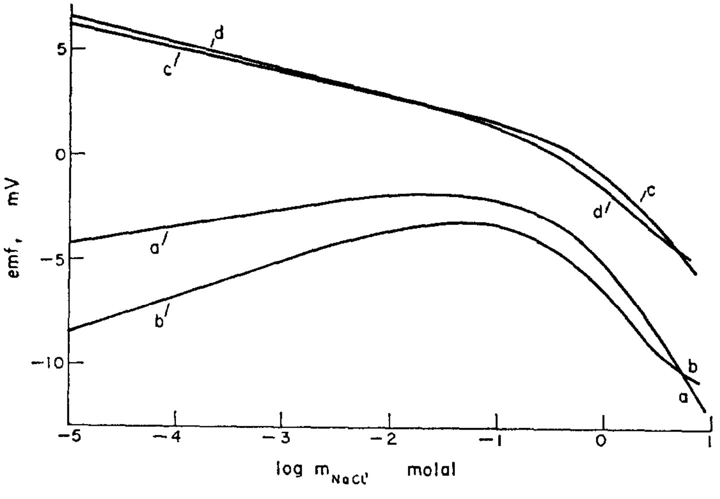

FIG. 1.—Liquid junction potentials calculated with the Henderson equation. *a–b:* for 1*M* KNO$_3$ bridge; *c–d:* for saturated KCl bridge; *a* and *c* using limiting conductivities; *b* and *d* using conductivities calculated for the respective concentrations.

The values of E_j plotted in Fig. 1 allow the calculation of the e.m.f. between the chloride bridge and the nitrate bridge (ΔE_j) for a junction obeying the Henderson equation. It is of interest to compare such calculated ΔE_j values with the experimentally available ΔE_j. For the reference solution of 0·1m sodium chloride, ΔE_j has been determined in 47 experiments as 7·5 ± 0·3 mV. Employing this value and the difference between the e.m.f.'s of columns *b* and *c* in Table I, the values listed in column *d* are obtained. Comparison with the Henderson equation values (column *e*) shows that the agreement is only fair, so that at least one of the bridges, and probably both, will contribute E_j's not following exactly the Henderson equation. It should be noted that the use of limiting conductivities reduces the agreement considerably.

When a saturated potassium chloride bridge is employed against a chloride-sensitive electrode, the leakage of potassium chloride into the test solution has to be considered. For test solutions containing a high chloride concentration such a leakage can be insignificant. For dilute chloride solutions it is necessary to allow for the contamination. Actually two effects of the contamination have to be considered: the first is simply the increase of the concentration of chloride; the second is the increase of the ionic strength of the solution, which affects the activity coefficient of the ions. The two effects can differ not only in magnitude but also in sense: in dilute solutions the two effects will in general oppose each other.

The contamination can be studied by observing the change of e.m.f. with time. After a period in which the e.m.f. changes due to the step-change in the activity of the test solution,[2] the e.m.f. assumes a steady final value when no appreciable contamination occurs, while an approximately linear decrease (or increase) of e.m.f. with time is found when contamination does occur. Two such examples of contamination are presented in Fig. 2.

The corrected e.m.f. (E_{corr}) can be easily evaluated from the experimental e.m.f. (E_{exp}) by using equation (1), which follows from the geometry of Fig. 2:

$$E_{\mathrm{corr}} = E_{\mathrm{exp}} - t(\mathrm{d}E_{\mathrm{exp}}/\mathrm{d}t)_{\mathrm{lin}} \qquad (1)$$

where the subscript "lin" denotes the linear part of the curve. The E_{corr} so obtained is plotted as open circles in Fig. 2.

The slope of e.m.f. against time in the linear part of the curve is controlled mainly by three factors: the rate of leak of the bridge solution into the test solution; the volume of the test solution; and the initial concentrations of the bridge solution and the test solution. In the case illustrated in Fig. 2 (where the bridge is a saturated potassium chloride solution) the rate of leak is about 5×10^{-7} mole of potassium chloride per hour, and the volume of the test solution is about 30 ml. Under these conditions no extrapolation is necessary for test solutions above 10^{-1} m; extrapolation can yield results within our experimental precision for solutions down to 10^{-3} m; between 10^{-3} and 10^{-4} m the intercept is accurate only within ±1 mV; below 10^{-4} m the extrapolation can give only qualitative estimates. These considerations apply to the results for the chloride bridge listed in column *b* of Table I.

The next point of interest is how the leakage of a concentrated electrolyte affects the activity coefficients in the test solution, through the change in the ionic strength. Under the conditions described above, the molality of the sample has been found to increase by about $1{\cdot}5 \times 10^{-5}$ m/hr. Thus for a 10^{-4} m sample of sodium chloride

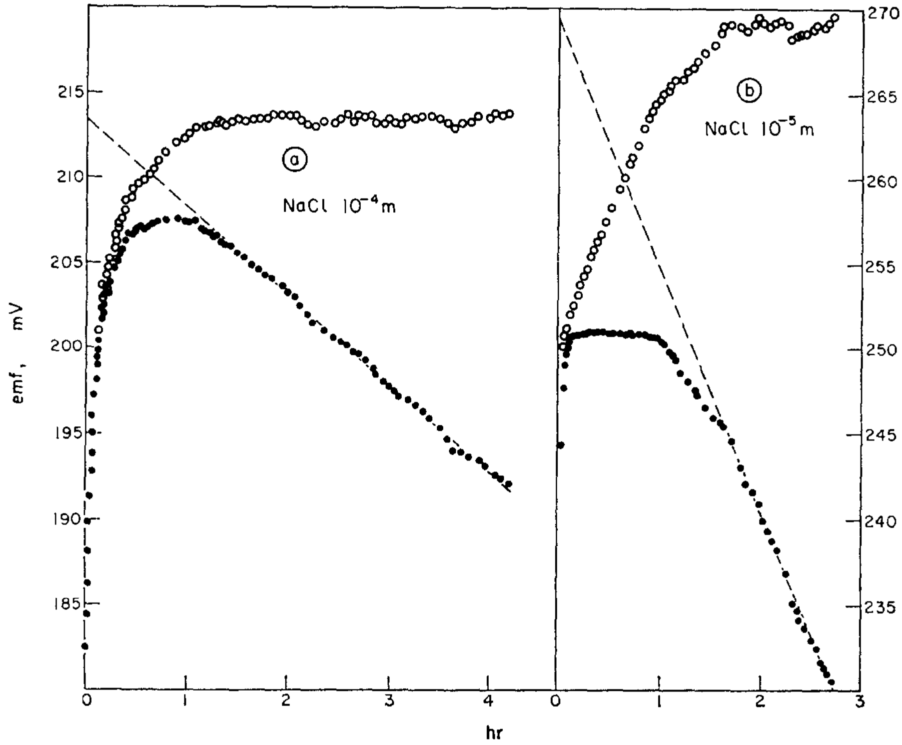

FIG. 2.—Change of e.m.f. with time for a chloride electrode soaked in 0·1 m NaCl. Filled circles: experimental results; open circles: corrected by use of equation (1); *a*— in 10^{-4} m NaCl; *b*— in 10^{-5} m NaCl.

the $\gamma_{\pm}$ would change after 1 hr of measurements from 0·995 to 0·994—an insignificant effect. For more concentrated test solutions the effect would be even smaller, as the relative change in ionic strength would be smaller. For more dilute test solutions the relative change in ionic strength will become more significant, but the actual effect on $\gamma_{\pm}$ will be negligible, as in one hour $\gamma_{\pm}$ can change only from 1·000 (for an infinitely dilute solution with no leakage) to 0·995 (due to the leakage). These considerations support our assumption that the change in $\gamma_{\pm}$ due to the change in ionic strength caused by the liquid junction may be safely neglected.

Choice of the reference solution

In order to obtain reproducible results with electrodes which have a standard potential E^{0} that is not constant, it is necessary to choose a reference solution and to assign to it a reference e.m.f. This has been stated briefly previously.[1] However there is a difference between the choice of a reference solution for a reference e.m.f., and the choice of a reference solution for a reference γ. As a new approach will now be suggested, this point requires some elucidation. Theoretically the best reference solution would be a very dilute one, so that its activity coefficient would be close enough to unity, and the various conventions for the single-ion activities would yield the same activity coefficients within the experimental accuracy. For example, in the aqueous solutions of sodium chloride, $\gamma_{\pm NaCl}$ is 0·965 at 10^{-3} m, while $\gamma_{\pm KCl}$ has the same value at the same concentration of potassium chloride. Thus at this concentration $\gamma_{\mathrm{Cl^-(McInnes)}} = \gamma_{\mathrm{Cl^-(Guggenheim)}}$ even though both coefficients still differ significantly from unity, since an error of ±0·5 mV corresponds approximately to 0·02 in γ. For a sodium chloride solution of 10^{-4} m, $\gamma_{\pm} = 0{\cdot}995$, so that this solution would be dilute enough for γ to be assumed to be unity even within the experimental precision of ±0·1 mV. Unfortunately the e.m.f.'s obtained with the best available chloride and sodium electrodes are not Nernstian at 10^{-4} m, as can be seen on plotting the results tabulated in Table I: at 10^{-4} m the e.m.f.'s (corrected for E_j) fall about 3 mV below the Nernst slope. Furthermore, measurements in such dilute solutions suffer from various experimental difficulties, especially the risk of contamination on preparation and during the measurement. From practical considerations the 0·1 m sodium chloride solution has been chosen as the reference solution. Such choice suffices for compiling a reproducible and unambiguous table of experimental e.m.f.'s for a set of electrodes even with a reasonably unstable $E°$, but still leaves open the choice of a reference γ for the comparison of the various conventions for $\gamma_{\mathrm{Cl^-}}$ and $\gamma_{\mathrm{Na^+}}$. The objections to the choice of the 10^{-4} m sodium chloride solutions have been stated above in connection with the reference solution for the e.m.f. One alternative approach is to use again the e.m.f. of the 0·1 m reference solution as the starting point for the calculation of γ. The great advantage of such an approach is that the e.m.f.'s of the reference solution are completely reproducible since they are chosen arbitrarily, while the e.m.f.'s of any other solution will in general be subject to some experimental error. However, this approach has at least one considerable disadvantage which did not apply to the choice of the 0·1 m solution as reference for the e.m.f. By assignment of the "correct" γ to the 0·1 m concentration according to some assumption, the coefficients calculated for the vicinity of the 0·1 m concentration will appear also to be nearly "correct", and the inconsistency of the assumption will become apparent (if at all) only at some distance from the 0·1 m concentration. On the other hand, when the very dilute solution is used as reference, the various γ's will all start near unity, and their divergence from the curve calculated with a wrong assumption will be marked in the interesting range of concentrations between 10^{-2} and 6 m (compare Figs. 3 and 4 with Fig. 5). Thus the method using the 0·1 m solution as reference is less sensitive than that using the very dilute solution.

A compromise was attempted in our previous work,[1] the 10^{-3} m solution of sodium chloride being used as basis for calculations. At this concentration the behaviour of the electrodes appears still to be Nernstian, the experimental results are fairly reproducible, and the various conventions yield the same γ, even though it is not unity. The results on the whole justified this approach, but the deviation of the γ's obtained for low concentrations was considerable, as was pointed out in the discussion of the results.

It appears worthwhile to compare the results obtained by the two approaches. For brevity we shall refer to the choice of the 10^{-3} m solution for reference as "approach I", while the choice of the 10^{-1} m solution will be referred to as "approach II". In practice, the difference between the two approaches is equivalent to a choice of two different standard potentials ($E°$) for the electrode, as can be seen from the following quantitative considerations. We employ an asterisk to mark the values corresponding to the reference solution of our choice. In the Nernstian range the relation between the e.m.f. (corrected for E_j) of the first reference solution (E_{I}^*), the standard potential

($E_I°$), the molality (m_I^*), and the activity coefficient taken from the literature using one of the single-ion conventions discussed (γ_I^*), is:

$$E_I^* = E_I° - \frac{RT}{F}\ln m_I^* - \frac{RT}{F}\ln \gamma_I^*. \tag{2}$$

So $E_I°$ is determined by the experimental E_I^*, the known m_I^* and the chosen γ_I^*. When approach II is tried, $E_{II}°$ is obtained similarly from well defined values. Obviously $E_I°$ should equal $E_{II}°$ had all our assumptions been correct. The fact is that $E_I° \neq E_{II}°$, so that the interchange of the two approaches is not trivial.

The following relations are easily deduced from equation (2):

$$E_I° - E_{II}° = E_I^* - E_{II}^* + \frac{RT}{F}\ln\frac{m_I^*\,\gamma_I^*}{m_{II}^*\,\gamma_{II}^*} \tag{3}$$

and for *any* concentration

$$\ln\frac{\gamma_I}{\gamma_{II}} = \frac{F}{RT}(E_I° - E_{II}°) = \text{constant} \tag{4}$$

It is thus evident that the γ's of one approach can be obtained from the γ's of the other approach merely by multiplication by the constant factor of $\exp[(E_I° - E_{II}°)F/RT]$.

In our case the activity coefficients γ_{Cl^-} have first been calculated by approach II and the equation

$$E = E° - E_j - \frac{RT}{F}(\ln m_{Cl^-} + \ln \gamma_{Cl^-}) \tag{5}$$

where E is the experimental value of e.m.f. appearing in Table I, E_j is taken from Fig. 1, and $E°$ is calculated from the reference solution of 0·1 m sodium chloride with E = 49·4 mV and the corresponding γ's taken from the literature; for the test of the MacInnes convention γ_{Cl^-} was taken as 0·770, while for the Guggenheim convention it was taken as 0·778.[3,4] These reference γ's are shown by asterisks in Figs. 3 and 4.

It should be noted that when approach II is adopted it is necessary to present the results in two separate figures, as $\gamma^*_{II(\text{Guggenheim})} \neq \gamma^*_{II(\text{MacInnes})}$, so that the calculated γ's appearing in one figure differ from the corresponding γ's appearing in the second figure. On the contrary, when approach I is adopted, a single figure suffices (*cf.* Fig. 5), as $\gamma^*_{I(\text{Guggenhiem})} = \gamma^*_{I(\text{MacInnes})}$.

In the results dealt with in this paper the scatter of e.m.f.'s at 10^{-3} m is small. The average value of 157·5 mV for the chloride bridge given in Table I compares well with the average of 157·6 mV obtained previously with the Ag/AgCl electrode.[1] The average value of 161·4 mV for the nitrate bridge is taken from 3 readings: 161·5, 161·3 and 161·4, taken at intervals of one month. It appears therefore that the use of approach I is justified in this case. The γ's calculated by using this approach are presented in Fig. 5.

The consistency of the results

The γ's corresponding to the two conventions discussed are drawn in Figs. 3–5 as continuous curves, while the γ's calculated with the aid of equation (5) are shown as points. The 24 sets of points plotted are based on the 24 values tabulated in Table I; these are average values, representing over 100 experimental measurements. The scatter of the points is slight between the concentrations 10^{-3} and 6 m, thus supporting

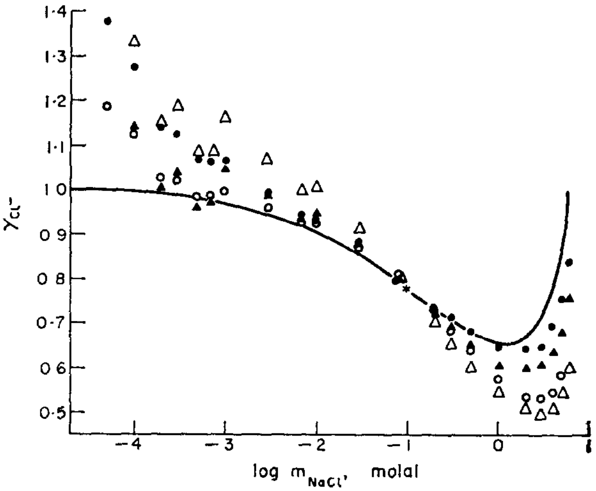

FIG. 3.—Single-ion activity coefficients calculated assuming the Guggenheim convention and using 0·1 m NaCl as standard.
Curve—interpolated from literature values. Circles—for KNO$_3$ bridge. Triangles—for KCl bridge. Open figures—without correction for E_j. Filled figures—corrected for E_j.

the precision of the results. Below 10^{-3} m the results obtained with the chloride bridge are considerably more scattered than those obtained with the nitrate bridge, as explained above.

It can be seen that in all cases the inconsistency between the theoretical curve and the experimental results grows rapidly below 5×10^{-4} m; this appears to be the concentration at which the chloride electrode ceases to behave as an ideal ion-specific electrode. Thus a valid comparison between the fit of the points to the theoretical curves can be made only for concentrations above 10^{-3} m. In this range the MacInnes

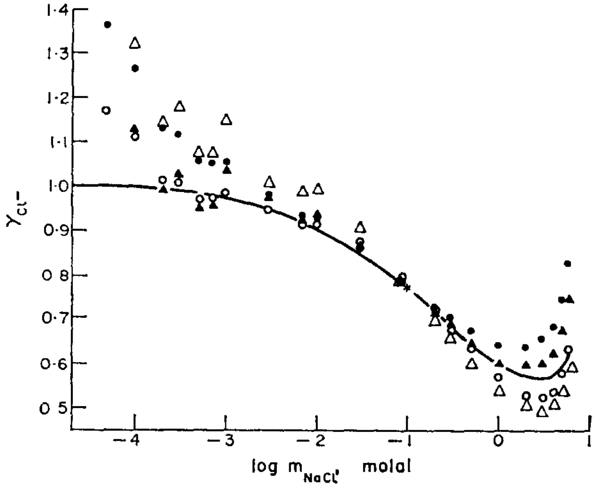

FIG. 4.—Single-ion activity coefficients calculated assuming the MacInnes convention and using 0·1 m NaCl as standard.
Symbols as in Fig. 3.

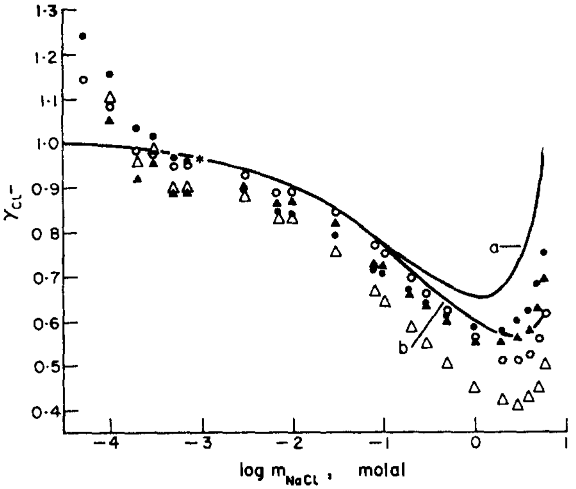

FIG. 5.—Single-ion activity coefficients 10^{-3} m NaCl as standard. *a*—Guggenheim convention; *b*—MacInnes convention. Symbols as in Fig. 3.

convention appears to give a better fit than the Guggenheim convention. To obtain a quantitative comparison the root mean square deviation from the theoretical curves has been calculated for the 16 concentrations between 10^{-3} and 6 m. The results are summarized in Table II.

Since our experimental precision yields γ's accurate within $\pm 0{\cdot}01$, it can be seen from Table II that approach I favours significantly the MacInnes convention. When approach II is used the experiments with the chloride bridge favour the MacInnes convention, while those with the nitrate bridge slightly favour the Guggenheim convention, but the difference in RMS deviation is still within the experimental error, so that it is not significant.

Similar calculations were carried out for the results without correction for E_j. The RMS deviations are well over 0·1 (all favouring the MacInnes convention). The only exception is the RMS deviation for the nitrate bridge without correction for E_j: for the Guggenheim convention it is 0·16, in line with the results quoted above, but for the MacInnes convention it is only 0·03—a better fit than that of any previous results, as can also be seen in Figs. 3–5. Thus the conclusion could be reached, if not all the evidence was considered, that the neglect of E_j gives more consistent results than allowance for E_j. The consistency in this case is probably due to the discrepancy

TABLE II.—ROOT MEAN SQUARE DEVIATION FROM THE THEORETICAL γ_{Cl^-} OF THE COEFFICIENTS CALCULATED FROM THE EXPERIMENTAL e.m.f.'S CORRECTED FOR E_j

		RMS deviation for Guggenheim convention	 MacInnes convention
Approach I	KCl bridge	0·13	0·04
	KNO_3 bridge	0·11	0·06
Approach II	KCl bridge	0·10	0·05
	KNO_3 bridge	0·06	0·08

between the real E_j's and those obtained with the Henderson equation, as remarked in the section dealing with the effects of E_j.

The following conclusions appear justified. When approach II produces a significantly better fit for one of the single-ion conventions, it is to be expected that approach I, had it been experimentally justified, would produce an even better fit for this convention. On the other hand the absence of significant fit on the use of approach II does not necessarily indicate that approach I would also fail to yield a significant difference of fit between the conventions. Approach I appears thus to be preferable whenever the experimental conditions allow it. Only if the electrode is suspected of non-Nernstian behaviour or if the readings are not reproducible at the low concentration reference solution is it advisable to employ approach II.

Finally, the effect of the use of different electrodes may be considered. The possibility of getting different results when using different makes of electrodes has already been pointed out.[5] As a concrete example the recent paper of Hansen *et al.*[6] illustrates how the use of 3 different chloride electrodes yields 3 different sets of results. According to the measurements reported, there is a considerable difference between the results obtained with an Ag/AgCl electrode of the second kind, and a solid membrane electrode, even though the final results are equivalent. This may be due to the fact that the method of measurement was different for each electrode. In our case comparison of column *b* in Table I of the present paper with Table I of reference[1] shows that the results obtained with the solid membrane chloride electrode agree within the experimental error with those obtained with the Ag/AgCl electrode. In fact, the range of agreement extends from 10^{-5} to 6 m sodium chloride, while the claim of the manufacturers[7] is only up to 1 m. The response time of the solid membrane electrode is also comparable with that of the Ag/AgCl electrode, so that in all respects the two electrodes appear to be equivalent in pure aqueous sodium chloride solutions.

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Zusammenfassung—Die EMK-Werte zwischen einer Chloridelektrode und einer Bezugselektrode wurden in wäßrigen NaCl-Losungen zwischen 10^{-5} und 6 m gemessen, wobei Brücken mit gesättigtem KCl und mit 1 M KNO_3 verwendet wurden. Der Effekt der verschiedenen Brückenlösungen wird berechnet und diskutiert. Die Konsistenz der Ergebnisse wird untersucht, wenn man die Annahmen nach MacInnes oder nach Guggenheim verwendet. Die Wahl verschiedener Bezugspunkte für die Standardisierung der EMK-Werte und Aktivitätskoeffizienten wird diskutiert. Die Ergebnisse mit einer Ag/AgCl-Elektrode zweiter Art und mit einer Chloridelektrode mit fester Membran werden verglichen.

Résumé—On a mesuré les valeurs de f.é.m. entre une électrode au chlorure et une électrode de référence en solutions aqueuses de NaCl entre 10^{-5} et $6M$, en utilisant des ponts de KCl saturé et de KNO_3 $1M$. On calcule l'influence des diverses jonctions liquides et en discute. On examine la consistance des résultats en admettant, soit la convention de Mac Innes, soit celle de Guggenheim. On discute du choix de différents points de référence pour l'étalonnage des f.é.m. et pour les coefficients d'activité. On effectue une comparaison entre les résultats obtenus avec une électrode Ag/AgCl de deuxième espèce et une électrode au chlorure à membrane solide.

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PREPARATION OF D-(—)-*trans*-1,2-DIAMINOCYCLOHEXANE-*N*,*N*,*N*′,*N*′-TETRA-ACETIC ACID AND ITS USE AS A SPECTROPOLARIMETRIC REAGENT FOR LEAD

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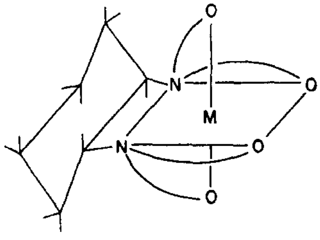
Summary—D-(−)-*trans*-1,2-diaminocyclohexane-*N*, *N*, *N*′, *N*′-tetra-acetic acid [D(−)DCTA] was prepared stereospecifically in good yield by the condensation of the resolved diamine, D-(−)-*trans*-1,2-diaminocyclohexane, with sodium chloroacetate at 16°, followed by use of a strong cation-exchanger to obtain the free acid. Distinct differences were noted in the infrared spectra of the optically active acid and the racemate. The molecular rotation of D(−)DCTA showed strong dependence on the pH of the solution. D(−)DCTA was used as a stereospecific chelometric reagent in the spectropolarimetrically monitored determination of lead.

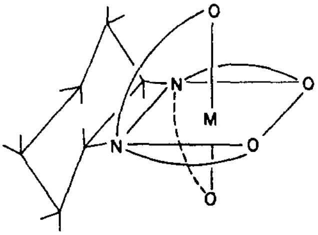
THE REAGENT *trans*-1,2-diaminocyclohexane-*N*,*N*,*N*′,*N*′-tetra-acetic acid (DCTA) was first prepared by Schwarzenbach and Ackermann[1] in their study on the effect of the positions of the nitrogen atoms on the thermodynamic stability of metal–ligand complexes for a series of diaminocyclohexanetetra-acetic acids. The complexes of DCTA with most metal ions are more stable than those of EDTA or 1,2-propylenediaminetetra-acetic acid (PDTA).[2] This greater stability (generally 1–2 units in log K for most of the metal complexes) can be attributed to the fact that during chelation, the carbon chain between the nitrogen atoms in both EDTA and PDTA has to be rotated to bring the nitrogen atoms into the same plane for chelation between the nitrogen atoms and the metal ion to occur. The thermodynamically preferred chair configuration of *trans*-DCTA, with the nitrogen atoms in equatorial positions, demands that very little reorientation of the nitrogen atoms is necessary for chelation to occur.

Commercially available *trans*-DCTA is a racemic mixture of the two possible optical isomers, D(−) and L(+). Ferrone attempted the resolution of DCTA into its optical isomes, using (+)-phenylethylamine, (+)-camphor sulphonate, and (—)-quinine, but none of these attempts gave a crystalline diastereoisomer. He also tried to prepare the L-(+)-isomer of the acid by direct synthesis from L-(+)-*trans*-1,2-diaminocyclohexane [L(+)chxn] and sodium chloroacetate, following the general method used in the preparation of ethylenediaminetetra-acetic acid, but obtained only a viscous syrup which would not crystallize upon acidification.[3] Dwyer and Garvan also failed in their attempt to resolve the racemic acid with (+)-cinchonine, but were successful in the resolution by using the (—)-*cis*-dinitrobis(ethylenediamine)cobalt(III) ion.[4] This procedure is very long and tedious and the yield is extremely low.

The work by Dwyer and Garvan showed that only two of the four possible isomers of the metal chelate were obtained,[4] the $(+)_{546}$[Co(−)DCTA]$^-$ and $(-)_{546}$[Co(+)-DCTA]$^-$ isomers, proving that both optical isomers of *trans*-DCTA are completely stereospecific in their reaction with the cobalt(III) ion. Models show that it is impossible to obtain the isomers $(+)_{546}[Co(+)DCTA]^-$ and $(-)_{546}[Co(-)DCTA]^-$ because of the fixed stereochemistry of the cyclohexane ring and its inability to accompany certain chirality, because of steric hindrances of the methylene groups of the ring and the acetato groups (see Fig. 1). Failure to racemize solutions of these optically active complexes at 100° with activated charcoal confirmed this conclusion experimentally. This conforms with Jaeger's theory that one configuration of the complex is incompatible with one optical isomer of the ligand.[5]



L*- $[M(D(-)DCTA)]^{n-}$



D*- $[M(D(-)DCTA)]^{n-}$

FIG. 1.—Stereospecificity of D(−)DCTA in forming L*-$[M\text{-}(D(-)DCTA)]^{n-}$ complexes.

D-(−)-*trans*-1,2-diaminocyclohexane-*N*,*N*,*N*′,*N*′-tetra-acetic acid [D(−)DCTA] was prepared by stereospecific condensation of the resolved diamine with concentrated sodium chloroacetate solution in a strongly basic medium, followed by the use of a strong cation-exchange resin to obtain the free acid.

Spectropolarimetric titrimetry is a relatively new analytical technique first described by Kirschner and Bhatnagar.[6] The optical rotation of the system is constantly monitored while the titration proceeds. An inflection in the change of the optical rotation indicates the end-point of the titration. Spectropolarimetric titrimetry has been applied to acid-base titrations, as well as to different metal systems.[7] Recent work by Pearson *et al.*[8,9,10] has shown the use of D-(−)-1,2-propylenediaminetetra-acetic acid as titrant for transition, heavy and lanthanide metals. The spectropolarimetric method offers several advantages over other chelometric methods, especially in choice of pH range for quantitative titration, because the pH range is not limited by the need to ensure a sharp indicator colour transition; the optically active ligand and stereospecifically formed complex serve as self-indicators. Since the observed rotation is essentially linear over large concentration ranges, the end-point is located by graphical extrapolation. The large molecular rotation values of many of the complexes make the method very sensitive.

In this work the synthesis and some properties of D-(−)-*trans*-1,2-diaminocyclohexane-*N*,*N*,*N*′,*N*′-tetra-acetic acid are described, together with its use as titrant for lead.

EXPERIMENTAL

Resolution of racemic trans-1,2,-*diaminocyclohexane and isolation of* D-(−)-trans-1,2- *diaminocyclohexane*

Technical grade racemic *trans*-1,2-diaminocyclohexane was distilled under reduced pressure, b.p. 75–80°/16 mbar. Then 200 g of racemic diamine were added dropwise with mechanical stirring to a solution of L-(+)-tartaric acid (350 g in 400 ml of water), the temperature being maintained below 55°. This mixture was allowed to cool to about 5° and kept cold for an hour, after which it was filtered (sintered-glass Büchner filter). The white crystals of the diastereoisomer, D-(−)-*trans*-1,2-diaminocyclohexane L-(+)-tartrate, were washed with 120 ml of ice water and sucked dry. The filtrate was set aside for later use in an attempt to isolate the L(+) isomer of the diamine. The crystals of the diastereoisomer were dissolved in the least amount of boiling water necessary (~325 ml), by adding the crystals in small portions to a beaker of hot water, with mechanical stirring to prevent burning of the product. A litre of absolute ethanol was added to the solution, which was then allowed to cool (with stirring) to about 5° during one hour, and then filtered. The specific rotation of a 1% solution of the diastereoisomer in water was determined to be +12·1° at 589 nm and this value was compared with the literature value[4] of +12·0°. This measurement served as the criterion of purity. The yield was 90%.

The diastereoisomer was suspended in water by stirring, and solid sodium hydroxide was added. The colour turned darker and the mixture separated into two layers. The upper layer was decanted off and distilled from solid potassium hydroxide under reduced pressure, b.p. 75–80°/16 mbar.

Preparation of D-(−)-trans-1,2-*diaminocyclohexane*-N,N,N′,N′-*tetra-acetic acid*

A solution of 280 g (3 mole) of monochloroacetic acid in 150 ml of water was cooled to 10° and a cold solution of sodium hydroxide, 240 g (6 mole) in 500 ml of water, was added dropwise with mechanical stirring, the temperature being kept below 16°. Then 58 g (0·5 mole) of the previously resolved D-(−)1,2-diaminocyclohexane were slowly added through a dropping funnel, the temperature being kept below 16° during the addition and for six days more and then being raised to and kept at 19° for an additional six days, the solution being stirred throughout. The pH was adjusted to 3·5 with concentrated hydrochloric acid and the solution evaporated on a steam-bath in a current of air to a volume of 600 ml. The solid sodium chloride was removed by filtration (sintered-glass Büchner funnel). The filtrate was poured into 2 l. of vigorously stirred absolute ethanol and stirred overnight to allow crystallization. The crystals were suspended in 600 ml of glacial acetic acid and heated, with stirring, to 40° in order to dissolve the disodium salt of D(−)DCTA. The undissolved sodium chloride was filtered off and washed with 30 ml of warm glacial acetic acid. The washings and filtrate were combined and added slowly to 3 l. of benzene and the mixture was stirred overnight. The viscous syrup deposited was crystallized by decanting off the benzene and pouring the viscous syrup into 2 l. of rapidly stirred acetone. This mixture was stirred for 1 hr and the crystals formed were allowed to settle out. The acetone was decanted off, 2 l. of fresh acetone were added, and the mixture was stirred overnight to dissolve traces of acetic acid. It was then filtered and the white solid was allowed to dry in air. The solid was dissolved in 1·5 l. of demineralized water and evaporated on a steam-bath to approximately 1 l., much of the acetic acid and acetone being thereby removed. The pale yellow solution was pumped onto a large heated ion-exchange column packed with Dowex 50W-X8, a strong cation-exchange resin which had been previously washed with 8 l. of hot 6*M* hydrochloric acid, followed by 12 l. of demineralized water, to remove traces of the iron(III) generally present in the material and to convert the resin into the acid form. The column was washed with 2 l. of cold demineralized water and these first 2 l. of pale yellow eluate were discarded, as they contained traces of acetic acid and only negligible amounts of the optically active material. The column was then heated to 95–100° and the active acid was eluted with ~44 l. of boiling demineralized water at a flow-rate of 10 l./hr until the eluate no longer showed optical activity. The eluate was reduced to about 400 ml by vacuum stripping and 600 ml of reagent grade acetone were added. After cooling of the solution overnight in an ice-bath, white crystals formed. They were collected on a medium porosity sintered-glass Büchner funnel and dried first in air and then overnight in a vacuum oven at 115°/4 mbar. The yield was 33%.

The specific rotation at 589 was −53·4° for a 0·5% aqueous solution (literature value[4] for the anhydrous acid −53·0°). M.p. 236–238° (decomp.), literature value[4] 237°. Calculated for $C_{14}H_{22}N_2O_8$: C 48·55%; H 6·40%; N 8·09%; O 36·96%; found C 48·8%; H 6·3%; N 8·2%; O 36·7%.

Visual chelometric titrations with standard lead solution (Xylenol Orange as indicator) showed 100·0 ± 0·15% purity.

Apparatus

A Perkin–Elmer Model 141 Photoelectric Polarimeter with a 0·1-m flow-through cell was used to monitor the titration. The titration vessel was constructed from a 125-ml Erlenmeyer flask with one glass tube attached at the bottom centre and another about one-fifth up the side, and was connected to the flow-through cell with Tygon tubing. A magnetic stirrer both mixed the solution and pumped it through the polarimeter cell. A 5-ml microburette with the tip immersed below the surface of the liquid was used to deliver the titrant.

Reagents

With the exception of the solution of D(−)DCTA, all solutions were prepared from reagent grade chemicals. D(−)DCTA, prepared as above, and reagent grade potassium hydroxide were dissolved in demineralized water and this solution was standardized by visual titration against standard lead solution at pH = 4·7, with Xylenol Orange as indicator. All solutions were stored in polyethylene bottles.

Effect of pH on the molecular rotation of D(−)*DCTA*

Dwyer and Garvan[11] reported that the molecular rotation of D-(−)-1,2-propylenediaminetetra-acetic acid varied as the pH was changed. Pearson *et al.*[8] also studied this pH dependence and attributed it to the degree of protonation of the ligand. A similar investigation was made with D(−)DCTA at the 5 wavelengths available on the instrument and the results are shown in Figs. 2 and 3.

Spectropolarimetric titration of lead

An aliquot of lead solution was buffered to pH 4·7 with sodium acetate–acetic acid buffer and diluted with demineralized water to 100 ml in the titration vessel. The flow-through polarimeter cell was inserted in the instrument, and the digital read-out set at zero. The titrant was relatively concentrated in order to minimize dilution effects. After each incremental addition of titrant, the rotation was read when it had stabilized, and the titration graph was plotted, a dilution correction

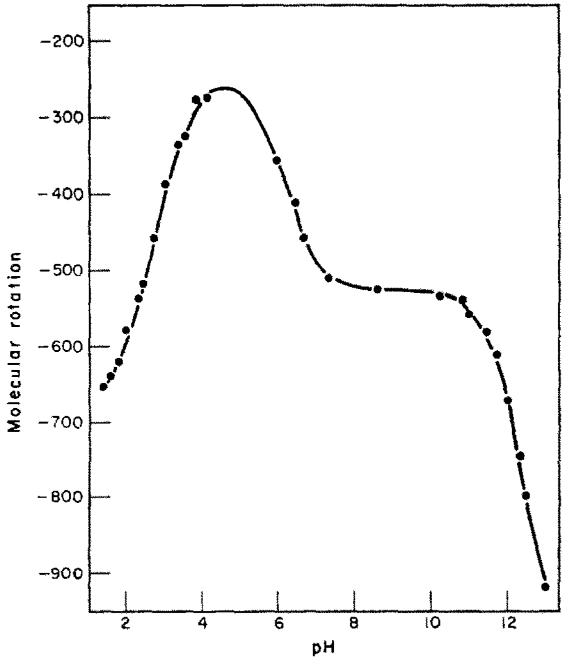


FIG. 2.—The molecular rotation of D(−)DCTA *vs.* pH at 365 nm, $\mu = 0{\cdot}50$ (KNO_3).

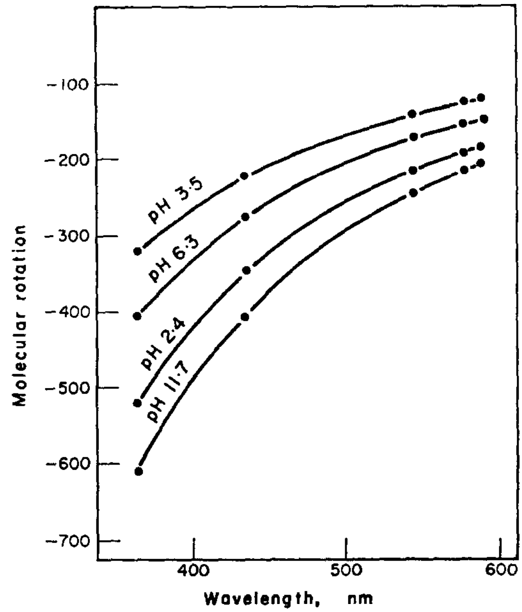


FIG. 3.—Optical rotatory dispersion spectra of D(—)DCTA at various pH values, $\mu = 0{\cdot}50$ (KNO_3).

being applied, and extrapolated to give the end-point. Generally only five points before and five after the end-point are needed.

RESULTS AND DISCUSSION

The change in the molecular rotation of D-(—)-DCTA with pH is due to successive dissociations of the ligand. The points of inflection of the curve occur at pH values near p*K* values for the racemic acid.

The infrared spectra of both the racemic and the D-(—)-isomer of *trans*-DCTA in Nujol mull were recorded on a Beckmann IR-12 instrument and showed distinct differences, Figs. 4 and 5. The weak broad band at 2550 cm^{-1} has been assigned to

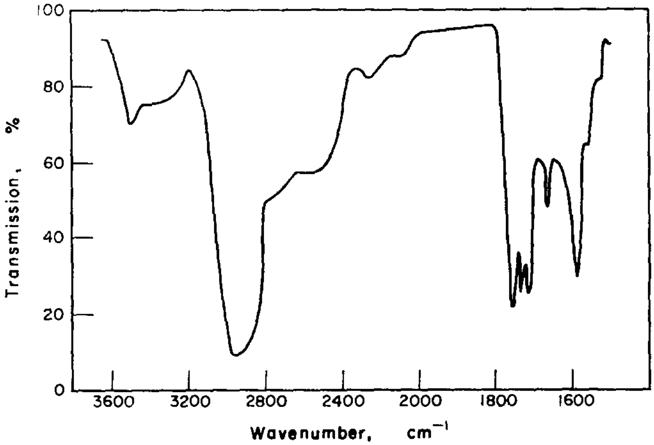


FIG. 4.—Infrared spectrum of racemic *trans*-1,2-diaminocyclohexane-*N,N,N',N'*-tetra-acetic acid.

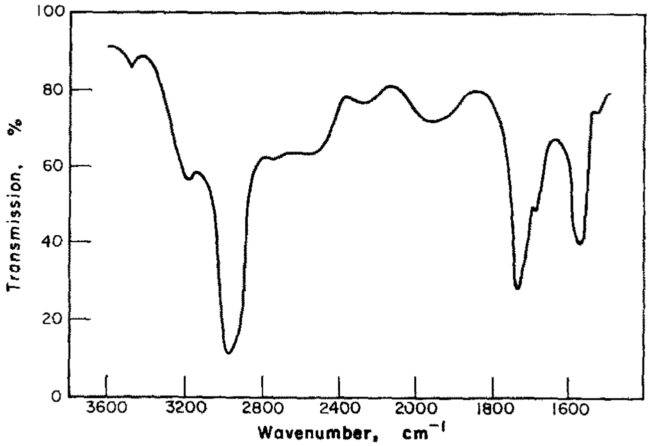


FIG. 5.—Infrared spectrum of D-(−)-*trans*-1,2-diaminocyclohexane-*N*,*N*,*N*′,*N*′-tetra-acetic acid.

the protonated nitrogen; this would suggest that the structure of the optical isomer could allow a higher degree of protonation of one of the nitrogen atoms. The carbonyl stretching bands in the neighbourhood of 1585–1735 cm^{-1} are not as sharp for the optically active DCTA as for the racemate; this suggests a greater degree of intra-molecular hydrogen bonding in the case of the optically active isomer. These conclusions appear to be consistent with the solubility differences: the racemate is very insoluble in water, whereas the optically active isomer is very difficult to crystallize from an aqueous solution. Similar results have been reported by Dwyer and Garvan in their studies of the infrared spectra of racemic and optically active 1,2-propylenediaminetetra-acetic acid.[11]

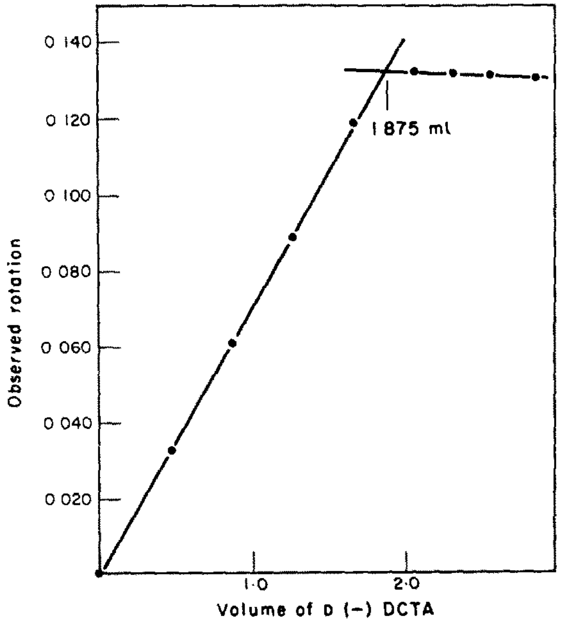


FIG. 6.—Spectropolarimetric titration of 2·0 mg of lead with D(−)DCTA at pH = 4·7 and 365 nm.

A typical titration plot for lead is shown in Fig. 6, and the results are shown in Table I. They agreed within experimental error with those obtained spectropolarimetrically with D-(−)-1,2-propylenediaminetetra-acetic acid and visually with EDTA. Although the molecular rotation of the lead–D(−)DCTA complex is somewhat greater than that of the lead–D-(−)PDTA complex at 365 nm, the sensitivity at this wavelength is not significantly greater. The wavelength of 365 nm was selected because it gave the greatest difference between the molecular rotations of the lead complex and the ligand.

TABLE I.—CONDITIONS AND RESULTS FOR THE SPECTROPOLARIMETRIC TITRATION OF LEAD WITH D-(−)-*trans*-1,2-DIAMINOCYCLOHEXANE-*N*,*N*,*N*′,*N*′-TETRA-ACETIC ACID

[D(−)DCTA], *M*	pH 4·7 buffer, *ml*	Lead Taken, *mg*	 Found, *mg**
0·08395	25·00	20·20	20·25 ± 0·03
0·05110	25·00	20·20	20·23 ± 0·01
0·005230	10·00†	2·020	2·036 ± 0·007

* Average of at least 3 determinations.

† Total volume of the solution was 50 ml, and a smaller titration cell was employed.

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Zusammenfassung—D-(−)-*trans*-1,2-Diaminocyclohexan-N,N,N′,N′-tetraessigsäure (D(−)DCTA) wurde in guter Ausbeute stereospezifisch durch Kondensation von optisch aktiven D-(−)-*trans*-1,2-Diaminocyclohexan mit Natriumchloracetat bei 16° und Freisetzung der Säure mit Hilfe eines Kationenaustauschers erhalten. Zwischen den Infrarotspektren der optisch aktiven Säure und denen des Racemats wurden deutliche Unterschiede gefunden. Die molare Rotation von D(−)-DCTA ist stark vom pH der Lösung abhängig. D(−)DCTA wurde als stereospezifisches chelometrisches Reagens bei der spektropolarimetrisch verfolgten Bestimmung von Blei verwendet.

Résumé—On a préparé stéréospécifiquement l'acide D-(—)-*trans*-1,2-diaminocyclohexane N,N,N′,N′-tétracétique (D(—)DCTA) avec un bon rendement par condensation de la diamine dédoublée, D-(—)-*trans*-1,2-diaminocyclohexane, avec le chloracétate de sodium à 16°, suivie de l'emploi d'un échangeur cationique fort pour obtenir l'acide libre. On a noté des différences marquées dans les spectres infra-rouges de l'acide optiquement actif et du racémate. Le pouvoir rotatoire moléculaire du D(—)DCTA s'est révélé être fortement dépendant du pH de la solution. On a utilisé D(—)DCTA comme réactif chélatométrique stéréospécifique dans la détermination contrôlée spectropolarimétriquement du plomb.

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EDTA TITRATION OF CALCIUM AND MAGNESIUM WITH A CALCIUM-SELECTIVE ELECTRODE

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Summary—Direct semi-automatic and automatic derivative potentiometric EDTA procedures for the determination of calcium and/or magnesium with a calcium-selective electrode are described. Calcium is titrated in the presence of magnesium at pH 12·0 and the total calcium and magnesium is determined at pH 9·7. Calcium in the range 1–8 mg and magnesium in the range 0·7–5 mg are determined semi-automatically with average errors of about 0·2 and 0·3% respectively and automatically with average errors of 0·4 and 0·7%. Titration times vary from a few seconds to a few minutes.

THE RECENT development of a large number of ion-selective electrodes has resulted in a renewal of interest in analytical potentiometry. During the past three years, a considerable amount of work has been published which deals with the use of such electrodes, and in particular of a calcium-selective electrode.[1–21] Liquid–liquid membrane as well as solid-membrane calcium-selective electrodes are now commercially available,[4,17] the former being more widely used. The electrode responds to the activity of the ionized calcium in the sample, which depends on the ionic strength of the sample. Therefore, the working curve, *E vs.* [Ca^{2+}], should be prepared with standards which have practically the same composition as the samples. Even with such precautions, direct potentiometric techniques are unlikely to give an accuracy better than ±1·2%, because the accuracy of measurements is seldom better than ±0·15 mV and the maximum slope of the working curve is 29·6 mV per activity decade at 25°. Titration techniques yield more accurate results than those obtained by the direct method, because the titration curve is reproducible and the equivalence point can be easily located. In practice, some easily distinguishable point on the titration curve (*e.g.*, a point of inflection or the mid-point of the section of maximum slope) is chosen as the "end-point" and it is assumed that the consumption of the titrant in going from this point to the equivalence point is small.[19] However, such titrations are time-consuming, requiring at least 20 min,[21] because many points are required for each titration curve and each potential measurement is made 30–60 sec after the addition of titrant.[5,16]

It is shown in the following presentation that the control unit of an automatic differential potentiometric titrator coupled with a recording electrometer and a constant-rate burette can be used for the automatic EDTA titration of calcium and/or magnesium with a calcium-selective electrode. It is not necessary to know the end-point potential, because the electronic circuit computes the second derivative voltage of the ordinary potentiometric curve, and this voltage is ideally suited to trigger a relay system which turns the burette off at the inflection point (end-point) of the titration.[22–25] It is also possible to determine calcium and/or magnesium semi-automatically by recording the potentiometric titration curve. The end-point is read from the plot after the titration is completed. Samples containing only calcium or magnesium are titrated at pH 9·7. In samples containing calcium and magnesium, calcium is automatically titrated at pH 12·0 in the presence of magnesium as magnesium hydroxide; total calcium and magnesium is determined at pH 9·7 and magnesium is calculated by difference. Titration times range from a few seconds to a few minutes.

EXPERIMENTAL

Apparatus

A block diagram of the automatic titration system is shown in Fig. 1. The automatic titration controller (S-29691, E. H. Sargent Co.) of the Sargent-Malmstadt titrator was used. The control unit is coupled with a direct-reading, constant rate, motor-driven, automatic burette (Model C, S-11120-10, E. H. Sargent Co.), which provides a titrant delivery rate of 1 ml/min (in the present work the delivery rate was ⅚ of the nominal because the available line voltage frequency was 50 Hz). The burette is plugged into the valve outlet on the back of the control unit. A special cell unit, shown in Fig. 2, was constructed. The unit consists of a beaker platform, a propeller-driven stirring system, an indicator electrode (Orion calcium-activity electrode, Model 92-20), a reference electrode (Coleman saturated calomel electrode, No. 3-512) and a delivery tip. Bakelite rings of different diameters can be inserted in the platform to hold beakers of various sizes. Most of the titrations were performed at room temperature, in a 50-ml beaker.

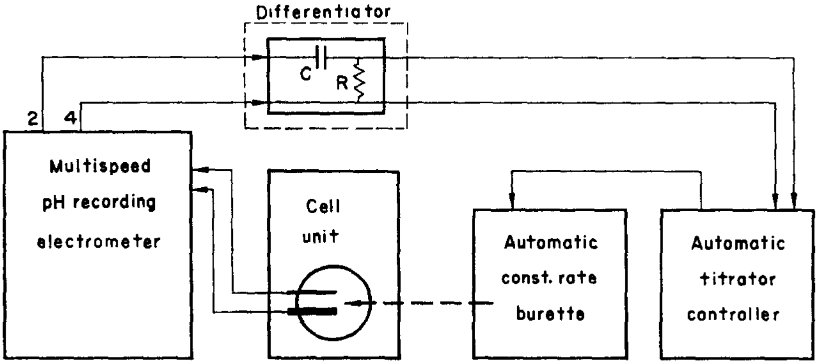

Fig. 1.—Block diagram of automatic titration system.

For automatic titrations the voltage between the electrode pair is fed to the input of a multispeed pH-recording electrometer (Model EUW-301 M, Heath Co.) and the output signal from points 2 and 4 of the chassis plug "U" is fed to the control unit. After the initial assembly and connection of the burette and the electrometer to the control unit, the usual operations consist of placement of sample vessel, pushing the automatic button on the control unit and reading the burette after the automatic termination of the titration. For semi-automatic titrations the control unit is not used and the burette is connected for actuation to the 110-V socket (second from bottom on side of recorder) of the recording electrometer.

Reagents

All solutions were prepared in demineralized water from reagent-grade materials.

Buffer solution. Glycine (37·5 g) dissolved in about 700 ml of water, adjusted to pH 9·7 with 2*M* sodium hydroxide, and diluted to 1 litre. The solution is kept refrigerated when not in use.

EDTA solution, 0·0600*M*. Standardized against standard zinc solution, which is prepared by dissolving reagent grade zinc (>99·9% Zn) in hydrochloric acid, Eriochrome Black T being used as indicator; stored in polyethylene bottles.

Magnesium solution, 0·01000*M*. Prepared from $MgSO_4.7H_2O$ and standardized against the EDTA solution.

Standard calcium solution, 0·01000*M*. Primary standard calcium carbonate is dried in an oven for 3–4 hr at 110° and 1·0009 g are dissolved in the least necessary amount of hydrochloric acid and diluted with water to 1 litre. When this solution was analysed gravimetrically or by titrating against the standard EDTA solution, after the addition of a known amount of standard zinc solution, with Eriochrome Black T as indicator, the results obtained agreed within 0·2% with the theoretical value.

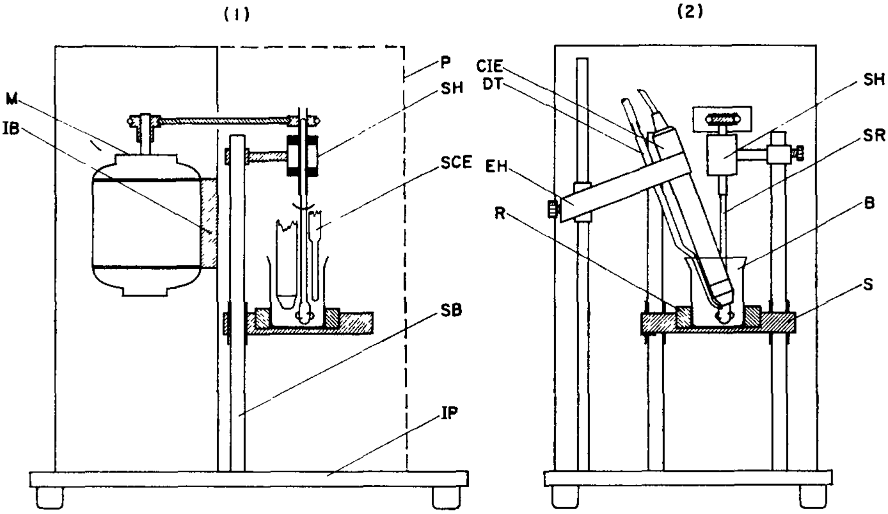

FIG. 2.—Left side-view (1) and front view (2) of the cell unit (scale 1:6). MC—Motor chamber, M—motor (Citenco, type 7 FA/47 200-230-volt a.c., 50 Hz, 1300 rpm), IB—insulation base plate of motor, P—protecting wire net, SH—stirring-rod holder with 2 ball-bearings, SCE—saturated calomel electrode, SB—slide bar, IP—iron plate, CIE—calcium ion electrode, DT—delivery tip (Sargent S-29704), EH—electrode holder (Orion Model 92-00-01), R—Bakelite ring, SR—stirring rod (Sargent S-76669-A), B—50-ml squat beaker, S—sliding platform.

Procedure

Preparation of cell unit and multispeed pH-recording electrometer. Place the stirrer slightly offset from centre and approximately 3 mm from the bottom of the beaker. Place the right-angled delivery tip immediately above the propeller and about 1 mm from the shaft of the stirrer, so that the delivery flow is directed at the shaft. Place the electrodes about 15 mm from the bottom and close to but not touching the sides of the titration beaker. Use small-diameter gum-rubber tubing to connect the tip of the burette to the delivery tip. Mount the complete assembly so that the beaker can be replaced without disturbing the electrode, burette and stirrer assembly. Adjust the scale of the electrometer to read from +50 mV to −150 mV, left to right. Set the chart speed at the desired value (usually 0·15 M/min) and turn the function switch to "Standby".

Semi-automatic titration of calcium and/or magnesium. Take a 25-ml aliquot of the sample in a 50-ml beaker and add 2 ml of buffer solution. Lock the burette "ON" by pressing its delivery push button and turning it by a one-fourth turn. Start the stirrer and after a few seconds turn the function switch to the "Record" position to obtain the titration curve for calcium plus magnesium. For the greatest accuracy calibrate the recorder for each titration, using the burette reading. Use this procedure when the sample contains only calcium or magnesium. Titrate calcium in another 25-ml aliquot of the sample without buffer but with 0·25*M* sodium hydroxide added to bring the pH to 12·0. Calculate the magnesium content by difference from the volumes of EDTA used, subtract also the difference in the blanks.

Automatic determination of calcium and/or magnesium. The procedure is the same as for the semi-automatic method except that at the beginning the function switch is turned to the "Measure" position and the titration is started by pushing the "automatic" button and is automatically terminated at the end-point.

When not in use the calcium electrode is stored in a $10^{-3}M$ calcium chloride solution.

RESULTS AND DISCUSSION

The calcium electrode responds rapidly to changes in calcium activity and with efficient stirring it can be used to follow the course of a complexometric titration of calcium and/or magnesium with continuous addition of titrant. The point of maximal rate of potential change is very close to the equivalence point. Thus at a delivery rate of 0·05 mmole of EDTA/min the end-point (mid-point of the section of maximum slope of the curve) is located beyond the equivalence point by about 0·02 ml of 0·06*M* EDTA. The electrode response to changes in magnesium activity is slower than for calcium and the equivalence point is overshot by 0·05 ml of 0·06*M* EDTA. The blank becomes larger, 0·07–0·10 ml, in automatic titrations. However, the precise definition of the end-point that the calcium electrode provides makes possible the accurate automatic titration of calcium and magnesium even with a blank of 0·10 ml.

The slope of the titration curve, the overall voltage change, and the blank, all depend on sample composition, buffer used, and on experimental conditions, *e.g.*, titrant delivery rate and concentration, stirring rate, size of beaker, position of delivery tip and depth of electrode immersion. The slope and the overall voltage change decrease whereas the blank increases slightly with increasing ionic strength of the test solution. Thus for the titration of 4 mg of calcium the rate of potential change near the equivalence point decreased from about 9 to 3 mV/sec, when the ionic strength of the test solution was increased from 0·03 (pure calcium chloride solution) to 0·4 (calcium chloride sample with added sodium chloride). The blank remained about the same for the semi-automatic method, but it increased for the automatic method by about 0·02 ml of 0·06*M* EDTA. Therefore, if the ionic strength of the test solution is high, for better accuracy with the automatic method the blank should be determined with standards closely approximating to the sample ionic composition. If the preparation of such standards is not easily feasible, the blank can be determined by analysing two portions of the sample differing slightly in magnitude, so that the ionic strength is about the same in both test solutions. For samples containing only calcium or magnesium the blank was determined by titrating standard calcium or magnesium solutions.

When the ionic strength was increased by addition of sodium chloride, the voltage between the electrode pair shifted to more positive potentials, because of sodium interference.[15] Therefore for high ionic strength the scale was adjusted to read from +100 mV to −100 mV. A span of 100 mV, with full scale from 0 to −100 mV, was used in the semi-automatic method for magnesium.

Ammonia/ammonium chloride, tris, ethylenediamine, and glycine buffers were tried. Partial complexing of calcium and/or magnesium, which results in errors in direct potentiometry, has no other effect except the shift of the titration curve. Such shifts were observed during precision studies, even for the same buffer and sample, but had no appreciable effect on the accuracy. Thus, while semi-automatic and automatic end-point potentials for replicates differed by up to 10 mV, the corresponding titrant volumes differed by less than 2%. The glycine buffer was chosen because it gave the greatest rate of potential change in the region of the equivalence point. The amount of buffer added should be such that the pH of the solution at the end-point is greater than 8. In the titration of calcium in presence of magnesium the amount of sodium hydroxide added is such that the pH of the solution at the end-point is greater than 11·2.

The differentiation shows up the signal noise. To minimize noise and the number of false signals, the following precautions were taken: (1) the upper three-quarters of the electrode body were wrapped in aluminium foil, which then was grounded to a common outlet with the electrometer, the burette, the cell unit base and the control unit; (2) the motor was shielded from the rest of the unit and grounded to a separate outlet; (3) a wire net was set in front of the cell unit; (4) the signal was overdamped by turning the damping control on the electrometer clockwise by at least a quarter-turn beyond the point where the pen stopped "jittering"; (5) a special electrode holder was used to avoid trapping of air bubbles on the porous disc; (6) efficient clockwise stirring at 1300 rpm was provided to accelerate the change of sample liquid in immediate contact with the electrode membrane, without drawing air into the solution.

Occasionally during the titration of total calcium and magnesium the addition of titrant was stopped automatically before the equivalence point was reached, usually near a point corresponding to the calcium content of the sample. False early end-points can be easily detected from the potential value shown on the electrometer. If one should occur near the end-point, the titration must be finished semi-automatically by depressing the manual button on the control unit. This is necessary because the control unit has a built-in 10-sec time delay circuit in the automatic control that over-rides the end-point signal. If desired, the 10-sec delay interval may be over-ridden for titrations less than 0·25 ml by releasing the delivery push button on the burette, actuating the automatic button, delaying for 10 sec, then engaging the delivery push button.

TABLE I.—TITRATION RESULTS FOR SAMPLES CONTAINING KNOWN AMOUNTS OF CALCIUM OR MAGNESIUM

Taken, *mg*		Found, *mg*		Error %	
Calcium	Magnesium	Semi-automatic	Automatic	Semi-automatic	Automatic
1·202		1·207	1·185	+0·4	−1·4
2·004		2·004	2·012	—	+0·4
4·008		4·016	4·004	+0·2	−0·1
6·012		6·012	6·012	—	—
8·016		8·008	8·040	−0·1	+0·3
		Av.		0·14	0·44
		Std. devn., for 4 mg Ca ($n = 6$)		0·38	0·60
	0·729	0·733	0·723	+0·5	−0·8
	1·216	1·221	1·199	+0·4	−1·4
	2·431	2·424	2·455	−0·3	+1·0
	3·647	3·647	3·651	—	+0·1
	4·86	4·84	4·88	−0·4	+0·4
		Av.		0·32	0·72
		Std. devn., for 2·4 mg Mg ($n = 8$)		0·34	1·10

Hundreds of samples containing known concentrations of calcium and/or magnesium in different amounts and in different ratios, were titrated to check the proposed method. Some representative data are shown in Tables I–III. The average errors in semi-automatic and automatic titrations were about 0·2 and 0·4% respectively for samples containing only calcium, 0·3 and 0·7% for samples containing only magnesium (Table I) and 0·3 (Table II) and 1·7% (Table III) for total hardness of synthetic samples containing only calcium and magnesium. The error for calcium and magnesium was larger in samples containing both these elements. The large error for magnesium in sample 6, Table III, actually amounts to less than 0·02 ml of titrant. The relative standard deviations for the semi-automatic and automatic titration of

TABLE II.—SEMI-AUTOMATIC TITRATION RESULTS FOR SAMPLES CONTAINING KNOWN AMOUNTS OF CALCIUM AND MAGNESIUM

Taken, *ppm*			Found, *ppm*			Error %		
Calcium	Magnesium	Total hardness as $CaCO_3$	Calcium	Magnesium	Total hardness as $CaCO_3$	Calcium	Magnesium	Total hard-ness
198·8	61·1	748	197·7	62·0	749	−0·5	+1·5	+0·1
158·5	49·1	598	159·2	48·5	597	+0·4	−1·2	−0·2
99·4	30·5	374	99·3	30·6	374	−0·1	+0·3	—
39·7	49·1	301	39·4	48·9	300	−0·8	−0·4	−0·3
59·5	36·8	300	59·1	36·3	297	−0·7	−1·4	−1·0
18·9	10·4	90	19·5	10·0	90	+3·2	−3·8	—
					Av.	1·0	1·4	0·3

TABLE III.—AUTOMATIC TITRATION RESULTS FOR SAMPLES CONTAINING KNOWN AMOUNTS OF CALCIUM AND MAGNESIUM

Taken, *ppm*			Found, *ppm*			Error %		
Calcium	Magnesium	Total hardness as $CaCO_3$	Calcium	Magnesium	Total hardness as $CaCO_3$	Calcium	Magnesium	Total hard-ness
198·8	61·1	748	199·0	61·7	751	+0·1	+1·0	+0·4
158·5	49·1	598	157·2	48·4	592	−0·8	−1·4	−1·0
99·4	30·5	374	99·9	31·2	378	+0·5	+2·3	+1·1
39·7	49·1	301	39·7	48·8	300	—	−0·6	−0·3
59·5	36·8	300	59·2	35·5	294	−0·5	−3·5	−2·0
18·9	10·4	90	19·1	11·5	95	+1·1	+10·6	+5·5
					Av.	0·5	3·2	1·7

4 mg of calcium were 0·38 and 0·6% respectively, whereas for 2·4 mg of magnesium they were 0·34 and 1·1%.

The first and third derivative curves were also used for the semi-automatic and automatic titrations respectively. They were obtained by differentiating the output signal from points 2 and 4 of the chassis plug "U" by a simple resistance-capacitance differentiator (Fig. 1. $R = 0{\cdot}5\ \mathrm{M\Omega}$, $C = 0{\cdot}47\ \mu\mathrm{F}$). Results obtained were less accurate and precise than those obtained by using the titration curve or its second derivative curve.

The semi-automatic method provides the best accuracy but it requires longer times than the automatic method. For greater accuracy, samples containing less than 0·02 mmole of titrated ions or more than 0·2 mmole per 25 ml of solution should be titrated with more dilute or more concentrated solutions respectively.

The regular voltage *vs.* volume curve for the titration of calcium, together with its recorded first derivative curve, are shown in Fig. 3. It can be seen that the first derivative end-point (Fig. 3B) occurs slightly later than the ordinary titration curve end-point (Fig. 3A).

To check the possibility of back-titration with the proposed method, calcium solutions were analysed indirectly, semi-automatically and automatically, by titrating

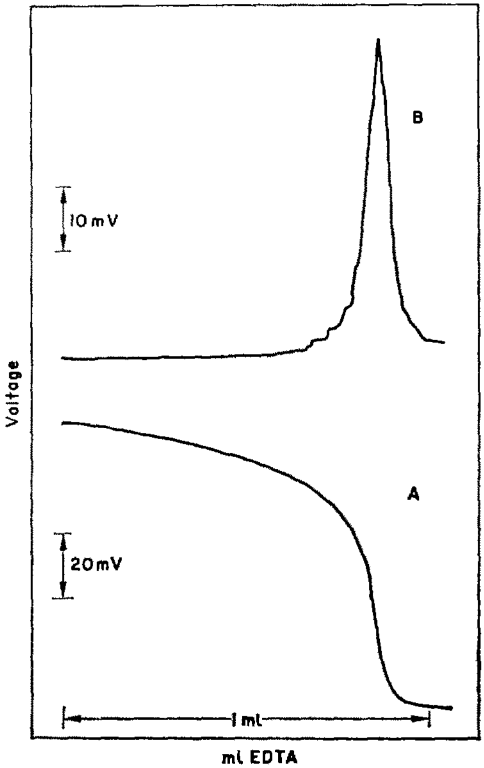

FIG. 3.—Recorded curves for the semi-automatic titration of calcium with EDTA. A—Ordinary titration curve. B—First derivative curve.

excess of EDTA with standard calcium solution. Results obtained were as accurate but less precise than those obtained for the direct titration of calcium with EDTA.

An attempt was made to improve the magnesium titration by substituting a $10^{-3}M$ magnesium chloride solution for the internal calcium chloride reference solution. The blank was slightly decreased, 0·03 ml compared with 0·05 ml, but the accuracy and precision remained the same, for both semi-automatic and automatic titrations.

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Zusammenfassung—Direkte halb- und vollautomatische derivativ-potentiometrische Verfahren zur Bestimmung von Calcium und/oder Magnesium mit EDTA und einer Calcium-selektiven Elektrode werden beschrieben. Calcium wird in Gegenwart von Magnesium bei pH 12,0 titriert und die Summe von Calcium und Magnesium bei pH 9,7. Calcium im Bereich 1–8 mg und Magnesium im Bereich 0,7–5 mg lassen sich halbautomatisch mit durchschnittlichen Fehlern von 0,2 bzw. 0,3%, vollautomatisch mit durchschnittlichen Fehlern von 0,4 bzw. 0,7% bestimmen. Die Titrationszeiten liegen bei einigen Sekunden bis einigen Minuten.

Résumé—On décrit des techniques EDTA potentiométriques dérivées directes, semi-automatiques et automatiques, pour le dosage du calcium et/ou du magnésium avec une électrode sélective du calcium. On titre le calcium en la présence de magnésium à pH 12,0 et le total calcium et magnésium est déterminé à pH 9,7. Le calcium dans le domaine 1–8 mg et le magnésium dans le domaine 0,7–5 mg sont déterminés semi-automatiquement avec des erreurs moyennes d'environ 0,2 et 0,3% respectivement et automatiquement avec des erreurs moyennes de 0,4 et 0,7%. Les temps de titrage varient de quelques secondes à quelques minutes.

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DETERMINATION OF Co, Cu, Fe, Ga, W, AND Zn IN ROCKS BY NEUTRON ACTIVATION AND ANION-EXCHANGE SEPARATION

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Summary—A neutron-activation method for the simultaneous determination of cobalt, copper, gallium, iron, tungsten and zinc in rocks is described. The method is based on anion-exchange separation in hydrochloric acid media. Chemical yield is higher than 97% for all elements, except for tungsten, where the recovery of the carrier is established by re-activation. The precision is about 1·3% for the iron determination and about 3% for cobalt, copper, gallium and zinc.

SINCE the pioneer work of Kraus and Nelson,[1] anion-exchange separation of metals in relatively concentrated hydrochloric acid media has been extensively used in analytical chemistry. In activation analysis, a large number of investigators have used this technique for radiochemical separations of a number of elements in various matrices. Applications to activation analysis of geological material, however, have been rather scarce.[2–5]

The only previously published neutron-activation method for rocks based on anion-exchange in hydrochloric acid media as a single separation step, seems to be a work on the simultaneous determination of copper, gallium and zinc, carried out in the authors' laboratory.[4] The present investigation is an extension of this work, including the determination of cobalt, iron and tungsten in addition to the three elements mentioned above. Instead of alkaline fusion, as used in the previous paper, hydrofluoric acid is used for decomposition of the samples. In this way a somewhat simpler method is obtained, giving results of higher precision and accuracy.

Although lengthy, the decomposition of the irradiated rock samples with hydrofluoric acid was found to possess several advantages compared to decomposition with sodium hydroxide as previously used.[4] First the disadvantage of introducing a solution of high salt concentration onto the anion-exchange column is avoided. Secondly, as silicon is removed during the dissolution step, there is no risk of obtaining reduced flow-rates through the columns because of precipitation of silica on the resin.

After dissolution of the evaporated sample in $9M$ hydrochloric acid, with boric acid as a complexing agent for the remaining fluorides, the resulting solution is added to the anion-exchange column. The individual elements are then eluted, after appropriate washing steps, with solutions of hydrochloric acid of gradually decreasing molarity (Co with $4M$, Cu with $3M$, Fe and Ga with $0{\cdot}5M$ hydrochloric acid, and finally Zn with $1M$ ammonia). The recovery of each element has been studied by means of separate radioactive tracer experiments, six for each element. The results, which are given in Table I, show that the recoveries are better than 97% for the five elements studied, and that a reproducibility of the order of 1% can be obtained. If samples and standards are treated the same, a separate step for chemical yield determination should be unneccessary.

In the course of the experiments, activity from ^{187}W was observed in the elution fractions containing copper. Tracer experiments showed that 30–40% of the tungsten was eluted together with copper, while the remaining activity was found on the column after the elution, probably because of hydrolysis. After the introduction of a re-activation step for chemical yield determination, this element was determined in the same fraction as copper.

In most of the zinc fractions, the 0·56-MeV γ-ray of ^{122}Sb was observed. It was shown by tracer experiments that antimony is quantitatively retained on the column until the elution step with $1M$ ammonia. In some samples, however, the fraction of antimony eluted even in this fraction was rather low. Furthermore, the complete exchange of radioactive and carrier atoms during the dissolution step is doubtful. The determination of this element was therefore omitted.

EXPERIMENTAL

Apparatus

Counting equipment. A 400-channel gamma-spectrometer with a well-type 75 × 75 mm NaI (Tl) crystal.

Anion-exchange columns. Columns of 12 mm internal diameter filled with Dowex 1-X8 (100–200 mesh, chloride form) to 85 ± 5 mm height of resin bed. Before use, the columns are equilibrated with $9M$ hydrochloric acid.

Reagents

Standards. The standards used for cobalt, copper and zinc are solutions of the respective metals in dilute nitric acid. For gallium, a solution of the metal in dilute sulphuric acid is used. The tungsten standard used is a solution of tungstic oxide in dilute ammonia. The following concentrations have been found suitable: Co, 0·5 mg/ml; Cu, 1·0 mg/ml; Ga, 0·2 mg/ml; W, 0·02 mg/ml; Zn, 2·0 mg/ml. About 100 mg of high purity iron metal is used as the iron standard.

Carrier solutions. The following concentrations are used: Co, 10 mg/ml; Cu, 4 mg/ml; Fe, 10 mg/ml; Ga, 1 mg/ml; W, 2 mg/ml; Zn, 10 mg/ml.

Treatment of samples and standards for irradiation

Accurately weighed standard rock samples (about 100 mg) are wrapped in sheets of aluminium foil. A composite standard of Cu, Co, Ga and Zn is prepared by sealing 100 μl of each standard solution in a silica ampoule. In a second ampoule 100 μl of the W standard are sealed. The Fe standard is wrapped in aluminium foil. The irradiations are carried out for 20 hr at a thermal neutron flux of about 3×10^{10} n . mm^{-2} . sec^{-1}, ten samples in each irradiation. The samples are allowed to stand for 30 hr, for the decay of ^{56}Mn and ^{24}Na activity.

Radiochemical separation procedure

The irradiated rock powder is transferred to a 250-ml polypropylene beaker containing 5 ml of concentrated hydrofluoric acid, 5 ml of concentrated nitric acid and 500 μl of each of the carrier solutions. After evaporation of the solution to dryness on a water-bath, an additional 5 ml of concentrated hydrofluoric acid are added, and the mixture is evaporated to dryness again. This step is repeated. The residue is dissolved in 10 ml of $9M$ hydrochloric acid + 1 ml of 2% boric acid solution. The solution is allowed to stand for at least 2 hr.

The irradiated standard solutions, after centrifugation of the ampoules at moderate speed, are transferred to a 50-ml volumetric flask. The iron metal standard is dissolved in a few ml of $9M$ hydrochloric acid and transferred to the same flask. The solution is diluted to the mark with $9M$ hydrochloric acid. Three aliquots of 5 ml each are transferred to separate 250-ml polypropylene beakers and treated as described above.

The sample solutions and the corresponding standard solutions are passed through the columns at a flow-rate of approximately 0·5 ml/min. When the solution has reached the top of the resin bed, washing is performed with three 5-ml portions of $9M$ hydrochloric acid. Cobalt is eluted with three 5-ml portions of $4M$ hydrochloric acid, copper and tungsten with four 5-ml portions of hydrochloric acid, iron and gallium with four 5-ml portions of $0·5M$ hydrochloric acid and zinc (and some antimony) with four 5-ml portions of $1M$ ammonia.

All the eluates are collected in 100-ml polyethylene screwcap bottles for gamma-activity measurements.

Activity measurements

The gamma-ray measurements of 12·8-hr ^{64}Cu (0·51 MeV), 13·8-hr ^{69m}Zn (0·44 MeV) and 14·0-hr ^{72}Ga (0·83 MeV) are started as soon as possible after the elution. In some samples, a minor correction for the contribution of the 0·48-MeV γ-ray of ^{187}W to the 0·51-MeV peak of ^{64}Cu has to be applied. The measurement of 24-hr ^{187}W (0·068 MeV) is postponed until 2 days after the elution, to reduce the ^{64}Cu activity of this fraction to a suitable level. Measurements of 5·3-y ^{60}Co (1·33 MeV), 45-d ^{59}Fe (1·29 MeV) and 245-d ^{65}Zn (1·11 MeV) in the respective fractions are accomplished after one week. Peak area calculations are performed after the method of Covell.[6]

The eluted fractions are essentially free of activities other than those already mentioned. In the cobalt fraction, activity of ^{233}Pa (from thorium) is observed in most samples. This activity, however, does not affect the measurement of the 1·33-MeV peak of ^{60}Co. Traces of the major activities ^{24}Na or ^{140}La due to incomplete washing could interfere in the measurements. The presence of these nuclides, as revealed by presence of the 2·75 MeV or 1·60 MeV γ-rays respectively, has not been confirmed in any sample.

In samples containing appreciable amounts of gold, difficulties might be encountered with interference from the 0·41-MeV γ-ray of ^{198}Au in the measurement of ^{69m}Zn. No such interference is indicated, however, in the present samples. In the zinc fractions, in addition to ^{122}Sb–^{124}Sb, trace activities of ^{59}Fe have been observed in a few samples. This interference is easily removed by spectrum stripping.

The results presented for zinc have been obtained from the measurement of ^{69m}Zn. Results calculated from the ^{65}Zn measurements, however, are in good agreement with those from ^{69m}Zn.

TABLE I.—CHEMICAL YIELD (%) OBTAINED FOR Co, Cu, Fe, Ga AND Zn

Experiment no.	Cu	Co	Fe	Ga	Zn
1	98·0	99·5	96·8	100·7	100·2
2	99·3	99·4	97·4	95·9	100·6
3	99·4	96·5	97·5	99·2	100·3
4	99·7	98·4	97·3	100·6	97·6
5	95·9	98·0	96·6	98·4	101·0
6	98·8	96·6	98·2	97·7	99·9
Average	98·5 ± 1·3	98·1 ± 1·3	97·3 ± 0·6	98·8 ± 1·3	99·9 ± 1·2

Chemical yield determination for tungsten

After measurement, the fractions containing tungsten are transferred to volumetric flasks and diluted to 100 ml with water after addition of 0·5 ml of concentrated hydrofluoric acid. After thorough mixing and shaking, 1·00 ml of each fraction is sealed in a polyethylene ampoule. After 30 min irradiation at a neutron flux of about $1{\cdot}5 \times 10^{11}\ \mathrm{n\,.\,mm^{-2}\,.\,sec^{-1}}$ and 2 days delay, the relative recovery of tungsten carrier in samples and standards is established by means of γ-spectrometry, and corrections are applied to the calculated results.

RESULTS AND DISCUSSION

The results obtained for the elements in question in five different U.S. Geological Survey standard rocks are shown in Table II. Five replicate determinations of each element are reported in all cases except for tungsten. The precision is indicated for each element by the calculated relative standard deviation of a single value.

In Table III, the mean values of the present work are compared with literature values obtained by neutron activation. For sample W-1, the "recommended values" from the recent compilation by Fleischer[7] are included in the Table. Correspondingly, the mean values from the compilation of Flanagan[8] for the other four standard rocks have been included. In several cases, however, these mean values are not especially useful for the discussion of accuracy, because they have been calculated from all

TABLE II.—CONTENT OF Fe, Cu, Ga, Zn, Co AND W IN FIVE U.S.G.S. STANDARD ROCKS

Standard rock	Total Fe as % Fe_2O_3		Cu, *ppm*		Ga, *ppm*		Zn, *ppm*		Co, *ppm*		W, *ppm*	
	6·78		59·5		21·4		81·8		14·9			
	6·66		57·6		19·9		84·1		14·9		0·42	
Andesite AGV-1	6·69	6·75 ± 0·07	56·2	57·9 ± 1·5	20·8	21·0 ± 0·7	85·8	81·1 ± 4·3	14·8	14·8 ± 0·2	0·42	0·45
	6·81		59·2		21·7		74·9		14·7		0·52	
	6·82		57·1		21·0		78·9		14·5			
	13·50		16·3		22·6		127·1		34·7			
	13·58		15·4		21·6		124·3		38·1		0·20	
Basalt BCR-1	13·27	13·40 ± 0·15	15·6	15·7 ± 0·4	21·7	22·2 ± 0·4	130·2	127·4 ± 2·2	36·0	36·2 ± 1·4	0·21	0·24
	13·24		15·6		22·6		127·2		36·8		0·31	
	13·40		15·4		22·4		128·4		35·2			
	2·74		9·01		22·4		80·1		4·44			
	2·70		9·22		22·6		81·3		4·05		0·03	
Granite G-2	2·57	2·65 ± 0·04	9·27	9·14 ± 0·16	22·4	22·5 ± 0·1	80·8	80·6 ± 1·1	4·54	4·35 ± 0·18	0·04	0·04
	2·60		8·93		22·4		80·6		4·39		0·05	
	2·64		9·29		22·6		80·4		4·35			
	4·28		35·3		22·7		97·1		6·37			
	4·29		33·4		21·9		96·6		6·11		0·11	
Granodiorite GSP-1	4·30	4·31 ± 0·09	31·3	32·7± 1·7	20·8	21·7 ± 0·8	93·8	96·7 ± 2·1	6·87	6·40 ± 0·30	0·13	0·12
	4·35		31·2		22·0		99·6		6·57			
	4·41		32·2		21·0		96·5		6·09			
	11·20		114·8		19·0		85·2		43·2			
	11·12		117·2		19·1		80·4		45·5		0·40	
Diabase W-1	11·06	11·12 ± 0·08	108·7	113·6 ± 3·7	16·7	18·4 ± 1·0	86·5	84·9 ± 2·4	43·2	44·5 ± 1·2	0·35	0·38
	11·03		116·4		18·5		86·5		45·7		0·39	
	11·21		110·7		18·7		85·6		45·1			
Mean relative standard deviation, %		1·25		3·0		2·9		2·7		3·3		

TABLE III.—COMPARISON OF PRESENT MEAN VALUES WITH PREVIOUS NEUTRON-ACTIVATION RESULTS AND AVERAGE VALUES FROM RECENT COMPILATIONS.[7,8]

Standard rock		Total Fe % Fe_2O_3	Cu *ppm*	Ga *ppm*	Zn *ppm*	Co *ppm*	W *ppm*
AGV-1	Present work	6·75	57·9	21·0	81·1	14·8	0·45
	Previous neutron-activation values	6·1[10]	52[4]	21[4]	87[4]	13·2[9]	
						14·7[10]	
						17[12]	
	Flanagan,[8] average	6·80	63·7	18·4	112	15·5	1·1
BCR-1	Present work	13·40	15·7	22·2	127·4	36·2	0·24
	Previous neutron-activation values	12·9[10]	13[4]	24[4]	115[4]	36[9]	
						36·3[10]	
						36[12]	
	Flanagan,[8] average	13·51	22·4	21·6	132	35·5	0·7
G-2	Present work	2·65	9·14	22·5	80·6	4·35	0·04
	Previous neutron-activation values	2·46[10]	6·7[4]	24[4]	77[4]	4·3[9]	
		2·76[11]				4·3[10]	
						5·0[12]	
	Flanagan,[8] average	2·77	10·7	20·7	74·9	4·9	0·4
GSP-1	Present work	4·31	32·7	21·7	96·7	6·40	0·12
	Previous neutron-activation values	4·0[10]	33[4]	24[4]	108[4]	5·2[9]	
						7·0[10]	
						8·5[12]	
	Flanagan,[8] average	4·33	35·2	18·8	143	7·5	0·5
W-1	Present work	11·12	113·6	18·4	84·9	44·5	0·38
	Previous neutron-activation values	10·71[10]	116[4]	20[4]	83[4]	41·6[9]	0·40[27]
		10·17[18]	112[14]	18[20]	85[25]	52[13]	0·46[28]
		12·20[19]	120[15]	18·3[22]	82·8[26]	49[14]	0·49, 0·27[29]
			110[16]	16·5[23]	76[18]	53·7[19]	0·58[31]
			116[17]	15·5[24]			
	Fleischer,[7] recommended value	11·09	110	16	82	50	—

data available, including those obtained by analytical techniques not especially suited for precision work in the trace concentration region. For a major element such as iron, however, these mean values should probably be good estimates of the "true" values.

The results obtained for each element are discussed in detail below.

Iron

Neutron-activation analysis has not been extensively used for iron determination in rocks so far. This is mainly due to the fact that good conventional chemical methods are available, which differentiate between the oxidation states of iron. The few neutron-activation data available so far for the standard rocks do not appear to be very promising. By the present method, however, iron can be determined with a precision that can be considered as satisfactory for most purposes. The fact that the mean values, with the exception of G-2, are in agreement with the average values of Flanagan[8] or the recommended value by Fleischer[7] within 1% or less, indicates that the accuracy of the results is good. The present method for determining total iron, although too detailed for routine determination of this element alone, should still be very useful for obtaining iron data simultaneously with the determination of other elements included in the scheme.

Copper, gallium and zinc

By the present method, the precision for the determination of these elements has been improved to about 3% from approximately 5% obtained in the previous work.[4] The copper results from this work are slightly higher than the previous values, especially at low copper content. The present results are believed to be more accurate, because the ^{64}Cu activity in the present case has been measured in a fraction essentially free from other activities, while in the previous work, ^{64}Cu was eluted in the same fraction as ^{72}Ga and ^{59}Fe. Interference from the ^{64}Zn(n, p)^{64}Cu reaction has been estimated to be negligible.

The gallium results from this work are about 5% lower on average. This is consistent with the fact that the gallium content of the standard solution used in the previous work, made from Ga_2O_3 which is very difficult to dissolve completely, was found to be 6% lower than that used in the present work, made from metallic gallium. The present results are also in better agreement with other literature data.

The mean values for zinc in the two sets of data are in reasonable agreement, although the difference is as high as 10% in the cases of BCR-1 and GSP-1.

Cobalt

This element can be determined by purely instrumental activation analysis, using an NaI detector,[9] a Ge(Li) detector,[10] or two NaI detectors coupled in coincidence.[12] The radiochemical values from this work, however, show higher precision than those obtained by the instrumental methods. The agreement of the present set of data with the previous values is reasonably good, especially with the work of Gordon *et al.*[10]

Tungsten

The results obtained for tungsten in this work are not as precise, mainly because of the low content of tungsten in the samples. The result for W-1, although slightly lower than previous literature data, is still in reasonable agreement with most of them.[27,28] The values cited by Flanagan[8] for the other standard rocks are from a work by Chan and Riley,[31] using a spectrophotometric method. These values are in considerable disagreement with those from the present work. Although a considerable number of elements can now be determined by some variant of instrumental activation analysis, it seems that the use of methods employing radiochemical separations is still justified, even for those elements which can be estimated instrumentally, if precise and accurate results are required. The main objection to such methods is that a large amount of time and work is often necessary. The present method, however, as well as similar methods based entirely on ion-exchange separations, should not be considered too unfavourable in this respect. A considerable number of samples can be handled simultaneously, and the column operations are well suited for automation.

Zusammenfassung—Ein Neutronenaktivierungsverfahren zur gleichzeitigen Bestimmung von Kobalt, Kupfer, Gallium, Eisen, Wolfram und Zink in Gesteinen wird beschrieben. Das Verfahren beruht auf Trennung durch Anionenaustausch in salzsauren Medien. Die chemische Ausbeute ist bei allen Elementen höher als 97%, außer bei Wolfram; hier wird die Ausbeute an Träger durch erneute Aktivierung ermittelt. Die Genauigkeit beträgt etwa 1,3% bei der Eisenbestimmung und etwa 3% bei Kobalt, Kupfer, Gallium und Zink.

Résumé—On décrit une méthode par activation de neutrons pour la détermination simultanée des cobalt, cuivre, gallium, fer, tungstène et zinc dans les roches. La méthode est basée sur une séparation par échange anionique en milieux acide chlorhydrique. Le rendement chimique est supérieur à 97% pour tous les éléments, à l'exception du tungstène, où la récupération de l'entraîneur est établie par réactivation. La précision est d'environ 1,3% pour la détermination du fer et d'environ 3% pour les cobalt, cuivre, gallium et zinc.

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CATALYTIC THERMOMETRIC TITRATIONS IN NON-AQUEOUS SOLVENTS BY COULOMETRICALLY GENERATED TITRANT

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Summary—Catalytic thermometric titrations have been developed for tertiary amines and salts of organic acids in acetic and propionic anhydride with titrant coulometrically generated at a mercury and/or platinum anode, hydroquinone being added to the solution titrated if the platinum anode is used. The results obtained are compared with those obtained by coulometric titration with the end-point detected either photometrically or potentiometrically.

IN A PREVIOUS communication we announced the principles of catalytic thermometric titration of bases by the coulometric generation of hydrogen ions in a mixture of acetic anhydride and acetic acid.[1] Mather and Anson[2] determined small amounts of bases and were the first to give a coulometric method for the titration of bases in a mixture of acetic acid and acetic anhydride, for the generating hydrogen ions by processes at a mercury anode. The end-point was detected potentiometrically, a slow and complicated procedure.

In the present paper we describe the catalytic thermometric titration of bases with coulometric generation of the titrant and compare the results obtained with mercury and platinum generator anodes. When the platinum anode is used, hydroquinone is added as anode depolarizer and source of hydrogen ions[2,3] in order to give a current efficiency of 100%. For the indicator reaction, use is made of the exothermic reaction between acetic or propionic anhydride and the water present, as well as of the addition reaction of acetic anhydride with the quinoid system, catalysed by hydrogen ions. The amount of water in this indicator reaction is of decisive importance for the shape of the titration curve in catalytic thermometric titration. Figure 1 shows the titration curve for pyridine in a supporting electrolyte consisting of a mixture of acetic acid and acetic anhydride (1:7) that was $0{\cdot}1M$ in sodium perchlorate. For observation of the effect of water alone, hydrogen ions were generated (in the absence of hydroquinone) on a platinum anode with a current of 2·7 mA. The curves obtained show that with a lower water content in the sample there is a lower increment in temperature after the equivalence point, and that the sharpest slope of the curve is achieved if the water content is under 0·4%.

Another possible indicator reaction is the addition of acetic anhydride to the quinoid system, also an exothermal process, which permits the determination of very weak bases as well, since it is possible to avoid even traces of water in the system.

Other organic solvents can also be used for anodic titrant generation. Thus we extended our studies to the system of mixtures of propionic anhydride and propionic

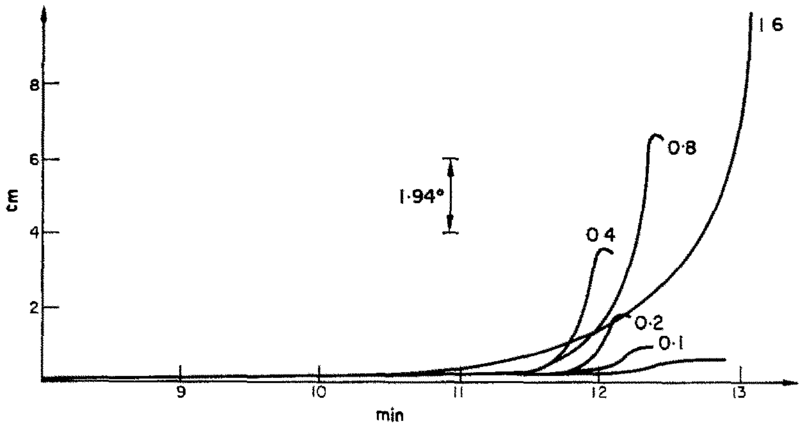

FIG. 1.—The effect of water in the indicator reaction on the shape of curves in catalytic thermometric titrations. The numbers on the curves represent the percentage of water added in the analysis.

acid, which also gave us satisfactory results. Coulometric generation of base in the catholyte permits the determination of acids, if the titration is carried out in acetone. Vaughan and Swithenbank[4] determined the titration end-point from the temperature increase when titrating different acids in acetone with butyltrimethylammonium hydroxide or by potassium hydroxide in methanol or isopropanol. Coulometric titration makes it possible to simplify this excellent method for the determination of acids by eliminating the addition of the titrant. We detected the titration end-point also on the basis of the endothermic effect appearing if the titration is done in a mixture of acetone and diacetone alcohol.

Coulometric titration simplifies the procedure and avoids errors due to volume change, difference in temperature between solutions, *etc.*

EXPERIMENTAL

Solvents and reagents

All chemicals used were either of *pro analysi* purity, or pharmaceuticals. Preparation and standardization of solutions have been described earlier.[1,5]

For the preparation of solutions free of water and of acetic anhydride, use was made of acetic acid (C. Erba, s.g. 1·051, RP grade) and propionic acid (C. Erba, s.g. 0·993, min. 99%, RP grade).

Acetic anhydride and propionic anhydride were used without special purification.

Sodium perchlorate was prepared from sodium hydroxide and perchloric acid and recrystallized several times.

The indicators were 0·25% solution of Crystal Violet in acetic acid, 0·25% solution of Methyl Violet in acetic acid, and 0·1% solution of Malachite Green in acetic anhydride.

Apparatus

Hydrogen ions were generated at a mercury anode (*ca.* 300 mm^2) at a constant current density of 3 or 9 μA/mm^2, or at a platinum electrode at a current of 0·9 or 2·7 mA. The platinum anode consisted of a platinum wire (16 mm long, diameter 0·5 mm) sealed into the bottom of the titration vessel. The cells were isolated during the determination in order to prevent the influence of outside temperature changes. The solution to be analysed was separated from the catholyte by a sintered glass disc, porosity 4.

The recorder of a Radiometer polarograph Po 3h was used to register the temperature indicated by the thermistor, or the change in photocurrent (in a large colorimeter[8]) resulting from the change in absorbance of the titrated solution. The thermistor was connected according to the diagram in Fig. 2, which also shows the generator circuit.

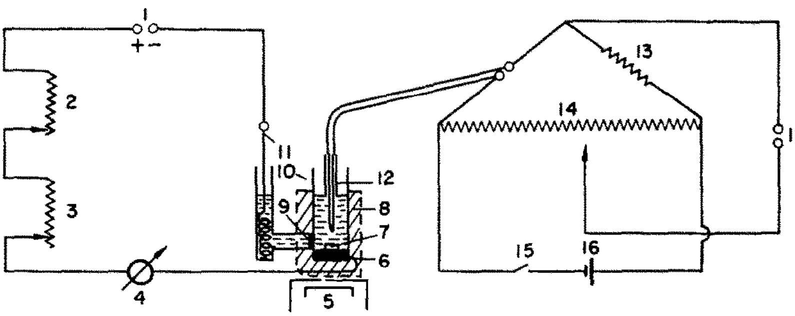

FIG. 2.—Schematic diagram of coulometric catalytic thermometric titration. 1—Source of d.c. (voltage stabilizer ST-12, RR Zavodi Niš). 2—10 kΩ semi-variable resistor. 3—100 kΩ semi-variable resistor. 4—Milliammeter BL 2 with scale in 0·01-mA divisions. 5—Magnetic stirrer. 6—Mercury anode. 7—Magnet. 8—Insulator. 9—Sintered-glass disc, porosity 4. 10—Coulometric titration cell. 11—Platinum cathode. 12—Thermistor (5 kΩ). 13—5 kΩ resistor. 14—10 kΩ rheostat. 15—Switch. 16—2·6-V battery. 17—Recorder.

Procedure

A supporting electrolyte was prepared, consisting of 0·1*M* sodium perchlorate in 1:7 acetic acid–acetic anhydride mixture. For end-point detection by the catalytic thermometric method, a definite volume of a 10% solution of water in acetic acid was added, so that the water content in the indicator reaction system amounted to below 0·2%. A solution of the substance to be analysed was prepared in the supporting electrolyte, and 7-ml samples were taken. In photometric titrations 14 ml of sample solution were used. The electrolysis was made at a constant current of 0·9 or 2·7 mA, and the sample weights were such that the time of electrolysis was about 10 min (with a precision of 0·1 sec.). When hydrogen ions were generated at a platinum electrode, about 2 mg of hydroquinone per ml was also added.

The left-hand cuvette of the adapted colorimeter was filled with pure solvent and illuminated with a yellow light-bulb; the right-hand cuvette was filled with the solution to be analysed, plus one drop of 0·25% Crystal Violet solution. For caffeine, Malachite Green was used as indicator, and since caffeine is a very weak base, the titration was done in acetic anhydride which was 0·1*M* in sodium perchlorate.

RESULTS AND DISCUSSION

The titration end-point was determined in three ways: potentiometrically,[2] photometrically,[3] and by catalytic thermometry. The end-point in catalytic thermometric titrations was determined from the graph of temperature against time, as illustrated in Fig. 3, curve A. If the amount of water in the indicator reaction is reduced from 2% to below 0·2% and the titration done in acetic anhydride, the detection of the end-point in catalytic thermometric titrations of bases is greatly simplified because the indicator reaction becomes instantaneous. The reproducibility is improved by a factor of almost 2. In addition, by reducing the amount of water or completely eliminating it in the indicator reaction, it is possible to determine even very weak bases. In determination of the weak base caffeine the changes in temperature at the end-point are fairly small. For example, after about 0·04 cb has passed, after the equivalence point, the change in temperature amounts to only 0·06–0·19°, yet it is possible to detect the end-point satisfactorily. The differential thermometric technique[6] is especially useful in this case.

As can be seen from Table I, bases have successfully been determined in amounts of 1–3 mg. For any particular substance the maximum deviation of results from the mean for the three methods amounts to ±1%. The average deviation of individual measurements is ±0·4%. The weak bases antipyrine ($\mathrm{p}K_b = 12{\cdot}40$ in water) and caffeine ($\mathrm{p}K_b = 13{\cdot}39$) have successfully been determined. We have not been able to

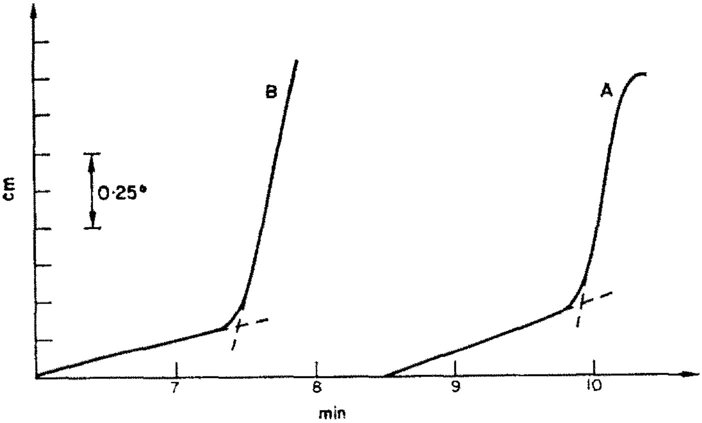

FIG. 3.—Catalytic thermometric titration curves for (*A*) 16 μmole of potassium acetate in acetic anhydride at constant current of 2·7 mA, (*B*) 6·7 μmole of benzoic acid in acetone at constant current of 1·5 mA.

determine caffeine by catalytic thermometric titration when using a mercury generator electrode, since during the titration, or rather at the equivalence point, there is no jump in the temperature rise. This confirms that in catalytic thermometric titration of very weak bases the equivalence point can be determined only by the acetic anhydride-hydroquinone indicator reaction, owing to the hindrance of water in the system titrated. The advantages of the platinum generator electrode are obvious.

The photometric titration curve is given in Fig. 4. Its shape depends on the indicator, photocell and source of light used. At the titration end-point, with Crystal Violet as indicator, there will be a maximum in the absorbance, because as hydrogen ions are generated and neutralize the base, the violet colour changes first to pure blue, and then to green and yellow. This maximum indicates the end-point (Fig. 4, curve 1). If Malachite Green is used as indicator, the titration end-point is determined from the inflexion point (Fig. 4, curve 2) since the colour change is from green to yellow.

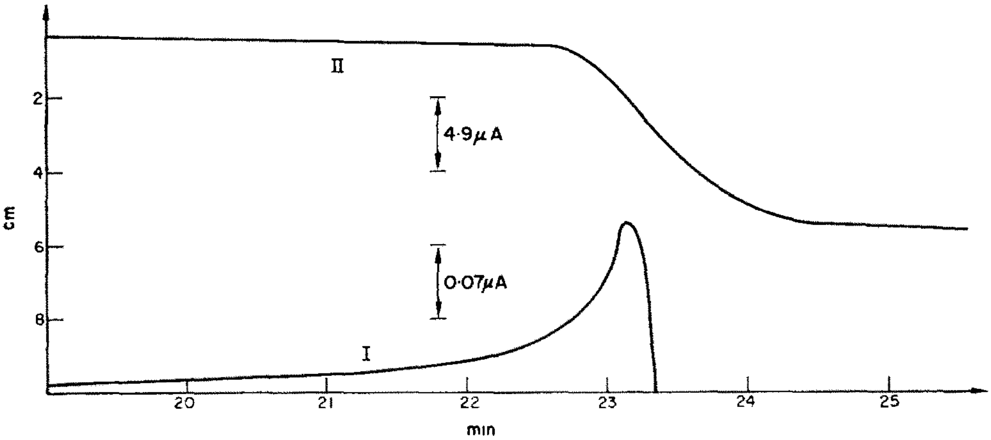

FIG. 4.—Photometric titration curve for 38·7 μmole of pyridine in acetic anhydride in the presence of: I—Crystal Violet as indicator; II—Malachite Green as indicator.

TABLE I.—COMPARISON OF RESULTS OBTAINED BY POTENTIOMETRIC, CATALYTIC THERMOMETRIC AND PHOTOMETRIC TITRATION BY COULOMETRIC GENERATION OF TITRANT, FOR SOME BASES IN ACETIC ANHYDRIDE (CURRENT 2·7 mA)

Substance titrated	Potentiometric titration						Catalytic thermometric titration						Photometric titration					
	Hg electrode			Pt electrode			Hg electrode			Pt electrode			Hg electrode			Pt electrode		
	n	Found, *mg*	m.d. %	*n*	Found, *mg*	m.d. %	*n*	Found, *mg*	m.d. %	*n*	Found, *mg*	m.d. %	*n*	Found, *mg*	m.d. %	*n*	Found, *mg*	m.d. %
K acetate	4	1·63	0·6	4	1·63	0·1	4	1·63	0·4	6	1·64	0·2	6	1·64	0·7	4	1·64	0·4
Na benzoate	4	1·90	0·3	4	1·91	0·2	6	1·93	0·5	6	1·92	0·4	4	1·94	0·5	4	1·93	0·2
Antipyrine	4	2·18	0·3	5	2·18	0·7	6	2·21	0·3	6	2·20	0·2	4	2·20	0·1	4	2·21	0·6
Quinoline	4	1·35	0·2	4	1·35	0·1	5	1·35	0·7	6	1·36	0·5	4	1·35	0·5	5	1·35	0·8
4-Picoline	5	1·31	0·8	5	1·31	0·5	5	1·32	0·5	7	1·32	0·6	4	1·30	0·5	4	1·30	0·3
Caffeine	3	2·41	0·2	5	2·42	0·6	—	—	—	9	2·44	0·5	3	2·42	0·3	4	2·44	0·4

n = number of titrations.
m.d. = Mean deviation, %.

TABLE II.—COMPARISON OF RESULTS IN THE DETERMINATION OF PYRIDINE BY DIFFERENT METHODS (CURRENT 2·7 mA)

	Potentiometric titration with 0·005*M* $HClO_4$ in acetic acid	Coulometric method, Pt anode				
				Photometric, in the presence of		
		Potentiometric	Catalytic thermometric	Crystal Violet	Methyl Violet	Malachite Green
No. of determinations	3	3	7	6	5	4
Found, *mg*	1·55	1·56	1·56	1·54	1·54	1·56
Average deviation, %	0·2	0·9	0·4	0·3	0·4	0·3

TABLE III.—COMPARISON OF RESULTS OBTAINED BY POTENTIOMETRIC, CATALYTIC THERMOMETRIC AND PHOTOMETRIC TITRATION BY COULOMETRIC GENERATION OF TITRANT FOR SOME BASES IN PROPIONIC ANHYDRIDE (CURRENT 0·9 mA)

Substance titrated	Potentiometric titration						Catalytic thermometric titration						Photometric titration					
	Hg electrode			Pt electrode			Hg electrode			Pt electrode			Hg electrode			Pt electrode		
	n	Found, *mg*	m.d.	*n*	Found, *mg*	m.d.	*n*	Found, *mg*	m.d.	*n*	Found, *mg*	m.d.	*n*	Found, *mg*	m.d.	*n*	Found *mg*	m.d.
Cinchonine	4	1·20	0·4	5	1·28	0·4	6	1·21	0·5	6	1·23	0·3	4	1·22	0·8	4	1·22	0·7
Pyridine	3	1·16	1·1	4	1·16	1·3	5	1·15	0·4	5	1·15	0·4	3	1·15	1·8	3	1·16	0·9
Triethylamine	4	0·81	0·3	5	0·83	0·7	6	0·82	0·4	9	0·83	0·8	4	0·84	1·0	3	0·84	1·1

n = number of determinations.
m.d. = mean deviation, %.

Methyl Violet behaves similarly to Crystal Violet, except that the maximum is less pronounced. Taking as example the determination of pyridine by different methods, it can be concluded that the results are in good agreement (Table II). The maxima when Crystal Violet is used as indicator are sharper if the platinum generator electrode is used.

Potentiometric titrations of bases with the coulometric generation of hydrogen ions were carried out according to Mather and Anson,[2] and took a very long time (30–40 min) because of discontinuous titration around the equivalence point.

In Table III comparative results are given of catalytic thermometric, potentiometric and photometric titrations of some bases in a mixture of propionic anhydride and propionic acid (7:1), which is $0{\cdot}1M$ in sodium perchlorate.

Coulometric determinations of acids in acetone or mixtures of acetone and diacetone alcohol as catholyte, with catalytic thermometric detection of the end-point by an exothermal or endothermal indicator reaction were carried out in a supporting electrolyte consisting of $0{\cdot}5M$ sodium perchlorate solution in acetone.

The acetone used as solvent should be dry. At higher water content in the acetone the temperature changes after the equivalence point are poor whereas at a low water content good titration curves are obtained, as illustrated in Fig. 3, curve B. The results are in good agreement with those obtained by other instrumental methods. Thus, for example, in six successive determinations of 0·8-mg samples of benzoic acid the average deviation amounted to 1·5%.

Acknowledgement—This work was supported partly by the Research Fund of the Autonomous Province of Vojvodina.

Zusammenfassung—Katalytische thermometrische Titrationen für tertiäre Amine und Salze organischer Säuren wurden entwickelt. Sie werden in Essigsäure- und Propionsäureanhydrid ausgeführt; der Titrant wird an einer Quecksilber- und/oder an einer Platinanode coulometrische erzeugt. Bei Verwendung der Platinanode wird der zu titrierenden Lösung Hydrochinon zugesetzt. Die Ergebnisse wurden mit solchen verglichen, die durch coulometrische Titration mit photometrischer oder potentiometrischer Endpunktsanzeige erhalten wurden.

Résumé—On a élaboré des titrages thermométriques catalytiques pour les amines tertiaires et les sels d'acides organiques en anhydrides acétique et propionique avec l'agent de titrage engendré coulométriquement sur une anode de mercure et/ou platine, de l'hydroquinone étant ajoutée à la solution titrée si l'on emploie l'anode de platine. Les résultats obtenus sont comparés avec ceux obtenus par titrage coulométrique avec le point de fin de réaction détecté soit photométriquement soit potentiométriquement.

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DOSAGE PROTOMETRIQUE DES HYDROGENES MOBILES A L'AIDE DE L'AMIDURE DE SODIUM

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Résumé—L'amidure de sodium est décomposé par les composés à hydrogène mobile avec dégagement stoechiométrique d'ammoniac qui est dosé par un acide titré. La technique proposée a été appliquée à des représentants de diverses familles; les résultats observés sont interprétés et l'intérêt pratique de la méthode discuté.

ON DÉSIGNE sous le nom de composés à hydrogène mobile des molécules dans lesquelles un ou plusieurs hydrogènes, peu ionisés ou non ionisés à l'état statique, sont cependant liés à l'atome porteur (C, O, N, S) par une liaison suffisamment polarisée pour permettre la formation d'une combinaison de type salin, par action des bases fortes:

$$A - H + B^- \rightleftharpoons BH + A^-$$

Les méthodes de détermination des hydrogènes mobiles font donc appel le plus souvent à l'utilisation de réactifs basiques. Ainsi, les hydroxydes d'ammoniums quaternaires[1,2] ou les alcoolates[3,4,5] ($B^- = OH^-$ et $B^- = RO^-$) permettent-ils le dosage protométrique des acides carboxyliques, des phénols et des thiols. Ces procédés ne sont en réalité qu'une extension de la protométrie classique dont ils accroissent le domaine d'application.

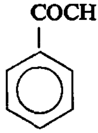
Les acidités plus discrètes, correspondant par exemple au remplacement de l'hydrogène dans l'acétylène ou le diphénylméthane, requièrent pour leur mise en évidence d'autres procédés qui empruntent le plus souvent leurs réactifs à la chimie organique préparative. La méthode la plus anciennement connue, due aux travaux de Tschugaeff et Zerevitinoff, utilise les organomagnésiens[6–9] et notamment l'iodure de méthylmagnésium dont l'attaque par un composé AH s'accompagne d'un dégagement de méthane aisément mesurable:

$$AH + CH_3MgI \rightarrow CH_4 + AMgI.$$

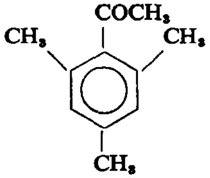
Plus récemment les hydrures complexes, et particulièrement $AlLiH_4$, ont été proposés comme réactifs titrants: ils sont décomposés par les composés de type AH avec libération stoechiométrique d'une molécule d'hydrogène:

$$4AH + AlLiH_4 \rightarrow 4H_2 + AlLiA_4.$$

Un des inconvénients fondamentaux de ces méthodes réside dans le caractère nucléophile du réactif alcalin qui se manifeste parfois préférentiellement au caractère basique; ainsi CH_3MgI révèle seulement 0,12 hydrogène mobile dans l'acétophénone, le réactif magnésien attaquant le carbonyle au niveau du carbone fonctionnel plutôt que d'éliminer un proton du CH_3. Cet inconvénient disparaît d'ailleurs dans le cas de la triméthyl-2,4,6 acétophénone dont l'attaque nucléophile est empêchée par encombrement stérique et pour laquelle 1H est régulièrement substitué dans le CH_3.



(0,12 H mobile[15])



(1 H mobile[15]).

Semblablement, $AlLiH_4$ a tendance à s'additionner sur les cétones plutôt qu'à attaquer les hydrogènes des carbones α. On pouvait donc penser que des agents plus fortement basiques réaliseraient avec plus d'efficacité la substitution au niveau des hydrogènes mobiles.

C'est pourquoi nous avons repris l'étude de l'utilisation de l'amidure de sodium. Ce réactif, essayé dès 1899 par Shryver[10] pour le dosage des phénols, fut repris en 1943 par Palfray et Sabetay[11] et appliqué au dosage des alcools; les auteurs ne poussèrent pas l'étude de ce procédé qui ne pouvait selon eux être utilisé "comme méthode de dosage que dans quelques cas particuliers". Plus récemment, Heilmann et Glenat ont vérifié, par la mesure de l'ammoniac évolué, la sodation d'alcools tertiaires acétyléniques à l'aide de l'amidure de sodium.[12]

La réaction de l'amidure de sodium avec les composés AH peut être schématisée comme il suit:

$$AH + NaNH_2 \rightarrow ANa + NH_3.$$

Les principaux problèmes techniques se situent, sur le plan pratique, au niveau du solvant, du réactif basique et de l'appréciation quantitative de l'ammoniac libéré.

(*a*) Le *solvant* choisi fut d'abord l'éther éthylique desséché sur sodium: les résultats qu'il donne paraissent plus réguliers que ceux observés par Palfray avec le benzène. Toutefois, on peut reprocher à l'éther une polarité insuffisante et un point d'ébullition trop bas. Après avoir essayé divers solvants (T.H.F., dioxanne, pyridine, D.M.F., diméthylaniline, diéthylaniline), nous avons retenu la diéthylaniline en raison de sa purification facile, de sa polarité basique et de son point d'ébullition élevé (Eb = 215°).

(*b*) *L'amidure de sodium* commercial conservé à sec s'altère rapidement avec dégagement d'ammoniac. Sa conservation sous huile de vaseline minimise cet inconvénient: le réactif renferme toujours de l'ammoniac mais il est facile de l'éliminer par un balayage d'azote et la décomposition spontanée en cours de dosage peut être tenue pour négligeable.

Signalons à titre indicatif que nous pratiquons actuellement des dosages avec un amidure commercial conservé en vase clos sous huile de vaseline depuis 1962, date de nos premiers essais.

(*c*) *Le dosage de l'ammoniac* dégagé peut être réalisé très simplement à l'aide du montage décrit plus bas et qui comprend une enceinte à dégagement sous agitation, balayée par un courant d'azote. L'ammoniac est entraîné à travers un réfrigérant ascendant et vient barboter dans une solution d'acide borique où il est neutralisé au fur et à mesure de son dégagement par un acide titré (indicateur rouge de méthyle + bleu de méthylène). Cette modalité de dosage est simple, elle a fait ses preuves dans l'évaluation de l'azote total en analyse biochimique,[13,14] et elle permet de suivre directement le dégagement d'ammoniac et d'apprécier facilement son terme.

On peut illustrer l'évolution de la réaction par deux types de courbes représentés ci-dessous. La courbe 1 mentionne les quantités d'acide titrant ajoutées en fonction du temps: après la période préliminaire de dégagement de l'ammoniac qui souille le réactif, l'évolution spontanée d'ammoniac devient pratiquement nulle, et la prise d'essai peut être introduite après 15 minutes environ.

On observe alors, après un temps variable, le dégagement gazeux dû à l'hydrogène mobile, la fin de la réaction étant marquée par le retour à un dégagement négligeable.

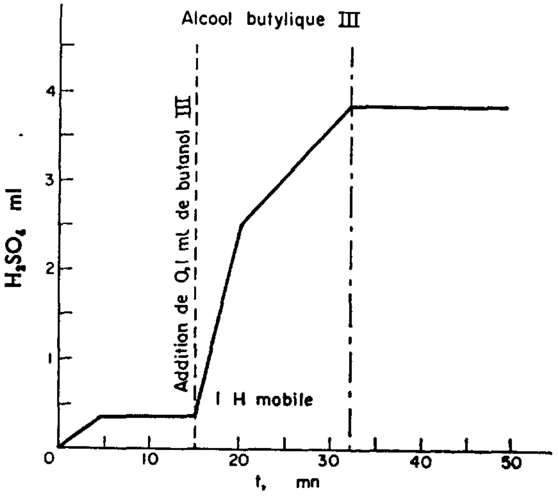
La courbe 2 traduit les mêmes résultats en exprimant l'intensité du dégagement gazeux par périodes de 5 minutes.

PARTIE EXPERIMENTALE

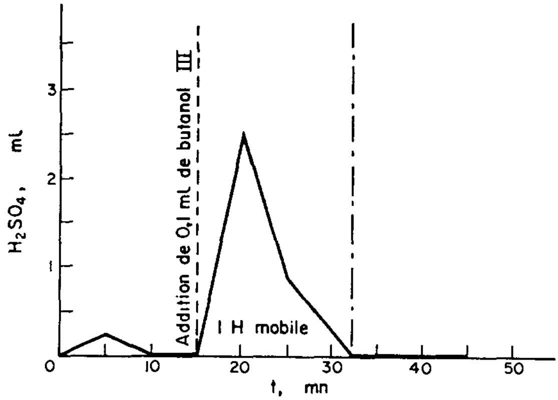
Réactifs

Solution d'acide sulfurique environ 0,5N étalonnée sur carbonate acide de potassium.

Solution tampon d'acide borique à 3%, de pH 5,5.



Courbe 1.



Courbe 2.

Solution de rouge de méthyle à 0,1 % dans l'alcool à 95°.
Solution de bleu de méthylène à 0,1 % dans l'alcool à 95°.
Amidure de sodium conservé sous huile de vaseline.
Diéthylaniline fraîchement redistillée après dessiccation sur baryte durant plusieurs jours.

Appareillage (*Fig. 1*)

Une fiole à trois tubulures (3) est munie d'une adduction d'azote gazeux qui traverse au préalable une fiole de Durand renfermant de l'acide sulfurique concentré (1).

Elle est surmontée par un réfrigérant vertical (4) relié à un bécher (5) contenant 50 cm³ de la solution d'acide borique, 8 gouttes de solution de rouge de méthyle, et 4 gouttes de la solution de bleu de méthylène.

La burette renfermant l'acide sulfurique titrant est disposée au-dessus du bécher.

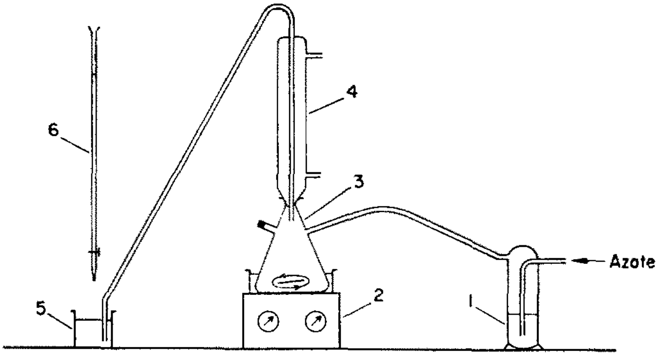


FIG. 1.—Appareillage.

Mode opératoire

Après passage d'un courant d'azote dans l'appareil, on introduit, au temps 0, environ 1 g d'amidure de sodium sous 10 cm³ de diéthylaniline. On met en route l'agitateur magnétique et on neutralise l'ammoniac au fur et à mesure de son dégagement en maintenant, par affusions ménagées de l'acide titrant, l'indicateur à sa teinte rose initiale. Après 10 minutes environ, cette coloration se stabilise et, vers la minute 15, on introduit rapidement la prise d'essai évaluée par double pesée ou par mesure à la pipette de précision pour les liquides de densité connue.

Le dégagement d'ammoniac se traduit par un virage de l'indicateur du rose au vert: l'addition immédiate d'acide sulfurique (retour à la teinte initiale) est poursuivie goutte à goutte jusqu'à stabilité de la coloration. Lorsque le dégagement est achevé, nous élevons la température du bain d'eau à 70°: ce changement des conditions provoque fréquemment un nouveau dégagement d'ammoniac évalué comme précédemment.

La courbe 3 illustre ce phénomène dans le cas de l'acétylacétone qui présente un hydrogène mobile à froid et deux à chaud (solvant = diéthylaniline).

La quantité théorique (n cm³) d'acide sulfurique correspondant à un hydrogène mobile est calculée en fonction de la prise d'essai p et du poids moléculaire M du composé analysé et du titre t de l'acide sulfurique titrant:

$$n = \frac{p}{tM}.$$

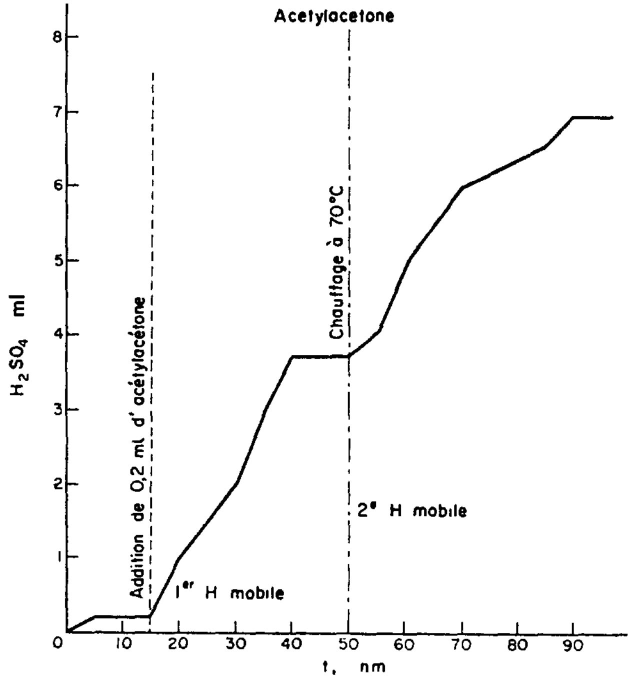
Le rapport entre la quantité d'acide réellement utilisée n et la quantité théorique correspond au nombre d'hydrogènes mobiles par mole.

Les essais effectués avec l'acide benzoïque et divers alcools montrent qu'on peut attendre de la méthode une précision de l'ordre de 3 %.

APPLICATION DE LA MÉTHODE DANS DIVERSES FAMILLES CHIMIQUES

Les résultats de cette étude sont regroupés dans le tableau I.

On y remarque certaines anomalies: ainsi, l'absence de réaction de l'acide benzoïque dans l'éther et la mauvaise réactivité du résorcinol et de l'hydroquinone dans ce solvant.



Courbe 3.

D'une façon générale, la révélation des hydrogènes mobiles se fait mieux dans la diéthylaniline:

—l'acide benzoïque, la pipéridine, le benzamide, l'urée, le phtalimide, le fluorène, inactifs dans l'éther, manifestent dans la diéthylaniline une ou plusieurs acidités vis-à-vis de l'amidure;

—avec l'acétylacétone, les alcools acétyléniques, l'acide salicylique, le malonate d'éthyle, on met en évidence dans l'éther un hydrogène mobile tandis que la détermination à chaud dans la diéthylaniline en révèle deux.

L'un des avantages de la méthode à l'amidure réside dans la possibilité de mettre en évidence les hydrogènes mobiles des cétones, l'amidure agissant plutôt par sa basicité que par son caractère nucléophile, à l'inverse des magnésiens[15,16] et de l'hydrure double d'aluminium lithium.[17]

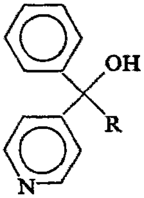
Intérêt de la technique proposée

La technique décrite est susceptible de rendre des services dans plusieurs domaines distincts:

(1) En tant que méthode de dosage d'un individu chimique connu: il paraît possible d'adapter le mode opératoire décrit en vue notamment du contrôle des médicaments.

(2) Dans l'élaboration des structures, l'utilisation des méthodes physiques demeure dans la plupart des cas la modalité de travail la plus efficace. Il peut néanmoins être utile de disposer en outre de méthodes chimiques simples. Citons, à titre d'exemple, la mise en évidence de la fonction alcool dans les alcools **I**, **II**, **III**, **IV** issus de la réduction alcoylante des diarylcétones.[18] Les composés de ce type dans lesquels R est

I



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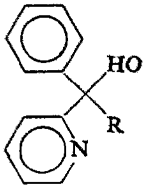

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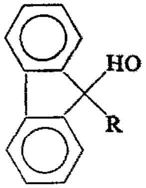

IV

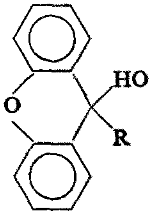

TABLEAU 1.

Composés essayés	Solvant	
	Ether éthylique	Diéthyl-aniline
Acides		
Benzoïque	0	1,00
Salicylique	0,85	1,97*
Phénols		
α-Naphtol	1	0,99
Résorcinol	0,05	1,14*
Hydroquinone	0,10	1,40*
Alcools		
Ethylique	0,98	
n Butylique	1,01	1,01
Butylique III	0.97	1,00
Cyclohexanol		1,00
Thiols		
Thiophénol		1,04*
Butylmercaptan		1,00
Carbonylés		
Acétophénone	1,01	1,03
Acétone	0,83	1,14
Acétylacétone	1,07	1,00; 1,90*
Esters		
Acétylacétate d'éthyle	1,01	1,36*
Malonate d'éthyle	0,96	1,00; 1,82*
Cyanacétate d'éthyle	1,01	1,01*
Amines		
Aniline	1,33	0,50*
Diphénylamine		1,00
Pipéridine	#0,00	0,97*
Morpholine		0,90*
Amides		
Acétamide	0,67	1,00*
Benzamide	#0	0,98
Acétanilide		0,93
Urée	0,20	2,07*
Thiourée		3,92
Uréthanne		1,40*
Salicylamide		0,98*
Benzène sulfonamide		1,99*
Imides		
Succinimide	#0,00	2,00
Phtalimide	#0,00	0,99*
Dérivés nitrés		
Nitrométhane		0,98*
Acétyléniques		
Hexyne	0,91	0,89
Méthyl pentynol	0,96	1,00; 2,00*
Ethynylcyclohexanol		1,00; 1,93*
Nitriles		
Cyanure de benzyle	1,28	2,01*
Acétonitrile	0,10	0,44
Propionitrile		0,40
Hétérocycles		
Carbazole	0,92	1,00*
Carbures		
Fluorène	#0,00	0,94*
Diphénylméthane	#0,00	0,16*
Amidine		
N-Phénylbenzamidine		1,95*

* Détermination effectuée à la température de 70°.

une chaîne azotée ne présentent pas en infra-rouge de bande OH visible, en raison de la liaison hydrogène alcoolique-azote basique; de plus, le proton de l'oxhydryle y est souvent peu visible en RMN. Or, l'analyse chimique a montré pour tous ces composés la présence attendue d'hydrogène mobile, confirmant ainsi la structure proposée (résultats rassemblés dans le tableau II).

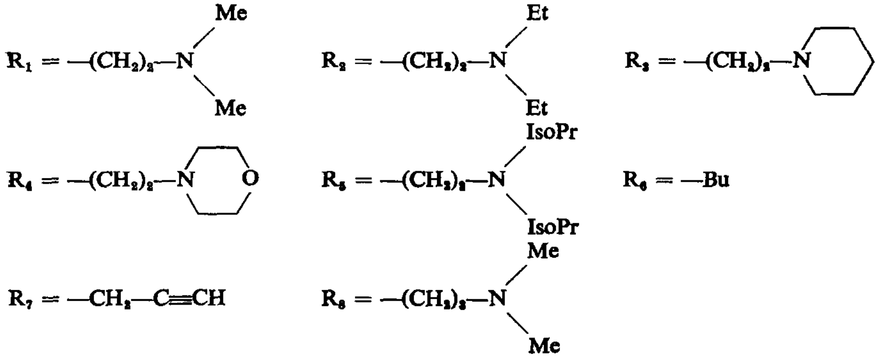

TABLEAU II.

Composé essayé	H mobile	Composé essayé	H mobile
I R_2	0,97	III R_1	0,95
R_8	1,02	R_2	1,05
		R_4	1,05
II R_1	0,98	R_5	1,01
R_2	1,04	R_6	0,94
R_3	1,01	R_8	0,98
R_4	1,00		
R_5	0,99	IV R_1	0,99
R_6	1,02	R_3	0,95
R_7	0,99	R_4	0,98

(3) Cette méthode peut enfin donner des indications sur la réactivité de diverses molécules organiques vis-à-vis des amidures alcalins. C'est un des domaines dont nous développons actuellement l'étude.

Summary—Sodium amide is decomposed by compounds containing active hydrogen, with stoichiometric release of ammonia, which can be determined by titration with acid. The proposed technique has been applied to representatives of various types of compound.

Zusammenfassung—Natriumamid wird durch Verbindungen, die aktiven Wasserstoff enthalten, unter stochiometrischer Freisetzung von Ammoniak zersetzt. Der Ammoniak kann durch Titration mit Säure bestimmt werden. Das vorgeschlagene Verfahren wurde auf Repräsentanten verschiedener Verbindungsklassen angewandt.

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SHORT COMMUNICATIONS

Estimation of thiosemicarbazide with chloramine–T

(*Received* 23 *April* 1969. *Revised* 29 *October* 1969. *Accepted* 23 *November* 1969)

THIOSEMICARBAZIDE is of importance in the characterization of aldehydes, ketones and polysaccharides and as a metal-complexing agent. The methods for its estimation reported so far are based on its oxidation by alkali metal hypohalites,[1,2] lead tetra-acetate,[3] and by chloramine-T at 60°,[4] are limited to the estimation of small quantities,[3] and are slow.

In the present investigations we examined the behaviour of certain oxidizing titrants towards thiosemicarbazide under various conditions. With dichromate, hexacyanoferrate(III), vanadate(V) and cerium(IV) oxidation occurred to a very limited extent even at high temperatures and in the presence of catalysts such as silver sulphate. However, the reaction between chloramine-T (CAT) and thiosemicarbazide (TSC) was found to proceed under certain experimental conditions with a mole ratio of 1:6, with a probable stoichiometric equation:

$$NH_2NHCSNH_2 + 6[CH_3C_6H_4SO_2NCl]^- + 6H_2O \rightarrow 6CH_3C_6H_4SO_2NH_2 + 6Cl^- + CO_2 + N_2 + NH_4^+ + H^+ + SO_4^{2-} \quad (1)$$

A direct titration of TSC at room temperature with chloramine-T with a visual or potentiometric end-point was not practicable, because the oxidation, though rapid, was not instantaneous, and a back-titration procedure was developed. The present method is rapid, with the added advantage that amounts of TSC up to 150 mg can be estimated.

EXPERIMENTAL

Reagents

Thiosemicarbazide was purified by recrystallization. About 2·0 g of the purified material were accurately weighed and dissolved in a litre of solvent to give an approximately 0·025*M* solution. Chloramine-T solution (~0·1*N*) was standardized by the iodometric method. All other reagents were of accepted grades of purity. Standard buffer systems[5] were used.

Preliminary studies

Known amounts of TSC solution were added to a known excessive volume of CAT in an iodine-flask. The reaction mixture was set aside for various intervals of time at room temperature, with occasional shaking. Then the excess of CAT left unconsumed was determined by back-titration. TSC and its oxidation products were found to have no action on the iodide used.

A typical set of results for the extent of oxidation of TSC in 30 min by an excess of CAT is given in Table I. It is seen that oxidation is slow at pH <1, faster in the pH range 1–3 and slower again at pH >5. Oxidation is fastest at pH 4, and TSC is quantitatively oxidized even with only a 40% excess of CAT. With a 10–20% excess, however, the reaction is complete only after 2 hr.

Detailed investigation of the TSC system has brought out the following facts.

(*i*) At any pH up to 10, TSC forms a complex with CAT, which rapidly decomposes in acidic solutions with a quick change of colour from orange-red to pale yellow and evolution of gaseous products. Thus the disappearance of the yellow colour and appearance of a white precipitate may be taken as a rough guide to the completion of oxidation of TSC with the required stoichiometry. The complex has a broad absorption band around 350 mμ, but attempts to establish its structure were not successful, owing to its instability and the rapid evolution of gaseous products.

(*ii*) At high pH (in presence of 2*M* sodium hydroxide) one mole of TSC consumes only about 10 equivalents of the oxidant. This is attributed to the decrease in the potential of the CAT-sulphonamide system with increase in pH.[6] However, the procedure could not be standardized for the estimation of TSC.

(*iii*) At low pH, presence of chloride (other than the very low concentration resulting from progressive consumption of CAT) in higher concentrations, was found to affect the oxidation, a lower

TABLE I.—EXTENT OF OXIDATION OF THIOSEMICARBAZIDE WITH CHLORAMINE-T

Medium	$\frac{\text{mmole CAT used}}{\text{mmole TSC taken}}$
0·502*N* H_2SO_4	5·54
0·100*N* H_2SO_4	5·70
pH 1	5·96
pH 2	5·96
pH 3	5·96
pH 4	6·00
pH 5	5·96
pH 6	5·90
pH 8	5·80
pH 10	5·75
pH 11–12	5·05
pH >12	4·90

TSC taken 0·3289 mmole: CAT taken 3·711 mmoles: time 30 min.

amount of oxidant being used than expected from equation (1). In the pH range 3–5 the presence of chloride up to 0·02*M* did not affect the oxidation.

(*iv*) The 1:6 stoichiometry holds only if the TSC is added to the CAT.

Recommended procedure

Prepare a solution of TSC (~0·025*M*) or of a TSC complex in sodium acetate–acetic acid buffer of pH 4. Add an aliquot containing 0·02–1·5 mmole to a measured excessive (~50–60%) volume of 0·1*N* chloramine-T solution in an iodine-flask and set aside for about 30 min, shaking occasionally. Rinse down with 20 ml of water, add 10 ml of 20% potassium iodide solution and 10 ml of 6*M* hydrochloric acid and titrate with 0·2*M* sodium thiosulphate. Run a blank with CAT solution alone. The

Table II.—ESTIMATION OF THIOSEMICARBAZIDE AND ITS COMPLEXES WITH CHLORAMINE-T

TSC taken, *mg*	TSC recovered, *mg*	TSC taken, *mg*	TSC recovered, *mg*
4·01	4·02	50·1	50·2
10·14	10·09	60·1	60·0
30·25	30·1	90·1	89·9
40·1	39·9	110·2	110·1
$Zn(TSC)_2SO_4$*		$Ni(TSC)_2(NO_3)_2$†	
Taken, *mg*	Found, *mg*	Complex taken, *mg*	Complex found, *mg*
2·33	2·34	2·22	2·23
5·83	5·84	4·88	4·86
11·66	11·68	5·56	5·58
13·45	13·42	9·78	9·82
23·32	23·36	11·11	11·16
37·6	37·7	16·65	16·73
48·4	48·4	24·45	24·51

* Prepared by mixing TSC and $ZnSO_4$ solutions in the stoichiometric proportions, scratching the beaker with a glass rod to induce precipitation, filtering off, washing with water, and drying at 40–50°. The composition was checked by standard methods of analysis.

† Prepared according to ref. 7.

number of g of TSC (*x*) in the experimental solution is given by

$$x = 7{\cdot}593y(V_1 - V_2)$$

where y is the normality of the thiosulphate, V_1 is the blank titration and V_2 the volume of thiosulphate used to titrate the excess of CAT left over after oxidation of TSC.

RESULTS AND DISCUSSION

There will, of course, be interference by any other species present that are oxidizable by CAT or which can oxidize iodide. In particular, thiocyanate and hydrazine (from which TSC is made) will interfere by reducing CAT. The method is useful, however, for analysis of TSC complexes of metals. Zinc and nickel appear to catalyse the oxidation, which was complete within 5 min when zinc and nickel TSC complexes were analysed.

Some typical results are given in Table II and include analyses of some TSC complexes. The values obtained are accurate within 0·5%.

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Summary—A rapid and accurate method for the estimation of thiosemicarbazide in aqueous solution has been developed based on its oxidation with chloramine-T at room temperature and pH 4. The effect of such variables as pH, mode of addition of reagents and concentration of chloride ion on the extent of oxidation has been studied.

Zusammenfassung—Eine schnelle und genaue Methode zur Bestimmung von Thiosemicarbazid in wäßriger Lösung wurde entwickelt. Sie beruht auf Oxidation mit Chloramin T bei Raumtemperatur und pH 4. Der Einfluß des pH, des Verfahrens bei der Zugabe der Reagentien und der Konzentration von Chlorid auf den Oxidationsgrad wurde untersucht.

Résumé—On a élaboré une méthode rapide et précise pour l'estimation du thiosemicarbazide en solution aqueuse, basée sur son oxydation par la chloramine-T à température ordinaire et pH 4. On a étudié l'influence de variables telles que le pH, le mode d'addition des réactifs et la concentration de l'ion chlorure sur le degré d'oxydation.

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Kinetochromic spectrophotometry—III.

Determination of fluoride by catalysis of the zirconium–Methylthymol Blue reaction

(*Received* 12 *November* 1969. *Accepted* 9 *December* 1969)

The majority of spectrophotometric methods for the determination of trace amounts of fluoride are indirect, and involve the bleaching action of the fluoride ion on soluble coloured complexes of zirconium with organic reagents such as Alizarin Red S[1] or Eriochrome Cyanine R.[2] Few direct colorimetric procedures for the determination of fluoride exist, but that based on the formation of a ternary complex between alizarin complexan, cerium and fluoride has been widely accepted and is number of g of TSC (x) in the experimental solution is given by

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RESULTS AND DISCUSSION

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EXPERIMENTAL

Reagents

The Methylthymol Blue (MTB) reagent solution (5 × $10^{-4}M$) and zirconium stock solution ($10^{-2}M$) were prepared and kept as previously described.[5] A stock solution ($10^{-2}M$) of analytical grade sodium fluoride was prepared, stored in a polythene container, and diluted to 5 × $10^{-5}M$ as required.

Preparation of calibration graph for fluoride

Transfer 0, 1·0, 2·0, 3·0, 4·0 and 5.0-ml portions of 5 × $10^{-5}M$ sodium fluoride solution to a series of six 50-ml volumetric flasks containing 10 ml of 5 × $10^{-4}M$ MTB solution and 7 ml of 5*M* hydrochloric acid. At reference time zero add by pipette 10 ml of $10^{-3}M$ zirconium solution to the first flask. After 30 sec dilute the solution to 50 ml with distilled water, mix and leave to stand. Repeat for the other flasks at 2-min intervals. Allow the solution to stand for 60 min. Measure the absorbance of each solution at 586 nm against a water blank, using 2-mm silica cells, and permit 2 min to elapse between measurement of successive solutions. Develop a blank and standards (containing 3·0 and 5·0 ml of 5 × $10^{-5}M$ fluoride solution) with each group of samples. The calibration graph extends over the range 0·01–0·095 ppm of fluoride (0·50–4·75 μg). The calibration graph must be established each day, owing to a slight but progressive decrease in sensitivity over the 5-day period during which the $10^{-3}M$ zirconium solution may be used.

RESULTS AND DISCUSSION

Reaction conditions

The measurements of the absorbance produced by fluoride samples are made at 586 nm, the wavelength of maximal absorption of the zirconium–MTB complex.[5] As in the previous reactions,[4,5] the age of the zirconium solution employed for the determination of fluoride has a pronounced effect on the reaction rate and sensitivity attainable. A $10^{-2}M$ zirconium stock solution in 0·0125*M* hydrochloric acid which was allowed to age for 2–7 days was found to be most satisfactory. An aliquot of this solution was diluted to $10^{-3}M$ and made 0·05*M* in hydrochloric acid. This solution could be used for up to five days. The MTB, hydrochloric acid and fluoride (or sample) solutions can be mixed in any order in the recommended procedure, but the zirconium solution must be added last and the solution should then be diluted to volume *immediately*. Provided that temperature variations are less than ±3°, reproducible reaction rates and sensitivities are obtained with day-to-day operation of the method.

Effect of hydrochloric acid, MTB and zirconium concentrations. Figure 1 shows the variation in net absorbance for 0·095 ppm fluoride with variation in hydrochloric acid concentration between 0·3 and 1·1*M*, for different development times. The highest sensitivity compatible with a uniform calibration curve is obtained after a development time of 60 min using a solution 0·7*M* in hydrochloric acid.

The effect of MTB concentration and the ratio of MTB:Zr concentration on the net absorbance for fluoride was investigated for 0·7*M* hydrochloric acid solutions. As shown in Fig. 2*a*, for a 60-min development period, a concentration ratio of 1:2 produces the highest sensitivity. As shown in Fig. 2*b*, the highest sensitivity after 60 min is obtained by using an MTB concentration of $10^{-4}M$.

Calibration graph and sensitivity

Unlike the linear calibration graph obtained for the determination of sulphate, the catalytic action of fluoride on the zirconium–MTB system consistently produced a smooth curve. The effect of development time upon the shape of the calibration curve measured against a water blank at 586 nm, is shown in Fig. 3. After 60 min the smoothest calibration curve is obtained for the range

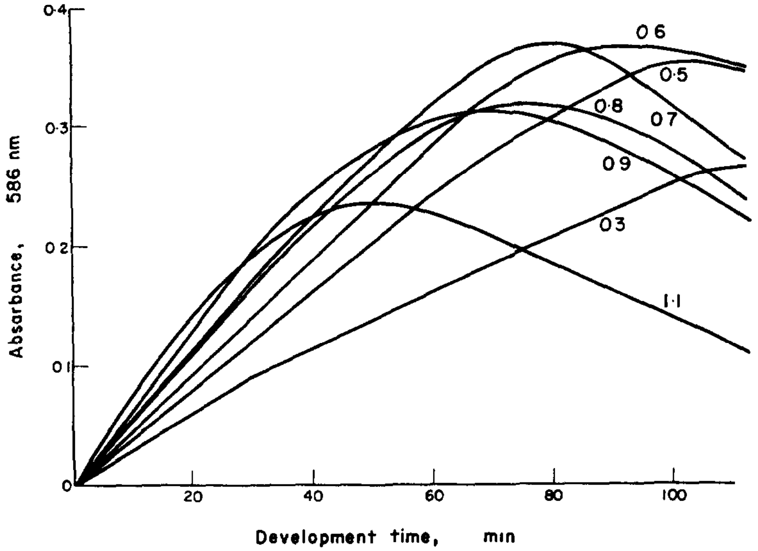
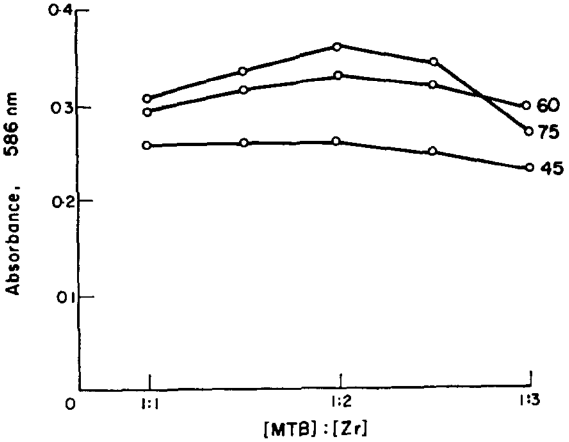


Fig. 1.—Effect of acidity on rate of development.
Net difference in absorbance of catalysed and uncatalysed reactions with varying concentration of HCl in final solution. $2 \times 10^{-4}M$ MTB; 0·3, 0·5, 0·6, 0·7, 0·8, 0·9, 1·1M HCl; 4·75 μg F^-; 2-mm cells, 586 nm.



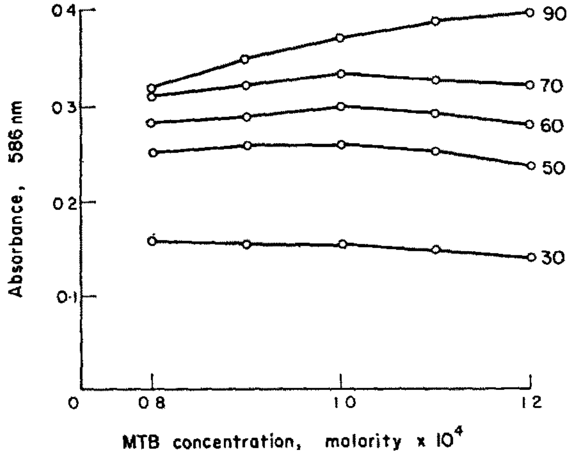
(a)

Fig. 2a.—Effect of MTB:Zr ratio at various development times.
Variation in net absorbance of catalysed and uncatalysed reactions for various MTB:Zr ratios, with development time. 0·7M HCl; $10^{-4}M$ MTB; 4·75 μg F^-. 2-mm cells, 586 nm. 1×10^{-4}, $1{\cdot}5 \times 10^{-4}$, $2{\cdot}0 \times 10^{-4}$, $2{\cdot}5 \times 10^{-4}$, $3{\cdot}0 \times 10^{-4}M$ $ZrOCl_2$. Development times in min.

0·25–4·75 μg of fluoride, with an effective molar absorptivity (4·75 μg of fluoride) of $3{\cdot}23 \times 10^4$ l.mole^{-1}.mm^{-1}. Owing to the curvature of the calibration graph, an effective molar absorptivity of $4{\cdot}00 \times 10^4$ l.mole^{-1}.mm^{-1} is obtained over the range 2·5–4·75 μg of fluoride.

Precision. The recommended procedure was used to determine 4·75 μg of fluoride repeatedly over a period of three months. The average net absorbance for 10 determinations after 60 min, in 2-mm cells, was 0·323 and the standard deviation 0·007.

Interference. The effect of diverse ions upon the kinetochromic action of fluoride on the zirconium–Xylenol Orange reaction, and of sulphate on the reaction between zirconium and MTB has



(b)

FIG. 2b.—Effect of MTB concentration.

Net difference in absorbance of catalysed and uncatalysed reactions for varying MTB concentrations at constant Zr:MTB ratio of 2:1. 4·75 μg F$^-$, 2-mm cells, 586 nm. 0·7M HCl; 8·0 × 10^{-5}, 1·0 × 10^{-4}, 1·1 × 10^{-4}, 1·2 × 10^{-4}M MTB; 1·6 × 10^{-4}, 1·8 × 10^{-4}, 2 × 10^{-4}, 2·2 × 10^{-4}, 2·4 × 10^{-4}M ZrOCl$_2$ respectively. Development times in min.

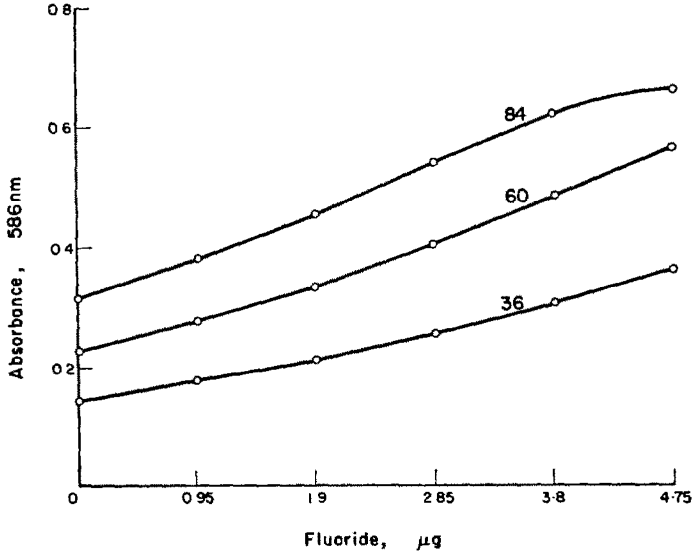


FIG. 3.—Effect of development time on calibration curve.

Variation in net absorbance of catalysed and uncatalysed reactions with fluoride concentration at different development times. 0·7M HCl; 10^{-4}M MTB; 2 × 10^{-4}M ZrOCl$_2$; 4·75 μg F$^-$, 2-mm cells, 586 nm, development times in min.

already been investigated.[4,5] Those ions which interfered in these procedures again showed similar effects. It was established that the presence of less than equimolar quantities of arsenate and phosphate ions, relative to the fluoride, caused serious additive interferences, but that sulphate could be tolerated when present in up to equimolar proportions with fluoride.

Removal of interference. Pretreatment of the sample solution, containing fluoride and interfering cations, with a strongly acidic cation-exchange resin such as Amberlite R-120[7] is effective in removing cationic interference from iron, manganese, thorium, vanadium, *etc.*

Procedures for the prior removal from solution of phosphate as the insoluble silver salt have been given by Fennell[8] and Colson,[9] while removal of sulphate interference has recently been described by Oliver[10].

CONCLUSION

The procedure described in this paper can be used to determine 0·25–4·75 μg of fluoride ion in aqueous solution, after a development time of 60 min, with an effective molar absorptivity of $3\cdot23 \times 10^4$ l.mole^{-1}.mm^{-1}. The method is more sensitive and also more rapid than the comparable method based on the catalytic action of fluoride on the zirconium–Xylenol Orange system.[4] It suffers from the same serious interference from phosphate, arsenate, and to a lesser extent, sulphate as that procedure, but is much freer from cationic interference than the cerium(III) or lanthanum alizarin complexan procedure, and has far greater sensitivity.

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Summary—The determination of 0·5–4·75 μg of fluoride ion by its catalytic action upon the slow reaction between Methylthymol Blue and zirconium(IV) in aqueous solution is described. Calibration curves obtained after 60 min under optimal conditions are smooth, and yield an effective molar absorptivity of $3\cdot23 \times 10^4$ l.mole^{-1}mm^{-1} at 586 nm. There is considerably less cationic interference than in the alizarin complexan–cerium(III) or lanthanum procedure, but more serious anionic interference is encountered when phosphate, arsenate and, to a lesser extent, sulphate ions are present in the sample solution.

Zusammenfassung—Die Bestimmung von 0,5–4,75 μg Fluorid durch seine katalytische Wirkung auf die langsame Reaktion zwischen Methylthymolblau und Zirkonium(IV) in wäßriger Lösung wird beschrieben. Nach 60 min unter optimalen Bedingungen erhaltene Eichkurven sind stetig und entsprechen einem effektiven molaren Extinktionskoeffizienten von $3{,}23 \cdot 10^4$ l mol^{-1} mm^{-1} bei 586 nm. Es gibt viel weniger Störungen durch Kationen als bei den Verfahren mit Alizarin-Complexan und Cer(III) oder Lanthan. Dagegen gibt es Störungen, wenn Phosphat, Arsenat, und in geringerem Maße, wenn Sulfat zugegen sind.

Résumé—On décrit la détermination de 0,5–4,5 μg d'ion fluorure par son action catalytique sur la réaction lente entre le Bleu de Méthylthymol et le zirconium (IV) en solution aqueuse. Les courbes d'étalonnage obtenues après 60 mn dans les conditions optimales sont régulières et donnent un coefficient d'absorption moléculaire réel de $3{,}23 \times 10^4$ l.mole^{-1}.mm^{-1}, à 586 nm. Il y a considérablement moins d'interférences cationiques que dans la technique Alizarine Complexan-cérium (III) ou lanthane, mais des interférences anioniques plus sérieuses sont rencontrées lorsque des ions phosphate, arséniate et, à un degré moindre, sulfate, sont présents dans la solution échantillon.

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ANNOTATION

Composition of the thorium(IV)–8–hydroxyquinoline adduct compound

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THE orange adduct, $Th(C_9H_6NO)_4 \cdot C_9H_7NO$, formed between thorium(IV) and 8-hydroxyquinoline (HQ) has been used as the basis of gravimetric and bromometric determinations of thorium for several years.[1,2] Surprisingly, however, the nature of this compound is not well understood, and there have been several conflicting studies regarding both its structure and composition.

Recent carbon-14 and infrared evidence[3] has strongly indicated that the additional HQ molecule is co-ordinated, as a zwitterion, to the central thorium ion, and is not merely an unco-ordinated crystal-lattice component as thought earlier. Similarly, in contrast to earlier work,[4,5] more recent work has suggested that the stoichiometry of the orange adduct prepared by conventional precipitation is not strictly 5:1.[6,7] Much of the analytical data supporting this recent claim, however, is not conclusive since the purported HQ:Th ratio (~4·8:1) was established solely by the bromometric determination of HQ in the precipitate; a determination of thorium was not made. In view of the difficulty in drying the adduct without partial loss of the thermally volatile molecule of HQ, it is possible that the results reflect the presence of water and/or the loss of some HQ. In a further report,[8] an HQ:Th ratio of 4·8:1 was also reported for the adduct prepared by precipitation from homogeneous solution.

In the present report, conclusive evidence is provided to show that the compound prepared by conventional precipitation is not the pure 5:1 adduct; two independent analytical procedures, each unambiguous, were used. The results show that the composition of the adduct is very difficult to reproduce from one preparation to the next.

The thermal reaction by which the tetrakis compound, $Th(C_9H_6NO)_4$, is prepared from the orange adduct has been reported many times, but there is considerable disagreement on the conditions required for the preparation.[1,9] A simple procedure for the preparation of the pure tetrakis compound is described in the present work.

EXPERIMENTAL

Stock solutions containing 1·4 mg of Th/ml were prepared from thorium nitrate hexahydrate (analytical-reagent grade) and adjusted to about pH 1·5 with freshly boiled nitric acid. The purity of all other chemicals was as previously described.[10]

The orange adduct was prepared as follows. A 25-ml portion of the thorium stock solution was diluted to 50 ml and the solution heated to 70°. A solution of HQ (0·143 g dissolved in 0·5 ml of glacial acetic acid and diluted to 7 ml with water) was slowly added, followed by a solution of ammonium acetate (2·0 g in 15 ml of water) added with stirring at a rate of 5 ml/min. Dilute aqueous ammonia (1·0*M*) was then added (5 ml/min) until the pH was 6–7. The final volume was adjusted to about 90 ml with water and the mixture allowed to digest for 1 hr at 70°. After filtration and washing with about 100 ml of hot water, the compound was dried in a stream of air for 3 hr and stored over phosphorus pentoxide. The compound was freshly prepared as required.

The molar ratio was established in two ways. (*i*) The thorium was determined by ignition[11] to ThO_2 at 900° and the HQ by bromometric titration,[10] and the molar ratio calculated (Table I). In one preparation, the compound was dried at 50° *in vacuo* for 72 hr before analysis. (*ii*) The ratio of the sublimed HQ to the residual tetrakis compound obtained on thermal conversion was determined. The conversion was effected quantitatively by heating (oil-bath) *in vacuo* (0·13 mbar) 150–200 mg of the adduct at 165–170° for 1½ hr. The sublimed HQ was collected in the initial portion of a U-tube immersed in a bath of solid carbon dioxide. A tiny droplet of moisture was observed below the HQ deposit in the U-tube. The sublimed HQ and residual tetrakis compound were separately dissolved in 4*M* hydrochloric acid and determined bromometrically, and the ratio HQ:ThO_4 was calculated (Table II). For the sample sizes taken, the deficiency of HQ (relative to ThO_4 . HQ) amounted to 2–4 mg, which is considerably more than the error expected in the bromometric titration.[10]

The same thermal procedure was used to prepare the pure tetrakis compound. The HQ and thorium contents were determined as described above. Analysis gave the following results: Th, 28·54 ± 0·04% (4 results; theoretical, 28·69%); HQ as Q^-, 71·37 ± 0·05% (10 results; theoretical, 71·31%); molar ratio Q^-: Th, 4·02 ± 0·01. The precision quoted is the standard error.

TABLE I.—ANALYSIS OF THE ORANGE Th(IV)-HQ ADDUCT

Th, %	HQ,* % (as Q^-)	Molar ratio HQ:Th
24·13†	72·62	4·84
±0·05	±0·04	±0·01
24·35†	73·54	4·86
±0·05	±0·05	±0·01
24·25†	74·28	4·94
±0·05	±0·06	±0·01
24·45¶	73·73	4·88

* HQ = 8-hydroxyquinoline.

† For the first three preparations, each result is the average of two determinations. The precision measure is the overall deviation.

¶ Compound dried *in vacuo* at 50° for 72 hr. For $Th(Q)_4 \cdot HQ$, Th = 24·33% and HQ, expressed as Q^- = 75·57%.

TABLE II.—MOLAR RATIO $HQ{:}ThQ_4$ IN THE ORANGE ADDUCT

HQ sublimed, *mg*	ThQ_4 residue, *mg*	Molar ratio $HQ{:}ThQ_4$
36·6	213·9	0·953
29·6*	184·4	0·913
24·8	155·3	0·889
23·7*	136·8	0·963
21·3	123·2	0·962

* Two determinations of the molar ratio were made on the material of a single preparation.

DISCUSSION

The data of Tables I and II, obtained by different analytical methods, show that the orange compound is deficient in HQ. Furthermore, the composition of the adduct varies (4·84:1 to 4·96:1) from one preparation to the next, even though the experimental conditions were not intentionally altered.

Since thermal loss of the additional HQ molecule is reported to begin at about 80°,[12,13] the samples were dried without heating to avoid any loss of the volatile species. Because of the mild drying conditions, the samples probably retained a small amount of moisture. The presence of moisture, however, would not affect the molar ratio of HQ:Th and $HQ{:}ThQ_4$.

The presence of water in the adduct was confirmed by the observation of moisture in the U-tube after the thermal reaction, and by infrared analysis. Under increasingly rigorous drying conditions, the integrated intensity of the broad absorption band centred at 3350 cm^{-1} (*e.g.*, spectrum B in reference 3) decreased, and became zero when the orange compound was dried *in vacuo* at 50° for 72 hr (spectrum A, reference 3). To minimize the effect of differences in sample size, a ratio of the integrated intensity of the 3350 cm^{-1} and 1100 cm^{-1} bands was made. Analysis of the anhydrous compound also yielded a value of HQ:Th significantly lower than 5:1 (Table I), although in this instance, there was the possibility of partial volatilization of the additional HQ molecule.

The variation in the results suggests that the composition is very sensitive to slight changes in the experimental conditions. This variation was obtained even though the amounts of thorium, HQ, ammonium acetate, aqueous ammonia, the rates of addition of each reagent, and the total volume of the final solution were kept reasonably constant in each preparation. In this regard, it is interesting that Cardwell *et al.*[14] observed that the composition of the compound is dependent on the rate at which the pH of the solution is adjusted. The results of the present study suggest that the sensitivity of the composition to such an experimental variable is even greater than previously thought, and that very carefully controlled experiments are required to attain reproducibility and perhaps, even a strict 5:1 stoichiometry. Variables such as the percent excess of HQ, method of pH adjustment, and temperature and time of digestion should be investigated. For example, in the present study, a 33% excess of HQ was used; this amount may not be sufficient to suppress thorium hydrolysis entirely as the pH is raised to its final value.

If it is assumed that the extent of hydrolysis is negligible and that the extra HQ molecule is coordinated to the central thorium ion and is monodentate,[3] it is reasonable to suggest that the deficient

HQ is replaced by co-ordinated water. The average composition can then be written as $Th(C_9H_6NO)_4 \cdot 0{\cdot}9C_9H_7NO \cdot 0{\cdot}1H_2O$. Simple calculation shows that the amount of bound water in the adduct would be about 0·2 mg/100 mg. This concentration is too small for detection by infrared analysis and could not lead to the droplet size observed in the U-tube. Therefore, the bulk of the water present in the orange adduct taken for analysis must have been unbound moisture.

In the past, erratic results have sometimes been reported in the bromometric determination of thorium by means of 8-hydroxyquinoline. In gravimetric work, some workers have ignited the precipitated adduct to ThO_2, or have thermally converted it to the tetrakis compound in order to obtain reproducible results. Clearly, the non-stoichiometry of the adduct and the thermal volatility of the additional HQ molecule detract greatly from the usefulness of the adduct as an analytical compound. A superior analytical compound is tetrakis(2-methyl-8-hydroxyquinolinato)thorium-(IV).[15] This easily prepared compound is stoichiometric and thermally stable.

Tetrakis(8-hydroxyquinolinato)thorium(IV) can be easily prepared in reasonably pure form by heating the orange adduct according to the procedure described earlier. The effect of varying the temperature, time and sample size was not investigated further. The main advantage in preparing the tetrakis compound *in vacuo* is that its oxidative decomposition cannot occur as readily as in air.

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Summary—The orange compound formed between thorium(IV) and 8-hydroxyquinoline by conventional precipitation is non-stoichiometric. The composition is very sensitive to experimental conditions; the average ratio of bound 8-hydroxyquinoline to thorium was found to be 4·9 : 1. The deficiency of 8-hydroxyquinoline is due either to partial hydrolysis of thorium, or to the presence of co-ordinated water. A simple procedure for the preparation of the pure tetrakis compound is described.

Zusammenfassung—Die orange Verbindung, die man durch konventionelle Fällung aus Thorium(IV) und 8-Hydroxychinolin erhält, ist nicht stöchiometrisch zusammengesetzt. Die Zusammensetzung hängt sehr empfindlich von den Versuchsbedingungen ab; das mittlere Verhältnis von gebundenem 8-Hydroxychinolin zu Thorium wurde als 4,9:1 gefunden. Der Abmangel an 8-Hydroxychinolin ist entweder durch teilweise Hydrolyse von Thorium oder durch Vorhandensein koordinierten Wassers begründet. Ein einfaches Verfahren zur Darstellung der reinen Tetrakis-Verbindung wird beschrieben.

Résumé—Le composé orange formé entre le thorium(IV) et la 8-hydroxyquinoléine par précipitation classique n'est pas stoechiométrique. La composition est très sensible aux conditions expérimentales; on a trouvé que le rapport moyen de la 8-hydroxyquinoléine liée au thorium est de 4,9:1. Le déficit en 8-hydroxyquinoléine est dû soit à une hydrolyse partielle du thorium, soit à la présence d'eau de coordination. On décrit une technique simple pour la préparation du composé tétrakis pur.

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END-POINT EVALUATION IN INSTRUMENTAL TITRIMETRY—II

CONFIDENCE INTERVALS IN EXTRAPOLATION OF LINEAR TITRATION CURVES

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Summary—The random titration error has been evaluated by single linear regression analysis of both linear branches of titration curves. As a simplification the confidence interval of a titration is estimated by substituting divergent linear confidence limits for the curved confidence limits of both branches of the curve. The influence of the angle between both branches upon the confidence interval of a titration has also been evaluated. The procedure has been proved advantageous by applying it to several amperometric and photometric titrations of lead and by comparing the results with those obtained by the complementary approach of Liteanu and Cörmös, and by the usual statistical treatment of end-points obtained by graphical extrapolation. The method allows a critical consideration of the experimental conditions with regard to the desired level of precision.

THE WIDESPREAD development and application of linear titration curves *e.g.*, photometric, amperometric, *etc.*, has made it necessary to study the attainable precision and accuracy of end-point evaluation.

The usual graphical procedure of linear end-point extrapolation based on linear segments of titration curve has been considered by many to be inadequate. Boulad[1] has proposed a simple calculation of the end-point which is taken as the intersection point of two straight lines, each being defined by two points before and beyond the equivalance point, respectively. Another simplified end-point evaluation has been developed by Lydersen[2] for conductometric titrations. As the ratio of the slopes of two adjacent branches of the titration curve is constant for a given titration system, the first branch of the titration curve can be characterized by a single point and the other one is represented by a straight line calculated by the method of least squares. In a series of papers, Liteanu and his co-workers[3–7] have shown the advantage of using single linear regression analysis of both linear segments of the titration curve. The end-point is calculated as the intersection point of both regression lines,[3,4] and the slope difference is also useful for the purpose.[7] The elimination of points with a suspiciously large deviation has been also discussed.[5] To evaluate an end-point confidence interval of a single titration (*cf.*, ref. 6), parallel linear confidence limits are substituted for the curved borders of confidence belts along the regression lines. The importance of having a sufficient number of experimental points has also been

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* Part I—*Talanta*, 1970, 17, 151.

stressed and the influence of the angle between both linear branches upon the confidence interval of a titration has been demonstrated by three experimental titration curves.[6]

One drawback to these contributions lies in the evident lack of experimental data necessary to check the influence of various sources of random experimental error in instrumental titrimetry. It has been difficult, therefore, to judge the validity of the conclusions reached.

In this paper a new simplifying approach to the evaluation of the confidence interval of a single titration is given. The results of a detailed study of random errors in a series of amperometric and photometric titrations, which is the subject of the next paper of this series,[8] are partially presented here to allow comparison of various approaches to the analysis of titration error and to illustrate the influence of the angle between both branches of the titration curve.

DERIVATION OF EQUATIONS

List of symbols

A_0, A_0' A_1, A_1'	Coefficients of estimated regression lines
c	Analytical (molar) concentration
$K =$	$s_{A_1}t - s_{A_1}'t'$; auxiliary symbol, equation (19)
$K_{\bar{x}} =$	$s_{A_1}t\bar{x} - s_{A_1}'t'\bar{x}'$; auxiliary symbol, equation (19)
n, n'	Numbers of pairs of experimental values x_i, y_i and x_i', y_i' respectively
s_{A_1}, s_{A1}'	Estimates of standard deviation of the slope values A_1 and A_1' respectively
s_{yx}, s_{yx}'	Estimates of standard deviation characterizing the distribution of y_i values either side of the estimated regression line
t, t'	Statistical *Student's* t-value taken from the Table for $n - 2$ or $(n' - 2)$ degrees of freedom and confidence level α
x, x'	Measured volumes of titrant
x_e	Consumption of titrant at end-point
Δx_e	Confidence interval of the end-point
x_i, x_i'	Experimental values of the measured volume of titrant
x_k	Chosen volume of the titration reagent
$\bar{x}, \bar{x}'$	Arithmetic means from the appropriate set of volume readings
x_{e_1}, x_{e_2}	Values limiting the confidence interval of the end-point
y, y'	Quantities of determinand
y_i, y_i'	Experimental values for the quantity of determinand
y_k	Actual value of the quantity of determinand corresponding to the value of x_k
$\tilde{y}_k$	Value of the quantity of determinand calculated for x_k, using the regression line
Δy_k	Confidence interval for y_k about the value of $\tilde{y}_k$
$\bar{y}, \bar{y}'$	Arithmetic means of all experimental values of y_i or y_i' respectively
α	Statistical confidence level
γ	Angle between linear branches of a titration curve

Note—The unprimed symbols refer to the branch before the equivalence point, the primed symbols refer to the branch of the curve beyond the equivalence point.

Statistical approaches to estimation of the confidence interval of a single titration

The random titration error is characterized by a confidence interval within which the end-point of a single titration can be found, at a certain probability level. The relation between the error in the measured values x_i, y_i, which are used for the end-point extrapolation, and the appropriate confidence interval, can be solved by single linear regression analysis on the assumption that for each of the fixed values x_i there is a distribution of the variates y_i which follows a normal Gaussian law. The variance of these distributions is constant and the average values of the distributions lie on the regression line.

For every actual value of x_k the corresponding confidence interval for y at a confidence level α is given by (*cf.* ref. 9)

$$\Delta y_k = 2ts_{yx}\sqrt{\frac{1}{n} + \frac{(x_k - \bar{x})^2}{\sum_{i=1}^{n}(x_i - \bar{x})^2}}, \tag{1}$$

expressing the spread either side of the value $\tilde{y}_k$ calculated from the expression for the estimated regression straight line[9] $\tilde{y}_k = A_0 + A_1x_k$ before the equivalence point.

Similarly, the branch of the titration curve beyond the equivalence point can be characterized by the straight line $\tilde{y}_k = A_0' + A_1'x_k$ with the corresponding confidence interval

$$\Delta y_k = 2t's_{yx}'\sqrt{\frac{1}{n'} + \frac{(x_k - \bar{x}')^2}{\sum_{i=1}^{n'}(x_i - \bar{x}')^2}}. \tag{2}$$

The values of *Student's t* are found in the statistical tables for a chosen probability, $(1 - \alpha)100\%$, and for the degrees of freedom $n - 2$, $n' - 2$, respectively.

The estimates of standard deviations corresponding to the distribution of the y-values either side of both regression lines are given by the expressions

$$s_{yx} = \sqrt{\frac{\sum_{i=1}^{n}(A_0 + A_1x_i - y_i)^2}{n - 2}} \tag{3}$$

$$s_{yx}' = \sqrt{\frac{\sum_{i=1}^{n'}(A_0' + A_1'x_i - y_i)^2}{n' - 2}}. \tag{4}$$

The confidence intervals form confidence belts with curved borders along both extrapolation straight lines (curves 1–4 in Fig 1). The geometrical interpretation of the confidence interval of a particular titration is also illustrated in Fig. 1. It would be possible to calculate its value as a difference between the outer intersects of the confidence limits, $x_{e_2} - x_{e_1}$. It is more convenient, however, to solve this problem by simplified models of confidence limits.

Liteanu and Cörmös have tried to find a suitable simplification by considering the confidence belts as limited by parallel straight lines at a distance of $\pm ts_{yx}$ or $\pm t's_{yx}'$ from both regression straight lines $\tilde{y} = A_0 + A_1x$, or $\tilde{y} = A_0' + A_1'x$, respectively, which is a rather subjective choice. The solution of the regression lines yields the expression for the end-point

$$x_e = \frac{A_0 - A_0'}{A_1' - A_1}. \tag{5}$$

The range of the confidence interval of the end-point, Δx_e, is limited by the confidence limits of x_{e_2} and x_{e_1},[6]

$$\Delta x_e = |x_{e_2} - x_{e_1}| = 2\frac{ts_{yx} + t's_{yx}'}{|A_1' - A_1|}. \tag{6}$$

A certain drawback to the method of parallel confidence limits consists in neglecting

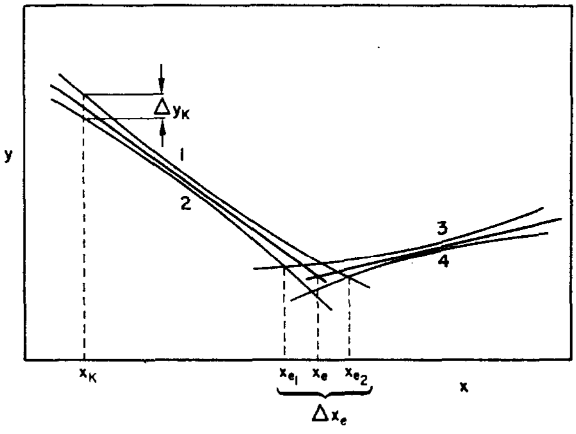

FIG. 1.—Theoretical shape of confidence belts along extrapolated branches of a titration curve.
Δy_k denotes the confidence interval for an actual value y_k either side of the calculated value $\bar{y}_k$.

the curvatures of the theoretical confidence belts (*cf.* Fig. 1) which may be pronounced in the middle part of the branch and close to the equivalence point.

This problem can be solved by another simplifying approach which will be presented here. The two confidence limits of the confidence belts are also assumed to be linear, but they are drawn through the mean point on the regression line, defined by $\bar{x}$, $\bar{y}$, where

$$\bar{x} = \sum_{i=1}^{n} x_i/n \tag{7}$$

$$\bar{y} = \sum_{i=1}^{n} y_i/n. \tag{8}$$

If it is assumed that the values of the only random variable y are normally distributed for each x, the confidence intervals of the slope values are represented by

$$\langle A_1 - ts_{A_1};\ A_1 + ts_{A_1} \rangle \tag{9}$$

$$\langle A_1' - t's_{A_1}';\ A_1' + t's_{A_1}' \rangle \tag{10}$$

where A_1, A_1' are the estimates of regression coefficients, s_{A_1}, s_{A_1}' are the estimates of standard deviations of the slope values of both regression straight lines, and the *Student's t, t'* values are chosen at the desired confidence level.

The estimates of standard deviations of the slopes are defined as follows

$$s_{A_1} = \frac{s_{yx}}{\sqrt{\sum_{i=1}^{n} (x_i - \bar{x})^2}} \tag{11}$$

$$s_{A_1}' = \frac{s_{yx}'}{\sqrt{\sum_{i=1}^{n'} (x_i - \bar{x}')^2}}. \tag{12}$$

The inherent assumption of this model consists in defining borders of confidence

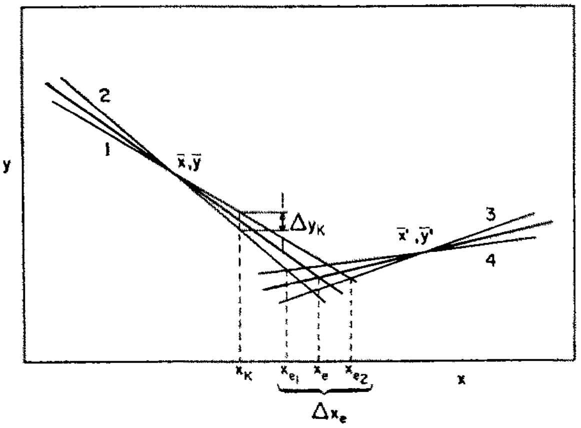

FIG. 2.—Model of divergent linear confidence limits along the extrapolated branches of a titration curve.
The linear confidence limits are given by: *1*—equation (13); *2*—equation (14); *3*—equation (15); *4*—equation (16).

belts as straight lines with slopes given by the confidence limits of the slopes of both regressions lines. It can easily be shown that these limits are identical with the asymptotes of the hyperbolically shaped borders of the confidence belts on both branches of the titration curves. Thus, the equations for the limits in Fig. 2 are obtained

$$y = A_0 - ts_{A_1}\bar{x} + x(A_1 + ts_{A_1}) \quad \text{(straight line No. 1)} \tag{13}$$

$$y = A_0 + ts_{A_1}\bar{x} + x(A_1 - ts_{A_1}) \quad \text{(straight line No. 2)} \tag{14}$$

$$y = A_0' - t's_{A_1}'\bar{x}' + x(A_1' + t's_{A_1}') \quad \text{(straight line No. 3)} \tag{15}$$

$$y = A_0' + t's_{A_1}'\bar{x}' + x(A_1' - t's_{A_1}') \quad \text{(straight line No. 4)} \tag{16}$$

The end-point of a titration to be evaluated can be calculated from equation (5) and is found within an interval defined by the intersect x_{e_2} of the straight line limits Nos. 1 and 3 and by the intersect x_{e_1} of the limits Nos. 2 and 4 (Fig. 2).

By solving the appropriate equations we obtain

$$x_{e_2} = \frac{A_0 - ts_{A_1}\bar{x} - A_0' + t's_{A_1}'\bar{x}'}{A_1' + t's_{A_1}' - A_1 - ts_{A_1}} \tag{17}$$

$$x_{e_1} = \frac{A_0 + ts_{A_1}\bar{x} - A_0' - t's_{A_1}'\bar{x}'}{A_1' - t's_{A_1}' - A_1 + ts_{A_1}} \tag{18}$$

Thus, the confidence interval of the titration is given by

$$\Delta x_e = |x_{e_2} - x_{e_1}| = 2\left|\frac{K(A_0 - A_0') + K_{\bar{x}}(A_1 - A_1')}{(A_1 - A_1')^2 - K^2}\right| \tag{19}$$

where

$$K = s_{A_1}t - s_{A_1}'t'$$

and

$$K_{\bar{x}} = s_{A_1}t\bar{x} - s_{A_1}'t'\bar{x}'.$$

In most practical cases, the values of K^2 in the denominator can be neglected since the value of the other term is greater by at least two orders of magnitude. Equation (19) can be simplified to

$$\Delta x_e = 2\left|\frac{K_{\bar{x}}}{A_1 - A_1'} + \frac{K(A_0 - A_0')}{(A_1 - A_1')^2}\right|. \tag{20}$$

Substituting from equation (5), we obtain the final form of the expression for Δx_e:

$$\Delta x_e = 2\left|\frac{s_{A_1}t(x_e - \bar{x}) + s_{A_1}'t'(\bar{x}' - x_e)}{A_1' - A_1}\right|. \tag{21}$$

Factors influencing the confidence interval of a titration

Besides the uncertainty in the measurement of variables, *e.g.*, the readings of the titrant volume and the physicochemical quantity taken for indication of the end-point, other important factors determine the level of the titration error, *viz.* the angle between both linear branches of the titration curve, the number of experimental points and their distribution upon the titration curve.

The influence of the angle upon the confidence interval of the titration can be shown, if the slope value of the regression line before equivalence is calculated, using expressions for the tangent of γ.

In the case of parallel confidence limits we thus obtain

$$\Delta x_e = 2\,\frac{ts_{yx} + t's_{yx}'}{1 + (A_1')^2}\,|A_1' - \text{cotan}\,\gamma|. \tag{22}$$

For the divergent linear limits the following expression can be written:

$$\Delta x_e = 2\left|\frac{[K(A_0 - A_0')(1 - A_1'\tan\gamma) + K_{\bar{x}}(1 + (A_1')^2)\tan\gamma](1 - A_1'\tan\gamma)}{[1 + (A_1')^2]^2\tan^2\gamma}\right|. \tag{23}$$

The symbols K and $K_{\bar{x}}$ were defined above [equation (19)].

TABLE I.—COMPARISON OF PRECISION IN SERIES OF AMPEROMETRIC TITRATIONS OF LEAD

Concentrations, M			Confidence intervals† Δx_e, μl		Statistical treatment of 10 end-points evaluated, by Δx_e, μl	
Lead	EDTA	$\lvert A_1' - A_1\rvert$*	Parallel limits	Divergent limits	graphical extrapolation	linear regression
1·50 × 10^{-4}	10^{-2}	0·747	19·2	18·7	8·7	11·7
0·75 × 10^{-4}	5 × 10^{-3}	0·407	24·6	28·9	27·8	30·2
0·60 × 10^{-4}	4 × 10^{-3}	0·332	26·7	27·5	31·0	29·9
0·30 × 10^{-4}	2 × 10^{-3}	0.181	35·6	34·8	39·6	50·5

* Expressed in galvanometer scale units per μl of titrant.
† Mean of 5 values calculated.

The dependence of the confidence interval of titration upon the angle γ is illustrated by the data in Tables I and II and in Figs. 3 and 4. If the slope of the branches beyond the equivalence point is low, an approximation $|A_1' - A_1| \approx -\tan\gamma$ can be accepted. The effect of the angle expressed as the slope difference $|A_1' - A_1|$ can be seen in Figs. 3 and 4, which also allow comparison of the ranges of confidence intervals obtained by various approaches. Further, the horizontal short lines denote

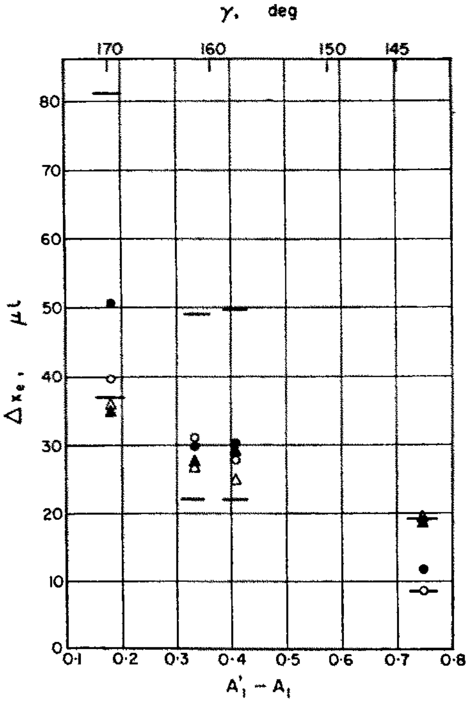

FIG. 3.—Comparison of confidence intervals of amperometric titrations of lead. The confidence intervals were evaluated from: ○, extrapolated end-points; ●, calculated end-points; △, mean value of 5 individual values obtained by the approach of parallel confidence limits; ▲, mean value of 5 individual values obtained by the approach of divergent confidence limits.

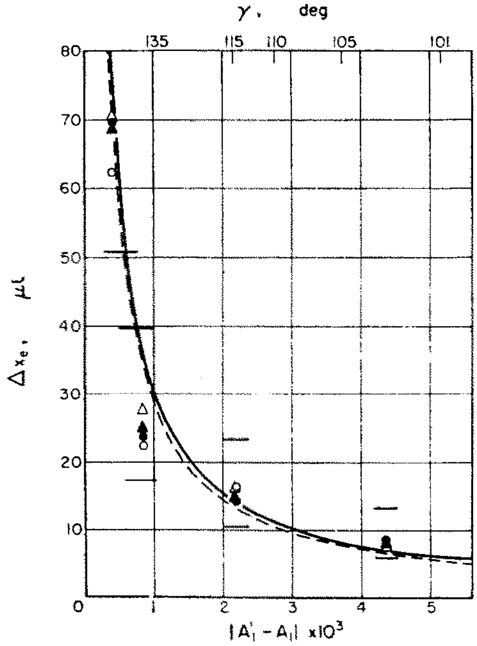

FIG. 4.—Comparison of confidence intervals of photometric titrations of lead. Full line represents the relationship according to equation (6), the dashed line according to equation (21). The legend for the points is the same as for Fig. 3.

TABLE II.—COMPARISON OF PRECISION IN SERIES OF PHOTOMETRIC TITRATIONS OF LEAD

Concentrations, M		$\lvert A_1' - A_1\rvert$*	Confidence intervals† Δx_e, μl		Statistical treatment of 10 end-points evaluated, by	
Lead	EDTA	$\times 10^3$	Parallel limits	Divergent limits	graphical extrapolation Δx_e, μl	linear regression
$1{\cdot}50 \times 10^{-5}$	10^{-3}	4·35	8·2	7·2	7·7	8·0
$0{\cdot}75 \times 10^{-5}$	5×10^{-4}	2·18	15·7	15·4	15·7	14·2
$0{\cdot}30 \times 10^{-5}$	2×10^{-4}	0·844	27·5	25·1	22·6	23·8
$0{\cdot}15 \times 10^{-5}$	10^{-4}	0·396	70·5	68·6	62·4	69·6

* Expressed in units of absorbance per μl of titrant.
† Mean of 5 calculated.

the limits where an actual value of confidence interval is found with a 90% probability. The calculation was based upon the $2ts$ estimates found by statistical treatment of the calculated end-points [equation (5)] of all titrations involved in one series. A double-sided confidence interval for the actual value of variance was taken into consideration. The χ-square distribution was employed and it was assumed that there is an equal probability in both directions of a deviation exceeding the calculated value of the confidence interval.

The values of the confidence intervals were calculated on the basis of data obtained by statistical treatment of a series of ten titrations which were evaluated either by graphical end-point extrapolation or by calculation using equation (5). The shift of estimates of Δx_e towards the lower limits can be attributed to the shape of the $(\chi)^2$ distribution. These confidence intervals can be compared with the average values of five intervals which were calculated for every single titration by both procedures indicated above. The individual confidence intervals which were obtained by all treatments studied are mostly found within the limits indicated, despite the perceptible differences especially at higher levels of experimental error. In Fig. 4, where the values of the confidence intervals of photometric titrations of lead are shown, a theoretical curve is traced showing the dependence of the confidence interval upon the difference in the slope values of both branches. The full line is for the approach with parallel confidence limits [equation (22)] and the dashed line is for the case of divergent linear limits [equation (23)]. For the evaluation of these functions the mean values of all four series of titrations were taken, *i.e.*, $s_{yx} = 3{\cdot}62 \times 10^{-3}$; $s_{yx}' = 2{\cdot}26 \times 10^{-3}$; $s_{A_1} = 2{\cdot}79 \times 10^{-5}$; $s_{A_1}' = 2{\cdot}68 \times 10^{-5}$. There is no appreciable difference between both theoretical curves, and the results of all the studied ways of treating experimental data are distributed close to these curves.

The range of the confidence interval depends also upon the number of experimental points employed for the computation of the regression lines. This factor can be seen from the general expressions for the confidence limits given by equations (1) and (2). The higher the numbers of experimental pairs n or n', the lower are the values of the discriminants, and the confidence belts become narrower. Consequently, the range of the confidence interval of titration is also narrower. This factor can also be illustrated by equation (21) for the divergent limits, since a greater number of variates accounts for lower values of the estimated standard deviation of the slopes, s_{A_1} and s_{A_1}'. The number of experimental pairs exerts an influence even upon the *Student's t* and t' values which are decreasing rapidly with increasing degrees of freedom.[9] To obtain a sufficient precision, it is usually necessary to take 6 or 8 pairs of readings at least for each of the extrapolation straight lines.[6] A greater number of experimental pairs does not lead to a more significant increase in precision.

Equation (21) for Δx_e in case of divergent confidence limits shows that the precision is increased for such an arrangement, when the set of experimental pairs being represented by the mean values of $\bar{x}$ or $\bar{x}'$, respectively, is situated sufficiently close to the equivalence point. This is counteracted by the requirement that the expressions $[\sum (x_i - \bar{x})^2]^{1/2}$ or $[\sum (x_i - \bar{x}')^2]^{1/2}$, respectively, should reach maximum values. An optimum arrangement satisfying both requirements is obtained for a case with gradually increasing density of experimental points on the linear part of the branch approaching the equivalence point.

EXPERIMENTAL

To study the random titration error lead was determined by two linear, instrumental methods, namely, photometric and amperometric titration with EDTA. Conditions were deliberately arranged so as to exaggerate the confidence intervals.

Apparatus

Polarograph. An LP55 model polarograph (Laboratory Instruments, Prague) was used in conjunction with a precise scale galvanometer.

Spectrophotometer. A Zeiss Spekol spectrophotometer was modified for spectrophotometric titrations.

Burette. A home-made syringe burette of 3–500 μl capacity was used. It was calibrated by weighing water delivered under medicinal paraffin. For 25 deliveries of 100 μl the standard deviation was 0·3 μl.

Procedures

Amperometric titrations. The mercury dropping electrode was used as indicating electrode in combination with a mercury pool as reference electrode. The applied potential difference was chosen so that the mean value of the limiting current was proportional to the unreacted lead ion concentration. The solution to be titrated (20 ml, ammonium tartrate buffer, pH = 8·5) was stirred and an inert atmosphere was maintained by passing a stream of nitrogen after each addition of titrant. The readings of the current oscillations were taken to evaluate the mean value (for details see ref. 8).

Photometric titrations. Xylenol Orange was used as indicator.[10] The titrations were carried out in a volume of 20 ml and the absorbance at 550 nm was measured. A titration curve with linear branches was obtained. The range of the linear segments of the curve depends upon the amount of indicator added and upon the pH value, pH = 5 being optimum.

In all titrations studied the experimental conditions were arranged so that the titration error was affected only by errors in the measured quantity and in measurement of the additions of the titrant. All other possible sources of error were carefully eliminated. All volumetric glassware was calibrated. The standard deviation for delivery from a 10-ml pipette was 0·002 ml, for example.

In all instrumental titrations 8–10 readings were taken on each branch of the titration curve, the sequence of the additions of titrant being even and identical within the series. In Fig. 5, one of the amperometric titration curves of $1{\cdot}5 \times 10^{-4}M$-lead chloride with $10^{-3}M$ EDTA is shown. The shape of the theoretical confidence belts can be compared with the simplified shapes of confidence belts obtained by both the treatments discussed. All details of our experiments and of the approaches used for an independent study of errors of all variables involved are given in Part III.[8]

The end-points of all these titrations were evaluated by graphical extrapolation and by the approach based upon single linear regression [equation (5)]. A programme for an electronic computer ODRA 1013 was developed to allow the rapid computation of the end-point and of its confidence interval by both procedures discussed.

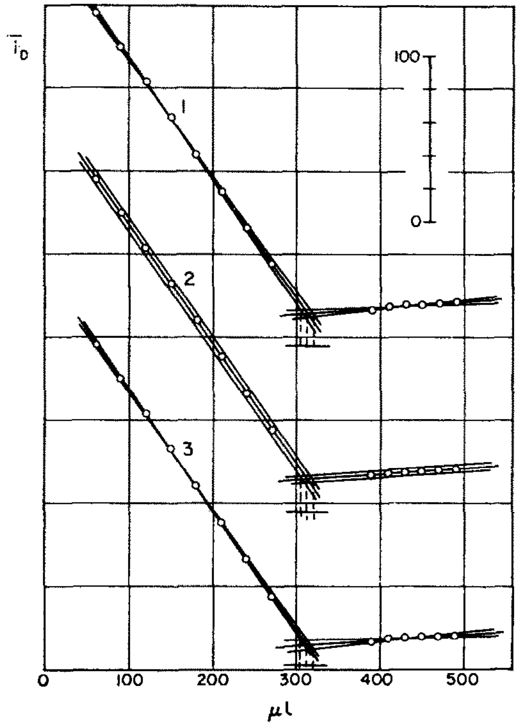

FIG. 5.—Evaluation of an amperometric titration of lead.
A 25-ml portion of $1\cdot5 \times 10^{-4}M$ $PbCl_2$ was titrated with $10^{-2}M$ EDTA. The confidence belts are limited by: *1*—theoretical borders resulting in single linear regression; *2*—parallel linear limits; *3*—divergent linear limits. The confidence intervals of the end-points are shown below each titration curve.

CONCLUSIONS

The analysis of the results obtained revealed that the end-point calculation based upon single linear regression leads to somewhat more accurate results than the common procedure of graphical end-point extrapolation.

The confidence intervals of tested instrumental titrations, calculated by both approaches, assuming either linear parallel confidence limits or linear divergent limits, are in good agreement with the results of the statistical treatment of the end-point data of each series. Under the experimental conditions studied both simplified approaches are capable of expressing the random spread of points on the linear branches of a titration curve. In these cases both linear simplifications of confidence belt borders sufficiently approached the hyperbolically curved theoretical limits near the equivalence point. Considering linear divergent limits, the greater the absolute values of the differences $|x - \bar{x}|$ and $|x - \bar{x}'|$, the better is the approach of the asymptotes to the curved limits. In our titrations, the y-values of the theoretical borders and of the asymptotes were approximately equal or deviated within 10% of the corresponding Δy_k value. As can be seen from the data summarized in Tables I and II, the divergent confidence limits approach can yield results which are in even closer accord with the data obtained by the statistical treatment of the end-point values.

From the practical point of view, both procedures for the evaluation of confidence intervals can be used to anticipate the level of random titration error from the experimental points of only one titration. In such a way, the optimum experimental conditions can be easily chosen to keep the titration error within desired limits.

The approaches studied also offer the possibility of a quantitative evaluation of some factors influencing the precision of instrumental titration. Besides the obvious requirement of a satisfactory level of precision in the measurements of both variables, there is an important effect of the value of the angle between both branches of the titration curve, or more explicitly, of the extent of the change in physical quantity per unit of the titration reagent added.

The study of the approach with divergent linear confidence limits pointed out the importance of the distribution of experimental points on the linear portions of both branches of the curve. For a higher precision to be obtained the density of readings should increase to a certain extent towards the equivalence point.

The use of computers for the analysis of titration error by the approaches discussed can eliminate the tedium of involved computations and offer further possibilities for a deeper study. Thus, a more reliable use of various methods of instrumental titrations could be achieved.

Zusammenfassung—Der zufällige Titrationsfehler wurde durch einmalige lineare Regressionsanalyse beider linearer Äste von Titrationskurven ermittelt. Zur Vereinfachung wird der Vertrauensbereich einer Titration durch Einsetzen divergenter linearer Vertrauensgrenzen beider Äste der Kurve abgeschätzt. Auch der Einfluß des Winkels zwischen beiden Ästen auf den Vertrauensbereich einer Titration wurde ermittelt. Die Vorteile des Verfahrens wurden durch Anwendung auf mehrere amperometrische und photometrische Titrationen von Blei nachgewiesen. Die Ergebnisse wurden mit solchen verglichen, die nach dem Komplementärverfahren von Liteanu und Cörmös sowie durch die übliche statistische Verarbeitung von graphisch extrapolierten Endpunkten gewonnen wurden. Das Verfahren erlaubt eine kritische Betrachtung der experimentellen Bedingungen im Hinblick auf die gewünschte Genauigkeit.

Résumé—On a évalué l'erreur de titrage fortuite par analyse de régression linéaire simple des deux branches des courbes de titrage. Dans un but de simplification, l'intervalle de confiance d'un titrage est estimé en substituant les limites de confiance linéaires divergentes aux limites de confiance incurvées des deux branches de la courbe. On a aussi évalué l'influence de l'angle entre les deux branches sur l'intervalle de confiance d'un titrage. On à démontré que la technique est avantageuse en l'appliquant à plusieurs titrages ampérométriques et photométriques du plomb et en comparant les résultats à ceux obtenus par l'approximation complémentaire de Liteanu et Cörmös, et par le traitement statistique usuel des points de fin de dosage obtenus par extrapolation graphique. La méthode permet une considération critique des conditions expérimentales par rapport au niveau de précision désiré.

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PREPARATIVE GAS CHROMATOGRAPHY OF VOLATILE METAL COMPOUNDS—I

SEPARATION OF ALUMINIUM, CHROMIUM AND IRON β-DIKETONATES

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Summary—The analytical gas chromatography of a range of fluorinated and unfluorinated β-diketonates of aluminium, chromium and iron has been studied in detail and conditions have been established for their complete separation; the complexes of trifluoroacetylpivaloylmethane show the best characteristics for this purpose. A range of liquid phases and column conditions have been considered and Apiezon substrates have been shown to give optimal resolution. The technique has been extended to a preparative scale with up to 0·1-g chelate samples, and the efficiency of the process demonstrated by the removal of 2% proportions of two metal complexes from a sample of the third. Implications of the technique for the purification of metals are discussed.

THE APPLICATION of preparative gas chromatography to the purification of metals as their volatile derivatives offers great possibilities, for this technique has a high separatory efficiency. However, developments in this field have been restricted both by the lack of volatility and by the high reactivity of many inorganic compounds. Analytical gas chromatographic separations of many β-diketonates are now well documented,[1] and although preparative separations have not yet been reported, the production of pure metal compounds by this method appears feasible. The β-diketonates are most attractive in this respect as many of them have both high volatility and thermal stability,[2] they are formed by a wide range of metals, often by quantitative extraction of the metal ion with the β-diketone,[3,4] and unlike many other metal compounds, they require no special handling techniques. We now report the first preparative gas chromatographic separation of metal complexes of this type.

Gas chromatographic separations of metal β-diketonates have usually been studied by injection of small samples onto short columns of low liquid phase loading. The aims of the work described in this paper were first to devise an optimal set of conditions for the complete resolution of a mixture of metal β-diketonates on the analytical scale, and secondly to increase sample size and adapt column parameters to a preparative scale with a view to purification of one complex by removal of others.

The aluminium, chromium and iron derivatives of a wide range of β-diketones were chosen for the initial examination. Several analytical separations of aluminium and chromium,[5,6] and aluminium and iron trifluoroacetylacetonates[7,8] have previously been achieved, but a complete separation of the chromium and iron complexes of the same β-diketone has not been reported. Sievers[9] claims a partial separation of the trifluoroacetylacetone derivatives of these metals on a polyethylene wax substrate, but the peaks are ill-defined and base-line return is incomplete. The separation of complexes with very similiar volatilities is often made more difficult by the existence of asymmetrical peaks and low column efficiencies, which are the result of undesirable column interactions.

In the work described in this paper, particularly good separations and minimization of undesirable column interactions were obtained with complexes of perfluoroalkanoylpivaloylmethanes. Previously published studies of these complexes have been mainly concerned with rare earth complexes,[10,11,12] and metal heptafluorobutanoylpivaloylmethanates.[13]

EXPERIMENTAL

General nomenclature

The following nomenclature is used for description of the β-diketonates. The abbreviations refer to the enolate ion used in the formation of the metal complex.

Pentane-2,4-dione (acetylacetone), AA
1,1,1-Trifluoropentane-2,4-dione (trifluoroacetylacetone), TFA
2,2,6,6-Tetramethylheptane-3,5-dione (dipivaloylmethane), DPM
1,1,1-Trifluoro-5,5-dimethylhexane-2,4-dione (trifluoroacetylpivaloylmethane), TPM
1,1,1,2,2-Pentafluoro-6,6-dimethylheptane-3,5-dione (pentafluoropropanoylpivaloylmethane), PPM
1,1,1,2,2,3,3-Heptafluoro-7,7-dimethyloctane-4,6-dione (heptafluorobutanoylpivaloylmethane), HPM

Reagents

Acetylacetone was obtained commercially. Trifluoroacetylacetone was prepared by the Claisen condensation of ethyltrifluoroacetate and acetone with sodium methoxide; dipivaloylmethane and its fluorinated analogues by the condensation of the appropriate esters and ketones with sodium hydride.

The aluminium, chromium and iron complexes were synthesized by the addition of the stoichiometric quantity of the β-diketone dissolved in ethanol, to an aqueous solution of the metal ion. The resultant solution was either buffered with sodium acetate or its pH was adjusted to *ca.* 7 by the addition of 4*M* ammonia solution. The precipitated metal chelate was filtered off, dried, and purified by sublimation under reduced pressure. The TPM complexes appeared initially as oils but solidified after standing for a few days.

For the preparative gas chromatographic studies the complexes were prepared from "Specpure" chromium metal, iron sesquioxide and hydrated aluminium chloride (Johnson, Matthey and Co.). All possible precautions were taken to exclude the introduction of any foreign ions during these preparations.

Gas chromatography—analytical separations

The Varian Aerograph Autoprep 700 fitted with a katharometer detector was used as a conventional analytical gas chromatograph. The injection port and detector block temperatures were maintained from 10 to 20° higher than that of the column, and a mixture of hydrogen and nitrogen (1:3 v/v) was used as the carrier gas. Samples (0–50 μl of 5 or 10% w/v solutions of the chelates in chloroform) were introduced into the glass-lined injection port of the apparatus with a microsyringe. A Pye "series 104" chromatograph equipped with a flame ionization detector was also used, samples (0–10 μl of 1000 or 2000 ppm solutions of the chelates in chloroform) being introduced directly on to the column.

Phase Separations Ltd. supplied the column packing materials and the Pye 104 columns were obtained pre-coiled. Before coating the celite supports were treated successively with 4*M* hydrochloric acid, water, 2*M* sodium hydroxide, water and methanol, and were then silaned with hexamethyldisilazane in petroleum ether, and coated by standard methods. The only exceptions to this treatment were the Universal B supports which were used as obtained, already coated. The procedure for the coating of Teflon with a liquid phase was that given by Kirkland.[14]

The following columns were used to obtain the analytical results.

(1) 0·46 m × 0·6 cm Cu, 5% SE-30 on PhaseSep N (60–80 mesh) (Autoprep)
(2) 1·8 m × 0·6 cm Cu, 10% SE-30 on PhaseSep N (60–80 mesh) or Chromosorb G (60–80 mesh) (Autoprep)
(3) 1·5 m × 0·6 cm glass, 10% SE-30 on PhaseSep N (60–80 mesh) (Pye 104)
(4) 1·8 m × 0·6 cm Cu, 10% SE-30 on Teflon (Autoprep)
(5) 1·8 m × 0·6 cm Cu, 10% Apiezon M on PhaseSep N (60–80 mesh) (Autoprep)

(6) 3·05 m × 0·6 cm Cu, 10% Apiezon L on Universal B (60–80 mesh) (Autoprep)
(7) 1·8 m × 0·6 cm Cu, 10% Diethylene glycol adipate (DEGA) on Chromosorb G (60–80 mesh) (Autoprep)

Gas chromatography—preparative separations

The Varian Aerograph Autoprep 700 was used as a preparative chromatograph combining automatic injection and collection systems, so that a single separation was continually repeated. The eluates were collected in liquid-air-cooled bottles supplied for the instrument. The column used was a 6·1 m × 9·5 mm aluminium tube packed with 15% Apiezon L on Universal B (44–60 mesh), supplied by Jones Chromatography and Co.

Universal B is a support material manufactured by Phase Separations Ltd., which has characteristics similar to a flux-calcined diatomite but is extremely inert, showing almost complete suppression of the adsorptive effect. This support proved greatly superior to white supports such as Chromosorb W or PhaseSep N (Phase Separations Ltd.) and also the alkaline surface support Chromosorb G. Universal B as purchased was found to have characteristics superior to PhaseSep N and Chromosorb G and W even after these had been subjected to successive acid and alkaline washes and hexamethyldisilazane treatment. It is largely to the use of this support that may be attributed the considerable improvement in resolution on both analytical and preparative columns. Pre-treatment of Universal B before coating did not produce better results than those obtained by using the ready-coated support as purchased.

TABLE I.—MAJOR FEATURES OF THE MASS SPECTRA OF THE ALUMINIUM, CHROMIUM AND IRON TRIFLUOROACETYLPIVALOYLMETHANATES

m/e	Ion	
612	$[Al(TPM)_3]^{+\cdot}$	$(M)^{+\cdot}$
555	$[Al(TPM)_3 - C(CH_3)_3]^+$	$(M - 57)^+$
543	$[Al(TPM)_3 - CF_3]^+$	$(M - 69)^+$
417	$[Al(TPM)_2]^+$	$(M - 195)^+$
367	$[Al(TPM)_2 - CF_2]^+$	$(M - 245)^+$
241	$(TPM\text{-}Al\text{-}F)^+$	$(M - 371)^+$
191	$[(TPM\text{-}Al\text{-}F) - CF_2]^+$	$(M - 421)^+$
637	$[Cr(TPM)_3]^{+\cdot}$	$(M)^{+\cdot}$
580	$[Cr(TPM)_3 - C(CH_3)_3]^{+\cdot}$	$(M - 57)^+$
442	$[Cr(TPM)_2]^+$	$(M - 195)^+$
385	$[Cr(TPM)_2 - C(CH_3)_3]^+$	$(M - 252)^+$
247	$[Cr(TPM)]^+$	$(M - 390)^+$
641	$[Fe(TPM)_3]^{+\cdot}$	$(M)^{+\cdot}$
584	$[Fe(TPM)_3 - C(CH_3)_3]^+$	$(M - 57)^+$
446	$[Fe(TPM)_2]^+$	$(M - 195)^+$
389	$[Fe(TPM)_2 - C(CH_3)_3]^+$	$(M - 252)^+$
377	$[Fe(TPM)_2 - CF_3]^+$	$(M - 264)^+$
251	$[Fe(TPM)]^+$	$(M - 390)^+$

The sample solution for the preparative separation of equal quantities of the metal TPM complexes was prepared by dissolving 0·4 g each of $Al(TPM)_3$, $Cr(TPM)_3$ and $Fe(TPM)_3$ in 6 ml of chloroform.

The sample solution for the separation of $Cr(TPM)_3$ from 2% $Al(TPM)_3$ and 2% $Fe(TPM)_3$ was prepared by dissolving $Cr(TPM)_3$ (2·88 g), $Al(TPM)_3$ (0·06 g) and $Fe(TPM)_3$ (0·06 g) in 15 ml of chloroform.

The gas chromatographic conditions used for each preparative separation were as follows:

sample: 0·5-ml injection

column temperature:	160–162°
injection temperature:	170°
detector temperature:	170–175°
collector temperature:	175–180°
filament current:	145 mA
attenuation:	×2
hydrogen/nitrogen flow-rate:	133 ml/min (30 psig).

Mass spectrometry

An A.E.I. M.S.9 double focusing mass spectrometer with direct injection probe was used in the characterization of eluates by means of the metal–$(TPM)_3^+$ and metal–$(TPM)_2^+$ ions. The major features of the mass spectra are given in Table I.

Emission spectrographic analysis

A Hilger-Watts large quartz spectrograph, with a high frequency plasma torch as the emission source,[15] was used to analyse the eluates from the preparative column. Chloroform solutions of the chelates were aspirated directly into the plasma.

RESULTS AND DISCUSSION

Analytical separations

The gas chromatographic behaviour of the aluminium, chromium and iron complexes of some fluorinated and unfluorinated β-diketones was studied on the analytical scale for two main reasons; to discover which complexes were potentially suitable for preparative scale elution by virtue of volatility and stability, and to find the conditions for quantitative separation of all three metals (which necessitated investigation of the interactions that occurred between the complexes and the chromatographic column). In general large samples of the complexes were injected into columns containing fairly high liquid phase loadings in order to approximate to preparative gas chromatographic conditions.

Unfluorinated β-diketonates. The major limitation in the gas chromatography of unfluorinated β-diketonates is their low volatility. Thus even if adequate separations could be obtained, the high column temperatures would certainly lead to decomposition on preparative columns. This prediction was confirmed for a mixture of the aluminium, chromium and iron acetylacetonates. All were eluted unchanged at 160° from column (1), but at the temperature of *ca.* 200° needed for their elution from column (2) breakdown of both the aluminium and iron complexes was indicated.

Almost complete separation was obtained for a mixture of the three metal dipivaloylmethanates from column (1) at 170° but retention times were similar to those of the acetylacetonates and no elution of discrete peaks could be obtained on longer columns.

Trifluoroacetylacetonates. The considerable increase in volatility afforded by fluorinated β-diketonates shows greater promise for preparative separations provided that adequate resolution can be achieved. Thus aluminium, chromium and iron trifluoroacetylacetonates were eluted individually from column (2) at 150° with retention times of 5½, 10 and 10½ min respectively.

However, despite variation of chromatographic parameters, complete resolution of the chromium and iron peaks was not achieved. This failure was attributed in part to adsorption effects which have been discussed by Veening and Huber[16] and by Uden and Jenkins.[17] These adverse characteristics appeared particularly severe for the trifluoroacetylacetonates but were greatly reduced for the perfluoroalkanoylpivaloylmethanates.

Trifluoroacetylpivaloylmethanates, pentafluoropropanoylpivaloylmethanates and heptafluorobutanoylpivaloylmethanates. The chromatography of chelates of these ligands with aluminium, chromium and iron was evaluated in the hope that they would show a combination of the favourable characteristics of the chelates containing tertiary butyl groups and of the enhanced volatility of the fluorinated β-diketonates.

Results obtained with silicone gum columns showed this hope to be partially realized. Improved separation was found between chromium and iron TPM complexes when compared with the trifluoroacetylacetonates but complete return to baseline could not be obtained. The use of PTFE support material [column (4)] reduced column efficiency to such an extent that no separation at all was observed.

It seemed possible that the PPM and HPM complexes might have shorter retention times and permit use of lower column temperatures, [Fe(TPM)$_3$ and Cr(TPM)$_3$ sublime at 58–62°/0·6 mbar; Fe(PPM)$_3$, Cr(PPM)$_3$, Fe(HPM)$_3$ and Cr(HPM)$_3$ sublime at 40–45°/0·6 mbar], but no reduction in retention time was found and resolution of the chromium and iron chelates was poorer. The elution pattern remained constant with variation of liquid phase loading, column and injection temperatures and increased sample size. Retention data are given in Table II and show the decrease in separation with increasing fluoroalkyl chain length.

TABLE II.—RETENTION TIMES OF THE ALUMINIUM, CHROMIUM AND IRON β-DIKETONATES ON SILICONE GUM RUBBER SE-30 [COLUMN (3) AT 160°C]

Sample	Ret. time, *min*	Sample	Ret. time, *min*	Sample	Ret. time, *min*
Al(TFA)$_3$	3½	Cr(TFA)$_3$	6½	Fe(TFA)$_3$	8
Al(TPM)$_3$	11⅜	Cr(TPM)$_3$	16¾	Fe(TPM)$_3$	22
Al(PPM)$_3$	13	Cr(PPM)$_3$	16¾	Fe(PPM)$_3$	19
Al(HPM)$_3$	16½	Cr(HPM)$_3$	21	Fe(HPM)$_3$	23

TABLE III.—RETENTION TIMES OF THE ALUMINIUM, CHROMIUM AND IRON β-DIKETONATES ON APIEZON M [COLUMN (5) AT 159°C]

Sample	Ret. time, *min*	Sample	Ret. time, *min*	Sample	Ret. time, *min*
Al(TFA)$_3$	3½	Cr(TFA)$_3$	6¾	Fe(TFA)$_3$	7½
Al(TPM)$_3$	9	Cr(TPM)$_3$	14¼	Fe(TPM)$_3$	20½
Al(PPM)$_3$	8	Cr(PPM)$_3$	10½	Fe(PPM)$_3$	12¾
Al(HPM)$_3$	8	Cr(HPM)$_3$	9¾	Fe(HPM)$_3$	11½

A considerable change was noted with Apiezon columns. It appeared that interaction with the chelates was much smaller than for the silicone gum rubber columns.[13] Table III gives the retention data for an Apiezon column.

The order of elution on the Apiezon column corresponded to ease of sublimation, and retention times were shorter than on the silicone gum column. The decrease in interaction with the liquid phase led to a marked improvement in the resolution of the chromium and iron peaks although the separation again deteriorated with increasing length of the fluorocarbon chain. Completely resolved peaks were obtained for the chromium and iron TPM complexes and it was found that further improvement in peak shape and reduction in retention time were attained by using a column of Apiezon L coated on Universal B support [column (6)].

It was concluded that preparative separations could best be performed with the TPM complexes on a column with a high loading of Apiezon L on Universal B.

Preparative separations

The effect of increasing the column dimensions and sample size was first investigated. An increase in peak resolution was obtained when an analytical scale injection was made into the preparative column (6·1 m × 9·5 mm aluminium, 15% Apiezon L on Universal B); 3½ min now separated the peaks instead of the 2 min on the 3·05-m column (6). The complexes could be eluted with reasonable retention times from the 6·1-m column at temperatures as low as 160°. Figure 1 shows that separation was still good when larger samples were injected (0·5 ml), containing equal weights (33 mg) of each complex.

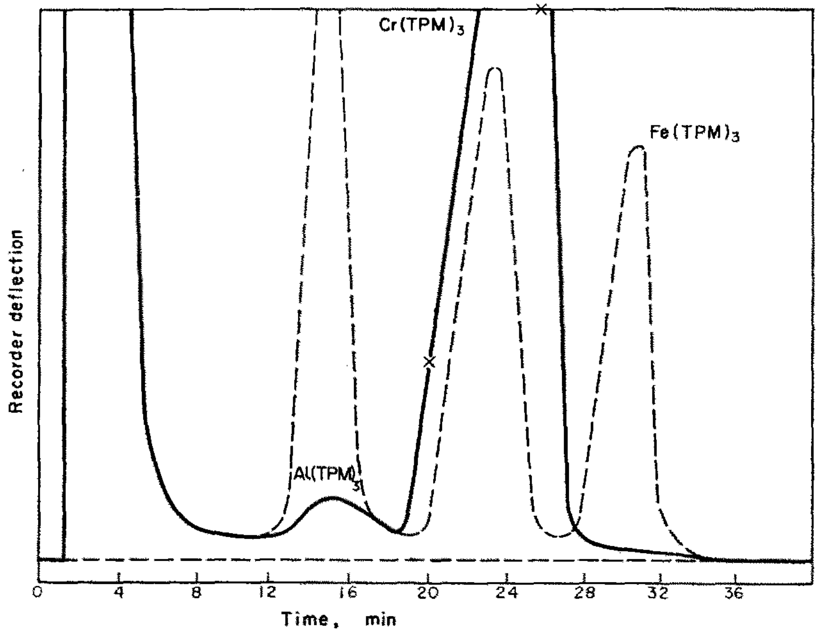

FIG. 1.—Chromatogram of the preparative separation of Cr(TPM)$_3$ from 2% Al(TPM)$_3$ and 2% Fe(TPM)$_3$. [– – – – – – – chromatogram of the separation of equal amounts (33 mg) of each chelate]

Sample: 0·1 g of total chelate injected. Column: 6·1 m × 9·5 mm Al, 15% Apiezon L on Universal B (44–60 mesh). Column temp. 162°C. Hydrogen/nitrogen flow-rate: 133 ml/min.

An attempt was then made to separate the chromium TPM complex from 2% w/w each of the aluminium and iron TPM complexes. A total of 0·1 g of mixed complexes was injected automatically in 0·5-ml portions with a syringe operated by an air piston. A small peak corresponding to the aluminium complex was observed in addition to the main chromium–TPM peak (Fig. 1) but the katharometer did not detect any iron complex. On comparing the chromatogram with that obtained in the earlier separation, it was assumed that either the iron had been eluted after the chromium peak but not detected, or it had been retained or decomposed on the column. Since the analysis of the collected chromium chelate showed very low levels of iron impurity, the assumption that the iron chelate was not emerging from the column in any considerable quantity during the collection period seems justified. Furthermore these low levels suggest that any iron possibly present as an impurity in the support material was not being leached out to any measurable extent.

No detectable quantity of iron complex could be trapped out between the end of the predicted position of the iron peak and the beginning of the next collection period. Nevertheless, as a general rule, a time lapse of some 5 min was allowed between the end of the chromium peaks and the reactivation of the injection cycle, thus giving a total time lapse of about 25 min between chromium collection periods.

By successive automatic injection 1 g of chromium trifluoroacetylpivaloylmethanate was collected in a bottle cooled in liquid air; this collection took place during the time between the crosses marked on the peak in Fig. 1. The aluminium, chromium and iron TPM complexes have melting points (60–80°) which are much lower than those of the corresponding complexes of most other β-diketones. These complexes, once molten, can be extensively supercooled and resolidify very slowly.

During the first few collection cycles the chromium complex was trapped out relatively poorly in the liquid-air cooled trap, remaining there as oil, recovery over the first five injections being about 45 %. Subsequently as solidification of the complex began, collection efficiency improved markedly, rising to over 80 % after 25 injections. Overall recovery for 1 g of collected complex was about 65 %. Improved trapping techniques, perhaps employing initial seeding of the trap with crystals of the complex or using an absorbing medium, should improve overall efficiency considerably. There was no indication that more than a very small proportion of the chromium complex was lost by adsorption or decomposition on the column.

Purity of the eluates. Chromium TPM complex which had been passed alone through the preparative column, and the chromium complex which had been separated from the aluminium and iron impurities, were analysed by plasma torch emission spectrography. The $Cr(TPM)_3$ passed alone through the column contained 0·055 % $Al(TPM)_3$ and $Fe(TPM)_3$ 0·028 %. The $Cr(TPM)_3$ separated from 2 % $Al(TPM)_3$ and 2 % $Fe(TPM)_3$ contained 0·091 % $Al(TPM)_3$ and 0·027 % $Fe(TPM)_3$. The impurity levels in the original sample of chromium trifluoroacetylpivaloylmethanate were also of this order.

The separation of the chromium complex from the aluminium and iron complexes appears most successful, the added impurity levels being reduced to about those in the original sample. A similar separation of the aluminium TPM complex from 2 % of impurities was attempted with the same preparative column, after the chromium TPM separations. The analysis of the aluminium complex showed that the iron had been effectively removed [less than 0·028 % $Fe(TPM)_3$ remaining] and that most of the chromium had been eliminated [0·28 % $Cr(TPM)_3$]. However, the level of the chromium impurity was higher than would have been expected from the well separated peaks on the chromatogram. As the column was purged in this case for 36 hr before purification of the aluminium complex, the probable explanation for the higher chromium level in the eluate is that a portion of the chromium chelate remained adsorbed or had otherwise interacted with the column material during the chromium purification experiment and was not removed by purging. Passage of the aluminium complex through the column then produced a displacement of the adsorbed chromium species which was then eluted with the aluminium complex. We have commented on this type of behaviour previously[17] for smaller samples where it is more pronounced for iron and aluminium chelates than for chromium chelates. However the much larger quantities of the chromium complex to which the column had been previously exposed in this experiment clearly made this behaviour more pronounced. A further separation, that of the iron trifluoroacetylpivaloylmethanate from 2 % each of the aluminium and chromium complexes was then attempted on the same column after a further lengthy period of purging. The results in this case showed that higher levels of the impurity chelates remained after separation even though resolution appeared good on the chromatogram. The further deterioration could be attributed once again to a build-up of both aluminium and chromium on the column. Better results could certainly be obtained in the latter experiments if fresh columns were used for the purification of each specific chelate. Considerable study must be made of this aspect of the technique in order to maintain high purities for the products.

CONCLUSIONS

The results demonstrate the feasibility of preparative scale separations of metal β-diketonates, even for a pair of metals such as chromium and iron, having complexes with very similar volatilities. The choice of ligand is of major importance to ensure maximal resolution and adequate volatility, while all chromatographic parameters must be fully explored and optimized during preliminary analytical investigations. Adsorption of chelates, a problem which is unlikely to be completely eliminated, suggests that eluates of the highest purity may best be obtained from a column which is used only for the purification of that particular metal complex.

The good purity levels obtained for the chromium complex suggest possibilities for the production of ultrapure metals by preparative gas chromatography. To produce significant amounts of pure metals however, considerable quantities of the complexes must be chromatographed as the proportion of metal in the complexes is low. It seems doubtful whether a batch process such as described here could be scaled up to separate sufficient quantities of complexes in a reasonable time, but studies now proceeding in the use of continuous gas chromatographic techniques may make commercial scale separations possible.

Work has been done by Van Hemert *et al.*[18] and Moshier *et al.*[19] which shows that pure metals may readily be regenerated from fluorinated metal β-diketonates by reduction with hydrogen gas at an elevated temperature.

Born–Haber calculations might be used to predict the relative stabilities of the metal-fluorine bonds formation of which could affect recovery of metals in other preparative applications.

Acknowledgements—The analyses of the eluates by the high-frequency plasma torch method were carried out in conjunction with Mr. S. Greenfield and the staff of the Analytical Research Department, Albright and Wilson Ltd., to whom the authors are indebted. The authors wish to thank Dr. J. R. Majer for his advice on mass spectrometry. One of us (C. R. J.) gratefully acknowledges the receipt of a maintenance grant from the United Kingdom Atomic Energy Authority, Aldermaston.

Zusammenfassung—Die analytische Gaschromatographie einer Anzahl fluorierter und nicht fluorierter β-Diketonate von Aluminium, Chrom und Eisen wurde in ihren Einzelheiten untersucht und die Bedingungen ermittelt, unter denen man vollständige Trennung erreicht. Die Komplexe von Trifluoracetylpivaloylmethan haben in dieser Hinsicht die besten Eigenschaften. Verschiedene flüssige Phasen und Säulenbedingungen wurden in Betracht gezogen; die beste Auflosung ergaben Apiezon-Träger. Das Verfahren wurde auf den präparativen Maßstab mit Chelatproben bis zu 0,1 g ausgedehnt. Die Wirksamkeit dieses Trennprozesses wurde durch Entfernung von 2 prozent-Anteilen zweier Metall-komplexe aus einer Probe des dritten demonstriert. Es werden Folgerungen für die Reinigung von Metallen diskutiert, die sich aus dem Verfahren ergeben.

Résumé—On a étudié en détail la chromatographie en phase gazeuse analytique d'une gamme de β-dicétonates fluorés et non fluorés de l'aluminium, du chrome et du fer et on a établi les conditions de leur séparation complète; les complexes du trifluoracétylpivaloylméthane montrent les meilleures caractéristiques dans ce but. On a considéré gamme de phases liquides et de conditions de colonne et l'on a montré que les substrats à l'Apiezon donnent la résolution optimale. On a étendu la technique à l'échelle préparative avec des échantillons de chélates jusqu'à 0,1 g et l'efficacité de la technique a été démontrée par l'élimination de deux complexes métalliques dans la proportion de 2% d'un échantillon du troisième. On discute des incidences de la technique sur la purification de métaux.

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SPECTROPHOTOMETRIC STUDY AND ANALYTICAL APPLICATION OF RARE EARTH TIRON COMPLEXES—I

DETERMINATION OF NEODYMIUM, HOLMIUM AND ERBIUM

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Summary—The absorption spectra of neodymium, holmium and erbium Tiron complexes in aqueous solution have been measured from 340 to 650 nm. The absorbance at the wavelength of maximum absorption band of an aqueous medium containing neodymium (pH 4·5), neodymium (pH 12·0), holmium (pH 5·0) and erbium (pH 5·0) Tiron complexes was about 4 (at 578 nm), 9 (at 571 nm), 9 (at 450 nm) and 5 (at 376 nm) times greater, respectively, than for the same quantities of the corresponding chlorides. The spectrophotometric determination of these elements has been investigated. Combining ratios of Tiron to rare earth have been found to be 3:2 and 2:1.

IN GENERAL, absorption spectra of tervalent rare earth ions in solution are complex and composed of sharp lines which arise from pure electronic transitions within the 4*f* subshell, which is shielded by the 5*s* and 5*p* outer shells from interaction with an ionic field. If the strength of the ionic field surrounding the rare earth ions is sufficient to penetrate the shielding, some absorption bands may be shifted in wavelength and enhanced in sensitivity. Such effects have been observed in the case of formation of chelate compounds.[1–3] Moreover, *O*,*O*-type ligands seem to be more effective for the enhancement of the sensitivity than *O*, *N*- and *N*,*N*-type ligands. Since Yoe first introduced Tiron (disodium 1,2-dihydroxybenzene-3,5-disulphonate), which is one of the *O*,*O*-type ligands, for the colorimetric determination of titanium and iron,[4] the reagent has been applied to the spectrophotometric determination of cerium,[5] molybdenum,[6] niobium,[7] uranium[8] and scandium.[9]

We have found that a few of the absorption bands of neodymium, holmium and erbium are enhanced remarkably when Tiron is reacted with these metal ions in weakly acidic and alkaline media. In the present paper, we describe the formulae and analytical application of these Tiron complexes.

EXPERIMENTAL

Reagents

Metal ion solutions. Standard solutions of neodymium, holmium and erbium chlorides were obtained by dissolving the 99·9% pure oxides in warm dilute hydrochloric acid and then removing the excess of acid by evaporation. The concentrations of these elements were determined by titration with EDTA, Xylenol Orange being used as the indicator.

Tiron. Tiron obtained from the Dojindo Co. Ltd. Research Laboratories was at least 95% pure and was used without further purification.

All other chemicals used were of analytical-reagent grade.

Procedure

A hydrochloric acid solution containing less than about 20 mg of the metal ions was transferred into a beaker and evaporated to near dryness on a water-bath. The residue was dissolved by adding 2 ml of 0·5*M* Tiron. Then for neodymium, holmium and erbium, 2 ml of 1·0% hexamine solution were added to the solution and the pH of the solution was adjusted to 4·5–5·0 with dilute hydrochloric acid

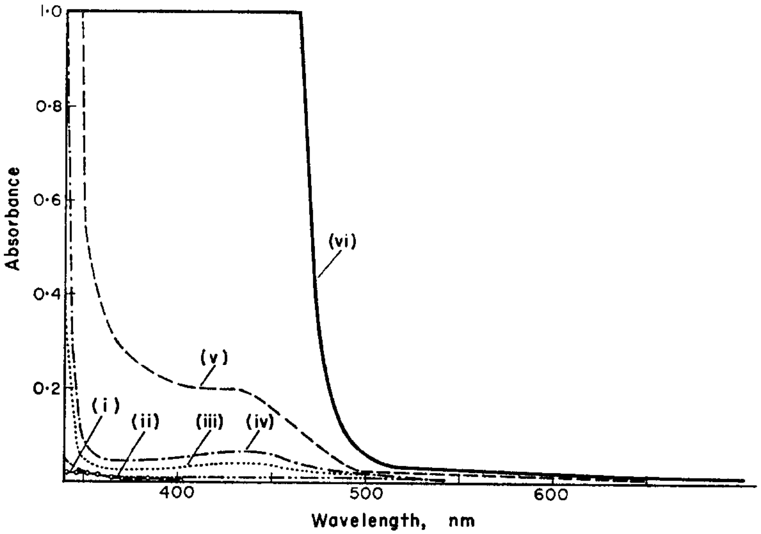

FIG. 1.—Absorption spectra of 0·1M Tiron solutions at various pH values. pH—(*i*) 4·9; (*ii*) 6·2; (*iii*) 7·1; (*iv*) 8·3; (*v*) 10·2; (*vi*) 12·2.

and sodium hydroxide solutions, or for neodymium, the pH was adjusted to 12·0 ± 0·5 with 0·1M sodium hydroxide. Then the solution was transferred to a 10-ml volumetric flask and made up to volume with water. The absorbance for neodymium, holmium and erbium at pH 4·5–5 and for neodymium at pH 12 was measured at 578, 450, 376 and 571 nm respectively. The concentration of the metal ions was obtained graphically from Beer's law plots. Water was used as a reference unless otherwise. All the experiments were carried out at 20–25°.

RESULTS AND DISCUSSION

Absorption spectra of 0·1M Tiron solutions at differing pH were measured between 340 and 650 nm (Fig. 1). With increase of pH, a broad absorption band gradually appears which gives a maximum at about 430 nm. In alkaline medium of pH 12, there is a strong absorption band at wavelengths below about 500 nm. Absorption spectra of aqueous solutions containing neodymium, holmium or erbium and an excess of Tiron were recorded from 340 to 650 nm as a function of pH (Figs. 2–4). The absorbances at the absorption maxima for neodymium Tiron complexes are 4·1 (at 578 nm), 4·0 (at 579 nm) and 8·6 (at 571 nm) times greater than that of the chloride and for holmium and erbium Tiron complexes at pH 5 the absorbances are about 9 (at 450 nm) and 5 (at 376 nm) times greater than those of the corresponding chlorides. Holmium and erbium Tiron complexes in alkaline media were not examined, because the main absorption bands occurred below 500 nm.

Figure 5 shows the variation of absorbance at the maxima of absorption bands for these metal complexes, as a function of pH. The absorption spectra for the neodymium complexes give almost identical patterns in the pH ranges 4·0–5·0 (α-type), 6·0–7·0 (β-type) and 11·5–12·5 (γ-type). The absorbances for holmium and erbium Tiron complexes are almost constant over the pH range 4·5–5·0.

Mole-ratio plots for the reaction at pH 4·5–5·0 gave the ratio of Tiron to lanthanide as 3:2. At pH 7 the same ratio (3:2) was found for Tiron:Nd, but in more alkaline media (pH 12) constant absorbance at 571 nm is not obtained until the mole-ratio of Tiron to neodymium is about 5. The absorption spectrum of the neodymium complex

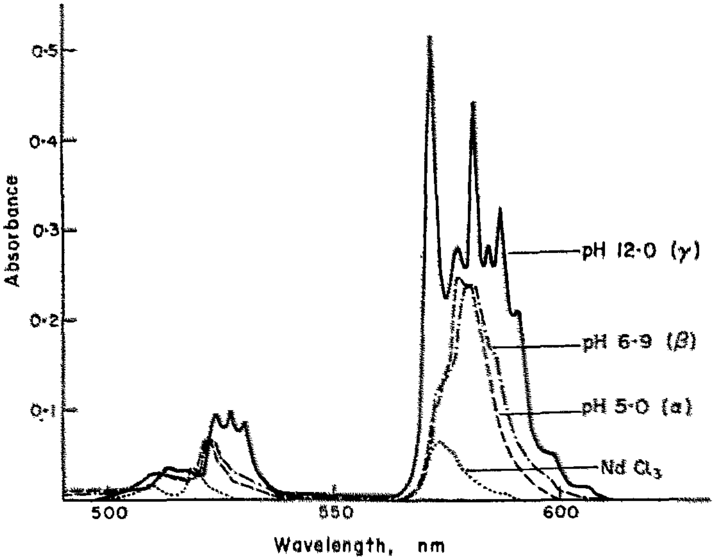

FIG. 2.—Absorption spectra of neodymium Tiron complexes at various pH values. Nd 0·00936*M*; Tiron 0·1*M*; measured *vs.* reagent blank.

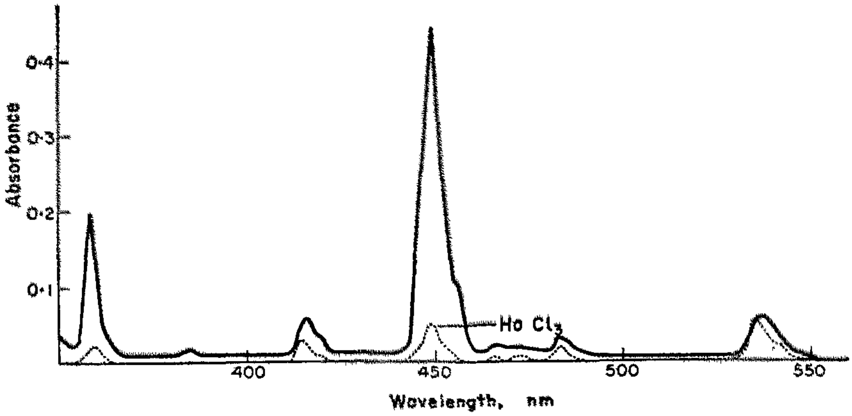

FIG. 3.—Absorption spectrum of holmium Tiron complex at pH 5·0. Ho 0·0125*M*; Tiron 0·1*M*.

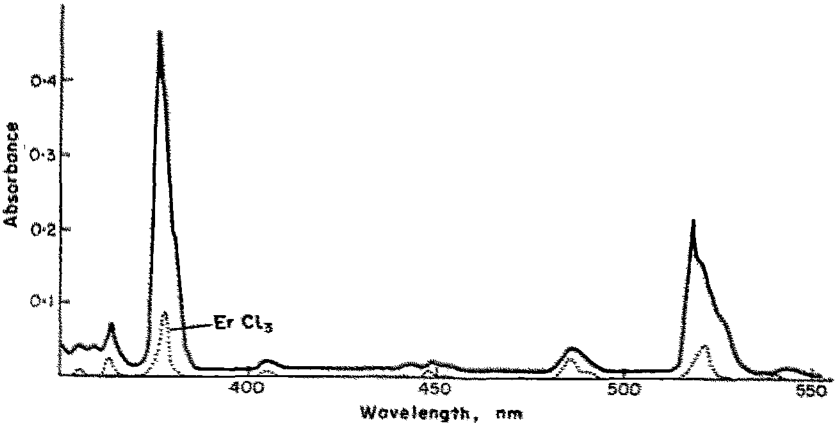

FIG. 4.—Absorption spectrum of erbium Tiron complex at pH 5·0. Er 0·0145*M*; Tiron 0·1*M*.

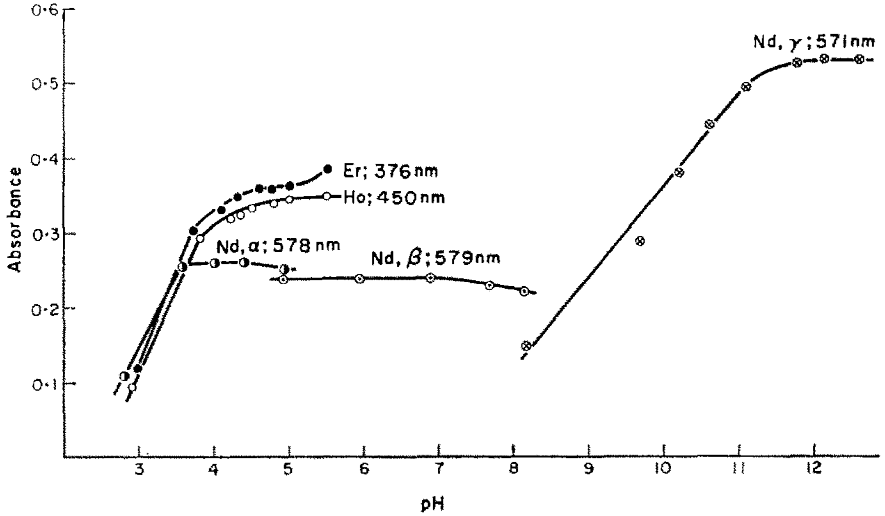

Fig. 5.—Variation of absorbance at the maxima of absorption bands, as a function of pH.

at pH 12 changes in a complicated manner as a function of the mole-ratio of Tiron to neodymium. Even in alkaline media, no hydrolysis of the metal is observed when the mole-ratio Tiron:Nd = 0·5. The spectrum at the mole-ratio Tiron:Nd = 3:2 almost corresponds to that of the β-type shown in Fig. 2. For determination of these metal ions, a tenfold excess of Tiron was taken as the minimum requirement.

The absorption spectra of these Tiron complexes are stable with time, especially in acidic medium. Even in alkaline medium (pH 12) the absorption bands of the neodymium Tiron complex remained constant for 24 hr, though the absorbance slightly increased because of a change in the absorption band of the reagent.

The systems follow Beer's law up to 4 mg/ml (Nd, pH 4·5, 578 nm), 2·5 mg/ml (Nd, pH 12, 571 nm), 4 mg/ml (Ho, pH 4·8, 450 nm), 5 mg/ml (Er, pH 4·8, 376 nm).

Effects of diverse ions

The effects of other rare earth ions on the determination of neodymium, holmium and erbium were investigated. The results are shown in Table I. Cerium ions do not interfere in acidic medium when the procedure is carried out with ascorbic acid added. Europium ions give an interference for holmium and erbium because the Tiron complexes have a broad absorption band below 550 nm. Ytterbium Tiron complexes (which have an absorption band below 430 nm) also give an interference for erbium.

Composition of the chelates

The continuous variation method was used to investigate the ratio in which Tiron combines with rare earths. The total concentration of neodymium and Tiron was maintained at $9{\cdot}5 \times 10^{-3}M$. The continuous variation plots at pH 4·5 (at 578 nm), 7·0 (at 579 nm) and 12·0 (at 579 nm) are illustrated in Figs. 6–8. The peaks at mole-fractions [Nd]/([Nd] + [Tiron]) of 0·40 and 0·33, indicate, combining ratios of 1·5 and 2 Tiron molecules per neodymium ion. For holmium and erbium at pH 4·8 the

TABLE I.—DETERMINATION OF NEODYMIUM, HOLMIUM AND ERBIUM IN SYNTHETIC SAMPLES CONTAINING DIVERSE METAL IONS

Metal ions added, *mg*		Nd (pH 4·5, 578 nm)* Found, *mg*	Metal ions added, *mg*		Nd (pH 12·0, 571 nm)† Found, *mg*
La	18·96	13·7$_0$	La	7·58	6·5$_8$
Ce	9·12	13·6$_0$	Ce	4·57	Interference
Pr	18·16	13·8$_5$	Pr	9·03	6·5$_8$
Sm	13·71	13·7$_0$	Sm	6·86	6·5$_0$
Eu	13·81	13·9$_0$	Eu	4·60	6·6$_0$
Gd	15·74	13·8$_5$	Gd	6·29	6·5$_5$
Tb	16·05	13·9$_0$	Tb	6·42	6·6$_0$
Dy	7·94	13·7$_5$	Dy	3·19	6·5$_5$
Ho	3·29	13·6$_0$	Ho	8·12	6·5$_0$
Er	19·85	13·6$_0$	Er	9·72	6·5$_8$
Tm	8·46	13·8$_5$	Tm	3·40	6·6$_2$
Yb	18·81	13·7$_0$	Yb	7·53	6·5$_0$
Lu	13·42	13·7$_5$	Lu	13·42	6·7$_8$
Y	8·03	13·6$_0$	Y	4·02	6·5$_8$
		Ho (pH 5·0, 450 nm)§ Found, *mg*			Er (pH 5·0, 376 mμ)‡ Found, *mg*
La	18·96	16·3$_4$	La	18·96	19·4$_0$
Ce	4·57	16·2$_5$	Ce	4·57	19·4$_0$
Pr	22·59	Interference	Pr	22·59	19·5$_5$
Nd	13·50	16·0$_0$	Nd	13·50	19·7$_5$
Sm	13·71	19·9$_0$	Sm	13·71	19·2$_4$
Eu	9·20	Interference	Eu	9·20	Interference
Gd	15·74	16·2$_5$	Gd	15·74	19·3$_5$
Tb	16·05	16·2$_0$	Tb	16·05	19·3$_5$
Dy	7·97	16·5$_5$	Dy	7·97	19·3$_0$
Er	19·85	16·5$_5$	Ho	16·44	19·3$_5$
Tm	8·38	16·6$_0$	Tm	8·38	19·5$_0$
Yb	7·53	16·6$_0$	Yb	7·53	Interference
Lu	13·42	16·7$_0$	Lu	13·42	19·4$_5$
Y	8·03	16·6$_0$	Y	8·03	19·5$_5$

* Taken—13·75 mg.
† Taken—6·75 mg.
‡ Taken—19·45 mg.
§ Taken—16·44 mg.

combining ratio is also 1·5:1. These Tiron complexes probably exist as binuclear complexes, Ln_2 (Tiron)$_3$.

However, the results of the continuous variation plots for neodymium, especially in alkaline media, are not always accurate because the spectra vary with concentration of Tiron. Therefore, the method of continuous variation was used again with lower concentrations of neodymium and Tiron. The ultraviolet absorption spectra as a function of pH are given in Fig. 9. Although the absorption bands are not observed if the pH is below 5·0, the bands having a maximum in a range 310–325 nm appear with increasing pH. The total concentration of neodymium and Tiron was $3{\cdot}03 \times 10^{-5}M$ and the absorbance was measured at 310 (pH 7·0) and 325 nm (pH 12·0), respectively. As shown in Figs. 7 and 8, the results correspond with those for the visible region.

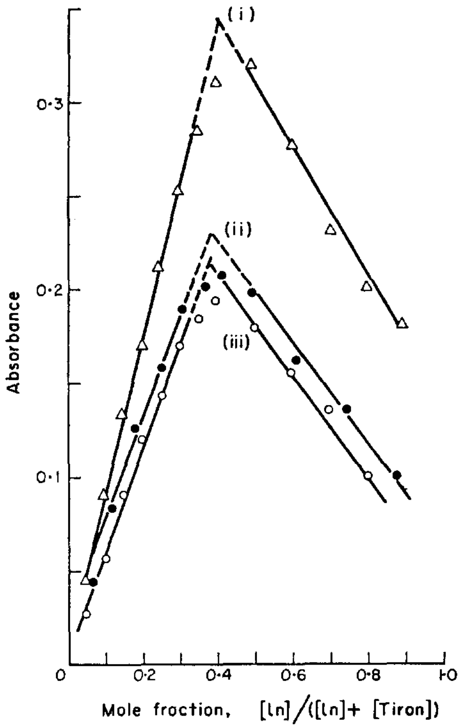

FIG. 6.—Continuous variation plots for neodymium, holmium and erbium in weakly acidic media.
(*i*) [Er] + [Tiron], 1·06 × $10^{-3}M$; pH 4·8; 376 nm
(*ii*) [Ho] + [Tiron], 9·96 × $10^{-3}M$; pH 4·8; 450 nm
(*iii*) [Nd] + [Tiron], 9·53 × $10^{-3}M$; pH 4·5; 578 nm.

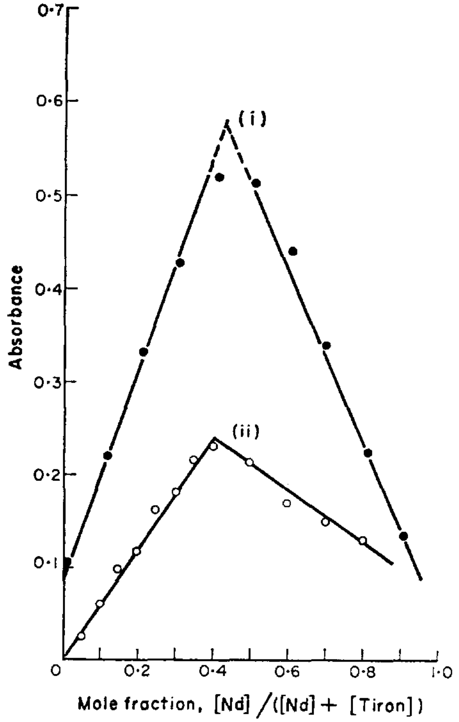

FIG. 7.—Continuous variation plots for neodymium in neutral media.
(*i*) [Nd] + [Tiron], 3·03 × $10^{-5}M$; pH, 7·0; 310 nm

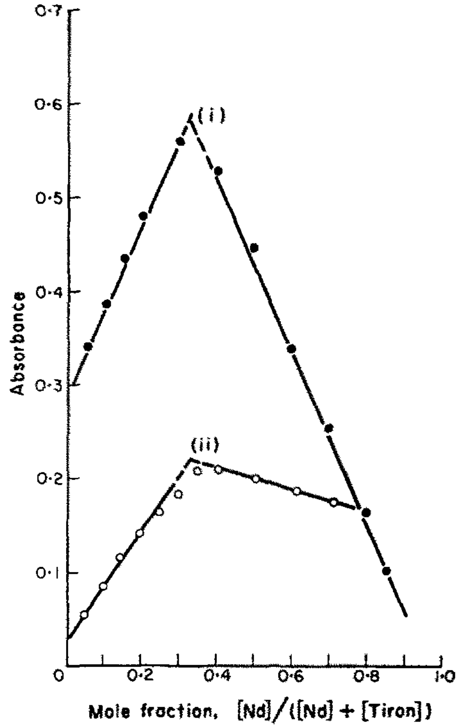

FIG. 8.—Continuous variation plots for neodymium in alkaline media.
(*i*) [Nd] + [Tiron], 3·03 × $10^{-5}M$; pH, 12·0; 325 nm
(*ii*) [Nd] + [Tiron], 9·53 × $10^{-3}M$; pH, 12·0; 579 nm.

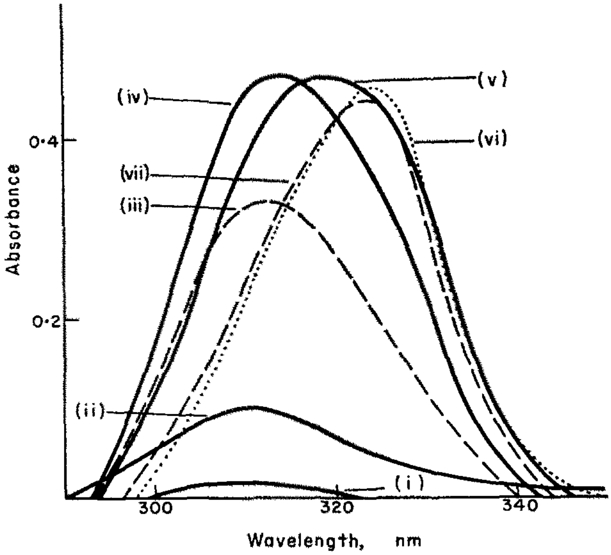

FIG. 9.—Variation of absorption spectra of neodymium complexes in ultraviolet region as a function of pH.
Nd, 6·06 × $10^{-5}M$; Tiron, 1·2 × $10^{-4}M$; reference, reagent. pH: (*i*), 5·0; (*ii*), 5·5; (*iii*), 6·0; (*iv*), 6·6; (*v*), 8·0; (*vi*), 10·0; (*vii*), 12·0.

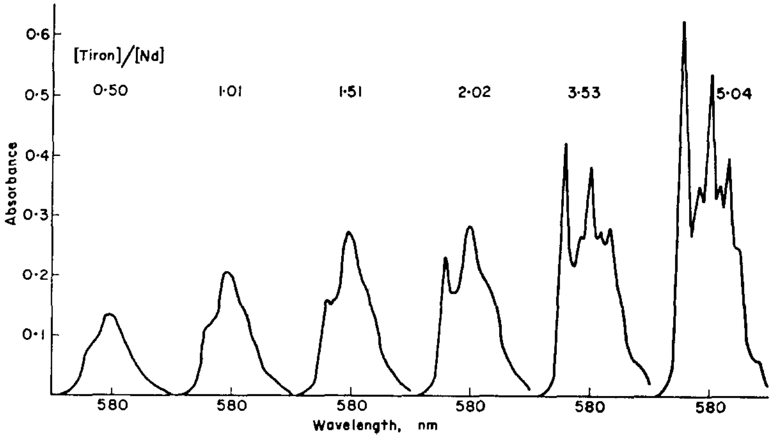

FIG. 10.—Variation of absorption spectra of neodymium Tiron complexes at pH 12 as a function of mole ratio of Tiron to neodymium.
Nd, $1 \cdot 24 \times 10^{-2}M$.

All the results from the continuous variation and mole-ratio plots at pH 4·5 and 7 show the combining ratio of 3:2 Tiron: Ln. At pH 12, there is a discrepancy between the continuous variation and mole-ratio plots; the continuous variation method may not be suitable here because the spectrum of the neodymium complex at pH 12 is remarkably dependent upon the concentration of the reagent, as shown in Fig. 10. The complexity and enhancement of the γ-type neodymium complex spectra may be explained by formation of higher order complexes, *e.g.*, Tiron:Nd = 5, which may be deduced from the results of the mole-ratio method and from the fact that the co-ordination number of rare earths may be as high as nine or ten.

Zusammenfassung—Die Absorptionsspektren der Tironkomplexe von Neodym, Holmium und Erbium in wäßriger Lösung wurden von 340 bis 650 nm gemessen. Die Extinktionen bei der Wellenlänge der stärksten Absorptionsbande eines wäßrigen Mediums mit den Tironkomplexen von Neodym (pH 4,5), Neodym (pH 12,0), Holmium (pH 5,0) und Erbium (pH 5,0) waren um die Faktoren 4 (bei 578 nm), 9 (bei 571 nm), 9 (bei 450 nm) und 5 (bei 376 nm) größer als mit den entsprechenden Mengen der betreffenden Chloride. Die spektrophotometrische Bestimmung dieser Elemente wurde untersucht. Als Verbindungsverhältnisse Tiron: seltene Erde wurden 3:2 und 2:1 gefunden.

Résumé—On a mesuré les spectres d'absorption des complexes Tiron des néodyme, holmium et erbium en solution aqueuse de 340 à 650 nm. L'absorption, à la longueur d'onde de la bande d'absorption maximale, d'un milieu aqueux contenant les complexes Tiron de néodyme (pH 4,5), néodyme (pH 12,0), holmium (pH 5,0) et erbium (pH 5,0) est environ 4 (à 578 nm), 9 (à 571 nm), 9 (à 450 nm) et 5 (à 376 nm) fois plus élevée, respectivement, que pour les mêmes quantités des chlorures correspondants. On a étudié le dosage spectrophotométrique de ces éléments. On a trouvé que les rapports de combinaison du Tiron à la terre rare sont de 3:2 et 2:1.

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APPLICATION OF THE UNTERZAUCHER METHOD TO THE DETERMINATION OF OXYGEN IN COKE

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Summary—The Unterzaucher method, used for the determination of oxygen in organic compounds and coal, has been adapted to the determination of oxygen in coke. Modifications were made to the conventional apparatus in order to eliminate any contribution made by the coke moisture to the determined oxygen content. The carbon dioxide produced from the combustion of the oxygen in the coke was estimated by a sensitive conductimetric method. Evidence is presented which indicates that additional liberation of oxygen from the coke mineral matter does not make a significant contribution to the total oxygen determined under the prescribed experimental conditions. The error of the determination is approximately 0·1%. A comparison is made between results obtained for a series of cokes and chars by the direct method and by an independent determination, based on neutron activation.

The oxygen content of coal is related to certain coal properties such as coking power, liability to spontaneous combustion and oxidation. It is also an indication of coal rank. Because of its importance, many attempts have been made to derive a suitable experimental technique for the determination of oxygen in coal. The methods proposed fall generally within two groups, based on oxidation[1–3] or reduction[4–6] of the carbonaceous material. Within recent years the well known Schütze-Unterzaucher[7,8] method used for the determination of oxygen in organic compounds has been further developed[9,10] and methods based on this approach, *i.e.*, the reduction of the volatile oxygen compounds by carbon either with or without the addition of a catalyst, have been used. A survey of the field is given by Crawford, Glover and Wood[11] who determined oxygen in coal by a procedure and apparatus similar to that described by Oita and Conway.[10] This technique was further adapted for our purposes.

The principal difficulty associated with the application of such methods to the determination of oxygen in coal is that relating to the breakdown of the coal mineral matter at the temperature of pyrolysis and the inability of the method to assess the contribution to the total oxygen content made by the oxygen present in the mineral matter.

In an attempt to surmount these difficulties, methods have been suggested which incorporate a process of demineralization,[12] but such techniques are generally tedious and may introduce further sources of error into the determination, by causing retention of halogens or water.

The oxygen content of high-temperature cokes used in foundry and blast-furnace practice generally lies within the range 0·2–1·0%. It bears a superficial relation to the oxygen content of the parent coal but is more closely associated with the conditions of carbonization, particularly the temperature.

Some oxygen remains in the coke mineral matter after carbonization, but from generally available information it is considered that the contribution made by the coke mineral matter to the determined oxygen content is probably considerably smaller than that made by the mineral matter of coal to its oxygen content. This was investigated during the course of the work described in this paper.

EXPERIMENTAL

The elimination of moisture and adsorbed gases from the sample

The results of previous work[13] has shown that complete release of moisture from the analysis sample was not attained until temperatures of the order of 350° were reached in the drying of the coke. In order to remove moisture and adsorbed gases, including oxygen, from the sample and at the same time to prevent their re-adsorption, a method was devised to permit their removal without withdrawal of the sample from the apparatus.

For this purpose, the pyrolysis tube of the conventional apparatus (*E*, Fig. 1) was extended to include a wide-bore tap *D* and an evacuation section *F* which would be heated to a temperature of approximately 350° by an electric heating tape. Provision was also made to apply vacuum and simultaneous heating to section *F* to remove adsorbed gases from the sample. After this pretreatment the sample was moved by means of a pusher and external magnet through tap *D* into the pyrolysis tube *E*.

The effect of mineral matter upon the determined oxygen content

The principal constituents of the mineral matter of coke are silicates, aluminates and ferruginous substances. The former substances are generally found in combination with alkalis or alkaline earths, and the iron is largely present as sulphide. It is possible that some of these substances could release oxygen on pyrolysis at high temperatures, but it is considered that the extent of such decomposition would be small at a pyrolysis temperature of 1050°, since the principal components of the mineral matter are dissociated to only a small extent at this temperature. Experiments were undertaken to confirm these observations.

Laboratory cokes 1–3 were prepared by the carbonization of various proportions of float-and-sink fractions of one coal. Cokes 4 and 5 incorporated additional shale in the blend, and cokes 21–24 were prepared from a further coal or coal/shale blend. Samples 1–5, 21 and 22 were carbonized to a maximum temperature of 950° and cokes 23 and 24 were heated to 1100°. Approximately 100 g were taken for each test.

The oxygen content of these cokes was determined, with a pyrolysis temperature of 1050°, and the results are presented in Table I. There was evidence that the amount of oxygen found increased as the mineral-matter content increased but such increases were not systematic (*cf.* the oxygen and mineral-matter contents of cokes 1 and 2, 4 and 5 and 23 and 24).

It is important to bear in mind the inherent variability of coal samples in assessing the significance of the differences in the determined oxygen contents of the various cokes. Furthermore, small differences in carbonizing conditions result in the production of cokes which may be considered to be homogeneous for practical purposes, but by comparison with chemical compounds display a considerable degree of heterogeneity. It is therefore to be expected that there will be a greater inherent variation in results in the work considered in this paper than would be the case when substances of uniform quality are used.

Further tests were undertaken in which some samples of the same cokes were demineralized by treatment with hydrofluoric and hydrochloric acids, washed free from halogens as completely as possible and dried. The oxygen contents of the demineralized samples were determined, with the results shown in Table II.

The oxygen content of four of the demineralized samples was found to be higher, by a mean value of 0·08% oxygen, than that of the corresponding samples containing mineral matter. The oxygen content of sample 3 was 0·14% lower than that of the corresponding mineral-containing sample. Further experiments were made using a thermobalance to establish the loss in weight of coke ash, of the shale used in the preparation of some of the samples, and of mixtures of graphite and shale where the reducing action of the carbon on the mineral matter could be studied. The average loss in weight between 830 and 1100° from four different samples of ash was 0·2%, and from mixtures of 90% graphite and 10% shale was 0·6%. The implication of these results is that a 100 mg sample of coke, having an ash content of 10% (a reasonable value for the ash content of a high temperature coke), could lose approximately 0·06% by weight by breakdown of mineral matter. This weight loss would not necessarily be entirely due to loss of oxygen. No measurable weight loss was observed when shale was heated under the same conditions.

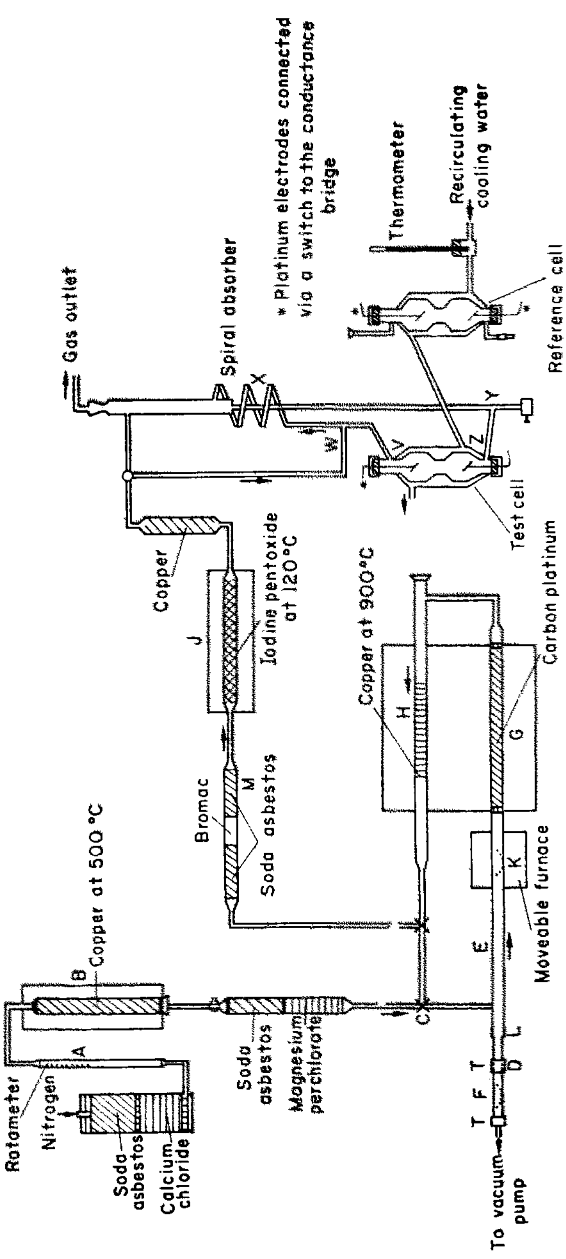


FIG. 1.—Apparatus for the direct determination of oxygen.

TABLE I.—THE RELATION BETWEEN DETERMINED OXYGEN CONTENT AND MINERAL MATTER FOR LABORATORY COKES

Sample	Blend composition	Oxygen % 1	Oxygen % 2	Oxygen % Mean	Mineral matter % d.b.†
1	Coal A (Floats)	0·79	0·75	0·77	1·23
2	Coal A (Floats and sinks)	0·85	0·84	0·84	1·49
3	Coal A (Floats and sinks)	0·92	0·90	0·91	3·69
4	Coal A (Floats, sinks and shale)	1·01	1·08	1·04	6·00
5	Coal A (Floats, sinks and shale)	1·25	1·20	1·22	10·71
21	Coal B	0·22	0·20	0·21	3·55
22	Coal B and shale	0·30	0·28	0·29	13·77
23	Coal B*	0·08	0·10	0·09	3·38
24	Coal B and shale*	0·16	0·16	0·16	14·61

* Carbonized at 1100°.
† Dry basis.

TABLE II.—THE EFFECT OF DEMINERALIZATION ON COKE OXYGEN CONTENT

Sample	Mean oxygen % d.m.m.f.† Before demineralization Mean	After demineralization Mean	Ash %*
1	0·78	0·93	0·08
2	0·86	0·94	—
3	0·94	0·80	—
4	1·10	1·18	—
5	1·36	1·39	0·24

* *cf.* Table I.
† Dry, mineral-matter-free basis.

The general conclusions forthcoming from these experimental results strongly indicated that there was little breakdown of mineral matter under the experimental pyrolysis conditions. Any small release of oxygen attributable to this cause was less than the overall error claimed for the determination.

The dependence of the determined oxygen content upon pyrolysis temperature

To establish whether complete release of oxygen from the carbon took place at or below 1050°, tests were carried out in which the sample was heated to this temperature without removal from the apparatus and the release of oxygen was measured at specific temperatures between 500 and 1000°. At each temperature the experiment was allowed to proceed (usually for about 20 min) until the amount of oxygen released was less than or equal to the blank value. The pyrolysis temperature was then increased, within 1–2 min, to the next highest level.

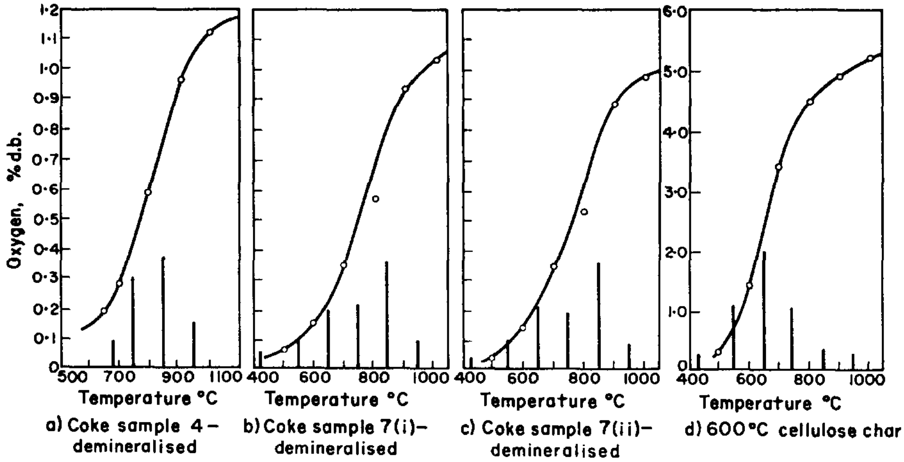
The results of these tests indicated that whilst the release of oxygen was not entirely complete at 1000°, the quantity liberated between 900 and 1000° and between 1000° and 1050° was quite small. The data are summarized in Fig. 2.

Higher pyrolysis temperatures were not considered to be feasible, because of the construction of the apparatus and the increased possibility of decomposition of the mineral matter.

A comparison of direct and indirect oxygen determination on cokes and chars

On the basis of the results of the preliminary experimental work the following technique was used to determine the oxygen content of several chars, laboratory cokes and commercial cokes, and the results were compared with corresponding values obtained by a neutron-activation method and with indirect estimates. Figure 1 shows the apparatus used.

Up to 150 mg of sample, crushed to pass a 0·06-mm mesh test-sieve, were weighed into a small platinum boat and introduced *via* the joint *L* into the evacuation side *F* of the pyrolysis tube. Oxygen-free nitrogen entered the apparatus *via* a rotameter *A* and purification train *B* containing copper wire at a temperature of 500° to remove the last traces of oxygen from the gas. The amount of residual oxygen in the cylinder gas appeared to be variable, and it was essential to carry out a periodic reduction



a) Coke sample 4—demineralised b) Coke sample 7(i)—demineralised c) Coke sample 7(ii)—demineralised d) 600°C cellulose char

FIG. 2.—Dependence of oxygen release on pyrolysis temperature.
The vertical lines represent difference values and hence rates of release.

of the resulting copper oxide by passing hydrogen through *B*, the frequency of this operation being indicated by the analytical precision. By manipulation of taps *C* and *D* the oxygen-free nitrogen was passed over the sample for 30 min at a rate of 25 ml/min. The nitrogen flow was then isolated from the sample and the temperature of *F* raised to about 350° by the surrounding heating tape; at the same time *F* was gradually evacuated to approximately 10 μbar. After 30 min the system was isolated from the vacuum, the heating tape removed and nitrogen allowed to leak into *F*. When the pressure was stable throughout the system the sample was moved by means of a pusher and magnet through the wide-bore tap *D* to a position just ahead of the furnace *G* containing the carbon-platinum catalyst at 900 ± 5°.

The conductance cells were now brought into a stable condition,[14] the pyrolysis furnace was moved over the sample in *E* and the temperature raised rapidly at approximately 150°/min to a final temperature of 1050°.

The volatile products of pyrolysis were carried by the nitrogen stream through the reaction tube *G* where at a temperature of 900° the carbon-platinum reagent converted the oxygenated gases into carbon monoxide. Sulphur compounds were removed from the gas stream by copper gauze at 900° in furnace *H*. The sulphur-free gases then passed successively through soda-asbestos to remove acidic gases, Bromac (bromine absorbed on activated charcoal) to remove any unsaturated hydrocarbons and a further soda-asbestos absorber (*M*) which removed any liberated bromine.

Carbon monoxide was finally oxidized to carbon dioxide by passage over iodine pentoxide at 118–120° (furnace *J*) and the iodine released in this reaction was removed by copper gauze before the conductimetric estimation of carbon dioxide was made. The basis of the conductimetric method is described by Strouts *et al.*[14]

The results of the first series of tests are presented in Table III, together with the results of oxygen determinations carried out on our behalf by the A.E.R.E., using neutron-activation analysis. These results included oxygen present as mineral oxygen and an approximate allowance for this oxygen was made by deducting 50% of the ash content from the total oxygen content. The adjusted results are shown in columns 6, 7 and 8 of Table III. For five of the samples, this adjustment amounted to 0·08% or less. Where available,values of oxygen content estimated by difference are included for comparison with the determined values.

The results for the two chars were about 0·5% higher by the activation method than by the chemical method, presumably because of partial retention of oxygen by these materials.[15]

There was better agreement between the values obtained for the five demineralized coke samples, the mean algebraic difference being 0·11% of oxygen with no indication of bias for either method.

In Table IV the results are given of further determinations which were carried out on samples of laboratory and commercial cokes. These samples were not demineralized. The experimental results expressed on the dry basis are compared with calculated values for oxygen.

The discrepancy between the determined and "difference" values of the oxygen content of the cokes varied between 0·89% (Sample 12) and 0·08% (Sample 17). The mean difference for samples 11, 13, 14, 16, 17 and 20 was 0·14%, four of the determined values being higher and two lower than the

TABLE III.—COMPARISON OF THE OXYGEN CONTENTS OF CHARS AND DEMINERALIZED COKES DETERMINED BY TWO METHODS AND BY CALCULATION

Sample	Direct determination, %			Oxygen by difference, % d.b.	Neutron activation, %			Ash %
	A	B	Mean		A	B	Mean	
Cellulose Char A	5·76	5·59	5·68	6·03	6·50	5·99	6·24	0·97
PVDC Char B	1·49	1·48	1·48	1·77	1·93	1·87	1·90	0·04
Coke 6	1·11	1·19	1·15	—	1·04	1·05	1·04	0·08
Coke 7	1·02	1·03	1·02	—	1·26	1·24	1·25	0·16
Coke 8	1·18	1·18	1·18	1·37	1·18	1·14	1·16	0·11
Coke 9	1·27	1·28	1·28	—	1·34	1·29	1·32	0·36
Coke 10	1·42	1·52	1·47	—	1·34	1·32	1·33	0·12

TABLE IV.—COMPARISON OF THE MEASURED AND CALCULATED OXYGEN CONTENTS OF COKES

Sample	Moisture %	% Dry basis										
		Ash	C	H	N	S	Cl	Mineral matter*	Oxygen by difference	Oxygen determined		
										A	B	Mean
11	2·80	6·01	89·13	0·68	1·54	1·25	0·08	6·84	1·73	1·74	1·88	1·81
12	3·70	8·72	84·39	0·83	1·59	1·86	0·03	9·96	3·20	2·30	2·32	2·31
13	1·65	6·08	89·38	0·83	1·26	1·43	0·00	7·03	1·50	1·49	1·35	1·42
14	0·98	3·66	92·94	0·58	1·46	0·73	0·01	4·15	0·86	0·71	0·74	0·72
15	0·36	10·37	87·59	0·31	0·95	0·69	0·03	10·91	0·21	0·60	0·54	0·57
16	0·90	11·79	85·84	0·23	0·78	1·18	0·05	12·58	0·52	0·75	0·67	0·71
17	0·55	11·42	86·41	0·28	0·70	1·46	0·02	12·39	0·20	0·26	0·30	0·28
18	1·16	10·70	86·88	0·40	1·11	1·21	0·02	11·51	0·08	0·51	0·55	0·53
19	0·40	11·76	86·21	0·26	1·02	1·53	0·04	12·78	−0·31	0·38	0·39	0·38
20	1·40	12·56	84·71	0·81	0·83	0·97	0·00	13·21	0·44	0·67	0·74	0·70

* Mineral matter (d.b.) = Ash + 2S/3.

"difference" values. The causes for greater divergence between the derived and determined results for samples 12, 15, 18 and 19 are not apparent.

The values of the "oxygen by difference" were obtained by subtracting the sum of the percentages of carbon, hydrogen, nitrogen, chlorine and mineral matter from 100. The total analytical error associated with all these determinations is approximately 0·5%, and the calculated oxygen may be in error by this amount. Whilst an error of this magnitude may not be too serious with respect to the calculated oxygen content of coal (which is frequently reported as oxygen plus errors) it is of the same order of magnitude as the oxygen content of many high-temperature cokes. Correction of the calculated results to a mineral matter free basis would not be expected to produce a significantly more accurate value for the calculated oxygen content of coke.

DISCUSSION

An examination of the relationship between the determined hydrogen, oxygen and moisture contents (Table IV) indicates that both hydrogen and oxygen contents tended in general to increase with the moisture content of the coke. Although experience suggests that a fraction of the moisture was not eliminated by heating at 350°, nevertheless the atomic ratio of hydrogen to oxygen was considerably greater than the stoichiometric ratio for water, suggesting that some of the hydrogen was originally in combination with the coke.

It is interesting that the amount of oxygen released from coke appears to be a function of pyrolysis temperature between 500 and 1000° (Figs. *2a*, *2b*, *2c*). There appeared to be a pronounced maximum rate of release of oxygen at 850°. For the cellulose char (Fig. *2d*) the maximum release occurred at a temperature of 650°. Apart from this maximum, there was a steady release of oxygen at temperatures between 650 and 850°, but a lower rate between 500 and 650° and above 850°. These observations could be of interest in relation to the nature of the carbon–oxygen bonding in cokes and carbons and may be worthy of further study.

The reduction in the amount of oxygen released above temperatures of 850–900° suggests that loss of oxygen from the coke substance was virtually complete at 1000–1050°.

The presence of mineral matter appeared in certain cases to make a small contribution to oxygen release, possibly due to the presence of carbonates, reformed by the action of moisture and carbon dioxide upon alkali or alkaline-earth oxides present in the mineral matter. On the other hand, the small amounts of additional oxygen detected in the presence of mineral matter may be accounted for on the basis of constituents of the mineral matter promoting catalytic liberation of oxygen from the coke.

As already stated, it is considered that the quantity of additional oxygen liberated in the presence of mineral matter is not significant by comparison with the overall error of the determination and the advantages in accuracy to be gained by demineralization of the coke are questionable.

The standard deviation of the analyses by the direct method described was slightly less than 0·05% (10 variates). The determined oxygen content was found to be related to the determined carbon content by the relationship

$$O = 43{\cdot}58 - 0{\cdot}44C \ (\%\ \text{d.m.m.f.})$$

the use of which results in a better value for the oxygen content than the "difference value" which is quoted in our Tables.

It does not appear to be essential with coke, as with coal, to remove the mineral matter from the sample prior to the determination of oxygen, but the coke must be crushed to pass a 0·06-mm mesh sieve.

It was found to be essential to calibrate and service the apparatus periodically. After approximately twenty determinations the oxygen content of a reference sample, *e.g.*, acetanilide, was determined, or a known amount of carbon dioxide was passed through the apparatus. With these precautions the precision of the determination can be maintained at better than 0·05%.

Acknowledgements—This work formed part of the programme of research of The British Coke Research Association. We are indebted to The Director for permission to publish this paper.

Zusammenfassung—Das zur Bestimmung von Sauerstoff in organischen Verbindungen und Kohle verwendete Verfahren nach Unterzaucher wurde der Sauerstoffbestimmung in Koks angepaßt. Die übliche Apparatur wurde abgeändert, um einen Beitrag der Feuchtigkeit des Kokses zum ermittelten Sauerstoffgehalt zu verhindern. Das durch die Verbrennung des Sauerstoffs im Koks entstandene Kohlendioxid wurde durch eine empfindliche konduktometrische Methode bestimmt. Es wird gezeigt, daß zusätzliche Freisetzung von Sauerstoff aus den Mineralbestandteilen des Kokses keinen wesentlichen Beitrag zum unter den Bedingungen der Vorschrift ermittelten Gesamt-Sauerstoffgehalt liefert. Der Fehler der Bestimmung beträgt etwa 0,1 prozent. Die an einer Anzahl von Koksen und Kohlen mit der direkten Methode erhaltenen Ergebnisse werden verglichen mit denen einer auf Neutronenaktivierung beruhenden indirekten Methode.

Résumé—La méthode d'Unterzaucher, utilisée pour le dosage de l'oxygène dans les composés organiques et la houille, a été adaptée au dosage de l'oxygène dans le coke. Des modifications ont été effectuées sur l'appareil ordinaire afin d'éliminer toute contribution apportée par l'humidité du coke à la teneur en oxygène dosée. Le gaz carbonique produit par la combustion de l'oxygène dans le coke a été dosé par une méthode conductimétrique sensible. On apporte des preuves indiquant que la libération supplémentaire d'oxygène de la matière minérale du coke ne contribue pas de manière significative à l'oxygène total déterminé selon les conditions expérimentales prescrites. L'erreur du dosage est d'approximativement 0,1 %. On effectue une comparaison entre les résultats obtenus pour une série de cokes et de produits de carbonisation par la méthode directe et par une détermination indépendante, basée sur l'activation de neutrons.

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MACRORETICULAR CHELATING ION-EXCHANGERS

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Summary—Two macroreticular chelating ion-exchangers have been prepared and characterized. One contains the iminodiacetate group and the second contains the arsonate group as the ion-exchanging site. The macroreticular resins show selectivities among metal ions similar to those of the commercially available microreticular chelating resins. Chromatographic separations on the new resins are rapid and sharp.

In recent years there has been an increasing interest in highly selective ion-exchangers.[1,2] The goal has been to achieve sharp separations of metal ions without the addition of complexing reagents to the eluent and to concentrate traces of metals from large volumes of very dilute solutions.

The inherent lack of selectivity of the conventional strong acid cation-exchanger, with a sulphonate ion-exchanging group, makes it unsatisfactory for the separation of many mixtures of metals. Even metal ions which are otherwise quite different from each other in their chemical behaviour are often unresolved by the sulphonate resin. For example, the equilibrium constant, $K_{\mathrm{Li}}^{\mathrm{M}}$, for the ion-exchange reaction

$$\tfrac{1}{2}\mathrm{M}^{2+} + \overline{\mathrm{Li}^{+}} = \tfrac{1}{2}\overline{\mathrm{M}^{2+}} + \mathrm{Li}^{+}$$

(the bars indicate the species in the resin) is 3·29 for Mg^{2+}, 3·47 for Zn^{2+}, 3·85 for Cu^{2+}, 3·93 for Ni^{2+} and 5·16 for Ca^{2+} on Dowex 50W-X8.[3] Separation of these metals on this resin must therefore rely on chemical reagents which bind some of the metals as rapidly eluted neutral or anionic complexes, while the others are not bound and remain on the resin.[4]

If the ion-exchanging group on the resin is able to form covalent complexes with metals—which the sulphonate group cannot—then the resin will exhibit a greater selectivity among them, due to variations in the strengths of the complexes. One such group is the iminodiacetate ion, $—N(CH_2COO^-)_2$. The commercial resin Dowex A-1 (Chelex 100) contains this exchange group. The selectivity constants for this resin, relative to calcium [$K_{\mathrm{Ca}}^{\mathrm{M}}$] are 4·9 for Mn^{2+}, 15·2 for Co^{2+}, 19·8 for Zn^{2+}, 52 for Ni^{2+}, and 500 for Cu^{2+}.[5] A second selective group is the phosphonate ion, $—PO_3^{2-}$, which is the ion-exchanging group in Duolite C-63. Selectivities of this resin relative to nickel [$K_{\mathrm{Ni}}^{\mathrm{M}}$] are 1·3 for Co^{2+}, 2·9 for Mn^{2+}, 20·5 for Zn^{2+}, and 53 for Cu^{2+}.[6] Both types of resin are weak acids, which is to say that the ionic group has a strong preference for hydrogen ion. Thus in both cases control of the pH of the eluent is all that is necessary for sharp separations of many metals from each other.

Many other chelating ion-exchangers have been studied.[1] The main limitation of these materials is that they are based on a gel or microreticular copolymer matrix.

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This means that the resin undergoes large changes in volume on conversion from one ionic form to another.[7] Such volume changes can disrupt the uniform packing of the resin in a column. In addition, with low degrees of swelling the rate of ion-exchange reactions becomes slow, which is undesirable in chromatography.

Over the past decade a new type of copolymer has been developed for use in ion-exchangers. It is called macroreticular, since it has a permanent macroscopic structure regardless of the ionic form.[8,9,10] In particular, there is an extensive network of large pores, up to 50 nm in diameter or even larger, throughout the interior of the resin beads.[11] This pore structure allows exchange reactions to proceed rapidly in any ionic form of the resin, even if the resin is placed in a non-polar solvent, such as hexane, which does not swell it. Several macroreticular strong acid cation-exchangers and strong and weak base anion-exchangers have become commercially available[12] and have found use in diverse analytical procedures.[13,14,15]

The results that have been published regarding the properties of chelating ion-exchangers, combined with the data on the macroreticular resins, suggested that the highly porous copolymer could serve as the basis of selective ion-exchangers with more satisfactory properties than the microporous materials. In this paper we report on some newly-prepared selective macroreticular cation-exchangers containing the iminodiacetate and the arsonate[16] groups. Synthetic procedures, properties, and chromatographic behaviour are discussed.

EXPERIMENTAL

Starting materials and reagents

XAD-1 macroreticular styrene–divinylbenzene copolymer was obtained from the Rohm and Haas Company, Philadelphia, Penn. The beads were washed with $2M$ hydrochloric acid, methanol and acetone, screened to 20–50 mesh, and dried under vacuum before use. All other chemicals were of the highest available purity, usually reagent grade.

*Synthetic procedures**

Iminodiacetate resin. The XAD-1 was chloromethylated with chloromethyl methyl ether in the presence of anhydrous tin(IV) chloride.[17] After washing and drying under vacuum, the chloromethylated copolymer was refluxed with $1M$ sodium iodide in acetone to convert it into the iodomethylated form.[18] The latter was heated for 10 days at 75° with diethyl iminodiacetate in acetonitrile, producing the diethyl iminodiacetate derivative of the copolymer. This was hydrolysed by heating with ethanolic sodium hydroxide to give the iminodiacetate resin.[19]

Arsonic acid resin. The XAD-1 was nitrated by heating with nitric–sulphuric acid mixture (40:60) for 2 hr at 60°. After washing and drying, the nitrated resin was reduced by refluxing with tin(II) chloride in hydrochloric acid for 2 hr, washed, and diazotized with nitrous acid at 0°. The beads were then washed with cold aqueous sodium carbonate solution and mixed with $0{\cdot}5M$ aqueous sodium arsenite at 25° for 1 hr and at 60° for an additional hour to obtain the arsonic acid copolymer.[20]

Characterization of products

Infrared spectra were obtained on a Beckman Model IR-10 Spectrophotometer; there were no noticable differences when the mineral oil mull and KBr pellet methods of sample preparation were used.

Relative volumes in the different ionic forms were determined by packing a column with resin in the sodium form, converting it into the other forms, and observing the volume of the resin bed in each case.

Hydrogen ion capacity was determined by the standard technique.[21]

Metal ion capacities were determined by equilibrating weighed samples (fully converted into the sodium form) with a measured amount of standard metal ion solution [copper(II), zinc or calcium]. An aliquot of the supernatant liquid was titrated with standard EDTA under appropriate conditions.[22] The results were checked by washing the sample free from the metal solution with demineralized water,

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* These are available in fuller detail from the senior author.

and treating the resin with 1*M* hydrochloric acid to displace the absorbed metal ions, which were then titrated with EDTA.

All capacities refer to the dry resin weight on a hydrogen-form basis.

Chromatography

A resin sample was equilibrated with buffer and packed into a chromatographic column, forming a bed about 100 mm long and 10 mm in diameter. Two ml of a mixture of metals (0·01*M* in each) in this buffer were added to the column. Elution was carried out with buffer solutions of various pH values at a flow-rate of 2 ml/min. Fractions were collected and analysed for relative metal ion concentrations with a Perkin–Elmer Model 290 Atomic Absorption Spectrophotometer under standard conditions for each metal.[23]

RESULTS AND DISCUSSION

Syntheses

The procedures described above are the optimum ones found in this work. Several other routes were studied in each case and were less satisfactory. The iminodiacetate resin could not be obtained from chloromethylated copolymer in as high capacity by reaction with disodium iminodiacetate, iminodiacetonitrile, or diethanolamine (procedures suggested in the literature for gel resins[1]). The procedure chosen, using diethyliminodiacetate as the aminating reagent, gave somewhat better results with iodomethylated XAD-1 (95% amination based on product nitrogen content) than with chloromethylated copolymer (70–80% amination).

The arsonic acid resin could not be obtained by reaction of chloro-iodomethylated copolymer with potassium arsenite or by refluxing XAD-1 with arsenic trichloride in the presence of aluminium trichloride catalyst, followed by hydrolysis (which was found to be a satisfactory procedure for preparation of a phosphonic acid resin, using phosphorus trichloride and aluminium trichloride[16]). It is possible that under milder conditions arsenic trichloride would be a satisfactory reagent for introducing arsenic into the copolymer.

Several other new macroreticular resins were prepared, but were not thoroughly characterized. Among the ion-exchanging groups attached to the copolymer were triphenylbenzylphosphonium and triphenylbenzylarsonium anion-exchangers and phosphonate cation-exchanger, all with exchange capacities greater than 1 mequiv per g of dry resin.

Properties of the resins

The iminodiacetate resin had a hydrogen ion capacity of 3·2 mmole/g and a copper capacity of 1·6 mmole/g. These values are similar to the respective capacities 2·9 and 1·5, published for Dowex A-1 or Chelex 100 gel-type iminodiacetate resins.[24] The high capacity is desirable for efficient operation in chromatography and other applications. The absence of ester in the resin was indicated by the lack of infrared absorption at 5·7 μm, absorption that was present prior to saponification of the diethyl iminodiacetate resin.

The volume was measured of the iminodiacetate resin in various ionic forms. There was no change in volume on interconversion between the Na^+, H^+, Cu^{2+}, and K^+ forms. Likewise, no volume change was observed when toluene or methanol was substituted for water in contact with the hydrogen or sodium forms. Dowex A-1, on the other hand, shows relative volumes of 0·45 for H^+, 0·55 for Zn^{2+}, 1·00 for Na^+ and 1·06 for K^+ forms in water, and 1·00 in water, 0·70 in methanol, and 0·47 in acetone for the sodium form.[7] These results suggest that the macroreticular chelating resin will be useful under a wider variety of conditions than the microreticular gel Dowex A-1.

The arsonate resin had a hydrogen capacity of 3·0 mmole/g. The metal ion capactities were 1·3 mmole Cu^{2+}/g, 1·4 mmole Zn^{2+}/g, and 1·1 mmole Ca^{2+}/g at pH 11, and 0·8 mmole Cu^{2+}/g at pH 3·5. Elemental analysis showed 6·4% nitrogen and (by difference) 16% oxygen in the final product. These results suggest the presence of other exchange groups in addition to the arsonate. A possible distribution of groups is 1·3 mmole arsonate/g, 1·0 mmole phenolate and 0·5 mmole azo/g (due to side-reactions of the diazonium intermediate), 3·3 mmole nitro/g (due to incomplete reduction), and 0·2 mmole carboxylate/g (due to oxidation of the copolymer during nitration). While the various side-products do affect the ion-exchange capacity of the arsonate resin, they would not interfere (with the possible exception of the carboxylate, which is only a small fraction of the total capacity) with the determination of the metal ion selectivity of the arsonate group.

The arsonate resin showed little volume change on conversion from one ionic form into another. Its exchange capacity is sufficient to allow use in various analytical

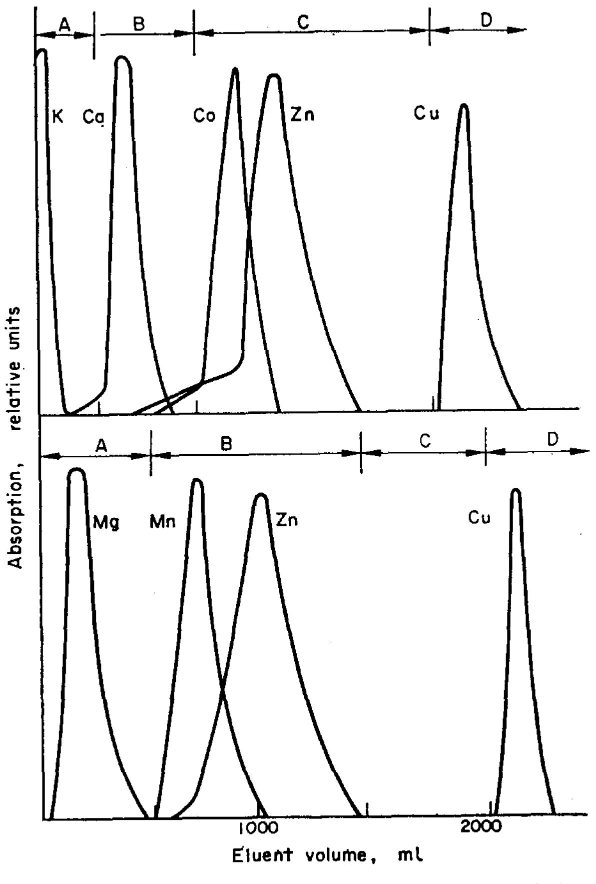

Fig. 1.—Chromatographic separations with the macroreticular iminodiacetate ion-exchange resin.
Buffer solutions: *A*—pH 4·3, *B*—pH 3·1, *C*—pH 2·0, *D*—pH 1·2.

applications, as the chromatographic results given below suggest. Unlike the iminodiacetate resin, which was gray, the arsonate resin was brick red in colour. It is likely that further synthetic studies would produce an arsonate resin with higher exchange capacity, fewer impurities, and a lighter colour.

Chromatography

Several mixtures of representative metal ions were used to test the selectivity of the two new macroreticular resins. Typical chromatograms are shown in Figs. 1 and 2.

The selectivity order for the macroreticular iminodiacetate resin is $K^+ < Mg^{2+} < Ca^{2+} < Mn^{2+} < Ni^{2+} < Co^{2+} < Zn^{2+} \ll Cu^{2+}$. Hering[1] determined the following order for a gel type iminodiacetate resin: $Na^+ < Mg^{2+} < Ca^{2+} < Co^{2+} < Zn^{2+} < Ni^{2+} \ll Cu^{2+}$, while Rosset[5] determined the selectivity of Dowex A-1 as $Mg^{2+} < Mn^{2+} < Co^{2+} < Zn^{2+} < Ni^{2+} \ll Cu^{2+}$. The elution order with the macroreticular chelating resin is therefore similar to that previously observed with the microreticular chelating resins.

The arsonate resin showed the selectivity order $Mg^{2+} < Ca^{2+} < Mn^{2+} < Co^{2+} < Ni^{2+} < Zn^{2+} \ll Cu^{2+}$. Persoz and Rosset[6] reported the following order of affinity for

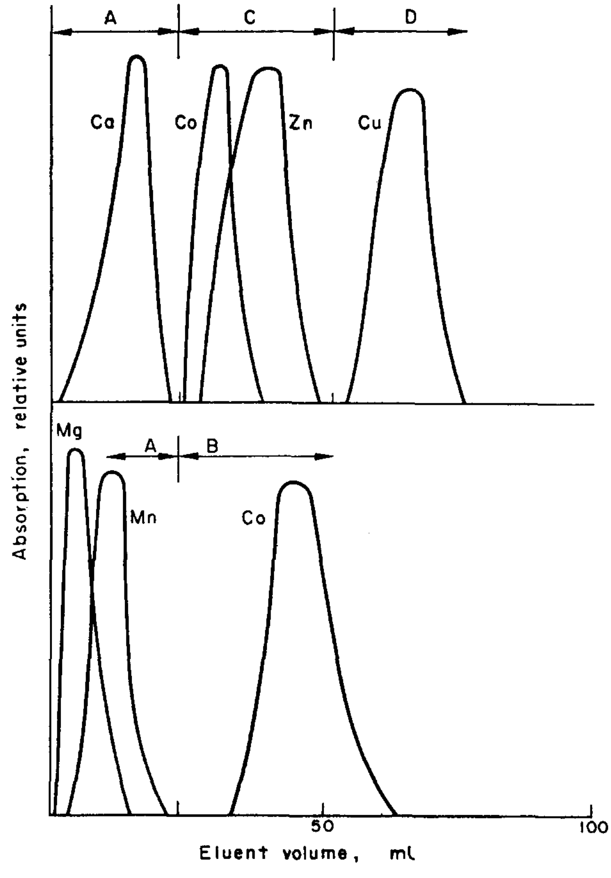

FIG. 2.—Chromatographic separations with the macroreticular arsonate ion-exchange resin.

Buffer solutions: *A*—pH 4·6, *B*—pH 3·5, *C*—pH 2·5, *D*—pH 1·5.

Duolite C-63, the phosphonate resin: $Mg^{2+} < Ca^{2+} < Ni^{2+} < Co^{2+} < Mn^{2+} < Zn^{2+} < Cu^{2+}$. The shift in position of the nickel and manganese is most likely due to the difference in co-ordinating properties between the arsonate and phosphonate groups.

The sharpness of the column separations would be improved if the ion-exchanger beads had been smaller and more uniformly sized. It is apparent, however, that sharp group separations can be carried out quickly with a short resin column and with suitable adjustments in the pH of the eluent. The eluent need not contain complexing agents, as is necessary with the strong acid cation-exchangers. The macroreticular resins should be useful under conditions in which the microreticular resins show unsatisfactory exchange rates and swelling behaviour.

Acknowledgement—The authors gratefully acknowledge the assistance of the Ion Exchange Division, Rohm and Haas Company, which supplied the starting materials.

Zusammenfassung—Zwei grob vernetzte chelatbildene Ionenaustauscher wurden dargestellt und charakterisiert. Einer enthält die Iminodiacetatgruppe, der andere die Arsenatgruppe als ionenaus tauschaktive Funktion. Die grob vernetzten Harze zeigen ähnliche Auswahleigenschaften unter Metallionen wie die handelsüblichen fein vernetzten chelatbildenden Harze. Chromatographische Trennungen an den neuen Harzen sind schnell und scharf.

Résumé—On a préparé et caractérisé deux échangeurs d'ions chélatants macroréticulaires. Le premier contient le groupe iminodiacétate et le second contient le groupe arsonate comme point actif pour l'échange d'ions. Les résines macroréticulaires montrent des sélectivités parmi les ions métalliques similaires à celles des résines chélatantes microréticulaires commercialement accessibles. Les séparations chromatographiques sur les nouvelles résines sont rapides et nettes.

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DETERMINATION OF SOME METHYLCARBAMATE INSECTICIDES BY A.C. POLAROGRAPHY AND CYCLIC VOLTAMMETRY

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Summary—The study of adsorption–desorption phenomena represents an important extension to the range of organic compounds that can be determined by electrochemical methods. The present work has utilized this approach for the determination of a range of methylcarbamate insecticides. The tensammetric behaviour of this class of compound at the mercury electrode has been investigated by a.c. polarography and the optimum experimental conditions for their analytical determination have been derived. Cyclic voltammetry has also been used to study the electrode process and by using the peak obtained on the cathodic sweep it was possible to extend the limit of detection to the ppm level.

A VARIETY of methylcarbamates are used in agriculture as insecticides. Among the most common are Carbaryl (1-naphthyl methylcarbamate), Aldecarb (formerly temik) (2-methyl-2-methylthiopropionaldehyde *O*-methylcarbamoyl oxime) and Butacarb (3,5-di-t-butylphenyl *N*-methylcarbamate), of which Carbaryl has been the most extensively studied.

The analytical methods available for the determination of this class of compound are numerous. Carbaryl has been determined both by classical methods[1,2] and a variety of spectrophotometric methods.[3–6] A number of thin-layer chromatography (TLC) methods[7–11] have also been developed of which the method of Benson and Finocchiaro[7,9] appears to be the most widely used for the determination of Carbaryl in vegetable matter. Kovacs[12] introduced an infrared method the merits of which were later compared with an ultraviolet and an alkaline distillation method.[13] Gas chromatographic (GLC)[14–19] methods are also in evidence, based mainly on the conversion of the carbamate into the corresponding phenol.

Substantially less work has been done on the determination of Aldecarb and Butacarb. Existing methods are confined to colorimetric,[20] GLC[21] and radiotracer[22] methods for Aldecarb, and a TLC/radiotracer determination[23] for Butacarb. No analytical method appears in the literature for the fourth methylcarbamate studied, Methiocarb (3,5-dimethyl-4-thiomethylphenyl *N*-methylcarbamate).

Very little investigation has been made into the electrochemical behaviour of methylcarbamates. Only Carbaryl has been determined by electrochemical techniques.[24,26] One method[24,25] is based on nitrosation of Carbaryl followed by oscillopolarography, while the other[26] involves the polarographic determination of the products resulting from nitration of the aromatic nucleus.

The present work describes a method for the direct determination of methylcarbamates, based on their adsorption–desorption phenomena. Both a.c. polarographic and cyclic voltammetric techniques have been used.

EXPERIMENTAL

Reagents

Methylcarbamates were obtained from the Ministry of Technology, Laboratory of the Government Chemist. The purity of each compound was checked by melting point determination, and where necessary they were purified by crystallization from methanol.

A $10^{-2}M$ stock solution of each compound was prepared. The solutions of Aldecarb and Carbaryl contained only 20% methanol, but because of low solubility those of Butacarb and Methiocarb were made with 100% methanol. Buffer solutions were prepared from analytical grade reagents.

Apparatus

Direct current polarograms were recorded on a Metrimpex polarograph type OH-102. A Kalousek cell with a separated saturated calomel electrode (SCE) was used. Capillary characteristics, measured at 0·0 V *vs.* SCE in $0{\cdot}1M$ potassium chloride were $t = 4{\cdot}41$ sec, $m = 1{\cdot}88$ mg/sec at $h = 0{\cdot}75$ m.

The a.c. peaks were measured with a Cambridge Univector and general-purpose polarograph with the Metrimpex polarograph as the current-output recorder. A Heyrovský cell was used with a mercury pool as the anode.

Cyclic voltammograms were obtained on a Chemtrix polarograph Model SSP-2 in the three-electrode mode. The working electrode was a hanging mercury drop electrode, Metrohm type E410. A silver wire and an SCE were used as counter and reference electrodes respectively.

Procedure

A sample containing from 0·05 to 10 μmole of the insecticide is added to 1 ml of buffer solution ($0{\cdot}5M$ boric acid/$0{\cdot}5M$ sodium hydroxide) in a 10-ml volumetric flask and diluted to volume with water/methanol so that the final solution contains 2% v/v methanol. As the methanol has an effect on the shape of the peak it is important that the methanol content in the final solution should not exceed this value. In the case of Butacarb, however, where solubility problems arise, it was found that 10% methanol could be tolerated without serious interference, assuming that 4 ml of buffer solution were used.

For the analysis of insecticide residues it is suggested that the volume of the methanol extract after clean-up should be reduced to 1–2 ml in a Kuderna evaporator.[27] The 10-ml collection flask is removed and the residue evaporated to dryness in a stream of nitrogen gas. Then 1 ml of methanol is added to the residue and an aliquot or the whole of this solution is used for analysis.

In the a.c. polarographic method the solution for analysis is transferred to a Heyrovský cell, deoxygenated with nitrogen for 3 min, and the a.c. peak is measured from 0 V *vs.* the mercury pool anode. For cyclic voltammetry, peaks were recorded over the potential range from 0 to −2·0 V *vs.* SCE, a mercury drop size of 25·2 mm^2 being used.

RESULTS AND DISCUSSION

None of the compounds studied shows conventional d.c. polarographic waves. However, on a.c. polarography all compounds showed current peaks at potentials in the region from −1·0 to −1·5 V. That these peaks were tensammetric in character was elucidated by the depression of the base line of the supporting electrolyte (Fig. 1), and the absence of a d.c. polarographic wave. The electrocapillary curves (Fig. 2) for these compounds showed that they were adsorbed over a voltage region either side of the electrocapillary maximum where maximum adsorption occurred. At high negative potentials the capacitive current coincides with that of the supporting electrolyte since at these potentials the surfactant is not present at the mercury–solution interface. These sharp capacitive peaks would therefore appear to be due to a desorption process, and as such reflect periodic changes in the capacity of the double layer. Contributory evidence of the tensammetric character of these peaks is the rectilinear dependence of the peak potential on the log of the concentration of insecticide. It is also worthy of note that small steps are observed in the d.c. curve for these compounds at potentials where tensammetric peaks occur. These adsorption steps are characteristically much smaller than conventional d.c. polarographic waves.

The pH dependence of the tensammetric peaks for Aldecarb, Butacarb and

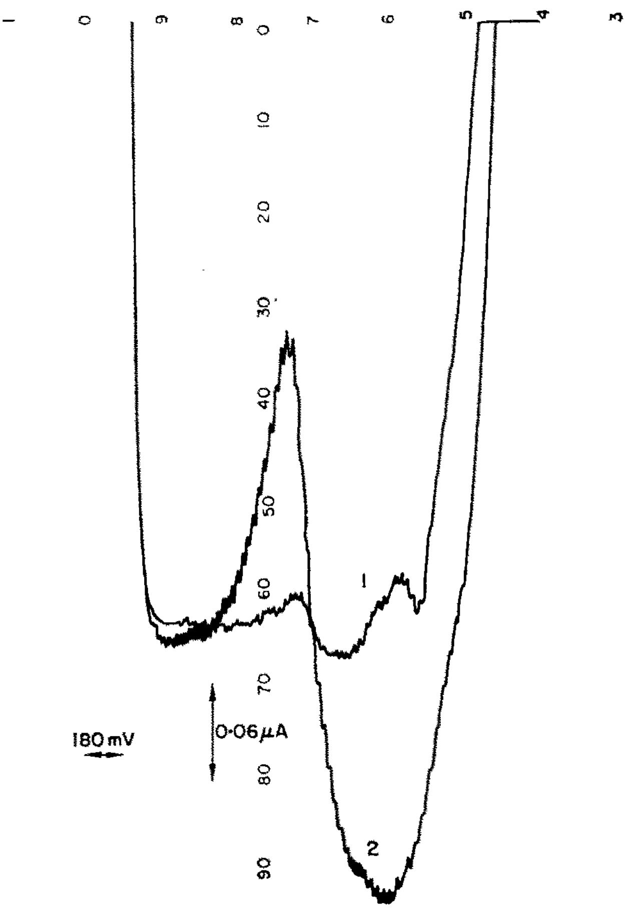

Fig. 1.—A.c. polarograms for: (1), 0; (2), 5 × $10^{-5}M$ Butacarb in 10% methanol at pH 8·98 (0·2*M* boric acid/0·2*M* sodium hydroxide); sensitivity 0·6 μA f.s.d.

Carbaryl are shown in Fig. 3. The optimum pH was found to be 8·4 (aqueous 0·5*M* sodium dihydrogen phosphate/0·5*M* sodium hydroxide buffer). The effect of variation of buffer concentration indicated that maximum peak height for Aldecarb, Methiocarb and Carbaryl was obtained in 0·05*M* buffer. Owing to the surface-active properties of the alcohols a maximum of 10% methanol could be tolerated. A 1–2% methanol solution was desirable. Because of the solubility of Butacarb, 10% methanol solutions 0·2*M* in buffer were necessary. A rectilinear dependence of peak current *vs.* concentration was obtained for all compounds and the results are summarized in Table I. The limit of detection for Aldecarb is $10^{-4}M$ as opposed to $10^{-5}M$ for the other compounds. This can be attributed to the solubility, molecular size and aliphatic nature of the compound.

The relationship between base-line depression and concentration of the surface-active carbamate is shown in Fig. 4 for Carbaryl and Aldecarb. A rectilinear relationship occurs over a limited concentration range, above which the form of a Langmuir isotherm is followed. This would appear to signify that the mercury surface is now completely covered with the adsorbed species.

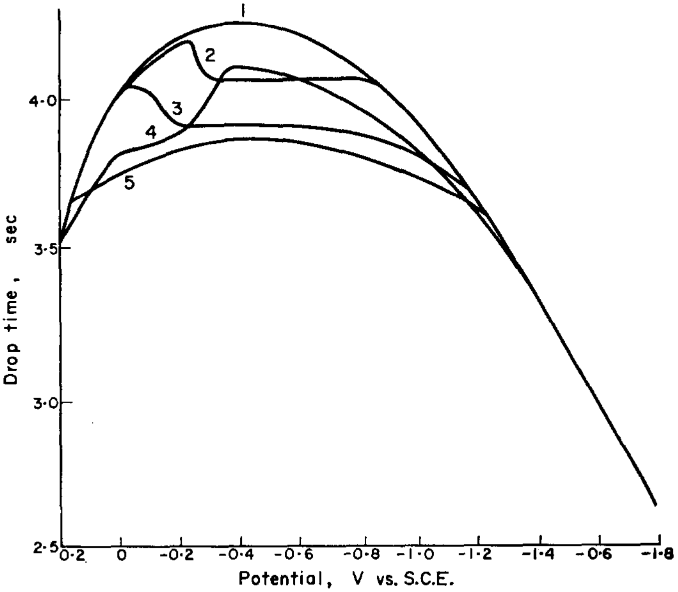

FIG. 2.—Electrocapillary curves for: (1), 0·05M boric acid/0·05M sodium hydroxide buffer in 2% methanol; (2), 5 × $10^{-4}M$ Aldecarb in 0·05M buffer/2% methanol; (3), $10^{-4}M$ Methiocarb in 0·05M buffer/2% methanol; (4), 5 × $10^{-5}M$ Butacarb in 0·2M buffer/10% methanol; (5), 2 × $10^{-4}M$ Carbaryl in 0·05M buffer/2% methanol.

The effect of various cations (0·1M as chlorides) and various anions (0·1M as sodium salt) on the tensammetric peaks was investigated. In the case of cations the desorption potentials are increasingly negative in the sequence $La^{3+} < Mg^{2+} < Li^{+}$. The observed effect will to some effect depend on the displacement capability of the cation and the solubility of the species in solution. In the case of the anions NO_2^-, NO_3^-, ClO_4^-, CO_3^{2-}, CN^-, SO_4^{2-}, the effect on peak height and peak potential

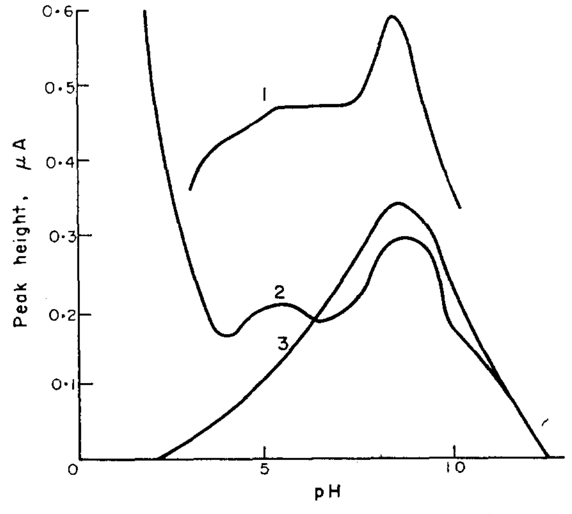

FIG. 3.—pH dependence of (1), 2 × $10^{-4}M$ Carbaryl, and (2), 5 × $10^{-4}M$ Aldecarb in 0·05M buffer/2% methanol; (3), 5 × $10^{-5}M$ Butacarb in 0·2M buffer/10% methanol.

TABLE I.—CONCENTRATION DEPENDENCES FOR METHYLCARBAMATES

Concentration of methylcarbamate M	Current, μA							
	a.c. polarography				cyclic voltammetry			
	B	C	M	A	B	C	M	A
2×10^{-6}	—	—	—	—	—	—	—	—
4×10^{-6}	—	—	—	—	0·40	—	0·40	—
6×10^{-6}	—	—	—	—	0·60	0·45	0·60	—
8×10^{-6}	—	—	—	—	0·87	0·60	0·75	
1×10^{-5}	0·05	—	0·05	—	1·10	0·70	1·00	—
2×10^{-5}	0·07	0·05	0·09	—	2·00	1·30	2·40	—
4×10^{-5}	0·17	0·09	0·22	—	4·40	2·40	4·70	
6×10^{-5}	0·28	0·14	0·29	—	6·60	3·20	7·60	0·30
8×10^{-5}	0·37	0·18	0·41	—	9·00	4·40	9·20	0·40
1×10^{-4}	0·49	0·24	0·52	0·06	11·00	4·80	11·40	0·50
2×10^{-4}	L.S.	0·50	L·S.	0·12	—	—	—	0·95
4×10^{-4}	—	1·00	—	0·28	—	—	—	1·70
6×10^{-4}	—	1·41	—	0·43	—	—	—	2·80
8×10^{-4}	—	1·73	—	0·59	—	—	—	3·75
1×10^{-3}	—	2·07	—	0·71	—	—	—	4·40

B—Butacarb; C—Carbaryl; M—Methiocarb; A—Aldecarb. L.S.—Limited by solubility.

follows no specific pattern. This is primarily because at negative potentials it is the cation that determines the capacity and structure of the double layer. However, an interesting observation is that the shifts in the desorption potentials caused by changing the nature of the halide ion follow the same sequence as the salting-out coefficient for benzene in aqueous solution[28] (Fig. 5). This phenomenon was first noticed by Gierst and Pecasse[29] in a study of the effect of anions on the adsorption–desorption of pyridine at the dropping mercury electrode. Only the effect of fluoride on the desorption potential for Butacarb is anomalous.

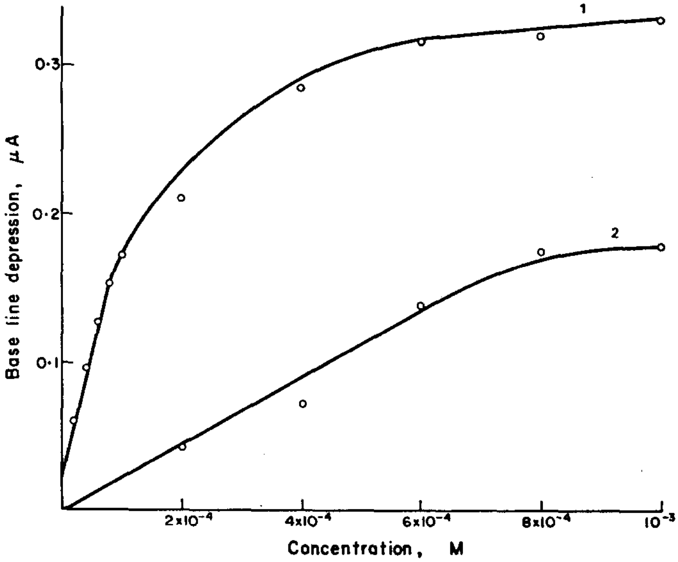

FIG. 4.—Base-line depression *vs.* concentration for (1), Carbaryl and (2), Aldecarb in 0·05M boric acid, 0·05M sodium hydroxide buffer (pH 8·4), 2% methanol.

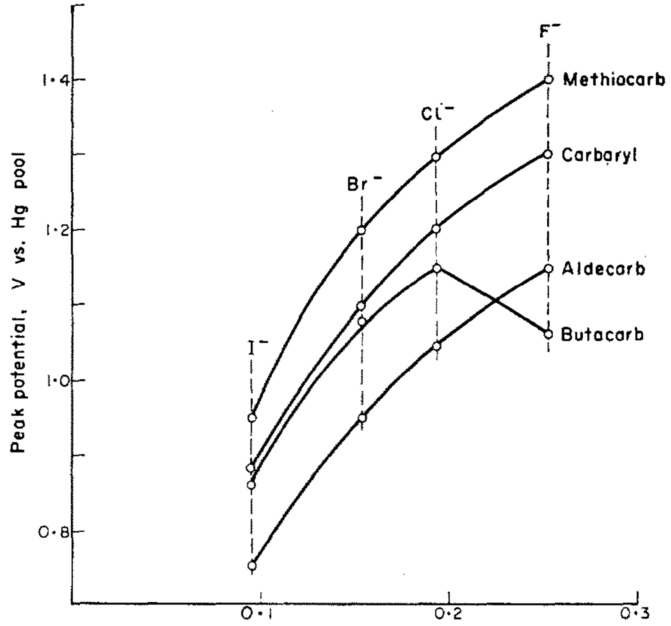

Fig. 5.—Relation between desorption potential of methylcarbamates on mercury, and salting-out coefficient for benzene; solutions as used for measurement of electrocapillary curves; halide concentration, 0·1*M*.

The extent of adsorption of the organic molecule is therefore not entirely governed by its own solubility. The solubility of the supporting electrolyte and any extraneous ions in solution must also be considered. This is an inherent drawback in the analytical utility of capacitive (tensammetric) peaks. The conditions under which the experiment is to be conducted must be clearly defined and closely adhered to.

Cyclic voltammetry

The cyclic voltammogram for Butacarb is shown in Fig. 6. A single cathodic–anodic peak is observed at the sweep rates used. The cathodic peak corresponds to

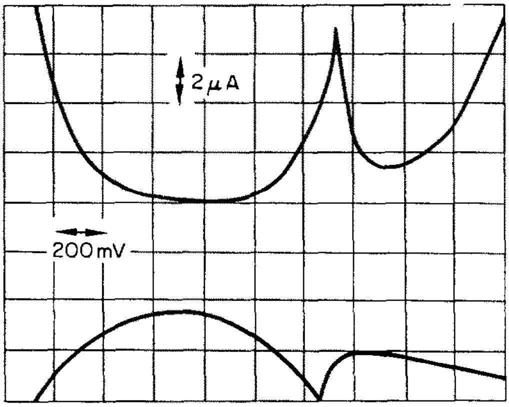

Fig. 6.—Cyclic voltammogram of 5 × $10^{-5}M$ Butacarb in 0·2*M* boric acid/0·2*M* sodium hydroxide buffer, 10% methanol. Scan rate, 4 V/sec.

the tensammetric peak described earlier caused by the desorption of the surface-active carbamate compound. This peak was utilized for analytical purposes. The anodic peak observed on the reverse scan is due to adsorption of the carbamate onto the electrode surface, replacing the cations of the supporting electrolyte. Methiocarb and Carbaryl show similar behaviour. Aldecarb shows in addition the capacitive peaks corresponding to adsorption of the surfactant on the cathodic scan, and desorption on the reverse scan.

A rectilinear dependence of peak current against concentration was observed for all compounds (Table I). Concentrations of the order of $5 \times 10^{-6}M$ (1 ppm) for Butacarb, Carbaryl and Methiocarb must be taken as the lower limit attainable with the apparatus used. The limit for Aldecarb is $5 \times 10^{-5}M$.

Acknowledgements—We wish to thank the Agricultural Research Council for the provision of a research assistantship for one of us (M. D. B.).

Zusammenfassung—Die Untersuchung von Adsorptions- und Desorptionserscheinungen stellt eine wichtige Erweiterung der Auswahl von organischen Verbindungen dar, die mit elektrochemischen Methoden bestimmt werden konnen. Die vorliegende Arbeit benutzte dieses Verfahren zur Bestimmung verschiedener Methylcarbamat-Insektizide. Das tensametrische Verhalten dieser Verbindungsklasse an der Quecksilberelektrode wurde mit Hilfe der Wechselstrompolarographie untersucht und die optimalen Versuchsbedingungen für die analytische Bestimmung solcher Substanzen ermittelt. Zur Untersuchung des Elektrodenprozesses wurde auch die cyclische Voltammetrie eingesetzt; mit Hilfe des Peaks, den man beim kathodischen Durchlauf erhält, ließ sich die Nachweisgrenze bis zum ppm-Bereich herabdrücken.

Résumé—L'étude des phénomènes d'adsorption–désorption représente une extension importante au domaine des composés organiques que l'on peut déterminer par des méthodes électrochimiques. Le présent travail a utilisé cette approache pour la détermination d'une série d'insecticides méthylcarbamatés. Le comportement tensammétrique de cette classe de composés à l'électrode de mercure a été étudié par polarographie en courant alternatif et l'on en a déduit les conditions expérimentales optimales pour leur détermination analytique. On a aussi utilisé la voltamétrie cyclique pour étudier le processus à l'électrode et en utilisant le pic obtenu sur le balayage cathodique il a été possible d'étendre la limite de détection au niveau de la *ppm*.

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CATALYTIC REACTIONS—I

MECHANISMS

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Summary—The mechanisms of some reactions used in catalytic analysis are discussed. The knowledge of the mechanism of a catalytic reaction can help in the development of new catalytic reactions and the choice of optimal conditions, and to show the possibilities for further increases in sensitivity.

THE RECENT intensive development of catalytic methods of analysis is a result of their high sensitivity combined with relatively simple procedures. More than 250 procedures are known for the determination of about 45 elements. Some monographs have been published[1–6] as well as the biennial reviews in *Analytical Chemistry*.

Many different types of catalytic reaction have been used for analytical purposes. In the present paper an attempt is made to generalize the results of investigations on the mechanisms of catalytic reactions in the hope that it will help in the development of new, *improved*, analytical procedures.

The homogeneous reactions used for the catalytic determinations of ions can be classified according to whether the catalytic ions change their oxidation state or not.

REACTIONS CATALYSED BY IONS THAT CHANGE THEIR OXIDATION STATE DURING THE REACTION

Most of the useful catalytic methods are based on reactions in this group, which includes the most sensitive reactions (sensitivity is usually 0·1–10^{-4} ppm, sometimes as low as 1 ppb) and hence those most frequently used.

A catalytic cycle frequently observed is:

$$\text{Red} + \text{M}^{(n+1)+} \rightarrow \text{P} + \text{M}^{n+} \qquad (1)$$

$$\text{M}^{n+} + \text{Ox} \rightarrow \text{M}^{(n+1)+} + \text{Q} \qquad (2)$$

where Red and Ox are the reagents of the redox reaction, and P and Q are the reaction products. The role of the oxidant Ox is simply to return the catalyst, the actual oxidant of Red, to its lower oxidation state, equation (2). Typical examples are transition metal ions in different oxidation states, such as vanadium, manganese, iron, copper, osmium, rhenium, or non-metal ions such as iodide and bromide.

A reaction of this type should be suitable for analytical purposes if the following two conditions are also satisfied:

(*a*) the oxidation potential E_{M} of the couple $\text{M}^{(n+1)+}/\text{M}^{n+}$ under the reaction conditions is higher than the potential E_{Red} of the couple P/Red and lower than the oxidation potential E_{Ox} of the couple Ox/Q, *i.e.*,

$$E_{\text{Ox}} > E_{\text{M}} > E_{\text{Red}}$$

(*b*) the direct interaction of Red with Ox which is thermodynamically permitted is hindered kinetically, whereas the oxidation of M^{n+} by Ox proceeds readily.

REACTIONS WITH ORGANIC SUBSTRATES

Reactions of this type usually involve the oxidation of an arylamine, phenol or dye-stuff. The oxidation of arylamines and phenols leads to the formation of coloured products, whereas the oxidation of dyestuffs most frequently involves decolorization. Thus the kinetics of such reactions are usually followed colorimetrically.

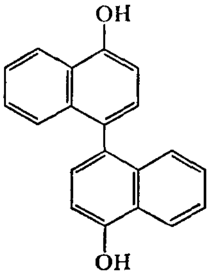
These oxidations are usually slow, but are catalysed by metal ions. When transition metal ions (and other one-electron oxidants) are used, the first step of arylamine or phenol oxidation is always homolytic:[7,8]

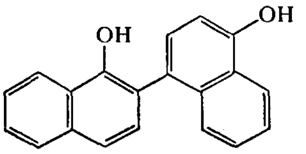
$$RH + M^{(n+1)+} \rightarrow R^{\cdot} + H^+ + M^{n+} \qquad (3)$$

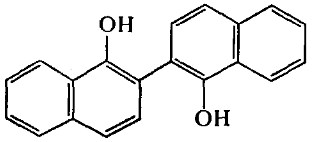
where $R^{\cdot}$ represents an arylamine radical $ArNH^{\cdot}$ or an aryloxy radical $ArO^{\cdot}$. The low ionization energy of arylamines and phenols permits the ready removal of the electron.[9] The radicals are also stabilized by conjugation of the unpaired $2p_z$ electron from nitrogen or oxygen with the π-electron system of the aromatic ring.[10] Reactants with substituents which increase the electron density in the conjugated system are oxidized more easily, therefore, than the corresponding non-substituted or electrophilically substituted compounds. Thus, the homolytic oxidation of polyphenols, arylamines, aminophenols, alkyl- and alkoxy-substituted phenols and arylamines proceeds very readily.[11–14]

The homolytic mechanism of the one-electron oxidation of these compounds by metal ions has been confirmed by kinetic data, initiation of polymerization processes, reduction of mercury(II) chloride, *etc.*[15–18] Direct evidence of the formation of free radicals has been provided by electron paramagnetic resonance.[19–24]

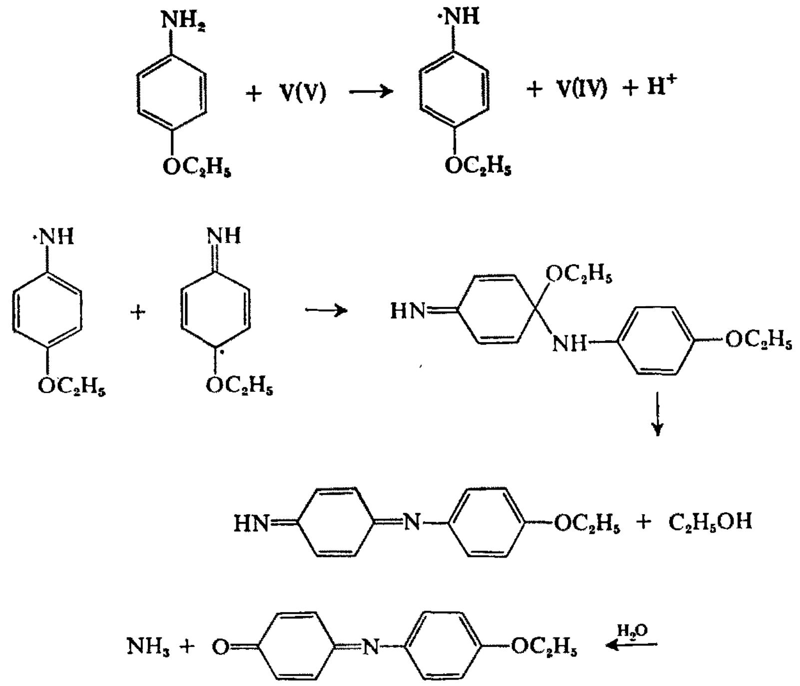
The large number of possible final reaction products arises because of the different ways in which the radical $R^{\cdot}$ can react further. These depend on its structure, reactivity and the reaction conditions,[7,14,25–28] and especially on the localization of the unpaired electron. For example, the localization of the electron at the 2 and 4 positions in the 1-naphthol radical results in the formation of three products when α-naphthol is oxidized by iron(III) chloride[29]:







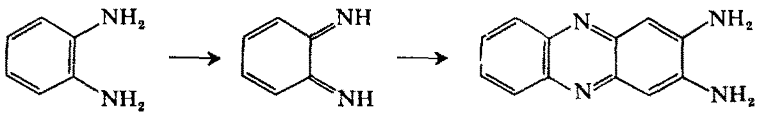
If a favoured position is hindered by a bulky substituent (such as phenyl, naphthyl, *etc*) at this position, the number of products is reduced. Less bulky substituents, however, do not prevent reaction at this position. Thus the catalytic oxidation of *p*-phenetidine by halates, with vanadium(V) as a catalyst, proceeds as follows[30]:



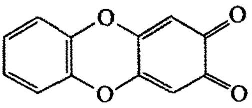
(4)

If the quinolide is stable it might form the final reaction product as in the oxidation of 1-methyl-2-naphthol (see ref. 14, p. 142).

Reaction of the radical in which the unpaired electron is localized *o*- to the —O or —NH group leads to the formation of heterocyclic compounds such as (see ref. 14, p. 149):

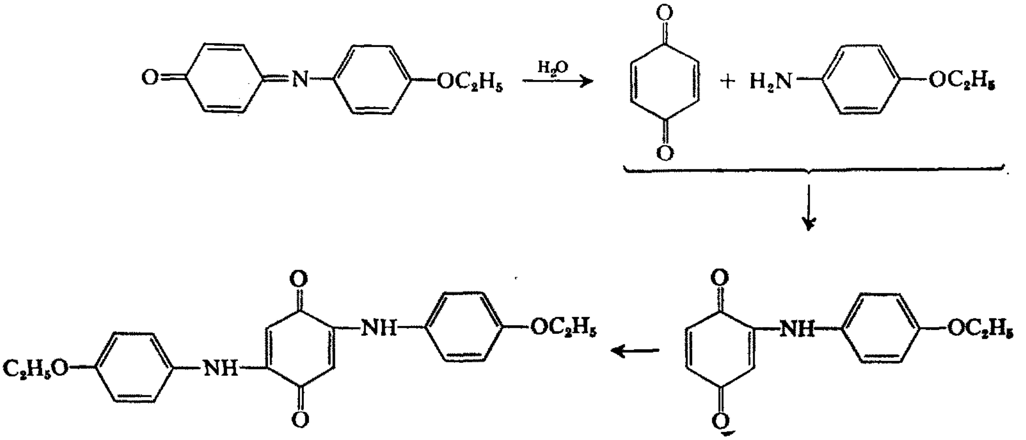


Catechol gives (see ref. 14, p. 146):



The formation of primary radicals from arylamines or phenols and their further reaction strongly depend on the acidity of the reaction medium. In acidic solutions the reactions usually lead to the formation of a smaller number of reaction products of relatively low molecular weight. There are many reasons for such a behaviour. Reaction (3) proceeds less easily in acidic solution, and the co-ordination of a metal ion with the free electron-pair of nitrogen or oxygen is more difficult in an acidic solution because of the competition of the hydrogen ions for the electron pair so that the radical formation is again hindered. The high rate of radical formation in alkaline solution increases the concentration of R$^\cdot$ so that the number of products likely to be formed is increased. Alkaline media also stabilize some types of radicals such as semiquinones, formed during the oxidation of polyphenols. The symmetric radical $^\cdot OPhO^-$ is formed.[31]

Acidity can also affect side-reactions such as hydrolyses, condensations, *etc.* Thus quinoneimines, formed during the oxidation of arylamines in neutral or alkaline solutions slowly hydrolyse to quinone and the amine. Further interaction gives mono- and diarylidoquinones as the final reaction products. Thus the oxidation of *p*-phenetidine shown by equation (4) in solutions of pH $\gg$ 5 proceeds further:[32]



(5)

Arylidoquinones are not very suitable as final reaction products for analytical procedures based on photometric measurements, because of their low water solubility; they form red-brown precipitates. This is yet another reason for avoiding alkaline reaction media for such reactions. Temperatures above 40–50° must be avoided because the rate of hydrolysis of quinoneimines according to equation (5) strongly increases on heating.

The disadvantage of the formation of polymeric or complex heterocyclic products (water-insolubility) is largely overcome by using compounds containing hydrophilic groups (OH, COOH, SO_3H *etc*). Thus sulphanilic acid, amino- and hydroxynaphthylsulphonic acids, aminocarboxylic acids, *etc*, have received great attention as reagents in catalytic analysis.[33–38] Alternatively, the solubility of the coloured reaction products can be enhanced by using water–organic solvent mixtures. Yatsimirskii and Philipov[39] used aqueous ethanol as solvent for the oxidation of 1-naphthylamine by potassium bromate, catalysed by molybdenum(VI).

Yatsimirskii has shown that the sensitivity of a catalytic method depends on the sensitivity of the method used to monitor the reaction.[6] Thus, when a spectrophotometric method is used, the reactants should be chosen so as to give a reaction product of high molar absorptivity. Quinoneimines and arylidoquinones are usually more intensely coloured than quinones, and their absorption bands fall in the spectral range where the sensitivity of the detectors is highest. These data, combined with those for the solubility of the corresponding compounds, indicate that quinoneimines are the reaction products most suitable for high sensitivity analysis.

Alternatively, the use of highly coloured products as indicator substances allows the reaction to be followed immediately after the start of the reaction, when the concentration x of the coloured reaction product is negligible compared to the initial reactant concentration C_0. The kinetic equation then simplifies to

$$\frac{dx}{dt} = kC_0 \tag{6}$$

where t is the time and k is the rate constant.

This equation gives a linear dependence between absorbance and time, which permits simple recording devices to be used and the time necessary for the analytical determinations to be shortened to 2–4 min.[40,41]

When both *o*- and *p*-positions in a phenol or arylamine molecule are hindered by bulky substituents, stable radicals are formed.[19] These radicals have molar absorptivities (in the visible part of the spectrum) of the order of 300–500 $\mathrm{l.\ mole^{-1}\ mm^{-1}}$ which makes them suitable for catalytic analysis purposes. Their main advantage is that usually reactions forming such radicals lead only to one product. Although the radicals are not very soluble in aqueous solution, organic solvent–water mixtures can be used as a reaction medium. However, such reactions have not yet been used in catalytic analysis, although their chemistry has been studied in some detail.[19]

Nature of the catalyst-reactant interaction

Most often, the first stage of the catalytic reaction is the substitution of water or another ligand attached to the metal ion, by the amine or phenol. In many instances this results in the formation of a charge-transfer complex. The catalyst, having free *d*-orbitals, acts as a strong Lewis acid and partially receives an electron from the highest energy nitrogen or oxygen orbital that is populated. The existence of such a complex was shown in the catalytic oxidation of *p*-phenetidine, discussed above.[42] The positively charged complex formed between the catalyst and the amine has an absorption band with a maximum at 540 nm and a molar absorptivity of 10^2–10^3 $\mathrm{l.\ mole^{-1}\ mm^{-1}}$. At temperatures below 5° the complex is comparatively stable but at higher temperatures an oxidation process takes place, which results in the formation of an arylamino radical:

$$\begin{aligned}\mathrm{V(V)} + \mathrm{H_2N\,.\,C_6H_4\,.\,OC_2H_5} &\rightarrow \mathrm{V(V)\ldots H_2N\,.\,C_6H_4\,.\,OC_2H_5}\\ &\rightarrow \mathrm{V(IV)} + {}^{\cdot}\mathrm{NH\,.\,C_6H_4\,.\,OC_2H_5} + \mathrm{H^+}\end{aligned} \tag{7}$$

The process proceeds further according to reaction scheme (4).

The formation of such complexes makes it easier to understand, for example, why titanium(IV) catalyses oxidation processes with oxygen-containing ligands but not with nitrogen-containing ones and why silver(I) preferentially catalyses oxidation reactions of nitrogen-containing reactants. Thus the arylamine or phenol chosen must be suitable for complexation with the catalyst. The pH of the medium must also be chosen so as not to decrease the degree of complexation with the catalyst.

Copper(II) in alkaline solution catalyses the oxidation of arylamines and phenols but in slightly acidic solutions it catalyses only the arylamine oxidation. This can be ascribed to the different stability of copper(II) complexes with oxygen- and nitrogen-containing ligands.

Complex formation between the catalyst and the reactant offers possibilities for the regulation of the selectivity of catalytic methods. The tendency of the amine or phenol to complex with metal ions can be modified if suitable substituents are introduced in the substrate molecule or if the acidity of the reaction medium is adjusted to a suitable value.

Indirect catalytic oxidation

In this process the catalyst takes part in a reaction which produces the actual oxidant of the other reactant. Thus copper, iron and titanium compounds catalyse the oxidation of many organic substances by hydrogen peroxide. Most frequently the role of the catalyst in these processes is to produce hydroxyl radicals from hydrogen peroxide, and these are the real oxidant. For example, Fenton's reagent acts as follows:

$$Fe^{2+} + H_2O_2 \rightarrow FeOH^{2+} + {}^{\cdot}OH \tag{8}$$

$${}^{\cdot}OH + RH \rightarrow H_2O + {}^{\cdot}R \tag{9}$$

Catalytic systems of this type are very useful for the oxidation of compounds with sterically hindered donor atoms or with donor atoms which do not tend to form complexes with the catalyst. In such instances small uncharged radicals with a high oxidation potential (such as $^{\cdot}OH$) can be produced by a catalytic reaction and used up for the oxidation of the substrate.

Another example of this type is the accelerating action of phenols and hydroxycarboxylic acids on the oxidation of arylamines catalysed by vanadium(V).[30,43–48] The tendency of oxygen donor atoms to complex with vanadium(V) is greater than that of nitrogen, so that charge-transfer complex formation and hence the oxidation processes with phenols proceed more readily than with arylamines. The phenoxy radicals produced oxidize the arylamine very rapidly, and therefore increase the overall reaction rate. These reactions are examples of activated catalytic processes, which will be discussed in detail in Part II.

The choice of a suitable oxidant for a catalytic oxidation is as important as the choice of the reductant, and is primarily governed by the two conditions stated in the introduction. Usually it is not difficult to find an oxidant with an oxidation potential higher than that of the reductant. The condition $E_{Ox} > E_M$, however, restricts the number of possible oxidants especially when the oxidation potential of the couple $M^{(n+1)+}/M^{n+}$ is high. For example, there are only two oxidants used in the catalytic reactions of silver(I)—persulphate ion[33] and cerium(IV)[49] which can oxidize silver(I) to silver(II) ($E_M{}^0 = 2{\cdot}00$ V). Sometimes this restriction can be overcome by using a suitable complexing agent to lower the oxidation potential of the couple $M^{(n+1)+}/M^{n+}$.[33] In such instances the complexes of the ligand with the form of the catalyst that participates in the rate-limiting reaction step must be labile. Examples of this type will be discussed in detail in Part II.

The main difficulties in choosing a suitable oxidant arise from the second condition—the existence of kinetic obstacles to direct interaction between the reductant and the oxidant. Oxidants such as permanganate, cerium(IV), manganese(III), and cobalt(III) which react readily with organic compounds are seldom used for catalytic oxidation process with organic substances. When hydrogen peroxide is used as an oxidant, the greatest difficulty is the purification of the reagents from commonly occurring metals ions such as Cu^{2+}, Fe^{3+}, Mn^{2+}, Co^{2+} which catalyse the oxidations by hydrogen peroxide even when present in very small amounts. However, these catalytic effects can become an advantage when such ions are to be determined: many sensitive analytical catalytic procedures have been developed for the determination of these ions, using hydrogen peroxide as the oxidant.[50–55]

Halates are very suitable as oxidants for catalytic oxidations of organic substrates. At 20–50° they usually react only very slowly with organic compounds in spite of their relatively high oxidation potential. However, under such conditions they can oxidize rapidly many metal ions, especially the lower oxidation states of molybdenum, tungsten, vanadium and osmium.

Persulphate is another oxidant often used in catalytic analysis. It readily oxidizes silver(I) and copper(I) to higher oxidation states and thus is used in catalytic methods for the determination of these elements. However, the measurable rate of the uncatalysed oxidation is a serious disadvantage. This arises because persulphate dissociates in solution to give sulphate radicals:

$$S_2O_8^{2-} \rightarrow 2\,{}^{\cdot}SO_4^- \qquad (10)$$

which themselves oxidize the organic compound. Other authors[56] consider that persulphate acts through the production of hydroxyl radicals:

$$ {}^{\cdot}SO_4^- + H_2O \rightarrow HSO_4^- + {}^{\cdot}OH \qquad (11)$$

REDOX REACTIONS WITH INORGANIC SUBSTRATES

Inorganic reductants used in catalytic reactions are usually monodentate and charged, and, of course, are smaller than the organic molecules discussed above. Typical examples are I^-, Cl^-, $S_2O_3^{2-}$, AsO_2^- and NH_3.

Reactions in which more than one electron is transferred have been postulated as proceeding by one- or two-electron mechanisms, that is, by several one-electron steps or by a simultaneous transfer of two or even more electrons. The one-electron scheme has been supported by numerous experimental data not only for such reactions as

$$\begin{aligned} &\mathrm{Ag(II)} + \mathrm{Fe(II)} \rightarrow \mathrm{Ag(I)} + \mathrm{Fe(III)} \qquad (12)\\ &\mathrm{Ag(I)} + \mathrm{Fe(II)} \rightarrow \mathrm{Ag^0} + \mathrm{Fe(III)} \end{aligned}$$

but also for more complicated reations as, for example, the oxidation of sulphurous acid with iron(III), catalysed by copper(II)[57]:

$$\begin{aligned} &\left.\begin{aligned} &\mathrm{Fe(III)} + H_2SO_3 \rightarrow \mathrm{Fe(II)} + {}^{\cdot}HSO_3 + H^+\\ &\mathrm{Fe(II)} + {}^{\cdot}HSO_3 + H^+ \rightarrow \mathrm{Fe(III)} + H_2SO_3 \end{aligned}\right\} \text{slow}\\ &2\,{}^{\cdot}HSO_3 \rightarrow H_2S_2O_6 \qquad (13)\\ &\left.\begin{aligned} &\mathrm{Fe(III)} + {}^{\cdot}HSO_3 + H_2O \rightarrow \mathrm{Fe(II)} + SO_4^{2-} + 3H^+\\ &\mathrm{Cu(II)} + {}^{\cdot}HSO_3 + H_2O \rightarrow \mathrm{Cu(I)} + SO_4^{2-} + 3H^+ \end{aligned}\right\} \text{fast}\\ &\mathrm{Cu(I)} + \mathrm{Fe(III)} \rightarrow \mathrm{Cu(II)} + \mathrm{Fe(II)} \end{aligned}$$

In some inorganic redox reactions, as for instance those involving thallium (III), *e.g.*,

$$\mathrm{Hg^0} + \mathrm{Tl(III)} \rightarrow \mathrm{Hg(II)} + \mathrm{Tl(I)} \qquad (14)$$

a two-electron mechanism is thought to occur.[58] Ashurst and Higginson, however, have shown that the kinetic data for similar reaction with iron(II) strongly indicate a one-electron mechanism:[59]

$$\mathrm{Fe(II)} + \mathrm{Tl(III)} \leftrightharpoons \mathrm{Fe(III)} + \mathrm{Tl(II)} \qquad (15)$$
$$\mathrm{Tl(II)} + \mathrm{Fe(II)} \rightarrow \mathrm{Tl(I)} + \mathrm{Fe(III)}$$

As Basolo and Pearson emphasized "at the present time there is no good evidence that simultaneous, or near-simultaneous, transfer of more than one electron in a true electron-transfer reaction ever occurs".[60]

In most instances the existence of a two-electron mechanism is connected with the transfer of an atom or a group of atoms from one reactant to the other, as, for example:[61]

$$O_2SO^{2-} + OCl^- \rightarrow O_2SO_2^{2-} + Cl^- \qquad (16)$$

It is of interest in this connection to quote the conclusions of Higginson[62] drawn after considering the mechanisms of many redox reactions:

(*a*) species derived from transition elements react by a set of one-electron steps;

(*b*) if both reacting species are derived from non-transition elements, two-electron reactions usually take place;

(*c*) if one of the reagents is a transition-element ion and the other compound is derived from a non-transition element, the one-electron mechanism occurs more often;

(*d*) if one of the reactants is a free radical, a one-electron reaction is to be expected.

In connection with catalytic analysis it is of interest to note that the reactions with the participation of transition-element species usually proceed by one-electron mechanisms. It can be seen that even in the few examples of two-electron reactions [of type (*c*)] the main reason that they were included in this group is that it had been impossible to detect the intermediates which correspond to one-electron mechanisms with the techniques then available. For this reason the importance of the application in this field of new physical methods such as EPR and NMR can hardly be overestimated.

The one-electron mechanism of many redox reactions catalysed by transition-element ions often results in the production of unstable intermediates. Duke has suggested the term "reactates" for such species,[63] which includes free radicals ($^{\cdot}SO_4^-$, $^{\cdot}OH$), atoms (Cl, O) or species in unfamiliar oxidation states [Mn(V), Sn(III)]. Many examples are known of the formation of reactates in the course of the catalytic reactions. For example, the role of $^{\cdot}SO_4^-$ and $^{\cdot}OH$ in redox reactions with $S_2O_8^{2-}$ and H_2O_2 has already been discussed.

The oxidation of hydrazine by iron(III), catalysed by copper(II),[64] proceeds through the formation of the radical $^{\cdot}N_2H_3$:

$$\begin{gathered}
N_2H_4 + \mathrm{Fe(III)} \xrightarrow{\text{fast}} {}^{\cdot}N_2H_3 + \mathrm{Fe(II)} + H^+ \\
{}^{\cdot}N_2H_3 + \mathrm{Fe(III)} \xrightarrow{\text{slow}} N_2H_2 + \mathrm{Fe(II)} + H^+ \\
{}^{\cdot}N_2H_3 + \mathrm{Cu(II)} \xrightarrow{\text{fast}} N_2H_2 + \mathrm{Cu(I)} + H^+ \qquad (17) \\
\mathrm{Cu(I)} + \mathrm{Fe(III)} \xrightarrow{\text{fast}} \mathrm{Cu(II)} + \mathrm{Fe(II)} \\
2\,{}^{\cdot}N_2H_3 \rightarrow N_4H_6 \rightarrow 2NH_3 + N_2
\end{gathered}$$

The catalytic effect is thus due to the greater reactivity of copper(II) in the oxidation of $^{\cdot}N_2H_3$ compared with iron(III), which is possibly due to the stronger tendency of copper(II) to complex with nitrogen-containing donors. The oxidation of iodide by dichromate, catalysed by iron(II), proceeds *via* the formation of Cr(V) and Cr(IV) as intermediates in the reduction of Cr(VI) and Cr(III) (see ref. 4, p. 309).

The catalysts of inorganic redox reactions act most often by a direct mechanism, by alternate oxidation–reduction processes with the oxidant and reductant. Thus in the oxidation of chloride by cerium(IV) the catalyst silver acts through the oxidation states Ag(I) and Ag(II).[49] The oxidation of iodide by halates in the presence of vanadium compounds proceeds *via* the consecutive formation of V(IV) and V(V).[65] Another example of this type of mechanism is provided by the oxidation of arsenic(III) with cerium(IV), catalysed by iodide or osmium(VIII). Thus, one of the most widely used catalytic reactions is considered[66] to proceed *via*

$$\begin{aligned} I^- + \mathrm{Ce(IV)} &\rightarrow \mathrm{Ce(III)} + I^0 \\ I^0 + \mathrm{As(III)} &\rightarrow \text{intermediate} \\ \text{intermediate} + \mathrm{Ce(IV)} &\rightarrow \mathrm{Ce(III)} + \mathrm{As(V)} + I^- \end{aligned} \tag{18}$$

An alternative is

$$\begin{aligned} I^0 + \mathrm{Ce(IV)} &\rightarrow \mathrm{Ce(III)} + I^+ \\ I^+ + \mathrm{As(III)} &\rightarrow \mathrm{As(V)} + I^- \end{aligned} \tag{19}$$

The catalytic action of osmium also involves its alternate reduction and oxidation.[67]

An indirect catalytic mechanism does sometimes occur, probably, for example, in the oxidation of ammonia by hydrogen peroxide, catalysed by copper compounds.[68] Copper(II) cannot oxidize ammonia, but it reacts with peroxide to form hydroxyl radicals, which oxidize the ammonia. The oxidation of iodide by hydrogen peroxide, catalysed by iron compounds, is probably another example of this type.[69]

In other instances, the catalyst is produced during the reaction as one of the reaction products, so that the process becomes autocatalytic, as in the oxidation of arsenite by iodate, catalysed by iodide:[70]

$$IO_3^- + 3AsO_2^- \rightleftharpoons I^- + 3AsO_3^- \tag{20}$$

Complex formation between the catalyst and the reagents during the reaction seems to be important in inorganic catalytic redox reactions although only in a few instances is there direct experimental evidence for intermediates of this type.[71,72] At the same time, many considerations indicate the formation of such complexes. For example, the addition of ligands that form stable, inert complexes with the catalyst usually results in an inhibition of the catalysis (ref. 6, p. 95). In some instances kinetic data are available for the formation of such complexes.[65]

The oxidation of many inorganic species used in catalytic analysis, such as chloride or ammonia, needs oxidants with higher oxidation potentials than those used to oxidize arylamines and phenols. For this reason oxidants such as cerium(IV), permanganate, chromate, molybdate, iodine and bromine are often used in such reactions, as are hydrogen peroxide, halates and other oxidants also used for oxidizing the organic compounds. For the same reason, the catalysts for these reactions are usually metal ions which in their highest oxidation state are strong oxidants [cobalt(III), nickel(III), silver(II), manganese(III), chromium(VI), osmium(VIII), vanadium(V), *etc.*]. Because of the higher oxidation potentials associated with the reagents and catalysts in this group of reactions, very often it is necessary to change the oxidation potential associated with either the catalyst or the oxidant by complex formation in order to fulfill the condition $E_{\mathrm{Ox}} > E_{\mathrm{M}} > E_{\mathrm{Red}}$, which makes possible the catalytic action of the metal ion.

The sole use of inorganic reactants is analytically advantageous in that there are usually no side-reactions, or further reactions of the monitored reaction product. Even in reactions where dimerization of inorganic radicals is possible, together with further oxidation [see for instance reaction scheme (17)], the number of compounds formed is restricted. The absence of a number of products in the system makes possible the application of *different* methods to follow the reaction kinetics and this widens the limits of application of catalytic analysis. Amperometric methods are a good example. They have been applied to catalytic methods for the determination of sulphides and sulphur-containing compounds, chromium, molybdenum, germanium, *etc.*, by the oxidation of iodide by hydrogen peroxide or of azide by iodine.[73–77]

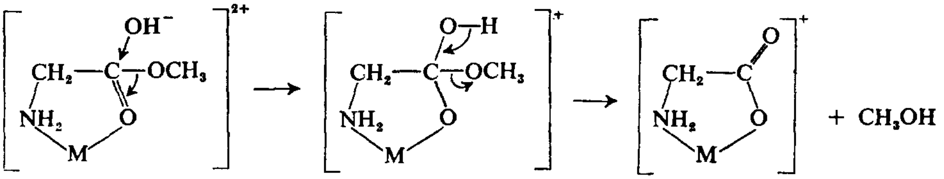
Polarography has similarly been applied in catalytic analysis, based on electrochemical reduction or oxidation processes with inorganic substances such as H^+, H_2O_2, NO_3^-, ClO_4^-, catalysed by metal ions.[78–81]

REACTIONS CATALYSED BY IONS NOT CHANGING THEIR OXIDATION STATE DURING THE COURSE OF THE REACTION

Reactions of this type include the catalytic rearrangement, decomposition, substitution and hydrolysis of organic and inorganic compounds in the course of which the catalyst does not change its oxidation state. The catalytic action can be due to the polarizing effect of the catalyst on bonds in the molecule of a reactant, or to the ability of the catalyst to bring the reactants together or to orientate them in a way suitable for the reaction to proceed.

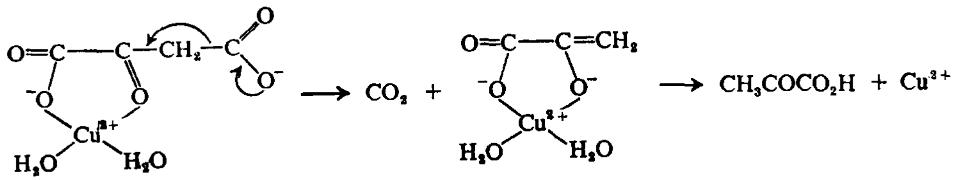
This group of catalytic reactions has not been developed as an analytical tool to such an extent as the preceding one, but it is important because it deals with reactions which make possible the determination of ions with filled outer *s*-, *p*- or *d*-electron shells, such as Al^{3+}, Ca^{2+}, Zn^{2+}, Cd^{2+} and Pb^{2+}.

The hydrolysis of amino-acid derivatives and phosphate esters is the most studied of this type of reaction. These reactions are catalysed by metal ions such as Cu^{2+}, Zn^{2+}, Mn^{2+} and Cd^{2+}. The metal ion catalyst forms a chelate with the reactant. The positive charge of the metal ion affects the electron distribution in the ligand in such a way as to facilitate the attack of the hydroxide ion. For example, in the hydrolysis of alkyl- and aryl-esters of glycine,[82] the metal ion causes an electron shift from the carbon atom of the carbonyl group, thus facilitating attack by hydroxide:



(21)

The decarboxylation of β-keto acids was first used in catalytic analysis by Bontchev and his co-workers.[83,84] For example the decarboxylation of oxaloacetic acid is catalysed by metal ions such as Zn^{2+}, Mg^{2+}, Mn^{2+} and Cu^{2+}. In the presence of copper(II), the decarboxylation proceeds as follows:



(22)

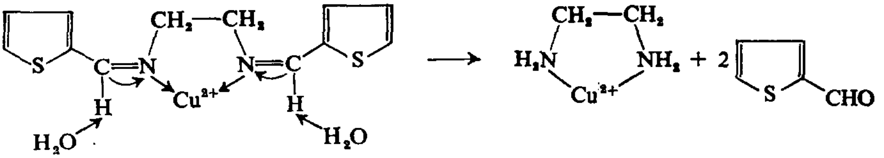
The catalyst forms chelates with both the substrate and the product, but the latter has a lower stability constant because of the change in inductive effect of the carboxyl group as it changes from the β- to the α-position. The substrate therefore displaces metal ion from the chelate with the product, and the cycle begins again. In such catalysed reactions any hindrance of chelate formation results in a decreased catalytic activity. Thus the presence of metal ions has no effect on the rate of decarboxylation of β-keto acids with a second carboxylic group too far from the keto group to form strong chelates, or on ketomonocarboxylic acids.[85] Hydrolytic reactions show the same dependence on the chelating ability of the substrate. Moreover, if the catalyst is already complexed by other ligands, so that the rate of substitution of these ligands by the substrate is very slow, or if stable inert complexes are formed with these ligands, the catalytic effect can decrease or even disappear.

Finally, the nature of the complex formed influences the catalysis. It was found, for example, in the catalytic decarboxylation of dimethyloxaloacetic acid that the catalyst forms two different complexes with the acid, only one of which can undergo decarboxylation.[86]

The metal ion acts in the catalytic, hydrolytic and decarboxylation reactions mainly because of its positive charge. It might be expected, therefore, that the effect of the dipositively charged ions will be of the same order and hence their overall catalytic action will depend on their complexing abilities. Numerous examples provide evidence for the validity of this assumption. In the hydrolytic reaction (21) the order of catalytic activity is

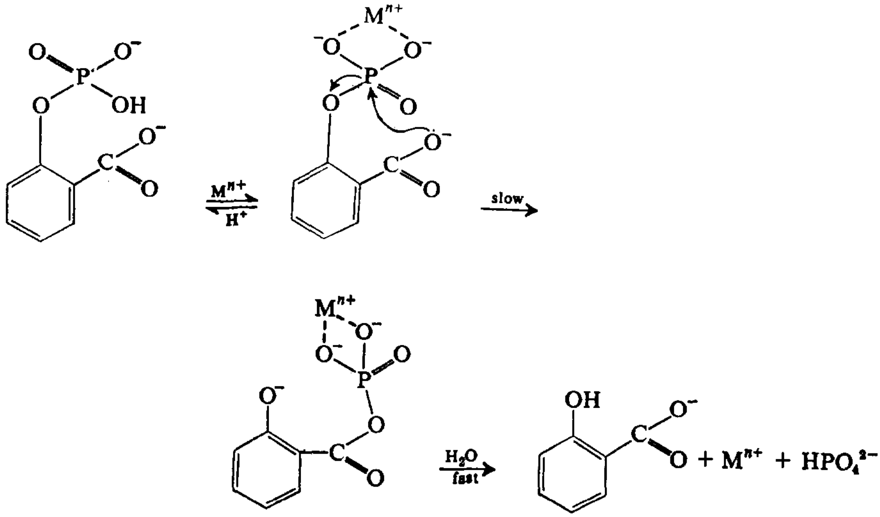
$$\text{Cu(II)} > \text{Co(II)} > \text{Mn(II)} > \text{Ca(II), Mg(II)}$$

which is identical with the Irving-Williams order. The same reasons are responsible for the evident connection between the position of the metal-ion catalyst in Sidgwick's classification[87] and the character of the donor atoms in the substrate molecule. Metal ions of the third group of this classification which bond to nitrogen more strongly than to oxygen are good catalysts for reactions of substrates with nitrogen donor atoms. In the hydrolysis of a Schiff's base, for example:



(23)

copper(II) and nickel(II) are the best bivalent catalysts (ref. 85, p. 220). For the same reason mercury(II), lead(II) and silver(I) are the most effective catalysts for the hydrolysis of thiol esters (ref. 85, p. 217). Similarly hydrolysis of substrates containing only oxygen donors is catalysed preferentially by metal ions of the first group of Sidgwick's classification, which tend to form complexes with oxygen in preference to other donors. Thus the hydrolysis of salicyl phosphate:



(24)

is catalysed by UO_2^{2+}, VO^{2+}, ZrO^{2+}, Fe^{3+} and Cu^{2+} whereas Ni^{2+}, Co^{2+}, Zn^{2+} and Cd^{2+} have no influence on the process.[88]

From an analytical point of view there are two main shortcomings of catalysed hydrolytic and decarboxylation reactions, namely, the low sensitivity and selectivity of these reactions. A comparatively large concentration of the catalyst is usually necessary to increase the reaction rate by a measurable extent. Yatsimirskii and Tikhonova,[89,90] the first authors to use a hydrolytic reaction in catalytic analysis, were able to determine 10 μg/ml of cadmium and 1 μg/ml of lead (total amounts of 250 μg of Cd^{2+} and 25 μg of Pb^{2+}), using the hydrolysis of the ethyl ester of cysteine. It is evident that this sensitivity is far less than that of a large number of other catalytic methods. The sensitivity of the decarboxylation reactions is also low. The catalytic effect becomes measurable at catalyst concentrations greater than about $10^{-3}M$, which is quite insufficient for trace analytical purposes. The sensitivity can be increased, however, by complexing the metal so as to increase the actual charge on the metal, as has been demonstrated[83,84] for the decarboxylation of oxaloacetic acid, which has been developed as a sensitive method for the determination of zinc.[84] The use of suitable complexing agents can contribute also to the selectivity of these catalytic reactions as will be discussed in Part II.

Catalytic substitutions of ligands in the co-ordination sphere of a metal ion are other examples of this group of reactions. They were first used in catalytic analysis by Asperger *et al.* for the determination of mercury.[91–94] These authors used the replacement of cyanide from hexacyanoferrate(II) by a water molecule:

$$[Fe(CN)_6]^{4-} + H_2O \rightleftharpoons [Fe(CN)_5H_2O]^{3-} + CN^- \qquad (25)$$

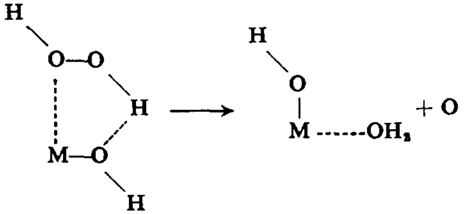
The reaction is monitored by adding nitrosobenzene, which readily replaces the water molecule in the inner co-ordination sphere of the product to form $[Fe(CN)_5PhNO]^{3-}$, a red-violet, soluble complex.[95]

The substitution of cyanide in hexacyanoferrate(II) by 2,2′-bipyridyl and 1,10-phenanthroline has also been used for the determination of mercury(II) and silver(I).[96,97]

The complete replacement of the cyanide ions in hexacyanoferrate(II) by water molecules gives $Fe(H_2O)_6^{2+}$, which is rapidly oxidized by atmospheric oxygen. The resulting iron(III) reacts with the unchanged hexacyanoferrate(II) and a blue colloidal solution of Prussian Blue is formed. Besides mercury(II), silver(I) and gold(III) also catalyse this reaction, which has been used for determination of these elements.[98–100]

The mechanism of these substitution processes and especially the role of the catalyst is at present not quite clear. It is worth noting, however, that the catalysts form stable complexes with the ligands whose substitution they catalyse.

The fact that in the reactions of this group the catalyst remains in the same oxidation state does not exclude the participation of the catalyst in oxidation processes. Thus the oxidation of iodide by hydrogen peroxide in acidic solution is catalysed by thorium(IV), zirconium(IV), hafnium(IV), niobium(V) and tantalum(V) which do not change their oxidation state during the course of the reaction.[6] In moderately acidic solutions they are present in the form of the corresponding oxo- or hydroxo-ions (for example ZrO^{2+}, $ThOH^{3+}$). Yatsimirskii has suggested[101] that the catalytic effect of these ions is due to the formation of cyclic peroxides, *e.g.*



(26)

The O—O bond is more labile in the complex, and it decomposes with the formation of free oxygen atoms, although it seems more probable that the reactates formed during the process are hydroxyl radicals, because the direct formation of oxygen atoms from the hydrogen peroxide molecule seems energetically less favourable than that of ˙OH. The reactates then oxidize the iodide. The catalyst does not react directly with the substrate and does not change its oxidation state during the reaction.

It is of interest to note that vanadium(V) and titanium(IV) oxo-ions, which are not among the catalysts for this reaction, catalyse the oxidation of thiosulphate by hydrogen peroxide as do Th(IV), Zr(IV), Nb(V), Ta(V) and Hf(IV).[6] If the role of the catalyst in these two reactions is only to produce reactates from H_2O_2 (or ˙OH) which then oxidize the substrate, the absence of a catalytic effect of V(V) and Ti(IV) in the first reaction is inexplicable. It seems possible, therefore, that the oxidation of the reductant occurs by interaction with a peroxide complex of the catalyst. When bond formation between the catalyst and the reductant is possible, and therefore a ternary complex can be formed, vanadium(V) and titanium(IV) catalyse the process (as for thiosulphate oxidation). If such a complex with the participation of the substrate cannot be formed [V(V) and Ti(IV) do not form iodide complexes] the oxo-ions of both elements do not influence the reaction (as for iodide oxidation).

Zusammenfassung—Die Mechanismen einiger bei der katalytischen Analyse verwendeter Reaktionen werden diskutiert. Die Kenntnis des Mechanismus einer katalytischen Reaktion kann bei der Auffindung neuer katalytischer Reaktionen und der Auswahl der besten Versuchsbedingungen von Nutzen sein. Ferner können Möglichkeiten zu weiterer Steigerung der Empfindlichkeit erkannt werden.

Résumé—On discute des mécanismes de quelques réactions utilisées en analyse catalytique. La connaissance du mécanisme d'une réaction catalytique peut aider dans le développement de nouvelles réactions catalytiques et le choix de conditions optimales, et montrer les possibilités de nouveaux accroissements de sensibilité.

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ACID DISSOCIATION AND SPECTROPHOTOMETRIC BEHAVIOUR OF 8-QUINOLINESELENOL IN WATER–DIOXAN MIXTURES

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Summary—The acid dissociation constants of 8-quinolineselenol, 8-quinolinol and 8-quinolinethiol in water–dioxan mixtures of varying solvent composition were determined potentiometrically or spectrophotometrically. The absorption spectra of 8-quinolineselenol in the same solvents were also obtained. The acid dissociation phenomena, stability towards oxidation and the absorption spectra of the reagents are discussed in connection with the existing forms. It is verified that 8-quinolineselenol exists as a zwitterion in water–dioxan mixtures of low or high dioxan content.

IN RECENT years, 8-quinolinethiol and 8-quinolineselenol have become of interest as analytical reagents.[1–4] 8-Quniolineselenol appears to be a more selective chelating agent than 8-quinolinol and 8-quinolinethiol, probably because of the lower electronegativity and larger size of the selenium atom.

Therefore, a study of metal complexes of 8-quinolineselenol is of value, especially as only a few studies of 8-quinolineselenol complexes have been reported.[2–4] This paper deals with a comparative study of the acid dissociation and spectrophotometric behaviour of 8-quinolineselenol, 8-quinolinethiol and 8-quinolinol in water–dioxan mixtures.

EXPERIMENTAL

Reagents

8-*Quinolineselenol.* The reagent was prepared by the modified method of Sekido, Fernando and Freiser.[3] The neutral salt of 8-quinolineselenol prepared from 8,8′-diquinolyldiselenide was dried under reduced pressure. This reagent was proved to be anhydrous and was stable for more than a week *in vacuo.*

The sodium salt of 8-quinolinethiol. 8,8′-Diquinolyldisulphide was first synthesized by the method of Edinger.[5] The sodium salt was then prepared by the following procedures. Pure disulphide, 5·5 g, was dissolved in a mixture of 20 ml of concentrated hydrochloric acid and 6 ml of 50% hypophosphorous acid, and the solution was heated under reflux for about 2 hr. The solution was cooled and filtered, and then a yellow precipitate was obtained by adding excess of saturated sodium hydroxide solution dropwise whilst a stream of nitrogen gas was passed through the solution. The pure sodium salt, obtained by recrystallization a few times from alcohol–ether, was dried *in vacuo.* The sodium salt prepared in this way was proved to contain 1–2 molecules of water of crystallization, and to be stable for several months under a nitrogen atomosphere.

8-*Quinolinol.* The reagent was reagent grade and was further purified by recrystallization from alcohol, m.p. 73·5–74·5°.

Dioxan. Commercial dioxan was treated with hydrochloric acid and metallic sodium and then distilled at 101·5–102·0°. Freshly distilled dioxan was further purified by freezing, and was used in a few days.

Carbonate-free sodium hydroxide solutions were prepared by the usual method and the other reagents used were reagent grade where possible.

Apparatus

pH meter. Horiba Model P, with glass and calomel electrodes, standardized against aqueous buffers (pH 4·01 and 6·86). The relationship between the pH meter reading (*B*) and the hydrogen ion concentration ($[H^+]$) in water–dioxan mixtures is defined as the following according to Van Uitert and Haas,[7]

$$-\log [H^+] = B + \log U_0 + \log \gamma_\pm \tag{1}$$

where U_0 is a conversion factor at zero ionic strength, $\gamma_\pm$ is the mean activity coefficient for the solvent composition and ionic concentration. The values of $\log U_0$ and $\log \gamma_\pm$ were taken from the data of Van Uitert and Haas,[7] and Harned and Owen,[8] respectively. Equation (1) was found to hold, with an error of 0·05 pH units, in this experiment.

Procedures

Nitrogen gas was bubbled through the sample solutions during titration, and the temperature was controlled to 25·0 ± 0·1° by circulating water through double-walled titration and reference cells. Titrations were made on the solutions which contain the reagents, perchloric acid and sodium perchlorate. The range of concentration was from $9{\cdot}4 \times 10^{-4}$ to $1{\cdot}0 \times 10^{-2}M$ for the reagents, and from $2{\cdot}0 \times 10^{-3}$ to $2{\cdot}0 \times 10^{-2}M$ for the acid, ionic strength varied from 0·001 to 0·1, and dioxan content ranged from 0 to 75% v/v.

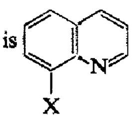
Spectrophotometric measurements were also made under various conditions; (*a*) in solvents of varying dioxan content, (*b*) at varying time, (*c*) in a stream of nitrogen gas, (*d*) by adding hypophosphorous acid as reducing agent.

CALCULATION

Acid dissociation of 8-quinolinol and its analogues takes place as follows

$$\mathrm{H_2R^+} \overset{k_{a_1}}{\rightleftharpoons} \mathrm{H^+ + HR \text{ and } H^+R^-} \tag{2}$$

$$\mathrm{HR \text{ and } H^+R^-} \overset{k_{a_2}}{\rightleftharpoons} \mathrm{H^+ + R^-} \tag{3}$$

where R is  (X = O, S or Se). The neutral and zwitterion forms are denoted by HR and H^+R^-, respectively, and k_{a_1} and k_{a_2} are stoichiometric acid dissociation constants. The formation function of the species HR and H_2R^+ corresponding to equations (2) and (3) is given by Bjerrum's method[13] as follows

$$\bar{N}_h - (\bar{N}_h - 1)\frac{[H^+]}{k_{a_2}} - (\bar{N}_h - 2)\frac{[H^+]^2}{k_{a_1} . k_{a_2}} = 0 \tag{4}$$

where $\bar{N}_h$ is the average number of hydrogen ions bound to each reagent molecule. Since the difference between the numerical values of k_{a_1} and k_{a_2} for the reagents is large, the first term of equation (4) is negligible in the acidic region and thus rearrangement of equation (4) leads to equation (5), similarly the third term is negligible in the basic region and equation (6) is obtained:

$$k_{a_1} = \frac{(2 - \bar{N}_h)}{(\bar{N}_h - 1)} [H^+] \tag{5}$$

$$k_{a_2} = \frac{(1 - \bar{N}_h)}{\bar{N}_h} [H^+] \tag{6}$$

$\bar{N}_h$ is calculated by means of equation (7)

$$\bar{N}_h = \frac{[HR]_0 + [H]_0 + [OH^-] - [H^+] - [OH]_0}{T_R} \tag{7}$$

T_R is the total concentration of the reagent, $[HR]_0$ is the concentration of the reagent in the HR or H^+R^- form, and $[H]_0$, $[OH]_0$, $[H^+]$ and $[OH^-]$ are the concentrations of perchloric acid titrated, sodium hydroxide added, free hydrogen ion and free hydroxide ion, respectively. In the case of 8-quinolinethiol the $[HR]_0$ term in the numerator of equation (7) can be omitted because the sodium salt is used. The values of $[OH^-]$ are calculated by employing the values of K_w in water–dioxan mixtures, given by Harned and Owen.[8]

On the basis of values of k_{a_1} and k_{a_2} obtained thus, the constants, K_{a_1} and K_{a_2}, which are good approximations to the thermodynamic constants,[7,9] are determined according to the following equations, with the use of mean activity coefficients given for hydrochloric acid by Harned and Owen.[8]

$$\mathrm{p}K_{a_1} = \mathrm{p}k_{a_1} \tag{8}$$

$$\mathrm{p}K_{a_2} = \mathrm{p}k_{a_2} + 2\log\left(\frac{1}{\gamma_\pm}\right) \tag{9}$$

where it is assumed that $\gamma_{\mathrm{H}^+} = \gamma_{\mathrm{R}^-} = \gamma_{\mathrm{H_2R}^+} = \gamma_\pm$ and $\gamma_{\mathrm{HR}} = 1$. Association of solutes which may be expected to take place in solvents of high dioxan content was ignored.

RESULTS AND DISCUSSION

Potentiometric studies

Results. A number of titrations for 8-quinolinol, 8-quinolinethiol and 8-quinolineselenol were performed. In order to examine the accuracy of k_{a_2} calculated according to equations (5), (6) and (7), the formation curves were checked by comparing the experimental and theoretical values (Fig. 1).

For 8-quinolinol the agreement is quite satisfactory, but for 8-quinolinethiol and 8-quinolineselenol good agreement was not always obtained, because of experimental error. The causes of error were proved to be oxidation of the reagents by air or dioxan and the glass electrode error. Therefore, much attention was paid, especially

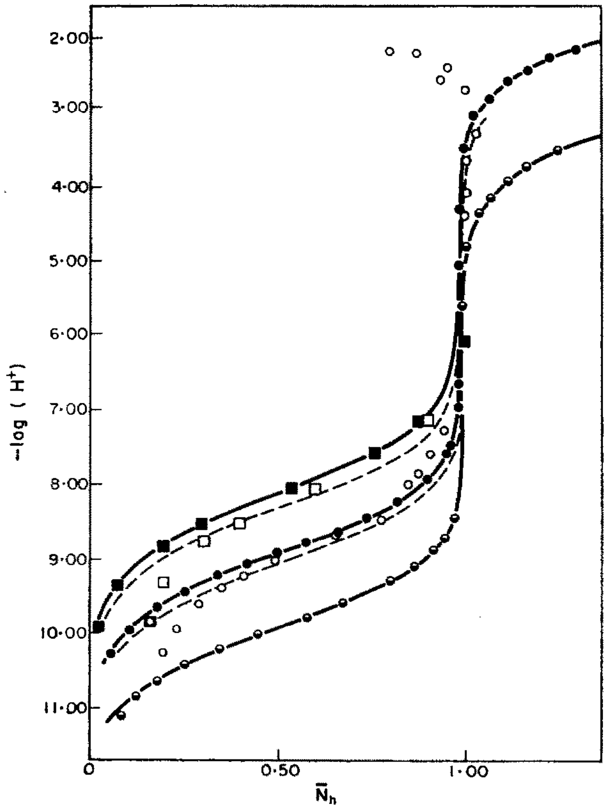


FIG. 1.—Formation curves for 8-quinolinol (—⊖—), 8-quinolinethiol (—●—, – –○– –) and 8-quinolineselenol (—■—, – –□– –) in 50% water–dioxan mixture. The plots (– –○– –, – –□– –) are erroneous data.

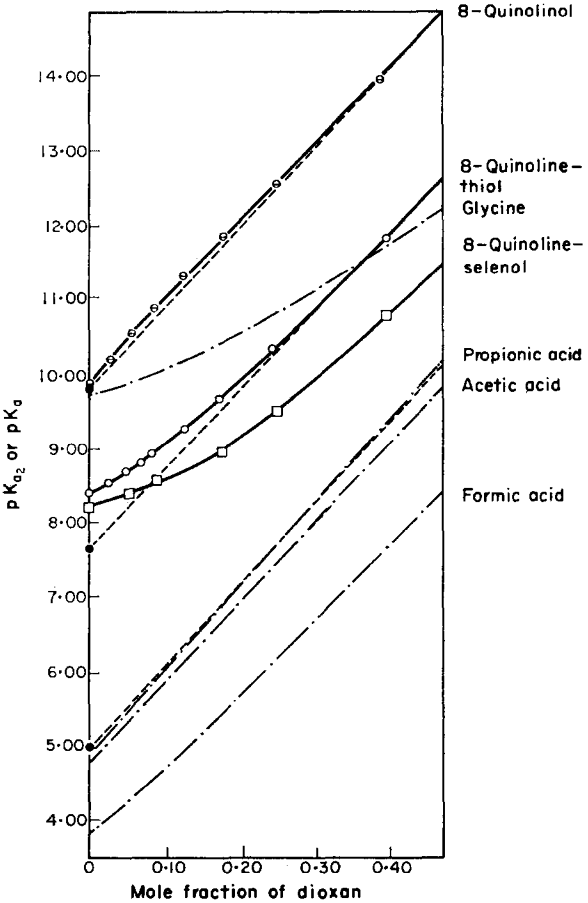


FIG. 2.—pK_{a_2} of the reagents and pK_a of monoprotic acids and glycine. Reliability of pK_{a_2} is ±0·07 for 8-quinolinol and 8-quinolinethiol, and ±0·1 for 8-quinolineselenol.

for 8-quinolineselenol, to titration procedure in order to minimize these errors. At first, titrations for 8-quinolineselenol were carried out under the same conditions as for 8-quinolinethiol, but the second equivalence point for 8-quinolineselenol did not coincide with that for 8-quinolinethiol. Disagreements of the formation functions corresponding to these titration curves are serious in the region $\bar{N}_h < 0{\cdot}5$ because of oxidation. Therefore the most reliable data for 8-quinolineselenol were obtained from the buffer region of the titration curve. To calculate the values of $\bar{N}_h$ for strongly acidic solution, the method of Irving and Rossotti[9] was applied to equation (7), otherwise serious disagreement for formation functions was observed in the region $-\log [H^+] < 3{\cdot}5$. The experimental results agreed with the theoretical ones. Only K_{a_1} for 8-quinolineselenol was determined spectrophotometrically. The acid dissociation constants (pK_{a_2}) obtained for these reagents are plotted as a function of dioxan content in Fig. 2.

Discussion. Activity coefficients in mixed solvents are defined as

$$\log \gamma = \log \gamma_0 + \log \gamma^* \tag{10}$$

where $\log \gamma$, $\log \gamma_0$ ($= \lim_{\mu \to 0} \gamma$) and $\log \gamma^*$ correspond to the total, primary and secondary medium effect, respectively. Then the following relationship would hold[10]

$$pK_a = pK_a^0 + 2 \log \gamma_0 \qquad (11)$$

where K_a and K_a^0 are the acid dissociation constants in the mixed solvent and in pure water, respectively. In the water–dioxan system the plots of $\log \gamma_0$ *vs.* mole fraction of dioxan in the range $n_2 = 0$–$0{\cdot}5$ have been found to be linear in the case of a monoprotic acid. Consequently the plots of pK_a *vs.* mole fraction of dioxan are linear. The values of pK_a of acetic acid, propionic acid, formic acid and glycine, which are given by Harned and Owen,[8] are shown in Fig. 2. The former three acids are monoprotic. In the case of glycine the zwitterion form is predominate in aqueous medium.

In Fig. 2, the pK_{a_2} values for 8-quinolinol, 8-quinolinethiol and 8-quinolineselenol are compared with pK_a for monoprotic acids and glycine. The values of pK_{a_2} all increase with mole fraction of dioxan. A substantially linear relationship is obtained for 8-quinolinol, but for 8-quinolinethiol there is deviation from linearity when the mole fraction is small.

In Fig. 2 the behaviour of the plot for 8-quinolinol is similar to that for acetic acid, and the behaviour for 8-qinolineselenol is similar to that of glycine. This suggests that in the neutral form, 8-quinolinol behaves as a monoprotic acid, and that 8-quinolineselenol as a zwitterion. For 8-quinolinethiol the behaviour is similar to that of 8-quinolineselenol in the region of low dioxan content but to that of 8-quinolinol in the region of high dioxan content.

If K_{aD} and K_{aC} are the acid dissociation constants for the neutral and zwitterion forms and K_t is the tautomeric constant, the following two equations hold:

$$\frac{1}{K_{a_2}} = \frac{1}{K_{aC}} + \frac{1}{K_{aD}} \qquad (12)$$

$$K_t = \frac{[\text{Zwitterion}]}{[\text{Neutral}]} = \frac{K_{aD}}{K_{aC}}. \qquad (13)$$

The values of pK_{aC} and pK_{aD} were evaluated from the results for pK_{a_2} and K_t. They are summarized in Table I.

TABLE 1.—EQUILIBRIUM CONSTANTS FOR 8-QUINOLINOL, 8-QUINOLINETHIOL AND 8-QUINOLINESELENOL IN WATER

	K_t	pK_{a_2}	pK_{aC}	pK_{aD}
8-quinolinol	0·04*	9·74	9·32	9·72
8-quinolinethiol	3·8†	8·36	8·26	7·68
8-quinolineselenol	1740‡	8·18	8·18	4·94

* Reference 11.
† Reference 12.
‡ Calculated value from the data of reference 3.

The calculated values of pK_{aD} are marked on the pK_{a_2} axis of Fig. 2. The black spot showing pK_{aD} for 8-quinolinol is in the vicinity of the straight line of pK_{a_2}, which suggests that 8-quinolinol behaves as the neutral form in water–dioxan mixtures.

Supposing that equation (11) is applied in this case, and that the reagent behaves only as the neutral form, the plots of pK_{a_2} *vs,* the mole fraction of dioxan are expected to be a straight line starting from the spot shown by values of pK_{aD} in Table I, and similarly for 8-quinolinethiol and 8-quinolineselenol. This is shown in Fig. 2. For 8-quinolinethiol, the plots of pK_{a_2} differ greatly from the expected when the mole fraction of dioxan is small but not when the mole fraction is higher. It is considered that this occurs because of a shift of the tautomeric equilibrium from the zwitterion to the neutral form with increase of the mole fraction of dioxan. Therefore, 8-quinolinethiol is considered to occur predominantly as the neutral form in the solvents with dioxan content > 70%, but 8-quinolineselenol is considered to be almost all in the zwitterion form in 75% water–dioxan mixture. This was also supported spectrophotometrically.

Spectrophotometric studies

Spectrophotometric measurements in water and water–dioxan mixtures were carried out both in air and in an atmosphere of nitrogen. Absorption spectra of 8-quinolinethiol, Fig. 3, are characterized by absorption maxima at 446, 316, 277 and 252 nm in water. The first two absorption bands have been attributed to the zwitterion form and the latter to the neutral form.[2] When the proportion of dioxan increases, the intensities of the first two bands decrease and those of the others increase (Fig. 3). The changes of the intensities for these bands suggest that the zwitterion form will be predominant in water and that the tautomeric equilibrium will be shifted towards the neutral form as the proportion of dioxan increases.

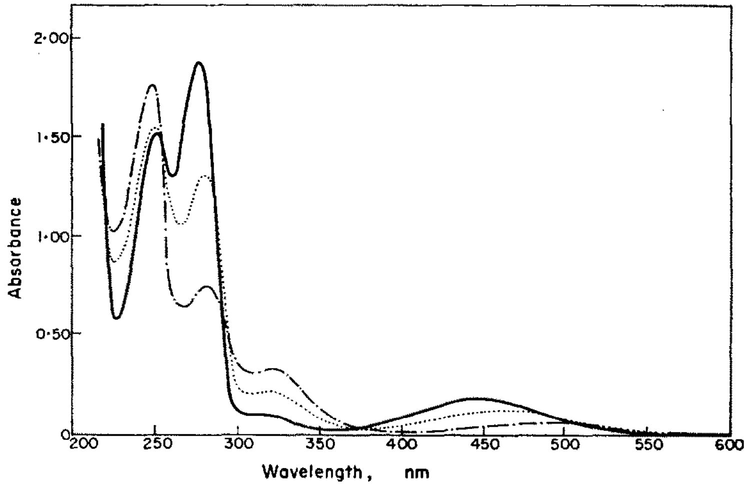


FIG. 3.—Absorption spectra of 8-quinolinethiol.
[NaR] = $1{\cdot}2 \times 10^{-4}M$, ($H_3PO_2$ or HCl added); pH = 4·2–5·1 Dioxan %: —— 0, ···· 30, —·— 50.

The absorption spectra for 8-quinolineselenol which were obtained in air were similar to those for 8-quinolinethiol. This fact is in conflict with the conclusion, obtained from potentiometric data, that the zwitterion form is predominant in spite of increase in dioxan content. However, different spectra, Fig. 4, were obtained when the measurements were made in an inert atmosphere and as quickly as possible. If the sample solution was allowed to stand for a certain time with the cell closed but in air, the spectra obtained become similar to those for 8-quinolinethiol. In Fig. 5, variation of the spectra as a function of time is represented. It is observed that the

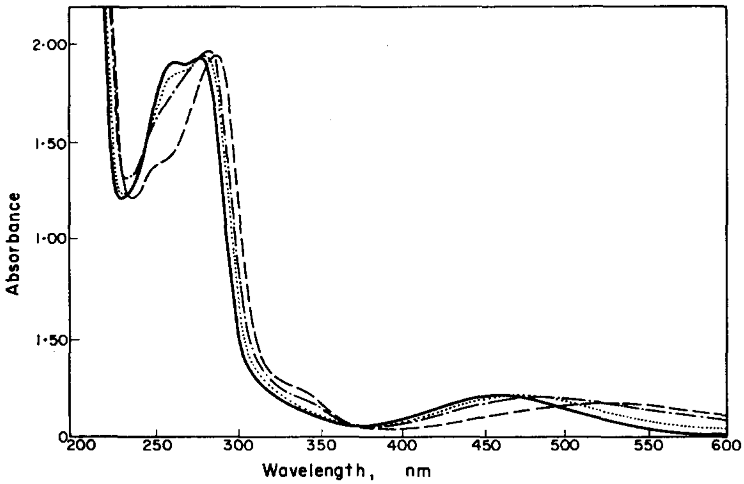


FIG. 4.—Absorption spectra of 8-quinolineselenol.
[HR] = 1·4 × $10^{-4}M$, [HCl] = 6 × $10^{-3}M$. Dioxan %: —— 0, ···· 30, —·— 50, — — 70.

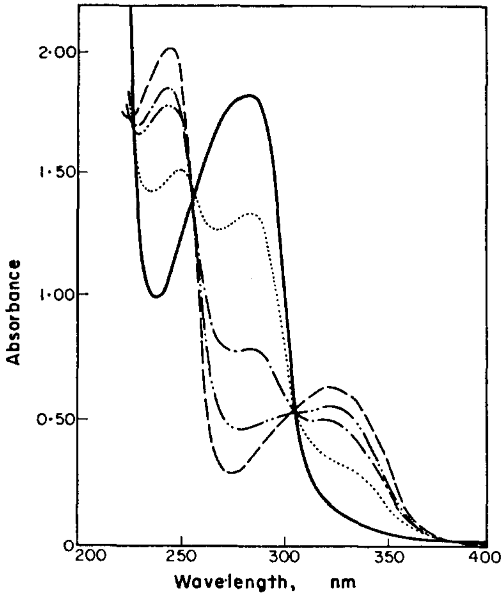


FIG. 5.—Variation of the spectra of 8-quinolineselenol in 50% water–dioxan mixture as a function of time.
[HR] = 1·2 × $10^{-4}M$, [$HClO_4$] = 5 × $10^{-3}M$. Time, *min*: —— 0, ···· 10, —·— 30, —··— 50. Diseleinde — —.

spectrum of 8-quinolineselenol approaches that of 8,8′-diquinolyldiselenide with time. The behaviour of the spectra for 8-quinolinethiol obtained under similar conditions was similar but the shifts were much slower.

To eliminate oxidation, measurements were carried out in the presence of hypophosphorous acid, and stable spectra were then obtained. In Fig. 4 it is shown that the absorption bands at 278 and 460 nm shift towards the red but the intensities of the bands change little with increase of dioxan content. The band at 260 nm shifts to red, and tends to overlap the band at 280 nm with increase of dioxan content. In other words the bands at 260, 278 and 460 nm undergo a blue shift as the solvent polarity is increased.

In Table II, spectrophotometric data obtained in this study or taken from the literature,[13] are summarized. All of the absorption coefficients are "apparent values" calculated from the total concentration of the reagent. Comparison suggests that the corresponding absorption bands undergo a red shift with decrease in basicity of ligand atoms. 8-Thiomethylquinoline has an absorption band at 251 nm which corresponds to the band at 252 nm of 8-quinolinol. 8-Selenomethylquinoline has a similar band at 252 nm. But the behaviour of the band at 260 nm for 8-quinolineselenol is different from these.

TABLE II.—ABSORPTION MAXIMA, *nm*, AND MOLAR ABSORPTIVITY (*l . mole*$^{-1}$ *. mm*$^{-1}$)

8-quinolinol		8-quinolinethiol		8-quinolineselenol	
λ	ε	λ	ε	λ	ε
430	6·4	446	160	460	130
304	263	316	82	320(sh*)	
270	284	277	1·80 × 10^3	278	1·60 × 10^3
239	3·24 × 10^3	252	1·44 × 10^3	260	1·50 × 10^3

8-thiomethylquinoline		8-selenomethylquinoline		8,8′-diquinolyldisulphide		8,8′-diquinolyldiselenide	
λ	ε	λ	ε	λ	ε	λ	ε
337	420	337	320	320		320	100
				310(sh*)		310(sh*)	
251	2·20 × 10^3	252	2·50 × 10^3	244		246	3·20 × 10^3
		232	2·10 × 10^3	232(sh*)		240(sh*)	

* Shoulder.

Consequently, the absorption bands at 278 and 460 nm for 8-quinolineselenol can be attributed to the zwitterion form, which correspond to the bands at 277 and 446 nm for 8-quinolinethiol and to 270 and 430 nm for 8-quinolinol. But the band at 260 nm for 8-quinolineselenol cannot be attributed to the neutral form. This suggests that in 8-quinolineselenol the zwitterion form is predominant in the solvent mixtures containing up to 70% dioxan. This conclusion agrees with the result obtained potentiometrically.

Acknowledgement—The authors acknowledge the invaluable assistance of Mr. Yoshiyuki Mido in this investigation.

Zusammenfassung—Die Säuredissoziationskonstanten von 8-Chinolinselenol, 8-Hydroxychinolin und 8-Chinolinthiol in Wasser-Dioxan-Gemischen wechselnder Lösungsmittelzusammensetzung wurden potentiometrisch oder spektrophotometrisch bestimmt. Die Absorptionsspektren von 8-Chinolinselenol in den selben Lösungsmittelgemischen wurden ebenfalls gemessen. Die Dissoziationseigenschaften, die Stabilität gegen Oxidation und die Absorptionsspektren der Reagentien werden in Verbindung mit den jeweils vorliegenden Formen diskutiert. Es wird nachgewiesen, daß 8-Chinolinselenol in Wasser-Dioxan-Gemischen mit niedrigem oder hohem Dioxananteil als Zwitterion vorliegt.

Résumé—On a déterminé potentiométriquement ou spectrophotométriquement les constantes de dissociation acide des 8-sélénolquinoléine, 8-hydroxyquinoléine et 8-thiolquinoléine dans des mélanges eau-dioxane de composition en solvant variable. On a aussi obtenu les spectres d'absorption de la 8-sélénolquinoléine dans les mêmes solvants. On discute des phénomènes de dissociation acide, de la stabilité vis-à-vis de l'oxydation et des spectres d'absorption des réactifs en relation avec les formes existantes. Il est vérifié que la 8-sélénolquinoléine esiste à l'état de zwitterion dans les mélanges eau-dioxane à basse ou haute teneur en dioxane.

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THEORY OF TITRATION CURVES—VII

THE PROPERTIES OF DERIVATIVE TITRATION CURVES FOR STRONG ACID–STRONG BASE AND OTHER ISOVALENT ION-COMBINATION TITRATIONS

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Summary—This paper deals with isovalent ion-combination titrations based on reactions that can be represented by the equation $M^{n+} + X^{n-} \rightarrow MX$, where the activity of the product MX is invariant throughout a titration, and with the derivative titration curves obtained by plotting $d[M^{+}]/df$ versus f for such titrations. It describes some of the ways in which such curves can be obtained; it compares and contrasts them both with potentiometric titration curves, which resemble them in shape, and with segmented titration curves, from which they are derived; and it discusses their properties in detail.

DERIVATIVE titrations are little known and rarely if ever performed, even though it is possible to envision circumstances in which they should have significant advantages over other more familiar titration techniques. Malmstadt and Roberts[1] performed some spectrophotometric titrations in which the reagent was added at a nearly, though not quite, constant rate from a conventional burette while the dynode voltage of a photomultiplier was amplified, inverted, and differentiated with respect to time by a simple R-C network. Recording the output of this network against time would have given a true derivative titration curve had the rate of reagent addition been constant, but Malmstadt and Roberts chose instead to use a second-derivative autotitrator to terminate the addition of reagent at the inflection point of that curve. A similar approach was later adopted by De Leo and Stern.[2] Zenchelsky and Segatto[3] performed derivative thermometric titrations in which the temperature of the titration mixture was sensed by a thermistor connected as one arm of a d.c. Wheatstone bridge; the out-of-balance voltage of this bridge was differentiated with respect to time by an R-C network, the output from which was filtered and recorded against time. Very heavy filtering had to be used to eliminate noise caused by stirring irregularities, power dissipation in the thermistor,[4] and other high-frequency phenomena, and severely distorted curves were obtained. Similar experiences were reported by Perchec and Gilot[5] and Bark and Doran.[6]

Recent advances in the art of signal processing should simplify the task of obtaining reasonably faithful derivative titration curves. There is no detector employed in titrations for which the signal/noise ratio is worse than it is for a dropping electrode in an amperometric titration, and the very low frequency of the noise (*i.e.*, the variation of instantaneous current during the drop-life) at a dropping electrode introduces a further complication, yet Kelley and Fisher[7] were able to obtain derivative polarograms conforming closely to theoretical expectations, by techniques that should be easy to adapt to the trivially different conditions arising in titrations. One obvious digital approach would be to compute successive values of $\Delta S/\Delta t$, S being the signal provided by the detector and t the elapsed time since the start of the titration, and plot them against t in a constant-rate titration. Signal smoothing or averaging would of course be advantageous. Another approach would be to equip the motor-driven burette (or other device used for reagent addition) with a transmitting potentiometer, or its equivalent, to furnish a signal proportional to the volume V of reagent added at any instant, thereby making it possible to compute $\Delta S/\Delta V$ and plot it against V, and further enabling anticipation circuitry to be added so that equilibration could be ensured for a reaction that becomes slow near the equivalence point.

Derivative titrations are based on the apparatus and experimental techniques of segmented titration-curve procedures, and, like the latter, are therefore more versatile than potentiometric titrations. Thermometric, spectrophotometric, conductometric, fluorometric, and other kinds of detectors can all be used in familiar ways, and the problem of selecting an indicator electrode that will respond to the concentration of some suitable species does not arise. Moreover, although derivative titration curves have shapes strongly reminiscent of the shapes of potentiometric titration curves, they have very different properties. Like a potentiometric titration curve, a derivative titration curve has a point of maximum slope that almost coincides with the equivalence point when the equilibrium constant, K_t, for the chemical reaction and the concentrations of the two reacting solutions are reasonably large. But the range of variation is much larger for the derivative than it is for the potential, and in addition the derivative undergoes a larger fraction of that variation in the immediate vicinity of the inflection point. For these reasons it is possible to locate the inflection point on a derivative titration curve even under conditions so unfavourable that none can be perceived on the corresponding potentiometric titration curve.

Comparison of derivative titration curves with the segmented ones from which they are obtained indicates that neither has much, if any, advantage over the other for end-point location in the extreme situations that arise when K_t and the concentrations of the reacting solutions are small. The segmented curve then has a wide region of curvature around the equivalence point, and end-point location consequently entails long extrapolations of the short linear portions. The discomfort and error thus produced will not differ materially from those caused by the fact that the derivative curve for the same titration is approximately linear for some distance on either side of the inflection point, so that it will not be possible to attain greater accuracy in locating the inflection point, and by the additional fact that the inflection point differs appreciably from the equivalence point under these extreme conditions. All of these considerations will be illustrated by Figs. 1 and 3.

It is when K_t and the concentrations of the solutions are moderately large that derivative curves will be superior to segmented ones for end-point location. Then, by appropriate selection of the experimental conditions, the derivative can be made to undergo a very large variation in the immediate vicinity of the equivalence point. This variation is so sudden and so sharp that it should permit far more precise and accurate end-point location than can be attained with segmented curves. It is of course well known that, other things being equal, sigmoid curves are superior for end-point location to segmented ones.

The advantage of derivative titrimetry is even more pronounced in the fairly common situation in which the solution being titrated contains two substances that can react with the reagent. Consider, for example, the thermometric titration of a mixture of zinc(II) and strontium(II) with ethylenediaminetetra-acetate in a medium in which zinc is not appreciably complexed. The zinc will react with the reagent first because the formation constant of its chelonate is much higher than that of the strontium chelonate. But the two enthalpies of formation differ so little (*ca.* 25%) that the end-point of the titration of zinc will be very difficult to locate with reasonable precision. On the corresponding derivative titration curve, however, the rate of change of temperature with respect to either time or volume of reagent would drop abruptly to a value only about $\frac{3}{4}$ as large, as the last of the zinc was titrated: inspection of computed titration curves suggests that the accuracy and precision attainable in the determination of zinc in this mixture can be little, if at all, inferior to those that can be secured in work with pure solutions.

Titration curves are also often employed for the evaluation of equilibrium and rate constants, and for these purposes derivative curves seem markedly superior to segmented ones. Equilibrium constants were first deduced from amperometric titration curves by Kolthoff and Laitinen[8] and by Bobtelsky and Jordan,[9] whose lead has been followed by many others; the ways in which they have been obtained from thermometric titration curves have been reviewed by Tyrrell[10]; any segmented-curve technique may be used in similar ways. In any case, the computation has to be based on the relatively small difference between the curve actually obtained and the one that would be obtained if the titration reaction were complete at every point, and precise results are therefore very difficult to obtain. Although the corresponding derivative curve really presents the same information, its shape is more sensitive to variations of the equilibrium constant.

The use of constant-rate titrimetry in studies of homogeneous kinetics was introduced by Cover and Meites[11] and Kozak and Fernando.[12] Its applications to date include studies of the rate of the disproportionation of uranium(V)[13] and the rate of the reaction between diphenyl sulphide and bromine.[14] One situation in which the superiority of derivative titration curves (which for purposes like this must portray the behaviour of the derivative with respect to time rather than volume of reagent) would be clearly evident would be that in which some side-reaction consuming the substance M^{n+} being titrated was induced by the main reaction. Other kinds of titrimetry would then reveal only that the end-point preceded the expected equivalence point; it would be easy to infer that the induced reaction was taking place, but its rate would not be at all easy to evaluate. Derivative titrimetry, on the other hand, would provide values of $d[M^{n+}]/dt$ that could be directly compared with those expected in the absence of the induced reaction, and the difference between these, and the manner in which it varied as the titration progressed, would be easy to interpret in mechanistic and kinetic ways.

Whether the advantages of derivative titrations for all these purposes can be realized in practice is of course a question that will have to be settled experimentally. To provide a firm basis for such work we have undertaken a detailed investigation of their theory for the simplest case: that of an isovalent ion-combination titration.[15] This has entailed a more extensive study of the properties of the third derivative of the titration curve than has been undertaken previously.

We shall consider the general equation

$$M^{n+} + X^{n-} = MX \tag{1}$$

omitting charges henceforth for simplicity of notation. Assuming that a $C_M{}^0F$ solution of M is titrated with a C_XF solution of X, we define the dilution parameter r and the titration parameter f by the equations

$$r = C_M{}^0/C_X \tag{2}$$

$$f = V_XC_X/V_M{}^0C_M{}^0 \tag{3}$$

where $V_M{}^0$ is the volume of the solution of M being titrated and V_X is the volume of the reagent added to it at the point under consideration. We assume that the equilibrium constant of the titration reaction

$$K_t = 1/[\mathrm{M}][\mathrm{X}] \tag{4}$$

is invariant and is satisfied at every point. Similar definitions and assumptions have been made and discussed in earlier papers in this series.[15,16]

The fundamental titration-curve equation for a titration involving reaction (1) is

$$[\mathrm{M}] = C_M{}^0\frac{1-f}{1+rf} + \frac{1}{K_t[\mathrm{M}]}\,. \tag{5}$$

We shall consider the derivative titration curve to be a plot of d[M]/df, which we shall henceforth denote by D, against f. Descriptions of this plot are applicable, *mutatis mutandis*, to one of d[X]/df against f.

Differentiation of equation (5) yields

$$D = -\frac{(rK_t[\mathrm{M}]^2 + C_M{}^0K_t[\mathrm{M}] - r)^2}{(1+r)C_M{}^0K_t(K_t[\mathrm{M}]^2+1)} \tag{6}$$

which is the fundamental equation of the derivative titration curve for an isovalent ion-combination titration. Figures 1, 2, and 3 show how the curve is affected by variations of K_t, r, and $C_M{}^0$, respectively. To facilitate comparisons of these curves we have normalized them by plotting D/D_0, rather than D itself, on the ordinate axis; D_0 is the value of D at $f = 0$. In any practical titration the value of [M] at this point would be indistinguishable from $C_M{}^0$, and the product $K_t(C_M{}^0)^2$ would also be very much larger than unity, although a few curves for which neither of these things is true are included in Figs. 1–3 to show degenerate forms. When both are true, the value of D_0 is given by

$$D_0 = -(1+r)C_M{}^0 \tag{7}$$

which is useful in interpreting most of the curves in these figures. It indicates, for example, that the decrease of D/D_0 as r increases, which is shown by Fig. 2, is partly attributable to an increase of D_0. The value of D at $f = 1$, which we shall represent by the symbol D_1, may be found by substituting $[\mathrm{M}] = 1/K_t^{1/2}$ into equation (6), and is given by

$$D_1 = -C_M{}^0/2(1+r) \tag{8}$$

Differentiating equation (6) yields a description of the slope dD/df of the derivative curve:

$$\frac{\mathrm{d}D}{\mathrm{d}f} = \frac{2(rK_t[\mathrm{M}]^2 + C_M{}^0K_t[\mathrm{M}] - r)^3(rK_t[\mathrm{M}]^3 + 3r[\mathrm{M}] + C_M{}^0)}{(1+r)^2(C_M{}^0)^2K_t(K_t[\mathrm{M}]^2+1)^3} \tag{9}$$

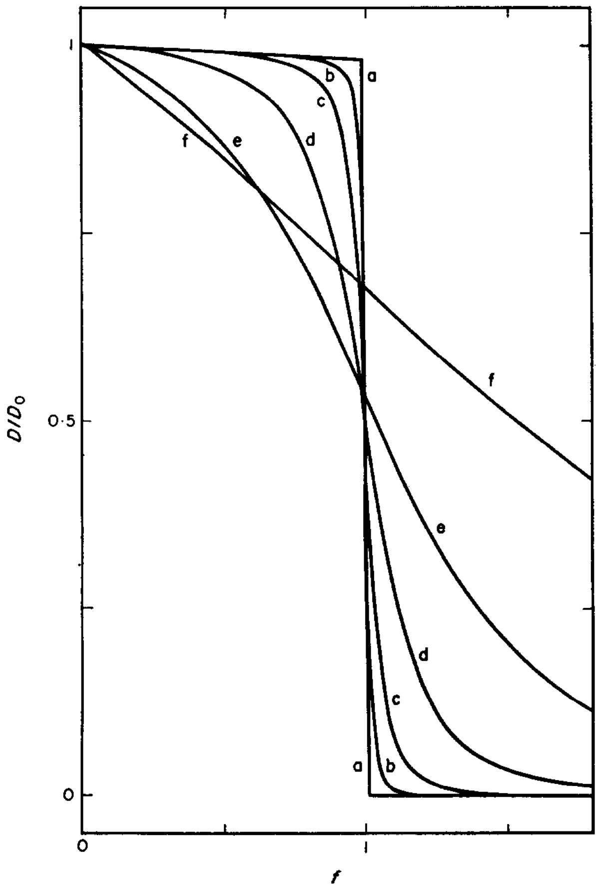

FIG. 1.—Calculated derivative titration curves.
$C_M{}^0 = 0{\cdot}1M$, $r = 0{\cdot}01$ and K_t = (*a*) 10^{10}, (*b*) 10^6, (*c*) 10^5, (*d*) 10^4, (*e*) 10^3, and (*f*) 10^2.

On introducing the expression for $K_t[\mathrm{M}]^2$ obtained by rearranging equation (5), it can be shown that

$$rK_t[\mathrm{M}]^2 + C_M{}^0K_t[\mathrm{M}] - r = C_M{}^0K_t[\mathrm{M}](1 + r)/(1 + rf).$$

Since the right-hand side of this equation must evidently be positive for all values of $f > 0$, and since the same thing is true of both the denominator and the quantity within the second parentheses in the numerator on the right-hand side of equation (9), $\mathrm{d}D/\mathrm{d}f$ must be positive everywhere, as is intuitively apparent.

At the equivalence point

$$\left(\frac{\mathrm{d}D}{\mathrm{d}f}\right)_1 = (4r + C_M{}^0K_t^{1/2})C_M{}^0/4(1 + r)^2. \qquad (10a)$$

On inspection of Fig. 2 it is clear that the choice of a small value of r is advantageous, because it maximizes the variation of D around the equivalence point in the same way that it decreases the necessity for applying a dilution correction in the parent segmented-curve technique. As a basis for estimating the relative precision of a derivative

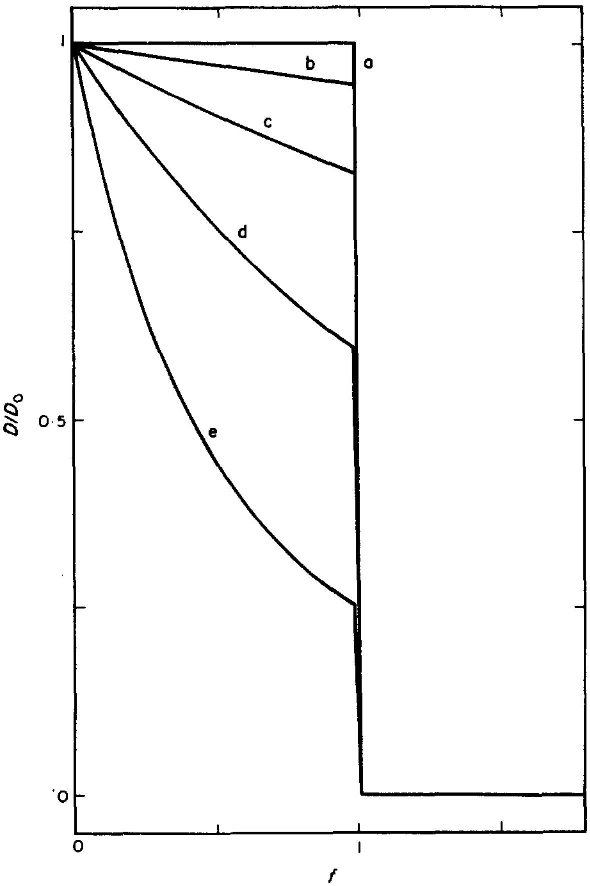

FIG. 2.—Calculated derivative titration curves.
$C_M{}^0 = 0{\cdot}1M$, $K_t = 10^{14}$, and r = (*a*) 0, (*b*) 0·03, (*c*) 0·1, (*d*) 0·3, and (*e*) 1.

titration we shall therefore rewrite equation (10*a*) in the approximate form

$$\left(\frac{\Delta D}{\Delta f}\right)_1 = (C_M{}^0)^2K_t^{1/2}/4\,. \tag{10b}$$

Benedetti-Pichler[17] defined the relative precision of a potentiometric titration as the value of Δf corresponding to a fixed uncertainty in the pH or indicator-electrode potential at the equivalence point. An exactly analogous definition seems inappropriate here, since there is very little basis for estimating the absolute uncertainty that can be expected in measuring a derivative signal. We shall instead assume that the uncertainty in the value of the derivative at the equivalence point is ±10% of its value at $f = 0$, so that $\Delta D_1/D_0 = \pm 0{\cdot}1$, and define the relative precision as the corresponding value of Δf. This appears to us to be an extremely conservative assumption, but experimentation will be needed to obtain a more reliable one.

Combination of equations (7) and (10*b*) with the assumption that again r will be made small, and the introduction of the description above of $\Delta D_1/D_0$, gives

$$\Delta f = \mp 0{\cdot}4/C_M{}^0K_t^{1/2}. \tag{11}$$

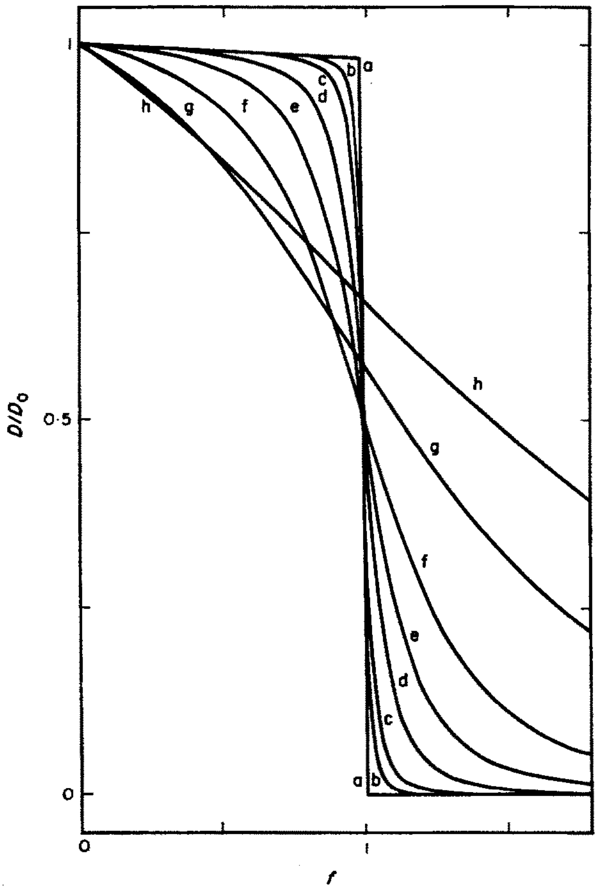

FIG. 3.—Calculated derivative titration curves.
$r = 0{\cdot}01$, $K_t = 10^{14}$, and $C_M{}^0 =$ (*a*) 1, (*b*) 10^{-5}, (*c*) 5×10^{-6}, (*d*) 2×10^{-6}, (*e*) 1×10^{-6}, (*f*) 5×10^{-7}, (*g*) 2×10^{-7}, and (*h*) $1{\cdot}1 \times 10^{-7}M$.

As usual,[18] it is the quantity $(C_M{}^0)^2K_t$ that governs the precision attainable in an isovalent ion-combination titration. The expected relative precision of a derivative titration is 0·4% even if $(C_M{}^0)^2K_t$ is as small as 10^4; this figure compares very favourably with the precision expected in an ordinary segmented-curve titration and is definitely superior to the corresponding figure for a potentiometric titration.

Differentiating equation (9) yields a description of the second derivative of the derivative curve:

$$\frac{d^2D}{df^2} = \frac{\begin{array}{c}-6(rK_t[M]^2 + C_M{}^0K_t[M] - r)^4\{[(K_t[M]^2)^3 + 5(K_t[M]^2)^2 \\ + 11(K_t[M]^2) - 1]r^2 - [K_t[M]^2 - 1](C_M{}^0)^2K_t + 8rC_M{}^0K_t[M]\}\end{array}}{(1 + r)^3(C_M{}^0)^3K_t{}^2[K_t[M]^2 + 1]^5} \tag{12}$$

At the equivalence point

$$\left(\frac{d^2D}{df^2}\right)_{r=1} = -3rC_M{}^0(2r + C_M{}^0K_t^{1/2})/2(1 + r)^3. \tag{13}$$

If $r = 0$, the second derivative vanishes at the equivalence point: like the corresponding potentiometric titration curve, the derivative titration curve has an inflection point that coincides with the equivalence point if there is no dilution during the titration. Moreover, when $r = 0$, equation (12) becomes

$$\left(\frac{\mathrm{d}^2D}{\mathrm{d}f^2}\right)_{r=0} = 6(C_{\mathrm{M}}^0)^3K_{\mathrm{t}}^3[\mathrm{M}]^4(K_{\mathrm{t}}[\mathrm{M}]^2 - 1)/(K_{\mathrm{t}}[\mathrm{M}]^2 + 1)^5. \tag{14}$$

The value of $K_{\mathrm{t}}[\mathrm{M}]^2$ exceeds 1 everywhere up to the equivalence point, is equal to 1 at the equivalence point, and is smaller than 1 everywhere beyond the equivalence point. Therefore, if $r = 0$, $\mathrm{d}^2D/\mathrm{d}f^2$ is positive at $f = 0$, remains positive until it vanishes at $f = 1$, and is negative for all values of f exceeding 1: there is only one point of inflection on the titration curve.

These things are also true if r is finite but very small. However, increasing r causes the terms in r^2 and r within the braces in equation (12) to increase rapidly, and there is a certain critical value of r at which $\mathrm{d}^2D/\mathrm{d}f^2$ just becomes equal to zero when $f = 0$. If r exceeds this critical value, $\mathrm{d}^2D/\mathrm{d}f^2$ is negative at $f = 0$, increases until it passes through zero at a point that corresponds to a point of minimum slope on the titration curve, attains positive values over a certain range of values of f, then decreases abruptly, passing through zero at a point that corresponds to a point of maximum slope on the titration curve, and finally remains negative for all values of f beyond this second inflection point. The critical value of r is approximately $1/(C_{\mathrm{M}}^0)^2K_{\mathrm{t}}$ and is thus indistinguishable from zero in practical titrations.

Decreasing either K_{t} or C_{M}^0 causes the value of $\mathrm{d}^2D/\mathrm{d}f^2$ at $f = 0$ to become more negative when r is finite, and narrows the range of values of f over which $\mathrm{d}^2D/\mathrm{d}f^2$ is positive. There is a degenerate case in which the second derivative never does attain positive values, so that there is no inflection point on the titration curve.

In connection with equation (13) it was stated above that the point of maximum slope coincides with the equivalence point if $r = 0$. In the light of the foregoing discussion, however, it can be seen that this is not true if r has any finite value, for then $\mathrm{d}^2D/\mathrm{d}f^2$ is negative at $f = 1$; in any real derivative titration (as in any real potentiometric titration[16]) the point of maximum slope precedes the equivalence point.

The locations of the inflection points, where the quantity within braces in equation (12) must vanish, are most conveniently described by equating this quantity to zero in the form

$$\frac{(C_{\mathrm{M}}^0)^2K_{\mathrm{t}}}{r^2}(1 - K_{\mathrm{t}}[\mathrm{M}]^2) + 8\left[\frac{(C_{\mathrm{M}}^0)^2K_{\mathrm{t}}}{r^2}\right]^{1/2}(K_{\mathrm{t}}[\mathrm{M}]^2)^{1/2} + [(K_{\mathrm{t}}[\mathrm{M}]^2)^3 + 5(K_{\mathrm{t}}[\mathrm{M}]^2)^2 + 11(K_{\mathrm{t}}[\mathrm{M}]^2) - 1] = 0. \tag{15}$$

This has the solution described by the equation

$$\frac{C_{\mathrm{M}}^0K_{\mathrm{t}}^{1/2}}{r} = \frac{4K_{\mathrm{t}}^{1/2}[\mathrm{M}] + (K_{\mathrm{t}}[\mathrm{M}]^2 + 1)^2}{K_{\mathrm{t}}[\mathrm{M}]^2 - 1} \tag{16}$$

from which the negative sign in the numerator of the general quadratic solution has been omitted because it can give rise only to negative or indeterminate values of $C_{\mathrm{M}}^0K_{\mathrm{t}}^{1/2}/r$, which are physically meaningless. From equation (16) it is again apparent that any inflection point must precede the equivalence point, so that $K_{\mathrm{t}}[\mathrm{M}]^2$ at the inflection point will exceed 1, if r has any finite value.

It is appropriate to begin by considering the locations of the inflection points when $C_M{}^0K_t^{1/2}/r$ is large, because this is the situation that is most important in practical titrations. The second inflection point, which is the point of maximum slope, will then occur just before the equivalence point, where $K_t[M]^2$ barely exceeds 1.* Substituting

$$K_t[M]^2 = 1 + \delta \qquad (\delta \ll 1) \tag{17}$$

into equation (16), replacing $(1 + \delta)^{1/2}$ by $1 + \delta/2$, we obtain

$$\frac{C_M{}^0K_t^{1/2}}{r} = \frac{4[1 + \delta/2] + (2 + \delta)^2}{\delta} = \frac{8}{\delta}. \tag{18a}$$

Comparison of equations (5) and (17) provides a value for δ:

$$\delta = C_M{}^0K_t[M](1 - f)/(1 + rf). \tag{18b}$$

By combining equations (18a) and (18b), letting $[M] = 1/K_t^{1/2}$ and $rf = r$ because the inflection point under discussion almost coincides with the equivalence point, we obtain

$$1 - f = 8r(1 + r)/(C_M{}^0)^2K_t. \tag{19}$$

Thus, for example, if $r = 1$ and $K_t = 10^{14}$, as would be the case for the titration of C^0F strong acid with C^0F strong base in an aqueous medium of low ionic strength at 25°, the point of maximum slope will occur at $(1 - f) = 1{\cdot}6 \times 10^{-13}/(C^0)^2$; this is quite close enough to the equivalence point to justify the approximations embodied in equation (19) unless C^0 is very small. It is unexpected that this result should be exactly identical with that for the point of maximum slope on the potentiometric titration curve under the same conditions.[16]

The location of the first inflection point when $C_M{}^0K_t^{1/2}/r$ is large can be obtained by noting that equation (16) becomes very nearly

$$\frac{C_M{}^0K_t^{1/2}}{r} = K_t[M]^2 \tag{20}$$

if $K_t[M]^2$ is large. As will presently appear, when $C_M{}^0K_t^{1/2}/r$ is large the point of minimum slope is close enough to the equivalence point to justify the approximation $(1 + rf) = (1 + r)$, and is yet far enough away from the equivalence point to justify writing $[M] = C_M{}^0(1 - f)/(1 + rf)$. Introducing these two simplifications into equation (20) and rearranging yields

$$1 - f = (1 + r)/(rC_M{}^0K_t^{1/2})^{1/2} \tag{21}$$

so that in the strong acid–strong base titration mentioned in the preceding paragraph, where $r = 1$ and $K_t = 10^{14}$ and where the point of maximum slope occurs at $(1 - f) = 1{\cdot}6 \times 10^{-13}/(C^0)^2$, the point of minimum slope occurs at $(1 - f) = 6{\cdot}32 \times 10^{-4}/(C^0)^{1/2}$.

As the value of $C_M{}^0$ decreases, the values of $(1 - f)$ at both of the inflection points increase, but that at the point of maximum slope increases much the more rapidly of

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* It is the ease with which situations important in practice can be described by simplifications like this that justifies the appearance of $K_t[M]^2$ in these equations. The superficially preferable course of solving equation (5) for [M] and differentiating with respect to f yields equations so complex that the useful simplifications are impossible to discern.

the two. The behaviour of these values in the typical case in which $r = 1$ is shown in Fig. 4. With equation (16) in mind, it is convenient to focus attention on the behaviour of $K_t[M]^2$ at the inflection points. As $C_M{}^0K_t^{1/2}/r$ decreases, the value of $K_t[M]^2$ at the point of minimum slope, which is large when $C_M{}^0K_t^{1/2}/r$ is large, decreases more and more; meanwhile the value of $K_t[M]^2$ at the point of maximum slope, which is barely above 1 when $C_M{}^0K_t^{1/2}/r$ is large, increases. There is a minimum value of $C_M{}^0K_t^{1/2}/r$ at which an inflection point is possible. This minimum may be found by differentiating equation (16) to obtain

$$\frac{\mathrm{d}(C_M{}^0K_t^{1/2}/r)}{\mathrm{d}(K_t[M]^2)} = \frac{(K_t[M]^2 - 1)[2/(K_t^{1/2}[M]) + 2(K_t[M]^2 + 1)] - [4(K_t^{1/2}[M] + (K_t[M]^2 + 1)^2]}{(K_t[M]^2 - 1)^2}. \quad (22)$$

On equating the numerator of the right-hand side of this equation to zero it is found that the minimum value of $C_M{}^0K_t^{1/2}/r$ occurs at $K_t[M]^2 = 4$. On substituting the latter value into equation (16), this minimum value of $C_M{}^0K_t^{1/2}/r$ is found to be 11. By combining these results with equation (5), it can be shown that

$$f = (22r - 3)/25 \quad (23)$$

at the point where the two inflection points coincide. This limiting value of f is represented by the small circle in Fig. 4. It is especially curious, because similar functions derived from titration curves have heretofore seemed to be uniformly

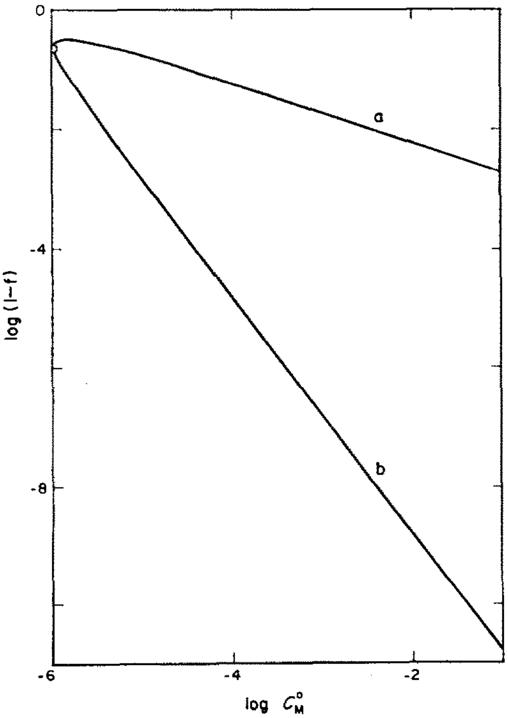

FIG. 4.—Effects of log $C_M{}^0$ on the values of $(1 - f)$ at (*a*) the first and (*b*) the second inflection points of titration curves for which $r = 1$ and $K_t = 10^{14}$.

monotonic, that the value of $(1 - f)$ at the point of minimum slope should pass through a maximum as this limit is approached.

All these considerations can be summarized as follows

1. If r is zero or extremely small the curve has only one inflection point: this is a point of maximum slope, and it coincides with the equivalence point if $r = 0$.

2. In a practical titration, in which r has a finite and appreciable value, there may be either two inflection points or none. There is no inflection point if $C_M{}^0K_t^{1/2}/r$ is equal to or less than 11; there are two inflection points if $C_M{}^0K_t^{1/2}/r$ exceeds this value. The first inflection point is a point of minimum slope; if $C_M{}^0K_t^{1/2}/r$ is very large, as will be true in practical titrations, the value of $K_t[\mathrm{M}]^2$ is large at this point, and its location is described by equation (21). The second inflection point is a point of maximum slope and must always precede the equivalence point; if $C_M{}^0K_t^{1/2}/r$ is large, the value of $K_t[\mathrm{M}]^2$ is barely above 1 at this point, and its location is described by equation (19). As $C_M{}^0K_t^{1/2}/r$ decreases, the value of $K_t[\mathrm{M}]^2$ at the first inflection point decreases while that at the second inflection point rises, and the ratio of the values of $(1 - f)$ at the two inflection points approaches 1. When $C_M{}^0K_t^{1/2}/r$ becomes equal to 11, $K_t[\mathrm{M}]^2$ becomes equal to 4 at each of the inflection points, and the corresponding values of $(1 - f)$ become equal to $(28 - 22r)/25$; the inflection points coincide and therefore vanish.

Zusammenfassung—Diese Arbeit befaßt sich mit isovalenten Ionenkombinations-Titrationen, die man durch die Gleichung $M^{n+} + X^{n-} \rightarrow MX$ darstellen kann, wenn sich die Aktivität des Produkts MX bei der ganzen Titration nicht ändert, sowie mit den differenzierten Titrationskurven, die man durch Auftragen von $\mathrm{d}\,[M^-]/\mathrm{d}f$ gegen f bei solchen Titrationen erhält. Die Arbeit beschreibt einige Verfahren, wie man solche Kurven erhalten kann; sie zeigt Ähnlichkeiten und Unterschiede zu potentiometrischen Titrationskurven, die ähnliche Form haben, und zu segmentierten Titrationskurven, von denen sie abgeleitet sind. Die Eigenschaften dieser Kurven werden bis ins Einzelne diskutiert.

Résumé—Ce mémoire traite des titrages par combinaison d'ions isovalents basés sur des réactions que l'on peut représenter par l'équation $M^{n+} + X^{n-} \rightarrow MX$, où l'activité du produit MX est invariante tout à travers un titrage, et des courbes de titrage dérivées obtenues en portant $\mathrm{d}[\mathrm{M}^+]/\mathrm{d}f$ par rapport à f pour de tels titrages. Il décrit quelques-unes des voies dans lesquelles de telles courbes peuvent être obtenues; il les compare et les oppose tant aux courbes de titrages potentiométriques, qui leur ressemblent en allure, qu'aux courbes de titrage segmentées, desquelles elles sont dérivées; et il discute en détail de leurs propriétés.

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SHORT COMMUNICATIONS

Mass spectrometric analysis of carbon monoxide–nitrogen mixtures

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THE PRODUCTS of a hydrocarbon flame burning in oxygen will contain combustion gases consisting largely of carbon monoxide, carbon dioxide and water. Analysis of samples of such mixtures with a conventional single-focussing mass spectrometer such as the A.E.I. M.S.2 or the Atlas CH 4 presents no difficulties. When, however, the oxidant is air, or the fuel contains nitrogen, or the samples withdrawn from the flame include some of the surrounding air, the analytical problem becomes more difficult. The most abundant ions in the mass spectra of both nitrogen and carbon monoxide are the molecular-ions which are responsible for nearly all the ion current. Both these ions have an integral mass of 28, so when a mixture of nitrogen and carbon monoxide is admitted to the mass spectrometer the ion currents due to CO^+ and N_2^+ ions cannot be separated and are responsible for a single peak in the mass spectrum. When such a state of affairs is encountered with other pairs of compounds it is frequently still possible to carry out a satisfactory analysis by using the mass peaks which are due to fragment ions. Some of these may make up a substantial part of the total ion current and differ in their occurrence and abundance for pairs of compounds having the same integral mass. From the mass spectra of carbon monoxide and nitrogen which are shown in Table I, it can be seen that the fragment ions are of low abundance so that any analysis based on the measurement of their ion currents would be subject to considerable error. Such an analysis made for example from the $^{12}C^+$ peak from carbon monoxide and the $^{14}N^+$ peak from nitrogen would have an error approximately 50 times that of a method based on the ion current due to the molecular ions.

TABLE I.—RELATIVE PEAK HEIGHTS FROM MASS SPECTRA

m/e	CO_2	CO	N_2
44	100	—	—
29	0·07	1·12	0·77
28	8·10	100	100
22	1·50	—	—
16	4·08	0·44	0·01
14	—	5·0	5·0
12	7·0	1·0	—

Relative sensitivities

Carbon dioxide $$\left(\frac{H_{44}}{H_{40}}\cdot\frac{P_{Ar}}{P_{CO_2}}\right) = 0{\cdot}83$$

Carbon monoxide $$\left(\frac{H_{28}}{H_{40}}\cdot\frac{P_{Ar}}{P_{CO}}\right) = 0{\cdot}77$$

Nitrogen $$\left(\frac{H_{28}}{H_{40}}\cdot\frac{P_{Ar}}{P_{N_2}}\right) = 0{\cdot}87$$

In fact, the masses of the molecule ions of carbon monoxide and nitrogen are not exactly the same; the precise mass of CO^+ is 27·994914, that of N_2^+ is 28·006148, and the difference is about 1 part in 2500.

The resolution of a single-focussing mass spectrometer operated under conditions of high sensitivity is only 1 part in 1000, so that CO^+ and N_2^+ mass peaks cannot be resolved. Modern double-focussing mass spectrometers such as the A.E.I. M.S.9 have resolutions of the order of 1 part in 70000 so that it is possible by using such an instrument to analyse mixtures of carbon monoxide and nitrogen directly by measuring the intensity of the ion currents at masses 27·994915 and 28·006148. These instruments are, however, extremely costly and a method was therefore developed in which the normal analytical routine of a single-focussing machine was modified to permit the analysis of mixtures of combustion products containing both carbon monoxide and nitrogen.

In conventional methods of gas analysis it is convenient to convert the inert carbon monoxide into carbon dioxide which can be absorbed by alkaline solutions. A number of procedures for carrying out this conversion have been devised, involving oxidation of carbon monoxide to carbon dioxide with molecular oxygen or solid metal oxides at high temperatures. These procedures are not sufficiently simple or quantitative to be useful. Recently, however, a suitable oxidant has been proposed for the conversion of carbon monoxide into carbon dioxide at room temperature. It consists of a mixture of iodine pentoxide and sulphuric acid adsorbed upon pumice and is available commercially in the form of a fine powder under the name of Schütze catalyst.

The method described in this paper involves the recording of mass spectra of a sample containing both carbon monoxide and nitrogen before and after conversion with the oxidant. The intensity of the peak at mass 28 would be reduced by an amount directly proportional to the increase in the 44-peak produced by the conversion of carbon monoxide into carbon dioxide. The amount of carbon monoxide in the sample could be calculated from either the decrease in mass-28 peak intensity or the increase in mass-44 peak intensity.

EXPERIMENTAL

Materials

Schütze catalyst was obtained from Kodak Ltd. All gases were obtained from the British Oxygen Co.

Apparatus

The inlet system of an A.E.I. M.S.2 mass spectrometer was modified by attaching a small Pyrex glass chamber into which a porcelain boat filled with the oxidant could be introduced. The chamber could be pumped out and isolated from both the pumping system and the mass spectrometer inlet by means of taps. The sample volume could be connected to the mass spectrometer by opening a tap.

Method

A sample was introduced into the inlet reservoir of the mass spectrometer from the sample volume and its pressure was measured by means of a diaphragm micromanometer. The mass spectrum was then recorded and the reservoir pumped out. A second sample was then admitted from the sample volume and the reservoir connected to the chamber containing the catalyst. The pressure was measured on the micromanometer and the mass spectrum again recorded.

Calculation of results

Let the pressure in the reservoir for the first sample be P and the pressure after oxidation be P', and p and p' be the partial pressures of any component before and after oxidation. Let the sensitivities of the mass spectrometer for carbon monoxide, carbon dioxide and nitrogen be S_{CO}, S_{CO_2} and S_{N_2}. If H is the peak height before oxidation and H' that recorded after oxidation, then, if no carbon dioxide is present initially,

$$\frac{H'_{44}}{S_{CO_2}} = p'_{CO_2}$$
$$= \frac{P}{P'} \cdot p_{CO}$$

The partial pressure of carbon monoxide in the original sample may thus be derived from H'_{44}. If carbon dioxide is present in the original sample then this must be corrected for, *i.e.*,

$$p_{CO} = \frac{P'[H'_{44} - H_{44}P'/P]}{PS_{CO_2}}$$

In either case the nitrogen concentration may be determined from the residual H'_{28} from

$$p_{N_2}' = \frac{H'_{28} - 0{\cdot}081H'_{44}}{S_{N_2}}$$

An additional check may be made by calculating the nitrogen concentration from the residual H_{28} as given by

$$p_{N_2} = \frac{[H_{28} - 0{\cdot}081H_{44} - H'_{44}P/P' + H_{44}P'/P]}{S_{N_2}}$$

In order to compensate for instrumental variations, it is common practice to use a standard substance, to express all sensitivities relative to the sensitivity for this substance, and to make a daily check on the sensitivity of the instrument for this one substance, thus avoiding a lengthy daily calibration for all gases. A suitable calibrating substance for this work is argon, and sensitivities for the three gases, expressed as a fraction of the argon sensitivity, are shown in Table I.

RESULTS AND DISCUSSION

The method was tested in a number of ways to check whether the oxidation of carbon monoxide to carbon dioxide was complete under all the experimental conditions expected to be encountered.

1. Mixtures of nitrogen and carbon monoxide were made in a gas mixing plant. The carbon monoxide content was varied from 84·81% to 12·00%.
2. The total pressure of the gas mixture at the inlet system of the mass spectrometer and hence over the oxidant was varied from 1·3 to 130 mbar.
3. The mixture of carbon monoxide and nitrogen was diluted with equal volumes of carbon dioxide to determine whether carbon dioxide had any effect on the oxidation.
4. A mixture of argon and carbon monoxide was oxidized and checked for any residual carbon monoxide.
5. Mixtures of carbon monoxide and nitrogen were oxidized at the gas inlet system of a gas chromatography apparatus to check both for complete oxidation and for the effect of varying the time of exposure of the gas to the oxidant.

TABLE II.—ANALYTICAL RESULTS ON BLENDED GAS MIXTURES

	P_1	P_2	Composition, %						
			Ar		CO		N_2		CO_2
Blend			50·3		42·6		7·7		—
Result	93·0	67·3	50·1	50·4	41·2	41·6	7·7	8·0	—
Blend			47·2		33·0		19·8		—
Result	101·7	73·5	48·0	48·3	32·1	32·6	19·9	19·1	—
Blend			50·7		24·2		25·1		—
Result	123·0	96·9	50·2	50·0	24·7	24·3	25·1	25·7	—
Blend			43·9		23·7		33·4		—
Result	70·0	52·5	45·2	45·7	25·7	25·9	29·9	29·3	—
Blend			55·5		9·2		35·3		—
Result	70·0	52·5	51·4	51·7	10·5	10·5	38·1	37·8	—
Blend			50·7		24·2		25·1		—
Result	53·0	39·3	50·4	51·0	24·6	24·9	25·0	24·1	—
Result	27·7	21·0	50·2	50·5	24·7	25·0	25·1	25·3	—
Result	12·2	8·1	50·5	50·1	24·8	24·8	24·7	25·1	—
Result	1·4	1·1	50·5	50·2	24·2	24·6	25·3	26·2	—
Blend			54·4		45·6		—		—
Result	111·0	83·8	52·0	52·4	48·0	47·6	—		—
Blend			10·0		22·8		25·8		41·4
Result	97·2	74·3	8·7	8·9	24·5	24·9	23·7	23·2	43·7

The results of carrying out these tests are summarized in Table II. It can be seen that the results are in fair agreement with the blend values. It is in fact very difficult to make up a gas mixture of known composition merely by connecting reservoirs of the components at different pressures and allowing free diffusion. The blend values are therefore derived only from the gas pressures of the reservoirs and should not be considered as standard compositions, from which the results may deviate by a few per cent. A good test of the method is the agreement between the pairs of results obtained by different methods. A conservative estimate of the errors would be 2–3%. The results are not affected by the pressure at which oxidation takes place and satisfactory results may be achieved at pressures of ~1 mbar. The oxidation of carbon monoxide is complete and is unaffected by the addition of an excess of carbon dioxide. In a series of experiments in which small volumes of carbon monoxide were swept with a stream of nitrogen over a boat containing the Schütze catalyst in the inlet system of a gas chromatography apparatus, the extent of oxidation was determined by measuring the peak area obtained for the carbon dioxide peak. The time of exposure of the carbon monoxide to the oxidant was varied both by altering the gas flow and admitting the sample at different times. The results obtained were in agreement with those reported above and the time of exposure could not be made sufficiently brief to demonstrate incomplete oxidation of a carbon monoxide sample.

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Summary—A method for the analysis of gas mixtures containing both carbon monoxide and nitrogen, by using a single-focussing mass spectrometer, is described. It involves measurement of the mass spectrum of a gas sample before and after conversion of the carbon monoxide present into carbon dioxide by means of the Schütze catalyst.

Zusammenfassung—Die Analyse von Kohlenmonoxid und Stickstoff enthaltenden Gasgemischen unter Verwendung eines einfach fokussierenden Massenspektrometers wird beschrieben. Das Massenspektrum einer Gasprobe wird zweimal gemessen: einmal vor und einmal nach der Umsetzung des vorhandenen Kohlenmonoxids zu kohlendioxid mit Hilfe von Schütze-Katalysator.

Résumé—On décrit une méthode pour l'analyse de mélanges de gaz contenant à la fois de l'oxyde de carbone et de l'azote en utilisant un spectromètre de masse à une seule focalisation. Elle comprend la mesure du spectre de masse d'un échantillon de gaz avant et après conversion de l'oxyde de carbone présent en gaz carbonique au moyen du catalyseur de Schütze.

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Analytical applications of mixed ligand extraction equilibria

Nickel–dithizone–phenanthroline complex

(*Received* 4 *December* 1969. *Accepted* 14 *January* 1970)

THE POPULAR metal reagent dithizone (diphenylthiocarbazone) normally is not useful as a reagent for nickel because the complex forms very slowly and is less intensely coloured than most dithizonates. Recently, however, it was discovered[1] that in the presence of pyridine or other nitrogen bases together with dithizone, a mixed ligand nickel complex of unusually high absorbance is formed relatively rapidly. This reaction is not only potentially useful as a highly sensitive method for nickel but should permit an independent evaluation of the equilibrium extraction constant for nickel dithizonate. Although this had been previously reported[2] to have the value of $10^{-2.9}$ with chloroform as solvent, a more recent publication[3] cited $10^{-0.2}$ as a more reliable value because a longer (10 day) equilibration period had been employed in order to overcome the slow rate of the nickel–dithizone reaction.

The extraction constant of the mixed ligand complex, $NiDz_2 \cdot phen$, (where Dz is the dithizonate anion and phen is 1,10-phenanthroline) is defined as the equilibrium constant of the reaction

$$Ni^{2+} + 2HDz_{org} + phen_{org} \xrightleftharpoons{K'_{ex}} NiDz_2 \cdot phen_{org} + 2H^+$$

and may be evaluated by using the expression

$$D = K'_{ex} \frac{[HDz]^2_{org}[phen]_{org}}{[H^+]^2} \mu_{Ni} \tag{1}$$

where μ_{Ni} represents the fraction of the total aqueous nickel concentration that is in the uncomplexed hydrated form, and the subscript org indicates a species in the organic phase.

obtained for the carbon dioxide peak. The time of exposure of the carbon monoxide to the oxidant was varied both by altering the gas flow and admitting the sample at different times. The results obtained were in agreement with those reported above and the time of exposure could not be made sufficiently brief to demonstrate incomplete oxidation of a carbon monoxide sample.

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The extraction constant of the mixed ligand complex, $NiDz_2 \cdot phen$, (where Dz is the dithizonate anion and phen is 1,10-phenanthroline) is defined as the equilibrium constant of the reaction

$$Ni^{2+} + 2HDz_{org} + phen_{org} \overset{K'_{ex}}{\rightleftharpoons} NiDz_2 \cdot phen_{org} + 2H^+$$

and may be evaluated by using the expression

$$D = K'_{ex} \frac{[HDz]^2_{org}[phen]_{org}}{[H^+]^2} \mu_{Ni} \quad (1)$$

where μ_{Ni} represents the fraction of the total aqueous nickel concentration that is in the uncomplexed hydrated form, and the subscript org indicates a species in the organic phase.

This reaction can be seen to be the sum of (*a*) the extraction of nickel dithizonate

$$\mathrm{Ni^{2+}} + 2\mathrm{HDz_{org}} \overset{K_{ex}}{\rightleftharpoons} \mathrm{NiDz_{2org}} + 2\mathrm{H^+}$$

and (*b*) the formation of the mixed ligand adduct in the organic phase

$$\mathrm{NiDz_{2org}} + \mathrm{phen_{org}} \overset{K_{AD}}{\rightleftharpoons} \mathrm{NiDz_2{\cdot}phen_{org}}$$

so that K'_{ex}, the mixed ligand extraction constant, can be seen to be the product of the extraction constant of nickel dithizonate, K_{ex}, and the organic phase mixed-ligand adduct formation constant, K_{AD}. Hence, if K_{AD} is known,[4] K_{ex} can be evaluated.

It was therefore decided to determine K_{ex}' in order to evaluate K_{ex} and to provide a rational basis on which to design a procedure for determining nickel by use of this reaction.

EXPERIMENTAL

Materials

All materials were of analytical reagent grade.

Extraction equilibration procedure

A 20-ml portion of a chloroform solution containing the desired concentrations of dithizone and phenanthroline was added to a 60-ml screw-cap vial, followed by 20-ml of an aqueous solution that was $1{\cdot}0 \times 10^{-4}M$ in nickel(II) and buffered to the desired pH with either formate or acetate buffer at an ionic strength of 0·1, and the vial was then closed with a fitted polyethylene thimble before capping. The mixture was then shaken for 60 min (found to be sufficiently long for equilibration), allowed to stand several minutes for phase separation, and then aliquot of the phase having the lower nickel content was analysed in the manner below. The nickel content of the other phase was then obtained by difference.

Procedure for determination of nickel (aqueous phase)

Buffer the sample containing up to 15 μg of Ni in 5–10 ml solution with ammonium chloride–ammonia (pH 10). Add 15·0 ml of chloroform solution of dithizone ($6 \times 10^{-4}M$) and phenanthroline ($3 \times 10^{-4}M$). Shake vigorously for 2 min. Let the phases settle, remove the upper (aqueous) layer with a pipette and aspirator. Add 20 ml of 0·2*M* sodium hydroxide and shake for 2 min. Deliver an aliquot of the chloroform phase through a dry filter paper into a 10-mm cuvette. Read the absorbance at 520 nm against a reagent blank prepared in the same way.

Procedure for nickel (chloroform phase)

Dilute an aliquot of the chloroform phase to 15·0 ml with chloroform, then proceed as for aqueous phase, starting at addition of sodium hydroxide.

RESULTS AND DISCUSSION

On the basis of preliminary studies it was found that although quantitative nickel extraction could be obtained from solutions having pH values as low as 3, this would require higher reagent concentrations and inconveniently long equilibration times. Therefore the procedure finally developed employed an ammonium chloride–ammonia buffer at pH 10. This pH could be varied within at least ±0·3 pH units without effect. The mixed ligand complex was stable enough towards alkali for 1–2*M* sodium hydroxide to be used without decomposition of the complex; however, shaking with 0·2*M* sodium hydroxide removed excess of dithizone with adequate efficiency. A calibration curve obtained by this procedure was found to be linear to better than 4 ppt and could be used on known nickel samples with an agreement of about 5 ppt (Table I). It is likely that the method could be extended to even lower levels of nickel, but it would probably be necessary to purify reagents before use, either by shaking with portions of dithizone–phenanthroline solutions for reagents of pH under 8–9 or, as with ammonia, distilling before use. Without any special effort being made to purify reagents, the blanks observed in this study had absorbances corresponding to about 0·6–0·8 μg of nickel. It should easily be possible to extend the method down to 0·05–0·10 μg of nickel by using 100-mm cells.

In the presence of phenanthroline, the rate of extraction of nickel (as a mixed ligand complex, of course) is much faster than with dithizone alone. In fact, the rate of extraction is related to processes involving mainly nickel phenanthroline complexes.[5] Nevertheless, the overall extraction is faster at higher pH values and equilibration can require as long as 30 min in the pH range 3–4. In evaluating

TABLE I.—ANALYSES OF NICKEL SAMPLES

Absorbance at 520 nm	Total nickel, μg Taken	Total nickel, μg Found	Error Abs., μg	Error Rel., *ppt*
0·128	2·33	2·28	−0·05	22
0·131	2·33	2·33	0·00	0
0·260	4·67	4·70	+0·03	6
0·259	4·67	4·68	+0·01	2
0·385	7·00	6·99	−0·01	1
0·385	7·00	6·99	−0·01	1
0·517	9·36	9·41	+0·05	5
0·516	9·36	9·39	+0·03	3
0·890	16·36	16·25	−0·11	7
0·900	16·36	16·43	+0·07	4

Calibration curve from least squares: $A_{520} = (0{\cdot}05453 \pm 0{\cdot}00021)W_{Ni} + 0{\cdot}0039$ where W_{Ni} is the weight of nickel, in μg.

extraction equilibria involving phenanthroline it is necessary to take into account the effect of metal–phenanthroline complex formation in the aqueous phase.[6,7] This can readily be done by evaluating μ_{Ni} in equation (1) from the expression

$$\mu_{Ni} = \{1 + \beta_1[\text{phen}] + \beta_2[\text{phen}]^2 + \beta_3[\text{phen}]^3\}^{-1} \qquad (2)$$

where β_1, β_2 and β_3 are the cumulative Ni^{2+}–phen formation constants, and [phen] is the phenanthroline concentration in the aqueous phase, obtained by dividing the organic phase phenanthroline concentration, $[\text{phen}]_{org}$, by the phenanthroline distribution constant $(K_{DR} = 10^{3{\cdot}0})$[7]. In Table II are

TABLE II.—EQUILIBRIUM EXTRACTION OF BIS(DIPHENYLTHIOCARBAZONATO)NICKEL(II)–PHENANTHROLINE INTO CHLOROFORM FROM WATER AT 25°C AND 0·1 IONIC STRENGTH

pH	log D_{Ni}	$-\log\,[\text{HDz}]^*_{org}$	$-\log\,[\text{phen}]^*_{org}$	$-\log\,\mu_{Ni}$	log K_{ex}'
4·75	1·50	3·21	4·21	2·7	5·1
3·80	0·43	2·66	4·00	3·3	5·4
4·25	0·66	3·17	4·06	3·1	5·6
4·80	1·28	3·21	4·21	2·7	5·0
				Mean	5·3 ± 0·3

* Initial concentration corrected for amount consumed in Ni reaction.

listed values of μ_{Ni} for various equilibrium runs, calculated from log $\beta_1 = 8{\cdot}60$, log $\beta_2 = 16{\cdot}70$, log $\beta_3 = 24{\cdot}25$,[8] and values of log K_{ex}' from equation (1). With the average value 5·3 for log K'_{ex}, and the previously determined[4] value 5·96 for log K_{AD}, the extraction constant for nickel dithizonate, $K_{ex} = K'_{ex} / K_{AD}$, yields a value log $K_{ex} = -0{\cdot}7$ which is in fair agreement with log $K_{ex} = -0{\cdot}2$, obtained from direct measurement by McClellan and Sabel[3] in a 10-day equilibration run. This not only confirms McClellan's interpretation of the low value of the previously reported log $K_{ex} = -2{\cdot}9$ but emphasizes the importance of 1,10-phenanthroline in substantially accelerating the rate of nickel extraction in this system.

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Summary—The mixed ligand nickel-dithizone–phenanthroline complex provides a sensitive method for determination of nickel and also permits evaluation of the extraction constant for nickel dithizonate. The value log $K_{ex} = -0{\cdot}7$ was obtained, in agreement with a value of $-0{\cdot}2$ obtained by others, and in contrast to an earlier value of $-2{\cdot}9$. The addition of phenanthroline substantially increases the rate of extraction.

Zusammenfassung—Der gemischte Komplex von Nickel mit Dithizon und Phenanthrolin bietet eine empfindliche Methode zur Bestimmung von Nickel und erlaubt auch die Ermittlung der Extraktionskonstanten von Nickeldithizonat. Der Wert log $K_{ex} = -0,7$ wurde erhalten; er stimmt überein mit dem von anderen Autoren erhaltenen Wert $-0,2$, nicht jedoch mit dem älteren Wert $-2,9$. Die Zugabe von Phenanthrolin erhöht die Extraktionsrate beträchtlich.

Résumé—Le complexe mixte nickel–dithizone–phénanthroline fournit une méthode sensible pour le dosage du nickel et permet aussi l'évaluation de la constante d'extraction pour le dithizonate de nickel. On a obtenu la valeur log $K_{ex} = -0,7$, en accord avec une valeur $-0,2$ obtenue par d'autres, mais en opposition avec une valeur plus ancienne de $-2,9$. L'addition de phénanthroline accroît nettement la vitesse d'extraction.

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Use of a filter in atomic-fluorescence spectroscopy

(*Received* 24 *June* 1969. *Revised* 12 *January* 1970. *Accepted* 22 *January* 1970)

In ATOMIC-FLUORESCENCE flame spectroscopy, the limit of detection (defined as the solution concentration producing a given signal:noise ratio, usually 2) may generally be improved by increasing (*a*) the intensity of the source of primary radiation, (*b*) the amount of sample reaching the flame, or (*c*) the signal:noise ratio by reducing noise or increasing the signal by using an optical system with a higher light-gathering power.

High-intensity light sources, mainly microwave-excited electrodeless discharge tubes, have been used to obtain very low limits of detection, particularly for zinc and cadmium.[1] Heated spray chamber burners[2,3] enable more sample to enter the flame, while separated flames[4,5] and diffusion flames[6] have reduced flame noise, consequently increasing the signal:noise ratio.

Attempts to increase the light-gathering power have incorporated lenses to focus radiation from the flame onto the monochromator slit,[7] and the use of a concave mirror to collect radiation from the opposite side of the flame to the monochromator and focus this onto the slit.[7,8] Although the use of a mirror increases the signal it also increases the noise so the limit of detection is often not improved. The light-gathering power of the conventional system is mainly limited by the *f*-number of the monochromator used to separate the signal from background radiation.

This communication reports on the use of an interference filter, with auxiliary optics of low *f*-number to obtain a large light-gathering power, in place of the conventional monochromator in atomic-fluorescence spectroscopy. The light-gathering power of this system will effectively be limited by the *f*-number of the auxiliary optics. The use of a filter in atomic-fluorescence spectroscopy has previously been suggested by Jenkins[9] and West.[10] The filter is used to attenuate background radiation rather than to select a certain fluorescence wavelength.

Most of the background radiation can be attributed to flame emission above 300·0 nm, so the filter–photomultiplier combination should have a low response in this region to reduce noise and photomultiplier fatigue. By choosing a filter with a suitably wide bandpass below 300·0 nm and a

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Most of the background radiation can be attributed to flame emission above 300·0 nm, so the filter–photomultiplier combination should have a low response in this region to reduce noise and photomultiplier fatigue. By choosing a filter with a suitably wide bandpass below 300·0 nm and a photomultiplier with suitable response characteristics in this region, it should be possible to use one filter–photomultiplier combination for the determination of several elements which have fluorescence wavelengths below 300·0 nm.

Because larger background scatter and flame noise signals result from the increase in light-gathering power, for a system incorporating a filter to show an advantage over conventional systems both signals must be limited. Background scatter has been reduced to a tolerable level by shielding the sources of primary radiation and using a light trap. The increase in flame noise has been limited by using a bandpass of the a.c. amplifier that rejects most of the flame–noise signal.

Results obtained with the filter–photomultiplier combination are compared with those from another non-dispersive detecting system, incorporating a solar-blind photomultiplier, that has previously been used in atomic-fluorescence spectroscopy analysis.[12,13] Also, results from the non-dispersive systems are compared with those obtained from a conventional dispersive system incorporating a monochromator.

EXPERIMENTAL

The arrangement of the apparatus is shown in Fig. 1.

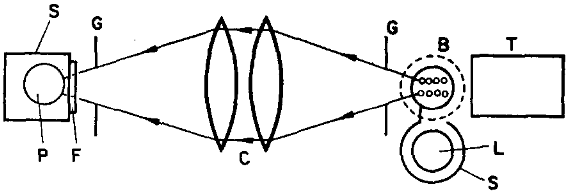

FIG. 1.—Arrangement of apparatus. *C*—condensing lenses, *B*—burner, *L*—lamp, *G*—stop, *P*—photomultiplier, *F*—filter, *S*—screening, *T*—light trap.

Primary sources of radiation

A Philips zinc vapour discharge lamp, operated from a variable transformer and a ballast leak transformer, was used for the investigation on zinc. A specially constructed mercury discharge tube (internal diameter 18·4 mm, length 0·20 m, argon gas pressure 2·7 mbar, weight of mercury 100 mg) was used for the determination of mercury. The lamp was operated on full-wave rectified, unsmoothed a.c. *via* a 100-ohm power resistor. The full-wave rectification unit was operated from a variable transformer supplied from a constant voltage source (Advance Volstat CV5 750A).

Aluminium screening, painted flat black, placed around the lamps, limited background scatter of radiation. A 50 × 20 mm hole in the screening allowed radiation from a selected region of the positive column of the mercury discharge and from the whole length of the zinc discharge to illuminate the flame. A protrusion on the detecting system side of this hole prevented radiation from the lamps entering the detecting system directly.

Flame

An air–town-gas flame was supported on an Evans Electroselenium burner head (from an EEL flame photometer model 100) the gases and sample solution being mixed in a spray chamber from a Unican SP90 atomic-absorption spectrophotometer. The holes in the burner head were aligned along the lens–filter axis. The flame produced by this burner had an approximate cross section of 20 × 10 mm and a height of 0·10 m. All gases were regulated with needle valves and monitored by flowmeters.

Detecting system

The condensing lenses were of quartz, diameter 80 mm, focal length 80 mm. The photomultiplier (R.C.A. 1P28) was housed in an aluminium box with a hole cut to the size of the photocathode. The filter (Baird-Atomic Prominent Ultraviolet Line Filter A.1.) was placed in front of this hole and secured with a black rubber washer which prevented stray radiation from entering at the edges of the filter. The spectral response of the filter–photomultiplier combination is shown in Fig. 2, curve *e*. An Isotopes Development Ltd. E.H.T. unit 532/D provided power for the photomultiplier, the signal from which was fed into a lock-in a.c. amplifier (Brookdeal Electronics Ltd. FL 355). The signal from the amplifier was then fed into a phase shifter–meter unit (Brookdeal Electronics Ltd. MS 320) the output from which was recorded on a Honeywell pen recorder. The 100 Hz reference signal for the phase shifter was obtained by the full wave rectification of the output of a 6·3-V transformer. A time constant of 1 sec was used for all measurements.

A light trap was constructed from a circular box, diameter 0·30 m, length 0·40 m, open at one end and lined with black velvet. This was placed on the opposite side of the flame to the detecting system, with the open end facing the flame, thus reducing the amount of background scattered radiation entering the detecting system.

Procedure

Standard 1000-ppm solutions of the elements were prepared by dissolving mercury(II) chloride in demineralized water, and zinc oxide in the minimum quantity of hydrochloric acid, and diluting with demineralized water. Less concentrated solutions were obtained by further dilution.

A photomultiplier voltage of 1·00 kV was used, and the lamp placed as close to the flame as possible (50 mm). The air flow-rate to the flame was fixed at 5·0 l./min and the fuel flow-rate for optimum signal-noise ratio was 1·6 l./min for both mercury and zinc. The aspiration rate of the solution was 3·1 ml/min.

The condensing lens system was placed 0·10 m from the center of the burner head and the aperture of the stop adjusted so that the lens system was just filled with radiation from the flame. The photomultiplier–filter position was adjusted by aspirating a zinc solution into the flame, irradiating with zinc resonance radiation and finding the position giving a maximum reading. The position of the burner head below the optical axis was adjusted until the signal resulting from scattering of primary radiation from the head was reduced to a tolerable level when the maximum gain of the amplifier was used. Approximately the middle third of the flame was focussed on to the photocathode. The fluorescence signal from a 1-ppm solution of both zinc and mercury remained essentially constant when the burner head was raised until the tips of the inner cones were just below the bottom of the front stop.

Choice of lamp operating conditions

The lamp currents were adjusted by means of a variable transformer to give a maximum fluorescence signal for a 1-ppm solution of the respective elements. The zinc lamp showed a maximum fluorescence signal at between 0·45 and 0·55 A and the mercury lamp at between 0·15 and 0·30 A.

Tests for scattering

Demineralized water was aspirated at all times when measurements were not being taken. To verify that the recorded signal was a fluorescence signal and was not caused by scattering within the flame the following procedure was used: with the amplifier at maximum gain, a 1-ppm mercury solution was aspirated and the flame irradiated with zinc 213·9-nm resonance radiation. No increase in signal above background resulted. A similar result was obtained with a 1-ppm zinc solution and mercury 253·7-nm radiation, and a 1-ppm lead solution with either mercury or zinc radiation.

Measurements made using a monochromator and solar-blind photomultiplier

To make a meaningful comparison of the results obtained when using a filter with those when using a monochromator, the condensing lenses and filter were replaced by a Jarrel-Ash 0·5-m grating monochromator incorporating an R.C.A. 1P28 photomultiplier. The flame was placed 40 mm from the entrance slit with the tips of the inner cones of the flame approximately 10 mm below the bottom of the slit. Both entrance and exit slits were set at 2·00 mm. The other parameters remained unchanged.

For measurements with a solar-blind photomultiplier, a Hamamatsu H.T.V. R.166 photomultiplier replaced the R.C.A. 1P28, the filter was removed and radiation from the flame was focussed directly onto the photocathode, all other parameters remaining unchanged.

RESULTS AND DISCUSSION

Table I lists the optimum lamp currents and limits of detection for zinc and mercury obtained with a monochromator, a filter–photomultiplier combination, or a solar-blind photomultiplier. Calibration curves of fluorescence signal against concentration for each system are essentially the same as

TABLE I.—LAMP CURRENTS AND LIMITS OF DETECTION FOR ZINC AND MERCURY

		Limit of detection, *ppm*		
Element	Lamp current, *A*	Monochromator	Filter	Solar-blind
Zinc	0·50	0·007	0·00001	0·00002
Mercury	0·30	0·02	0·002	0·00025

those obtained by Mansfield *et al.*,[11] being approximately linear from the limit of detection up to 5 ppm for zinc and 1000 ppm for mercury.

The limit of detection for zinc is improved by a factor of 700 by replacing the monochromator with a filter. This result is accounted for by the increased light-gathering power of the optical system, and a larger portion of the flame being focussed onto the photocathode. The optimum limit of detection of 10^{-6} ppm for zinc is an improvement on other recorded values obtained by using a Philips zinc vapour discharge lamp.[8,11]

For mercury, the limit of detection with the present filter and photomultiplier is an order of magnitude lower than that obtained by using a monochromator. This smaller improvement (compared with that obtained for zinc) is accounted for by the increase in light-gathering power being partially offset by the approximately 10-fold decrease in response of the filter-photomultiplier combination at 253·7 nm compared with that at 213·9 nm, Fig. 2, curve *e*. The optimum limit of detection of $2{\cdot}5 \times 10^{-4}$ ppm obtained with the solar blind photomultiplier is an improvement on the value of 0·08 ppm obtained by Browner *et al.*[7] from an aqueous solution in an air–hydrogen flame, and on the value of 0·1 ppm obtained by Mansfield *et al.*[11] from an aqueous solution in an oxy-hydrogen flame.

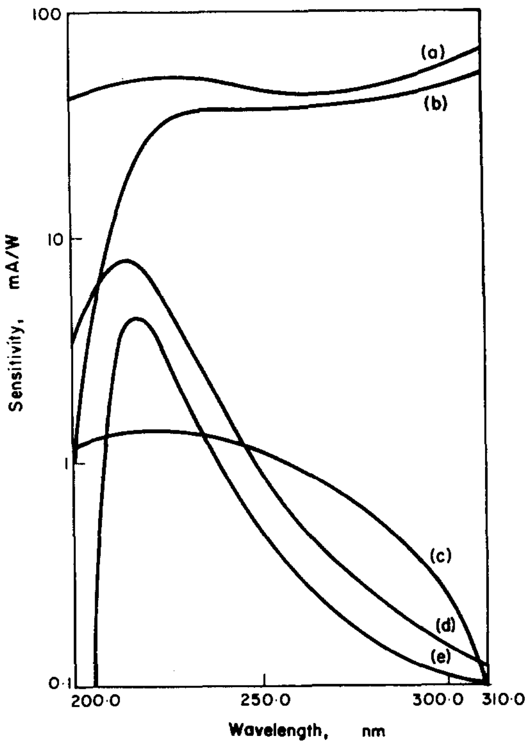

FIG. 2.—Approximate spectral response characteristics for various photocathodes and filter-photocathode combinations.
(*a*) S19; (*b*) S5; (*c*) Hamamatsu R166;
(*d*) Baird-Atomic Prominent Ultraviolet Line Filter A.1. and S19 photocathode;
(*e*) Baird-Atomic Prominent Ultraviolet Line Filter A.1. and S5 photocathode;

The spectral response characteristics of the filter–photomultiplier combination and the solar-blind photomultiplier are compared in Fig. 2, curves *e* and *c*. The combination shows an approximately 5-fold greater sensitivity than the solar-blind photomultiplier at 213·9 nm, while the solar-blind photomultiplier shows an approximately 5-fold greater sensitivity at 253·7 nm. Experimentally, the sensitivity of the solar-blind photomultiplier was found to be approximately 5-fold greater at 213·9 and 253·7 nm compared with the curve estimated from published data, Fig. 2, curve *c*. Consequently, the apparent signal from a given concentration of zinc was approximately the same with either system, but that from a given concentration of mercury was approximately an order of magnitude greater when the solar-blind photomultiplier was used. The flame-noise signal for the solar-blind photomultiplier was approximately twice that for the combination.

Comparisons have been made with a single solar-blind photomultiplier. Manufacturers state that it is extremely difficult to reproduce the solar-blind photocathode to an exact sensitivity, so that a 5-fold variation in sensitivity compared with published figures is quite possible. The use of a photomultiplier with an S19 response, Fig. 2, curve *a*, in place of the R.C.A. 1P28 with an S5 response, Fig. 2, curve *b*, would enhance the sensitivity of the filter-photomultiplier combination in the short-wavelength region, Fig. 2, curve *d*, the response around 300·0 nm being little affected.

Because of differences in apparatus it is difficult to compare accurately results of various recorded investigations. The most valid comparison of limits of detection obtained when a filter–photomultiplier combination, a solar-blind photomultiplier or a monochromator is used, is that in which results are obtained under otherwise identical experimental conditions, as in the present investigation.

The results of this investigation confirm that limits of detection can be improved by using a filter in place of a monochromator in atomic-fluorescence spectroscopy. With a suitable choice of filter and photomultiplier the 200·0–300·0 nm region can be covered with a single combination, giving comparable results to those from a solar-blind photomultiplier. For other wavelength regions a filter–photomultiplier combination should provide superior limits of detection compared with a monochromator, providing background noise, from the flame or other source of ground-state atoms, is low. In particular, the filter–photomultiplier combination should be most useful in conjunction with the carbon filament.[14]

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Summary—A detecting system incorporating an interference filter is described for use in atomic-fluorescence spectroscopy analysis in the 200·0–300·0 nm spectral region. Results obtained by using this system are compared with those from a detecting system incorporating either a monochromator or a solar-blind photomultiplier. Improvements of approximately 700-fold and 10-fold respectively in the limits of detection for zinc and mercury result from replacing the monochromator with the filter, while results with the filter are similar to those from a solar-blind photomultiplier. Limits of detection of 10^{-5} ppm for zinc and $2{\cdot}5 \times 10^{-4}$ ppm for mercury, both in aqueous solutions aspirated into an air–town-gas flame, are an improvement on other published results for these elements, obtained by atomic-fluorescence flame spectroscopy.

Zusammenfassung—Ein Nachweissystem mit Interferenzfilter zum Gebrauch bei der atomfluoreszenzspektrometrischen Analyse im Spektralbereich 200–300 nm wird beschrieben. Damit erhaltene Ergebnisse werden verglichen mit solchen, die mit anderen Nachweissystemen, entweder mit Monochromator oder mit tageslichtblindem Photomultiplier erhalten wurden. Bei den Nachweisgrenzen von Zink und Quecksilber erzielt man Verbesserungen um den Faktor 700 bzw. 10, wenn man den Monochromator durch das Filter ersetzt; dagegen sind die Ergebnisse mit dem Filter ähnlich wie mit dem tageslichtblinden Photomultiplier. Nachweisgrenzen von 10^{-5} ppm für Zink und $2{,}5 \times 10^{-4}$ ppm für Quecksilber, jeweils in wäßrigen Lösungen in eine Luft–Stadtgas–Flamme gesaugt, bedeuten eine Verbesserung gegenüber anderen publizierten Ergebnissen, die durch Atomfluoreszenz-Flammenspektrometrie an diesen Elementen erhalten wurden.

Résumé—On décrit un système détecteur comprenant un filtre interférentiel pour emploi en analyse par spectroscopie de fluorescence atomique dans la région spectrale 200,0–300,0 nm. Les résultats obtenus en utilisant ce système sont comparés à ceux d'un système

détecteur comprenant soit un monochromateur, soit un photomultiplicateur aveugle à la lumière solaire. Il résulte des améliorations d'approximativement 700 fois et 10 fois respectivement dans les limites de détection pour le zinc et le mercure du remplacement du monochromateur par le filtre, tandis que les résultats avec le filtre sont semblables à ceux d'un photomultiplicateur aveugle à la lumière solaire. Des limites de détection de 10^{-5} *ppm* pour le zinc et 2,5 × 10^{-4} *ppm* pour le mercure, tous deux en solutions aqueuses aspirées dans une flamme air–gaz de ville, sont une amélioration par rapport à d'autres résultats publiés pour ces éléments et obtenus par spectroscopie de flamme de fluorescence atomique.

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Thermometric titration of sulphate

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A VOLUMETRIC determination of sulphate with barium ions is often preferred to a gravimetric one despite difficulties with reliable detection of the end-point. Visual end-point detection is most vulnerable to interferences, because barium cations form only rather weak complexes with indicators. Frequently the colour change is not well defined and standardized titration conditions are usually required. However, the situation can be improved considerably by employing instrumental end-point detection. These methods were recently reviewed in connection with the determination of sulphur in organic samples.[1] Application of a specific ion-sensitive electrode for this purpose was reported recently.[2]

We have investigated the possibility of thermometric end-point detection and its applicability to practical sulphate determination. Thermometric titration of sulphate by barium ions was reported by Dean and Watts[3] and later by Mayr and Fisch[4] but with controversial results. Determination of sulphate by precipitation with barium ions is also mentioned in work on injection enthalpimetry.[5]

EXPERIMENTAL

Apparatus

A modified a.c.-thermistor bridge by Richards[6] with an LTC 23F thermistor was used to detect the temperature changes. The output of this bridge, which was used at a sensitivity of 5 V/deg was fed into a Servoscribe recorder; 50-ml or 100-ml polytetrafluoroethylene (PTFE) beakers mounted in a block of polystyrene foam served as titration vessels. Efficient and constant mixing was provided by a vibrating paddle mounted on the glass body of the thermistor.[7] The paddle was driven by a V-1 vibrator (Advance Instruments Ltd.) at 50 Hz. A motorized Agla micrometer syringe was used in the early experiments but was later replaced by a Radiometer ABU-12 burette. The titrant and all other solutions were kept in a water thermostat in order to minimize the temperature drift.

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Reagents

Barium perchlorate, 1–2*M* aqueous solution, was standardized gravimetrically. Organic sulphur compounds were microanalytical standards and all other chemicals were analytical-reagent grade. Distilled demineralized water was used in all experiments.

RESULTS AND DISCUSSION

Effect of ethanol

An ethanol (or acetone)–water medium is frequently used, particularly in sulphate titrations with visual indicators. It was found that the stoichiometry of the precipitation depends on the concentration of ethanol (Fig. 1). Adsorption of soluble sulphate on freshly precipitated barium sulphate was suggested as a possible explanation of negative errors observed in the earlier thermometric work.[3,4] It is therefore conceivable that concentrations of ethanol above 50% v/v eliminate this co-precipitation. Other surface-active compounds such as thymol were found to have no effect on the stoichiometry of the reaction. It should be noted from Fig. 1 that the results at concentrations of ethanol less than 50% have much lower precision than those at above this level.

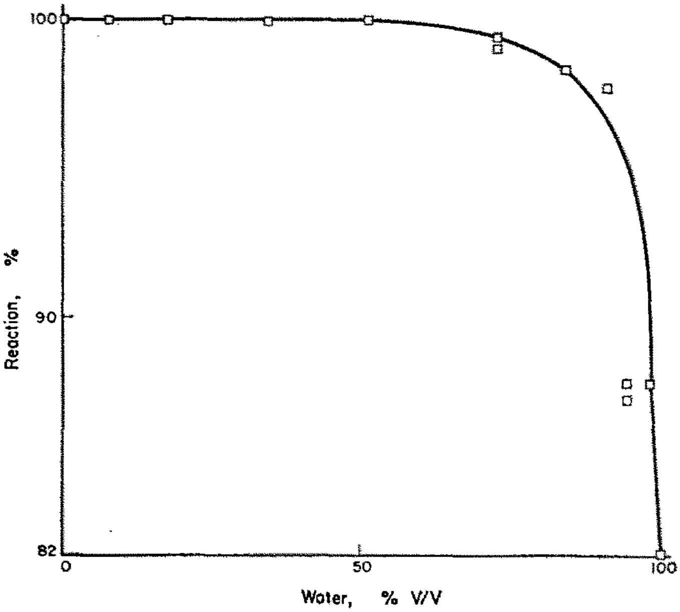

FIG. 1.—Effect of composition of ethanol/water mixture on the stoichiometry of the titration of 1 ml of 0.1*N* sulphuric acid.

Determination of sulphate

Results of determinations of sulphate both in inorganic and organic samples (following oxygen flask combustion or fusion with sodium peroxide) are summarized in Table I. The general procedure for a titration is as follows.

The sample, containing 1–25 mg of sulphate, is placed in a PTFE beaker and diluted to 30 ml with ethanol and water (together with 1 ml of a 10% solution of perchloric acid) in such proportions as to give a 70% ethanolic solution. After equilibration in a water-bath for approximately 10 min the beaker is fixed in the polystyrene block and the vibrator switched on. Depending on the size of the sample, the burette speed, recorder chart speed and the bridge sensitivity are adjusted to give a suitable rate of deflection; typical chart speeds are 30 or 120 mm/min. From the rate of addition of titrant and chart speed the volume of barium perchlorate can be calculated and hence the amount of sulphate present.

For the given volume of titration mixture the temperature rise is approximately 0·1° per ml of 0·1*N* sulphuric acid. The titration itself takes approximately 1–3 min to complete. The minimum

TABLE I.—ANALYSIS OF SULPHUR COMPOUNDS

Sample	Amount taken *mg*	S, % Theory	S, % Mean found	Rel. std devn., %§
H_2SO_4	0·9807	32·7	31·8	1·6
H_2SO_4	2·451	32·7	33·2	2·2
H_2SO_4	4·902	32·7	33·0	3·6
H_2SO_4	9·804	32·7	32·7	1·1
H_2SO_4	24·50	32·7	32·2	1·6
Na_2SO_4	14·20	22·5	22·9	1·8
Sulphonal*	10–13	28·1	28·9	7·1
Sulphonal†	10–13	28·1	27·0	1·6
Benzyl* thiuronium chloride	19–24	15·8	16·3	2·7

* After oxygen flask combustion.
† Following fusion with 1–2 g of sodium peroxide.
§ Calculated from at least 7 determinations.

amount of sulphate which can be determined by this method with reasonable accuracy is about 1 mg.

Interferences from various inorganic compounds were also investigated both in equimolar amounts and in a slight excess. No interference was found from excess of iron(III) chloride, copper(II) chloride, nickel choride or silver nitrate. Interferences from excess of sodium fluoride can be eliminated by addition of boric acid. Phosphate and arsenate do not interfere in equimolar concentrations but low results for sulphate were found if they were present in higher concentrations. When an inorganic compound was present which was precipitated on addition of the ethanol, low results were always obtained.

CONCLUSIONS

The proposed method is very rapid and suffers from only a few interferences. On the other hand-the accuracy is lower than in other instrumental methods. This might be due to the fact that the short titration time which is required for the semi-adiabatic arrangement is not long enough for barium sulphate to be formed exactly stoichiometrically, because of adsorption phenomena which occur during the precipitation.

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Summary—Direct thermometric titration of sulphate with a solution of barium perchlorate is proposed. The stoichiometry of the titration is shown to be critically dependent on the concentration of ethanol in the titration medium. The titration is rapid and suffers from only a few interferences.

Zusammenfassung—Die direkte thermometrische Titration von Sulfat mit einer Lösung von Bariumperchlorat wird vorgeschlagen. Es wird gezeigt, daß die Stöchiometrie der Titration empfindlich von der Äthanolkonzentration im Titrationsmedium abhängt. Die Titration geht schnell und unterliegt nur wenigen Ströungen

Résumé—On propose un titrage thermométrique direct du sulfate avec une solution de perchlorate de baryum. On montre que la stoechiométrie du titrage dépend de manière essentielle de la concentration de l'éthanol dans le milieu de titrage. Le titrage est rapide et ne souffre que de seulement quelques interférences.

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Di-n-butyl carbamoylphosphonate as an extractant of inorganic ions from hydrochloric acid solutions

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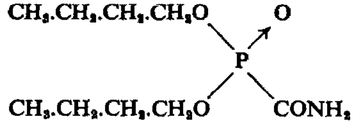
DI-n-BUTYL CARBAMOYLPHOSPHONATE (DBCP)* was found to extract readily the elements scandium, zirconium, hafnium, thorium, protactinium, uranium and neptunium from their solutions in nitric acid.[1]

This study comprises the measurement of the extracting ability of DBCP for 33 elements from their solutions in 0·5—12*M* hydrochloric acid. A 0·1*M* solution of DBCP in chloroform was used as the extractant. In most cases radioisotopes of the elements were used as tracers for the extraction experiments. Extraction coefficients of uranium(VI) and thorium were determined spectrophotometrically.[2,3]

EXPERIMENTAL

DBCP was synthesized in the laboratory[4] and purified by recrystallization from ethanol. It is a white crystalline solid (m.p. 175–176°) with the structure



The radioisotopes used were prepared as described earlier.[1] For the determination of the distribution ratio, *D*, 1 mg of the element was added to hydrochloric acid solutions of various concentrations, except in the cases of neptunium, technetium and protactinium, where the behaviour of carier-free ^{239}Np, ^{99m}Tc and ^{233}Pa was studied. The distribution ratios were measured as in our earlier work.[1]

RESULTS AND DISCUSSION

The obtained *D* values for all the elements studied are compiled in Fig. 1 in a graph of log *D vs* molarity of hydrochloric acid. Elements showing *D* values less than 10^{-2} are presented in a single group. An examination of Fig. 1 shows that the univalent and bivalent ions studied are non-extractable in the whole range of acidity 0·5–12*M* hydrochloric acid, showing *D* values lower than 10^{-2}. Of the trivalent ions, only indium and chromium show less than 1% extraction in the whole range of acidity, while all the others, including the lanthanides, show high extraction values in acidities greater than 6*M* hydrochloric acid. It is important to note here that among the trivalent ions, scandium was the only one extracted by DBCP to an appreciable extent from nitric acid solutions, while, with the exception of cerium(IV), lanthanides are extracted by DBCP only 5% or less from this medium.[1] A striking difference is observed between the behaviour of niobium and tantalum, the former being much the more extractable (maximum for Nb 92% and for Ta 16%, both from 10*M* hydrochloric acid).

The maximum extraction values of zirconium and hafnium are 96% and 98% respectively from 12*M* hydrochloric acid. They present larger differences at the lower acidities. Among all the elements studied, thorium shows the highest extractability. It is extracted nearly quantitatively even from

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* Originally named by the authors as *N*-(di-n-butylphosporo)urea, (N–DBPU).

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Di-n-butyl carbamoylphosphonate as an extractant of inorganic ions from hydrochloric acid solutions

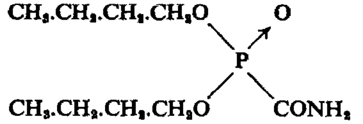
(*Received* 9 *October* 1969. *Accepted* 24 *January* 1970)

DI-n-BUTYL CARBAMOYLPHOSPHONATE (DBCP)* was found to extract readily the elements scandium, zirconium, hafnium, thorium, protactinium, uranium and neptunium from their solutions in nitric acid.[1]

This study comprises the measurement of the extracting ability of DBCP for 33 elements from their solutions in 0·5—12*M* hydrochloric acid. A 0·1*M* solution of DBCP in chloroform was used as the extractant. In most cases radioisotopes of the elements were used as tracers for the extraction experiments. Extraction coefficients of uranium(VI) and thorium were determined spectrophotometrically.[2,3]

EXPERIMENTAL

DBCP was synthesized in the laboratory[4] and purified by recrystallization from ethanol. It is a white crystalline solid (m.p. 175–176°) with the structure



The radioisotopes used were prepared as described earlier.[1] For the determination of the distribution ratio, *D*, 1 mg of the element was added to hydrochloric acid solutions of various concentrations, except in the cases of neptunium, technetium and protactinium, where the behaviour of carier-free ^{239}Np, ^{99m}Tc and ^{233}Pa was studied. The distribution ratios were measured as in our earlier work.[1]

RESULTS AND DISCUSSION

The obtained *D* values for all the elements studied are compiled in Fig. 1 in a graph of log *D vs* molarity of hydrochloric acid. Elements showing *D* values less than 10^{-2} are presented in a single group. An examination of Fig. 1 shows that the univalent and bivalent ions studied are non-extractable in the whole range of acidity 0·5–12*M* hydrochloric acid, showing *D* values lower than 10^{-2}. Of the trivalent ions, only indium and chromium show less than 1% extraction in the whole range of acidity, while all the others, including the lanthanides, show high extraction values in acidities greater than 6*M* hydrochloric acid. It is important to note here that among the trivalent ions, scandium was the only one extracted by DBCP to an appreciable extent from nitric acid solutions, while, with the exception of cerium(IV), lanthanides are extracted by DBCP only 5% or less from this medium.[1] A striking difference is observed between the behaviour of niobium and tantalum, the former being much the more extractable (maximum for Nb 92% and for Ta 16%, both from 10*M* hydrochloric acid).

The maximum extraction values of zirconium and hafnium are 96% and 98% respectively from 12*M* hydrochloric acid. They present larger differences at the lower acidities. Among all the elements studied, thorium shows the highest extractability. It is extracted nearly quantitatively even from

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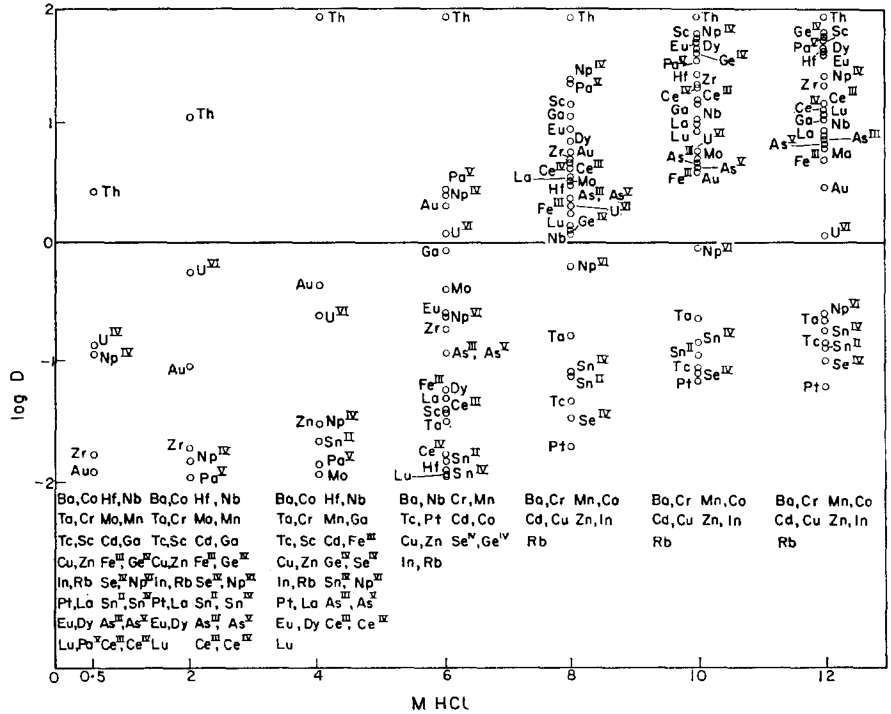

FIG. 1.—Log *D* values in 0·1*M* DBCP–HCl system [the values for As(III) and Ge(IV) correspond to the extraction by chloroform].

4*M* hydrochloric acid, while the extraction of carrier-free protactinium is very small up to this acid concentration. The extraction of uranium in the form of UO_2^{2+} is relatively high even at low acidities, with a maximum value of 87% from the 10*M* acid. The distribution ratios of carrier-free neptunium (IV) and (VI) are very different at all acid concentrations studied, the former being always the more extractable [maximum extraction values are 98% and 49% for neptunium(IV) and (VI) respectively from 10*M* hydrochloric acid].

Blank experiments with the pure solvent did not show any measurable extraction for any of the elements examined except for arsenic(III) and germanium(IV) which are extracted to a high degree by chloroform.

In summary, the extraction ability of DBCP is greater at high hydrochloric acid concentrations, a trend which was also observed for the extraction from nitric acid solutions.[1] On the other hand fewer elements are extracted from nitric acid solutions, which means that the selectivity of this new extractant is lower when the extractions are carried out from hydrochloric acid solutions. There are reasons to believe that the phosphoroamide moiety in the structure of DBCP is important in the extraction and future work is planned for the study of the extraction mechanism and the structure of the solvates involved.

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Summary—The extraction of 33 elements by a 0·1*M* solution of di-n-butyl carbamoylphosphonate in chloroform has been investigated as a function of hydrochloric acid concentration. The results show that this new extractant readily extracts most of the elements in a high oxidation state, including the trivalent rare earths, from hydrochloric acid at concentrations greater than 6*M*.

Zusammenfassung—Die Extraktion von 33 Elementen durch eine 0,1 *M* Lösung von Di-n-butylcarbamoylphosphonat in Chloroform wurde in Abhängigkeit von der Salzsäurekonzentration untersucht. Die Ergebnisse zeigen, daß dieses neue Extraktionsmittel die meisten höherwertigen Elemente extrahiert, einschießlich der dreiwertigen seltenen Erdenen, wenn die Salzsäurekonzentration höher als 6 *M* ist.

Résumé—On a étudié l'extraction de 33 éléments par une solution 0,1*M* de carbamoylphosphonate de di-*n*-butyle en chloroforme, en fonction de la concentration en acide chlorhydrique. Les résultats montrent que ce nouvel agent d'extraction extrait aisément la plupart des éléments qui sont dans un état d'oxydation élevé, y compris les terres rares trivalentes, de l'acide chlorhydrique à des concentrations plus grandes que 6*M*.

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LETTER TO THE EDITOR

Determination of manganese(II) in the presence of vanadium(V) and chromium(VI)

SIR,

Since Lingane and Karplus[1] in 1946 introduced the determination of Mn(II) by titration with $KMnO_4$ in pyrophosphate solution, this method of analysis is frequently used. Both Mn(II) and Mn(VII) are converted into Mn(III), which forms a very stable complex with pyrophosphate. Since the intense red colour of the complex precludes the use of a colour indicator, the titration is generally performed potentiometrically. The titration may be performed at pH 1–8, but the potential break at the equivalence point is maximal at pH 6–7. Furthermore, several components that interfere at low pH values do not do so at pH 6–7.[2] Vanadium(V), however, if present in more than small amounts, interferes at pH 6–7. At lower pH this interference is eliminated,[1] but other difficulties then arise. Chromium(VI), often present after oxidative attack on samples containing chromium, interferes by oxidizing Mn(II) to Mn(III) in the solution used.

We have found that amounts of vanadium up to 100 mg do not interfere at pH 6–7, but that larger amounts make the potential stabilization very slow, although the final result is still correct. The effect of chromium can be eliminated if the Cr(VI) is first reduced to Cr(III) by addition of 210 mg of sodium nitrite (for a maximum of 1 mmole of dichromate), followed by dilution to about 100 ml, adjustment to pH 1 with alkali or hydrochloric acid, heating at 40° for a few minutes, addition o 500 mg of urea and heating near the boiling point for 30 min (to remove excess of nitrite and the gases evolved in that process), then addition of this solution to 300 ml of saturated sodium pyrophosphate solution, adjustment to pH 6–7, and, after an hour, titration potentiometrically with permanganate. If larger amounts than 100 mg of vanadium are present, the titration is performed at 60°. The increased temperature is necessary to give rapid potential equilibration. An alternative is to add most of the titrant at room temperature and the rest after heating the solution to 55–60°. The rest period of an hour when chromium is present is necessary because the formation of the chromium complex with pyrophosphate is slow, as noted by Scribner,[3] who first developed this method of preventing chromium from interfering.

Relative errors ranged from 0·0% to +0·3% for up to 1200 mg of vanadium present (15 experiments), and from +0·2% to +0·5% for 50 mg of chromium (6 experiments). Experiments with 100 mg of chromium gave errors of +0·7%.

I thank C. Slagt, Miss J. de Neef, and J. F. G. van der Grift for experimental help.

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25 *September* 1969

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KOMPLEXE DER ANTHRANIL-*N*,*N*-DIESSIGSÄURE MIT METALLEN IN DER OXYDATIONSSTUFE +4—I

ZIRKONIUM UND HAFNIUM

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(*Eingegangen am* 31. *Juli* 1968. *Revidiert am* 25. *Octobre* 1969. *Angenommen am* 31. *Januar* 1970)

Zusammenfassung—Spektrophotometrische Untersuchungen zeigten, daß Zirkonium und Hafnium mit Anthranil-*N*,*N*-diessigsäure (ANDA) in wäßriger Lösung Komplexe der Zusammensetzungen Me:ANDA = 1:1 und 1:2 bilden. Die stufenweisen Bildungskonstanten bei pH 1 betragen für Zirkonium $k_1 = 20 \pm 5$ und $k_2 = 1{,}42 \cdot 10^5$, für Hafnium $k_1 = 10 \pm 5$ und $k_2 = 1{,}22 \cdot 10^5$.

Die chelatisierende Wirkung der Anthranil-*N*,*N*-diessigsäure (ANDA) auf eine Anzahl Metalle in der Oxydationsstuf +2, +3 und +4 wurde in früheren Arbeiten behandelt.[1] Aufbauend auf die Spektrophotometrie farbloser Me–ANDA-Komplexe[2] werden in der vorliegenden Arbeit die Ergebnisse einer UV-Untersuchung der durch ANDA mit Zirkonyl- und Hafnylionen gebildeten Komplexe aufgezeigt. Durch Ermittlung der Zusammensetzung und Stabilität der gebildeten Komplexe sollen Bedingungen erarbeitet werden, unter denen die photometrische Bestimmung von Hafnium in Gegenwart von Zirkonium möglich ist.

EXPERIMENTELLER TEIL

Apparate

Die Absorptionskurven im UV-Bereich wurden mit dem automatischen Spektrophotometer Unicam SP 800 aufgenommen. Alle Absorptionsmessungen wurden mit einem VSU 1 C. Zeiss (Jena, DDR)-Spektrometer durchgeführt. Die Schichtdicken der verwendeten Küvetten sind in der Zeichenerklärung der betreffenden Abbildungen angegeben. Sofern keine anderen Angaben gemacht wurden, diente als Bezugsflüssigkeit bidestilliertes Wasser. Die pH-Werte der Lösungen wurden mit einem pH-Meter Typ MV 11 Clamann und Grahnert (Dresden, DDR) bestimmt.

Reagenzien

Zur Herstellung der $5 \,.\, 10^{-3}M$-Lösung des Dinatriumsalzes der Anthranil-*N*,*N*-diessigsäure wurden 1,2654 g synthetisiertes ANDA[3] in 2 Äquivalentgramm Natrium hydroxid gelöst, wobei bidestilliertes Wasser bis zu 1 Litre hinzugefügt wurde. Der Titer der stabilen Lösung wurde komplexometrisch bestimmt.[3]

Zirkonylchlorid. Die entsprechende Menge $ZrOCl_2.8H_2O$ (Loba-Chemie Fischamend, Wien, *p.a* oder Johnson Matthey "Specpure") wurde in $10^{-1}M$ Perchlorsäure gelöst. Das verwendete Zirkonylchlorid war nicht hafniumfrei. Die Bestimmung von Zirkonium wurde gravimetrisch durchgeführt.

Hafniumchlorid. Die entsprechende Menge metallisches Hafnium "Spectral rein" wurde in konzentrierter Salszäure *p.a.* unter Zusatz einiger Tropfen konzentrierten Fluorwasserstoffs *p.a.* gelöst. Anschließend wurde das Hydroxid mit Ammoniak gefällt und bis zur negativen Reaktion auf Chlorid gewaschen. Die Auflösung des Hafniumhydroxid geschah in der kleinsten Menge warmer Salzsäure und die Ergänzung bis zur Marke mit $10^{-1}M$ Perchlorsäure. Zur Bestimmung der Bildungskonstanten wurde Hafniumoxidchlorid (Johnson Matthey "Specpure", London) verwendet.

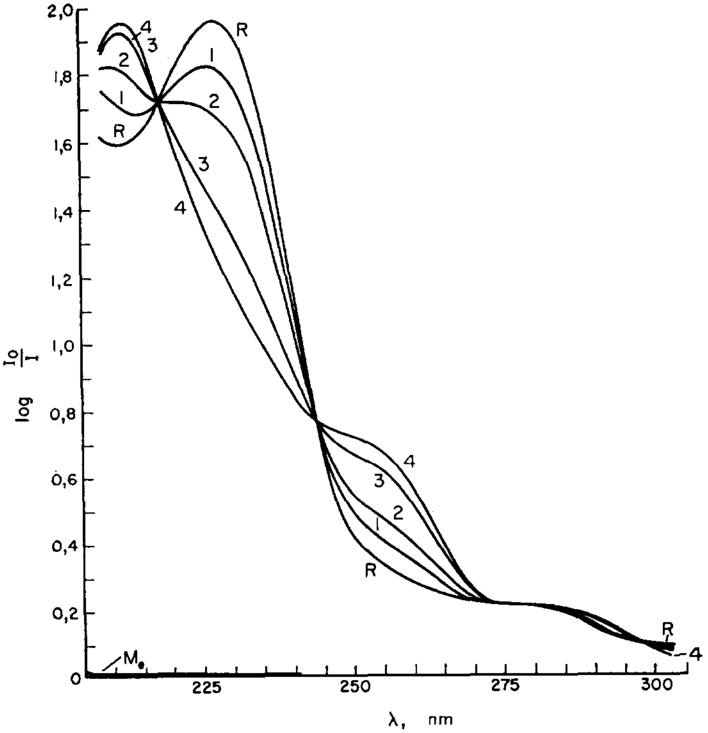
Natriumperchlorat (VEB Laborchemie Apolda, DDR). Zwecks Bestimmung der Bildungskonstanten wurde eine $1M$ Natriumperchlorat-Lösung in Wasser bzw. in $10^{-1}M$ Perchlorsäure benutzt.

Das bei sämtlichen Untersuchungen verwendete Lösungsmittel war eine $10^{-1}M$ Perchlorsäurelösung.

ERGEBNISSE UND DISKUSSION

Die Reaktionen, die zwischen Anthranildiessigsäure und Zirkon- bzw. Hafniumoxidchlorid stattfinden, treten durch Vergleich der Form der Absorptionskurven der Verbindung Zr-ANDA (Abb. 1A, Kurven *1* bis *4*) bzw. Hf-ANDA (Abb. 1B, Kurven *1* bis *4*) mit denen der Reaktanten (Kurven *R* und *Me*) hervor. Die Abbildungen zeigen die starke Absorption des Liganden in diesem Spektralbereich sowie die Ähnlichkeit, die zwischen den Kurven der beiden Reaktionsprodukte ohne charakteristische Absorptionsbanden besteht.

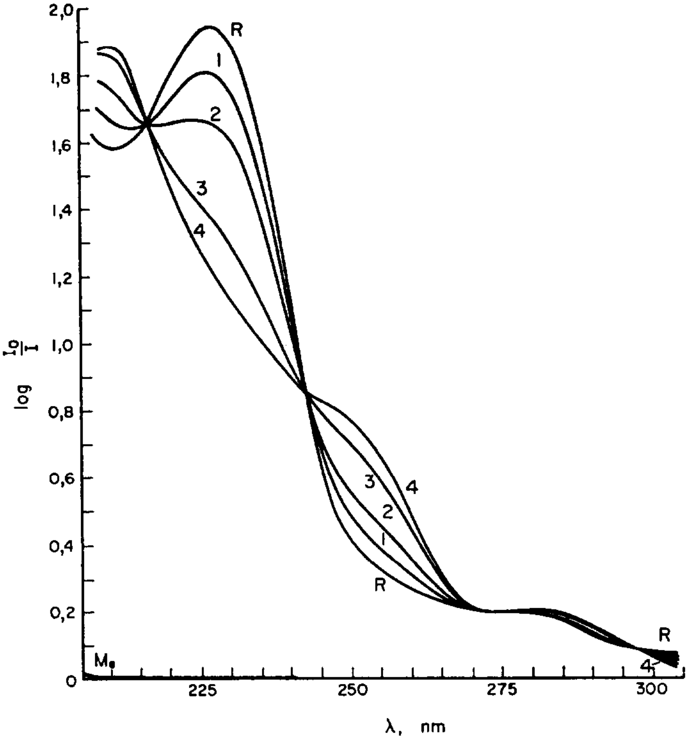
Um den optimalen pH-Wert der Komplexbildungsreaktion zu finden, wurden die Absorptionskurven der Zr-, Hf-ANDA-Komplexe bei unterschiedlichen pH-Werten aufgetragen. Die Wahl der pH-Werte ist einerseits durch die Fällungsmöglichkeit des Liganden, andererseits durch die Hydrolyse des MeO^{2+}-Ions begrenzt. Abbildung 2 zeigt für die Reaktion zwischen ZrO^{2+} und ANDA durch die Bildung des isosbestischen Punktes das Vorhandensein eines Gleichgewichts bei den pH-Werten zwischen 0, 7 und 2. Bei höheren pH-Werten (Kurve *4*, pH = 3) liegt kein Gleichgewicht mehr vor. Der Hf-ANDA-Komplex verhält sich ähnlich. Der optimale pH-Wert für beide Systeme beträgt 1. Er wird mit Hilfe einer $10^{-1}M$ Perchlorsäurelösung erhalten.



1A

Abb. 1.—Absorptionskurven des Systems Zr-ANDA (Diagramm A) und Hf-ANDA (Diagramm B)

Konstante Ligandkonzentration: $1{,}2 \cdot 10^{-3}M$. Kationenkonzentration: 0 (Kurve *R*), $1 \cdot 10^{-4}M$ (Kurve *1*), $2 \cdot 10^{-4}M$ (*2*), $3 \cdot 10^{-4}M$ (*3*), $4 \cdot 10^{-4}M$ (*4*),$5 \cdot 10^{-4}$ M (*5*). Bezugslösung: bidestilliertes Wasser. Schichtdicke 2 mm.



1B

Die zeitliche Verfolgung der Bildung der Zr-, Hf-ANDA-Komplexe in Abhängigkeit vom pH-Wert ergibt, daß die Reaktion bei pH-Werten zwischen 1 und 3 praktisch augenblicklich stattfindet und die gebildeten Komplexe wenigstens 3 Stunden stabil sind.

Die Ionenstärke der Lösungen wird mit Hilfe einer 1*M* Natriumperchloratlösung bei einem Wert $\mu = 0{,}25$ konstant gehalten.

Natur und Zusammensetzung der Zr-, Hf-ANDA-Komplexe

Es werden die Absorptionskurven für eine Reihe von Lösungen aufgenommen, in denen die Menge des Liganden konstant, die Menge des Metallions hingegen veränderlich ist. Für den Zr-ANDA-Komplex erhält man Diagramm A, für den Hf-ANDA-Komplex Diagramm B in Abb. 3.

Die Bildung der isosbestischen Punkte zwischen der Kurve des reinen Liganden (*1*) und den Kurven der Komplexe bis zum Erreichen des Verhältnisses Me:ANDA = 1:2 (Kurve *4* in Diagramm A und *5* in B) weist auf das Bestehen eines Gleichgewichts zwischen dem Me-$(ANDA)_2$-Komplex und dem Ligandüberschuß hin. Ebenfalls bringt die Unmöglichkeit, Gleichgewichte bei einem Überschuß an Metallionen zu erkennen (Kurven *7* bis *9*), die Tatsache zum Ausdruck, daß die Zr-, Hf-ANDA-Systeme keine polynuklearen Komplexe bilden.

Die beiden isosbestischen Punktpaare zeigen für die zwei Systeme Zr-$(ANDA)_2$ und Hf-$(ANDA)_2$ eine geringe Wellenlängenverschiebung. Die isosbestischen Punkte im

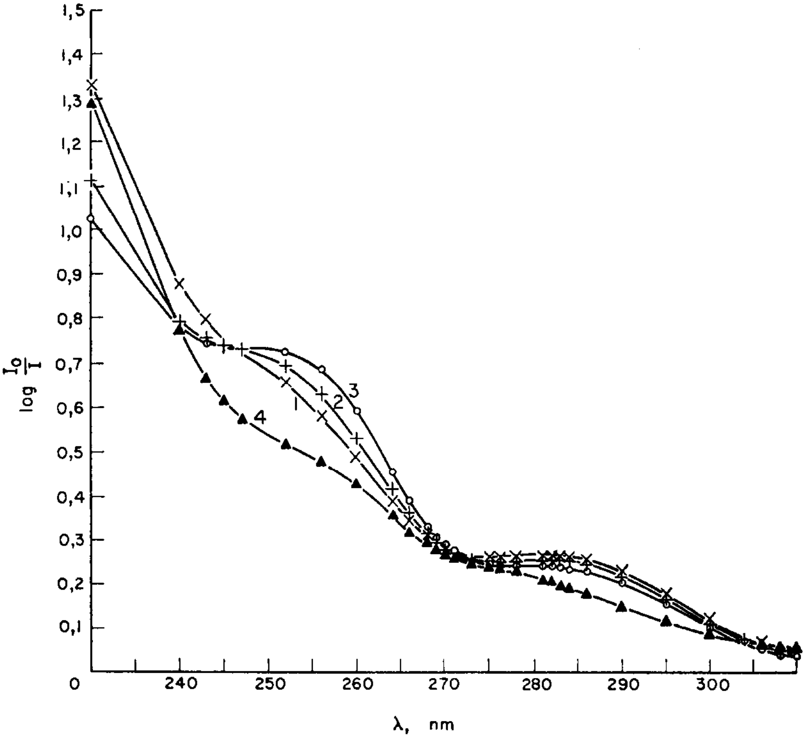


Abb. 2.—Absorptionskurven des Zr-ANDA-Komplexes mit der Konzentration 2 . $10^{-4}M$ bei unterschiedlichen pH-Werten.
Kurve *1* für pH 6 = 0,7; Kurve *2*, pH = 1; Kurve *3*, pH = 2 und Kurve *4*, pH = 3. Schichtdicke 20 mm.

Bereich kleinerer Wellenlängen sind für den Zr-ANDA-Komplex λ_{iso} mit ungefähr 243,5 nm und für den Hf-ANDA-Komplex λ_{iso} mit ungefähr 242,5 nm gleich. Beim λ_{iso} des Zr(ANDA)$_2$-Komplex weist der Hf-(ANDA)$_2$-Komplex eigene Absorption auf. Diese Tatsache macht bei dieser Wellenlänge die Bestimmung von Hafnium in Gegenwart von Zirkonium unter der Bedingung möglich, daß das Verhältnis Me:ANDA = 1:2 eingehalten wird.[4] Die beiden anderen isosbestischen Punkte der betrachteten Systeme im Bereich größerer Wellenlängen (ungefähr 300 nm für den Zr-(ANDA)$_2$-Komplex und 297 nm für den Hf-(ANDA)$_2$-Komplex) bringen grundsätzlich die spektrophotometrische Bestimmungsmöglichkeit von Zirkonium in Gegenwart von Hafnium bei λ_{iso} des Hf-(ANDA)$_2$-Komplexes zum Ausdruck.

Der spektrophotometrische Beweis für das Vorhandensein eines 1:1 Komplexes, dessen Bildung wahrscheinlich ist, läßt sich durch eine graphische Erweiterung von Abb. 3 führen. Da das registrierende Spektrophotometer zu gedrängte Kurven liefert, wurden manuelle spektrophotometrische Messungen gemacht und die Kurven für den Zr-ANDA-Komplex in vergrößertem Maßstab in Abb. 3, AI und II eingetragen. Auf diese Weise werden noch zwei weitere isosbestische Punkte bei ungefähr 253 nm (Abb. 3AI) und 268 nm (Abb. 3AII) erhalten, die einem Gleichgewicht zwischen den Komponenten mit den Verhältnissen Me:ANDA > 1:2 (Kurve mit dem Symbol ▲ in Abb. 3AI, II) und dem Metallionüberschuß (Kurve ○) entsprechen.

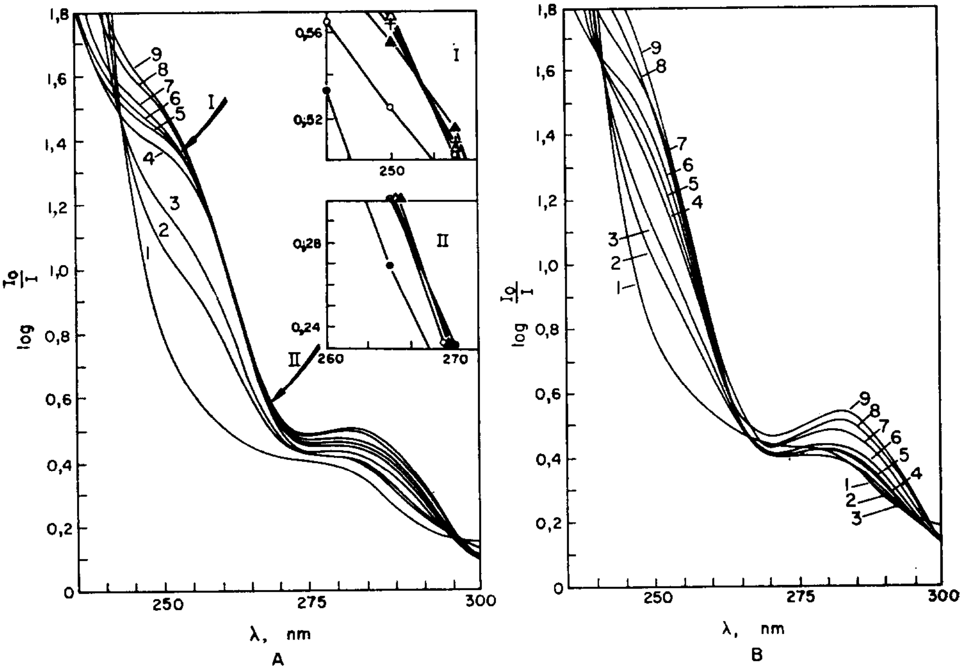


Abb. 3.—Absorptionskurven der Zr-ANDA-(Diagramm A) und Hf-ANDA (B)-Verbindungen.
Konstante Konzentration des Liganden: $2 . 10^{-4}M$. Konzentration MeO^{2+} für das Diagramm A: 0 (Kurve *1*); $0{,}4 . 10^{-4}M$ (*2*); $0{,}6 . 10^{-4}M$ (*3*); $1 . 10^{-4}M$ (*4*); $1{,}2 . 10^{-4}M$ (*5*); $1{,}5 . 10^{-4}M$ (*6*); $2 . 10^{-4}M$ (*7*); $10 . 10^{-4}M$ (*8*); $30 . 10^{-4}M$ (*9*); für das Diagramm B: 0 (Kurve *1*); $0{,}4 . 10^{-4}M$ (*2*); $0{,}6 . 10^{-4}M$ (*3*); $1 . 10^{-4}M$ (*4*); $1{,}2 . 10^{-4}M$ (*5*); $1{,}5 . 10^{-4}M$ (*6*); $2 . 10^{-4}M$ (*7*); $20 . 10^{-4}M$ (*8*); $30 . 10^{-4}M$ (*9*). Schichtdicke: 20 mm.
Für Diagramm A I und II ist die Konzentration des Liganden konstant = $1{,}6 . 10^{-4}M$ und die des ZrO^{2+} Ions veränderlich: $4 . 10^{-5}M$ (●); $8 . 10^{-5}M$ (○); $1{,}2 . 10^{-4}M$ (▼); $1{,}6 . 10^{-4}M$ (×); $2 . 10^{-4}M$ (△); $6{,}4 . 10^{-4}M$ (⊙). Schichtdicke: 10 mm.

Unter der Annahme, daß sich Hafnium analog verhält, kann demnach gesagt werden:

(*a*) In den zwei untersuchten Me-ANDA-Systemen liegen keine polynuklearen Komplexe vor;

(*b*) die Komplexbildung findet nacheinander in zwei Schritten statt (Verbindung 1:1 und 1:2).

Obwohl bekannt ist, daß eine Anzahl spektrophotometrischer Methoden zur Bestimmung der Komplexzusammensetzung nur bei der Bildung eines einzigen Komplexes gültig ist, wurde geprüft, bis zu welchem Ausmaß die Komplexzusammensetzung der untersuchten Systeme mit Hilfe dieser Methoden ermittelt werden kann. Auf diese Weise kamen zur Anwendung:

Methode des isosbestischen Punktes nach Asmus[5]

Im Falle der Zr-, Hf-ANDA-Komplexe (Abb. 4) zeigt die Überschneidung der Tangenten für den Molenbruch 0,65 das Verhältnis Zr, Hf:ANDA = 1:2, ohne

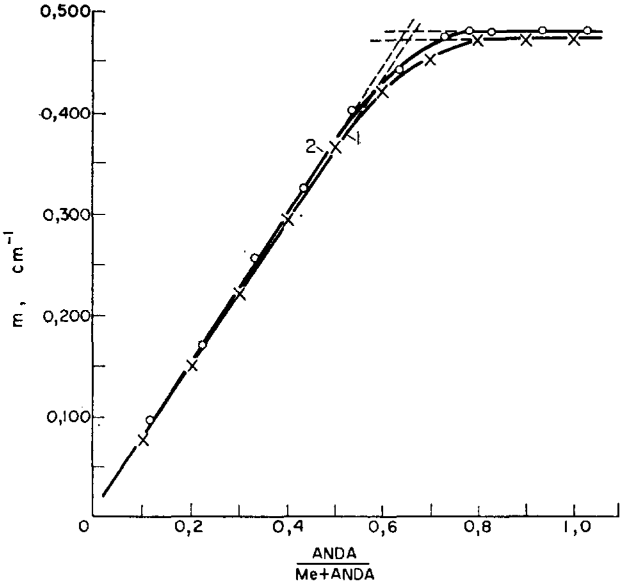


ABB. 4.—Methode des isobestischen Punktes für den Hf-ANDA-Komplex, (Kurve *1*) und den Zr-ANDA-Komplex (Kurve *2*). $\lambda = \lambda_{iso} = 247{,}5$ nm für Kurve *1* und 273 nm für Kurve *2*. Konzentration der Proben $2 \cdot 10^{-4}M$. Schichtdicke: 20 mm.

dabei den geringsten Hinweis auf das Vorliegen der betreffenden 1:1-Komplexe zu geben.

Methode der molaren Verhältnisse[6]

Im Falle der Zr-ANDA- und Hf-ANDA-Komplexe weist die Methode auf die Bildung einiger Me-ANDA-Verbindungen mit der Zusammensetzung 1:2 hin.

Demnach ergibt sich: Unter der Bedingung, daß mehrere Komplexe vorhanden sind, die im selben Spektralbereich absorbieren, geben die erhaltenen Ergebnisse nicht den wirklichen Zustand der untersuchten Zr-, Hf-ANDA-Systeme wieder. Weiterhin ist anzunehmen, daß der Bildungsgrad des Komplexes mit der Zusammensetzung 1:1 geringer ist als derjenige mit der Zusammensetzung 1:2.

Stabilität der Zr-, Hf-ANDA-Komplexe

Um die aufeinanderfolgenden Bildungskonstanten der beiden Systeme zu berechnen, wurde die spektrophotometrische Methode nach Newman und Hume[7] angewendet. Aus Abb. 3 ist ersichtlich, daß bei der Wellenlänge der isosbestischen Punkte, die die Komplexe Me:ANDA = 1:2 kennzeichnet, die Komplexe mit der Zusammensetzung 1:1 eine veränderliche Absorption aufweisen. Es ist demnach vorteilhaft, bei $\lambda = 243$ nm für den Zr-ANDA-Komplex bzw. bei $\lambda = 242$ nm für den Hf-ANDA-Komplex oder bei angenäherten Wellenlängen zu arbeiten. Es wurde bei konstanter Ionenstärke in $2 \cdot 10^{-1}M$ Natrium perchlorat lösung gearbeitet.

Wenn das Verhältnis der beiden aufeinanderfolgenden Konstanten k_2/k_1 genügend groß ist, kann man die Bildungskonstante k_1 in Gegenwart eines Überschußes von

Metallionen (M_t) gegenüber dem Liganden (X_t) bestimmen. Ein Metallionenüberschuß ist außerdem wegen der Absorption des Liganden im gesamten Absorptionsbereich beider Systeme vorteilhaft.

Für die Metallionenkonzentration $6 . 10^{-3}M$ und die Ligandenkonzentration $8 \cdot 10^{-5}M$ wurde der molare Extinktionskoeffizient aus der Beziehung $E_1 = A_0''/X_0$ berechnet. (A_0'' = gemessene Absorption des ersten Komplexes; X_0 = Ligandenkonzentration). Für den Hf-ANDA-Komplex wurde $E_1 = 4{,}25 \times 10^3$ berechnet.

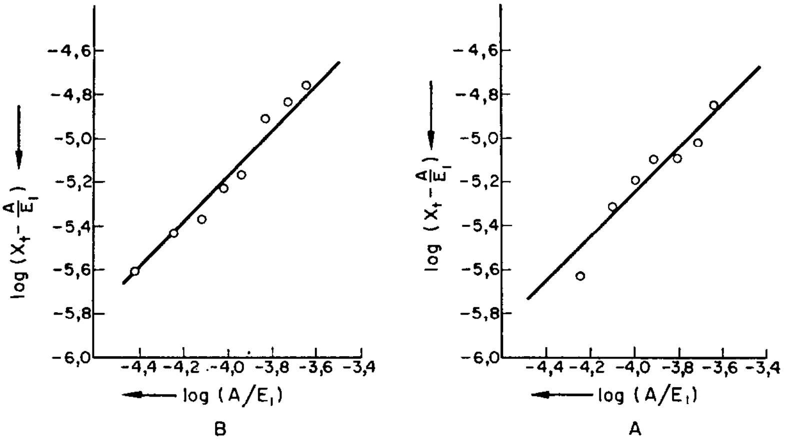


Abb. 5.—Bestimmung der ersten Bildungskonstante des Zr-ANDA-Komplexes (A), bzw. des Hf-ANDA-Komplexes (B).
Konstante Konzentration von $MeOCl_2$ $10^{-3}M$; veränderliche Konzentration von ANDA im Bereich von $4 . 10^{-5}M$ bis $24 . 10^{-5}M$. λ = 243 nm (A) bzw. 242 nm (B). Bezugslösung: Maßlösung ohne ANDA. Schichtdicke: 10 mm.

Im Falle der weiter oben erwähnten Bedingungen wurde die Beziehung (Gleichung F19 von Newman und Hume.[7])

$$\log\left(\frac{A}{A_0''}X_0\right) = q\left\{\log\left(X_t - q\frac{A}{A_0''}X_0\right)\right\} + \log k_1$$

angewendet. Es wurde weiterhin angenommen, daß zwei Komplexe vorhanden sind, von denen einer absorbiert, daß $[MX_2] = 0$, und daß E (der molare Extinktionskoeffizient des Metallions) gleich Null ist. Der Koeffizient q, mit welchem der Ligand an der Reaktion teilnimmt, wird für diesen Fall gleich 1 gesetzt. Indem das linke Glied der Gleichung in Abhängigkeit vom Ausdruck in der geschweiften Klammer graphisch dargestellt wird, werden die Geraden in Abb. 5 erhalten, und zwar A im Falle des Zr-ANDA-Komplexes und B im Falle des Hf-ANDA-Komplexes. Die mit 1 gleiche Neigung bestätigt die gute Wahl des Wertes q.

Aus dem Schnittpunkt mit der Abszisse wurde die erste Bildungskonstante $k_1 = 20 \pm 5$ für den Zr-ANDA-Komplex (bei $\lambda = 243$ nm) und $k_1 = 10 \pm 5$ für den Hf-ANDA-Komplex (bei $\lambda = 242$ nm) erhalten. Wie die Konstanten erkennen lassen, bilden sich Verbindungen mit sehr geringer Stabilität. Die Hafniumverbindung ist verhältnismäßig unstabiler als die Zirkoniumverbindung.

Um die zweite Bildungskonstante zu ermitteln, hätten zwei Wege eingeschlagen werden können. Man hätte den zweiten niedrigen Komplex berechnen können, wobei der vorhin bestimmte Wert für k_1 zu beachten gewesen wäre, oder es hätte das

Endglied in der Reihe der sukzessiven Komplexe berechnet werden können. Die letzte Alternative besitzt den Vorteil, nicht an die Fehler gebunden zu sein welche die Bestimmung der ersten Konstante begleiten. Sie fordert jedoch für die Berechnung von E_n, den molaren Extinktionskoeffizienten des Komplexes mit der maximalen Koordinationszahl, die Verwendung eines großen Ligandüberschusses. Da der Ligand im gesamten Wellenbereich, in dem die Komplexe absorbieren, ebenfalls stark absorbiert, ist dieser Weg nicht gangbar. Deshalb wurde zur Berechnung von k_2 für beide Zr-, Hf-ANDA-Systeme eine modifizierte Form der Newman und Hume D9-Gleichung benutzt:

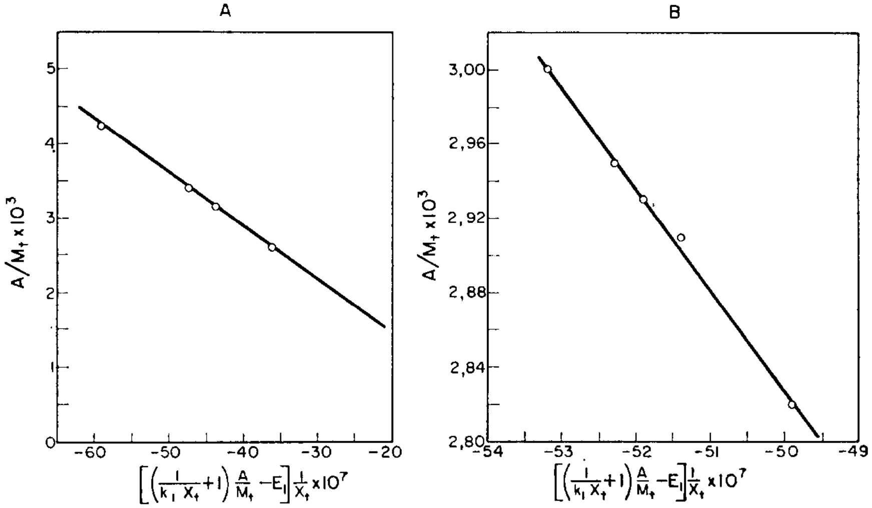


ABB. 6.—Bestimmung der zweiten Bildungskonstante des Zr-ANDA-Komplexes (Diagramm A) und des Hf-ANDA-Komplexes (Diagramm B). Konstante Konzentration von ANDA 6 . $10^{-4}M$ = veränderliche Konzentration von MeO^{2+} im Bereich von 4 . $10^{-5}M$ bis 24 . $10^{-5}M$; $\lambda = 253$ nm (A) und 250 nm (B). Bezug = Meßlösung ohne MeO^{2+}. Schichtdicke: 10 mm.

$$\frac{A}{M_t} = -\frac{1}{k_2}\left\{\left[\left(\frac{1}{k_1 x_t} + 1\right)\frac{A}{M_t} - E_1\right]\frac{1}{x_t}\right\} + E_2$$

Diese Gleichung entspricht den Eigenschaften der in Betracht gezogenen Systeme. Bei der Bestimmung der Bildungskonstante des zweiten Komplexes der beiden Systeme wurde bei der Wellenlänge des isosbestischen Punktes der betreffenden äquimolaren Komplexe oder bei λ-Werten, die diesen sehr angenähert waren, gearbeitet. Im Falle des Zr-$(ANDA)_2$-Komplexes wurden die Bestimmungen bei $\lambda = 253$ nm und im Falle des Hf-$(ANDA)_2$-Komplexes bei $\lambda = 250$ nm ausgeführt. Auch in diesem Fall wurde in einer $2 \cdot 10^{-1}M$ Natriumperchloratlösung gearbeitet.

Trägt man aus obiger Gleichung A/M_t gegen den Ausdruck in der geschweiften Klammer auf, so erhält man Geraden. Diagramm A gilt für den Zr-$(ANDA)_2$-Komplex und B für den Hf-$(ANDA)_2$-Komplex. Aus der Neigung wurde die Konstante $k_2 = 1{,}42 \cdot 10^5$ für Zr-$(ANDA)_2$ und $k_2 = 1{,}22 \cdot 10^5$ für Hf-$(ANDA)_2$ berechnet. Wie die Größe der k_2-Konstanten erkennen läßt, bilden sich Me-$(ANDA)_2$-Komplexe von mittlerer Stärke.

Als globale Bildungskonstante erhält man für das Zr-ANDA-System $K = k_1 \times k_2 = 2{,}80 . 10^6$ und für das Hf-ANDA-System $K = 1{,}2 . 10^6$.

Summary—Spectrophotometric studies have shown that zirconium and hafnium form complexes with anthranil-*N*,*N*-diacetic acid (ANDA) in aqueous solution, with the compositions Me:ANDA 1:1 and 1:2. The conditional stepwise formation constants at pH 1 were found to be $k_1 = 20 \pm 5$ and $k_2 = 1{\cdot}42 \times 10^5$ for zirconium, and $k_1 = 10 \pm 5$ and $k_2 = 1{\cdot}22 \times 10^5$ for hafnium.

Résumé—Des études spectrophotométriques ont montré que le zirconium et le hafnium forment des complexes avec l'acide anthranil-*N*,*N*-diacétique (ANDA) en solution aqueuse, avec les compositions Me:ANDA 1:1 et 1:2. On a trouvé que les constantes de formation étagée à pH 1 sont $k_1 = 20 \pm 5$ et $k_2 = 1{,}42 \times 10^5$ pour le zirconium et $k_1 = 10 \pm 5$ et $k_2 = 1{,}22 \times 10^5$ pour le hafnium.

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GLEICHZEITIGE SPEKTROPHOTOMETRISCHE BESTIMMUNG DES ZIRKONIUMS UND HAFNIUMS

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Zusammenfassung—Zirkonium kann in Gegenwart von Hafnium ultraviolettspektrophotometrisch bei den isosbestischen Wellenlängen 218,2; 243,5 oder 298,5 nm mit Anthranil-*N*,*N*-diessigsäure in verdünnter saurer Lösung bestimmt werden. Konzentrationen im Bereich 2–36 μg/ml (Zr) und 3–70 μg/ml (Hf) können bestimmt werden. Liegen beide Elemente vor, so können 2,5–80% Zr in Hf oder umgekehrt mit einem Fehler von 3–4% bestimmt werden.

ANTHRANIL-*N*,*N*-DIESSIGSÄURE (ANDA) bildet mit den Ionen ZrO^{2+} und HfO^{2+} Chelatkomplexe. Hierüber wurde schon in einer früheren Arbeit[1] berichtet. Untersuchungen über die Gleichgewichte mit Hilfe der Methode des isosbestischen Punktes zeigten eine kleine Verschiebung der Lage der isosbestischen Punkte der beiden Systeme Zr-$(ANDA)_2$ und Hf-$(ANDA)_2$. Diese Tatsache läßt sich zur Bestimmung von Zirconium in Gegenwart von Hafnium und umgekehrt ausnutzen.

ERGEBNISSE UND DISKUSSION

Die Absorptionskurven für die Komplexe Zr-ANDA und Hf-ANDA bei konstanter Ligandmenge, bei einem Ligandüberschuß und bei steigender Kationenmenge zeigt Abb. 1 Diagramm A und B in Citat 1. In beiden Fällen bilden sich je drei isosbestische Punkte. Sie liegen für den Komplex Zr-ANDA bei ungefähr 218 nm, 243,5 nm und 298 nm, für den Komplex Hf-ANDA aber bei ungefähr 216,5 nm, 242,5 nm und 297 nm. Diese isosbestischen Punkte bleiben bis zu einem Verhältnis Me:ANDA = 1:2 bestehen.

Nachher weisen die entsprechenden Punkte Extinktionen auf, die mit der anwesenden Kationenmenge steigen. Somit muß eine Ligandmenge eingesetzt werden, die ein Verhältnis Me:ANDA = 1:2 sichert. Außerdem bedingt der mittlere Wert der Komplexstabilitätskonstanten die Verwendung eines Ligandüberschusses, damit eine vollständige Komplexierung der Kationen erreicht wird. In den isosbestischen Punkten (siehe Abb. 1) haben alle Kurven von *R* (Eichkurve des reinen Liganden) bis zu Kurve *4* dieselbe Extinktion. Betrachtet man für beide Systeme je zwei isosbestische Punkte aus demselben Wellenlängenbereich, so ergibt sich:

(*1*) Bei 218 nm besitzt das System Zr-ANDA eine Extinktion, die konstant und gleich ist der des Liganden. Demgegenüber weist aber das System Hf-ANDA eine progressiv kleinere Extinktion auf als der Ligand, abhängig von der Zunahme der HfO^{2+}-Ionenmenge.

(*2*) Bei 216,5 nm ist die Extinktion des Systems Hf-ANDA konstant und gleich der des Liganden. Hier steigt die Extinktion des Systems Zr-ANDA proportional mit der Zunahme der anwesenden ZrO^{2+}-Ionenmenge.

(*3*) In analoger Weise könnte man bei 243,5 nm (isosbestischer Punkt für das System

Zr-ANDA) Hf in Gegenwart von Zr und bei 242,5 nm (isosbestischer Punkt für das System Hf-ANDA)Zr in Gegenwart von Hf- bestimmen.

(*4*) Bei ungefähr 297 nm wird man die anwesende Zirkoniummenge und bei ungefähr 298 nm die Hafniummenge bestimmen können.

Für solche Bestimmungen kann man zwei Wege einschlagen, welche anschließend beschrieben werden.

Absorptionskurvenverfahren

Hier gibt es zwei Varianten: Wasser als Bezugsflüssigkeit bzw. Blindprobe als Bezugsflüssigkeit.

Wasser als Bezugsflüssigkeit. In diesem Fall sind die experimentellen Bestimmungen analog denen aus Abb. 1. Für jeden einzelnen isosbestischen Punkt müssen jedoch die Arbeitsbedingungen so gewählt werden, daß sie zu optimalen Werten der Extinktion führen.

Als Beispiel ist in Abb. 1 Diagramm A das Gebiet um den isosbestischen Punkt von 218 nm für den Zr-ANDA-Komplex und im Diagramm B das Gebiet um den isosbestischen Punkt von 297 nm für den Hf-ANDA-Komplex dargestellt. Den isosbestischen Punkten von 243,5 nm (für das System Zr-ANDA) und 242,5 nm (für das System Hf-ANDA) entsprechen die Diagramme A beziehungsweise B aus der Abb. 1 (in Citat 1).

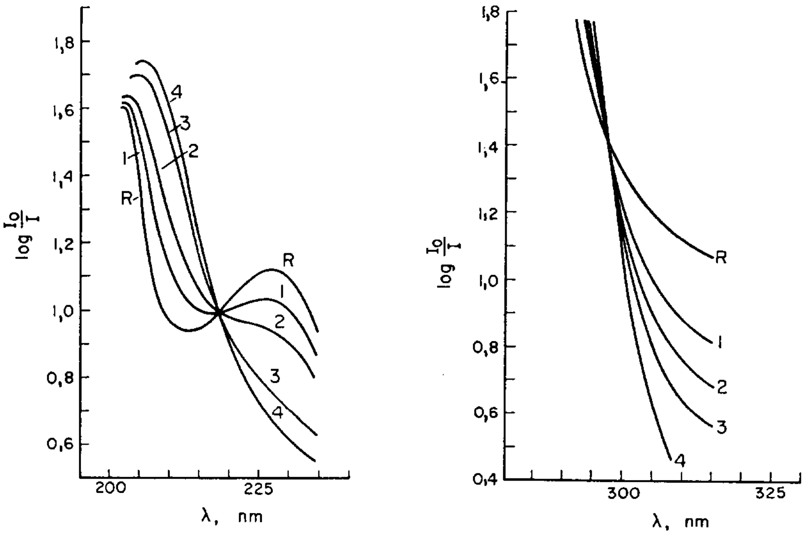
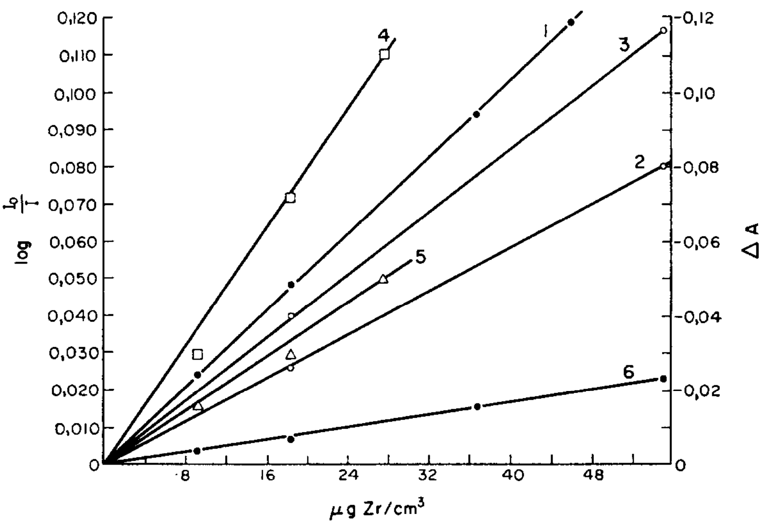


Abb. 1.—Absorptionskurven der Komplexe.
A: Zr-ANDA-Konstante Ligandkonzentration: 1,2 . $10^{-3}M$. ZrO^{2+}-Konzentration: 0 (Kurve *R*), $10^{-4}M$ (Kurve *1*), 2 . $10^{-4}M$. (*2*), 4 . $10^{-4}M$ (*3*), 5 . $10^{-4}M$ (*4*). Schichtdicke: 1 mm. *B*: Hf-ANDA. Konstante Ligandkonzentration: 1,6 . $10^{-3}M$. HfO^{2+}-Konzentration: 0 (Kurve *R*), 2 . $10^{-4}M$ (Kurve *1*), 3 . $10^{-4}M$ (*2*), 4 . 10^{-4} (*3*), 6 . 10^{-4} (*4*). Schichtdicke: 20 mm. Bezugslösung für A und B = bidestilliertes Wasser.

Der Extinktionswert bei den entsprechenden Wellenlängen wird aus der graphischen Darstellung ermittelt. Abgelesen wird die Differenz zwischen der Extinktion der zu analysierenden Probe und der Eichprobe (Kurve *R*). Für eine genauere Ablesung der Extinktion wurde ein Epidiaskop oder eine Handlupe verwendet.



2A

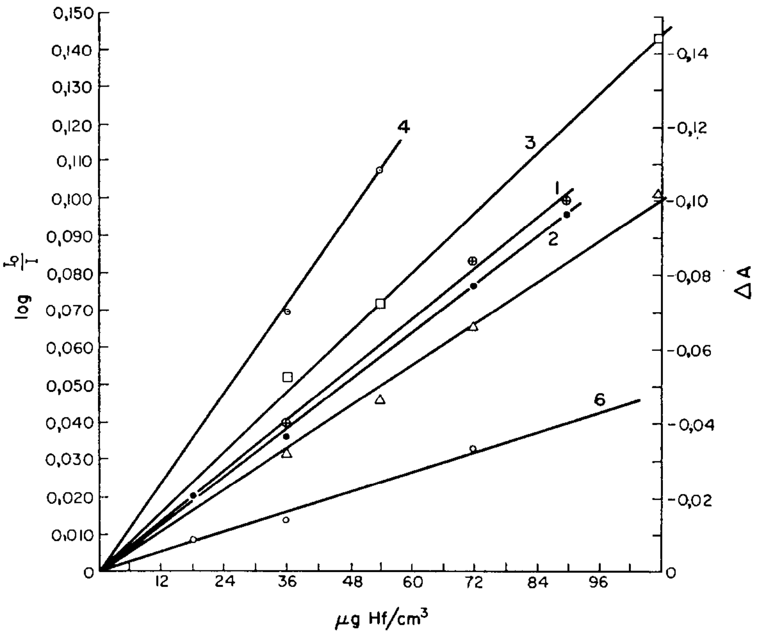
Abb. 2.—Eichkurven der Systeme.
Zr-ANDA (Diagramm A)

Kurve Nr.	Bezug	*nm*	Ligandkonzentration, *mM*	Schichtdicke, *mm*
1	bidest. Wasser	216,5	1,2	1
2	bidest. Wasser	242,5	1,6	2
3	bidest. Wasser	297	1,6	20
4	Blindlösung	215,5	1,2	2
5	Blindlösung	242,5	1,2	2
6	bidest. Wasser	297	2,6	5

Auf diese Weise (Abb. 2) werden die Eichkurven für den Komplex Zr-ANDA (Diagramm A) in den drei isosbestischen Punkten des Systems Hf-ANDA: 216,5 nm (Kurve *1*), 242,5 nm (Kurve *2*) und 297 nm (Kurve *3*) und auch die Eichkurven für den Komplex Hf-ANDA (Diagramm B) in den drei isosbestischen Punkten des Systems Zr-ANDA: 218,5 nm (Kurve *1*), 243 nm (Kurve *2*) und 298 5 nm (Kurve *3*) aufgestellt.

Die Absorptionskurven der Gemische (Zr + Hf)-ANDA haben dieselbe Form wie die Kurven *1–4* aus Abb. 3. Auch in diesem Fall werden für jedes Gebiet um die Wellenlänge des isosbestischen Punktes die Bedingungen so festgelegt, daß man optimale Werte für die Extinktionen erhält. Die aus einem Diagramm bei $\lambda = 216{,}5$ nm abgelesene Extinktion bezogen auf die Eichkurve (*R*) entspricht dem Komplex Zr-ANDA und die bei $\lambda = 218$ nm dem Komplex Hf-ANDA.

Ebenso entsprechen auch die abgelesenen Extinktionen aus einem analogen Diagramm wie Abb. 3 bei $\lambda = 242{,}5$ nm dem Komplex Zr-ANDA und bei $\lambda = 243{,}5$ nm dem Komplex Hf-ANDA. Für das Gebiet größerer Wellenlänge ($\lambda = 297$ nm, 298 nm) wird jede einzelne Kurve des Gemisches Zr + Hf aufgestellt, bei 297 für den Komplex Zr-ANDA, bei 298,5 nm, für den Komplex Hf-ANDA. Diese Messungen sind in Tabelle I für Zirkonium und in Tabelle II für Hafnium wiedergegeben. Aus den



2B
Hf-ANDA (Diagramm B)

Kurve Nr.	Bezug	*nm*	Ligand-konzentration, *mM*	Schichtdicke, *mm*
1	bidest. Wasser	218,2	1,2	1
2	bidest. Wasser	243,5	1,2	2
3	bidest. Wasser	298,5	1,6	20
4	Blindlösung	217,5	1,2	2
5	Blindlösung	243,5	1,6	2
6	bidest. Wasser	243	2,0	1,03

Kurven *1*, *3*, *4* und *6* (Diagramm A) und Kurven *2*, *5* und *6* (Diagramm B): Ordinate log I_0/I. Bie den anderen ist ΔA als Ordinate aufgetragen.

ersten 7 Spalten, die sich auf die oben beschriebenen Methoden beziehen, folgt, daß der prozentuale Fehler im Durchschnitt nicht 3% überschreitet.

Eine andere Möglichkeit Zirkonium in Gegenwart von Hafnium, aber nicht umgekehrt, zu bestimmen, entspringt aus einer besonderen Lage der Absorptionskurven beider Systeme im Wellenlängengebiet von 272–276 nm. Werden die Bedingungen so festgelegt, daß die Extinktion einen optimalen Wert aufweist, so erhält man die Diagramme aus Abb. 4, A für den Komplex Zr-ANDA, B für den Komplex Hf-ANDA und C für das Gemisch (Zr + Hf).

Bei 272–276 nm weist der Komplex Hf-ANDA eine konstante Extinktion auf. Sie ist gleich der des Liganden (Kurve *R*) und unabhängig von der anwesenden HfO^{2+}-Menge. Der Komplex Zr-ANDA zeigt eine Extinktion, die proportional mit der ZrO^{2+}-Menge in dem Reaktionsmedium wächst. Die Eichkurve für den Komplex Zr-ANDA bei $\lambda = 272{,}5$ nm ermöglicht die Bestimmung des Zirkonium (Tabelle I, Spalte B). Der durchschnittliche prozentuale Fehler beträgt ungefähr 4%.

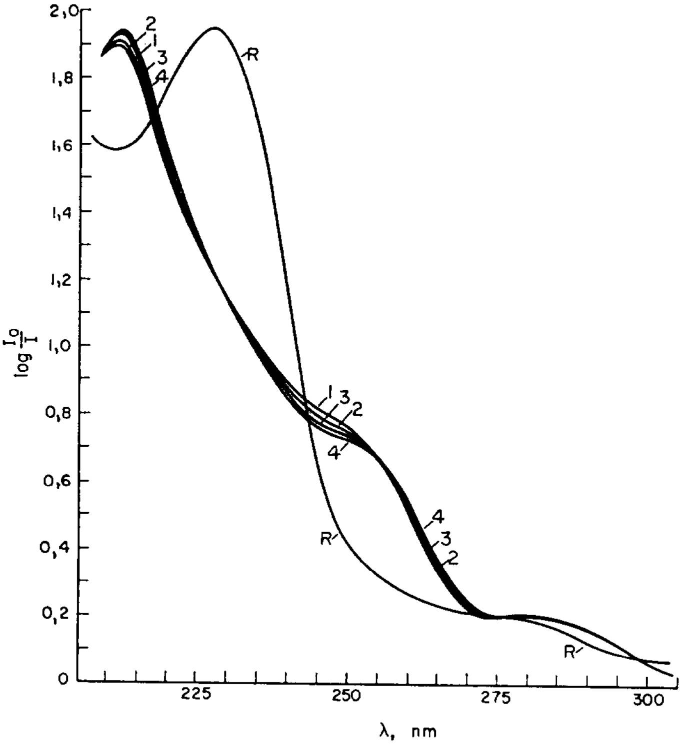


ABB. 3.—Absorptionskurven des Systems (Zr + Hf)-ANDA. Konstante ANDA-Konzentration: 1,2 . $10^{-3}M$. ZrO^{2+}-Konzentration: 0 (Kurve *R*), 1 . $10^{-4}M$ (Kurve *1*), 2 . $10^{-4}M$ (*2*), 3 . $10^{-4}M$(*3*), 4 . $10^{-4}M$ (*4*). HfO^{2+}-Konzentration: 0 (Kurve *R*), 4 . $10^{-4}M$ (Kurve *1*), 3 . $10^{-4}M$ (*2*), 2 . $10^{-4}M$ (*3*), 1 . $10^{-4}M$ (*4*). Bezugslösung: bidestilliertes Wasser. Schichtdicke: 2 mm.

Blindprobe als Bezugsflüssigkeit. Mit denselben Probelösungen, die zur Aufstellung der Diagramme aus Abb. 1 dienten, werden Absorptionskurven aufgenommen. Hier wird jedoch als Bezugsflüssigkeit eine Blindprobe verwendet (Kurve *R* aus Abb. 1). Man erhält so die Diagramme aus Abb. 5, A für den Komplex Zr-ANDA und B für Hf-ANDA. Auf diese Weise wird die Extinktion des Liganden kompensiert. Die Schnittpunkte der Kurven untereinander und mit der Nullinie stellen die isosbestischen Punkte in der neuen graphischen Darstellung dar. Da die Prinzipien dieselben sind, ist auch die Arbeitsweise analog mit der aus dem Verfahren 1.

Bei der Wellenlänge des isosbestischen Punktes des Komplexes Zr-ANDA wird die Extinktion für den Komplex Hf-ANDA abgelesen und umgekehrt. Bei 215,2 nm und bei 242,5 nm wurden die Eichkurven *4* und *5* aus Abb. 2, A für Zr-ANDA aufgestellt. Die in Tabelle I, Spalte 10–13 wiedergegebenen Werte zeigen, daß der prozentuale Fehler 3 % nicht überschreitet. Für den Komplex Hf-ANDA wurden die Eichkurven *4* und *5* aus Abb. 2B bei $\lambda = 217{,}5$ nm bzw. bei 243,5 nm aufgestellt. Die in Tabelle II Spalte 8–11 wiedergegebenen Werte zeigen, daß bei den angegebenen Mengenverhältnissen der durchschnittliche prozentuale Fehler 3 % beträgt. Der isosbestische Punkt von 297–298 nm kann bei diesem Verfahren nicht ausgewertet werden, weil die Extinktionsdifferenzen zu klein sind. Die Anwendung einer Skalenausdehnung würde wahrscheinlich auch hier eine Bestimmung ermöglichen. Infolge

TABELLE I.—SPEKTROPHOTOMETRISCHE BESTIMMUNG DES ZIRKONIUMS IN GEGENWART VON HAFNIUM

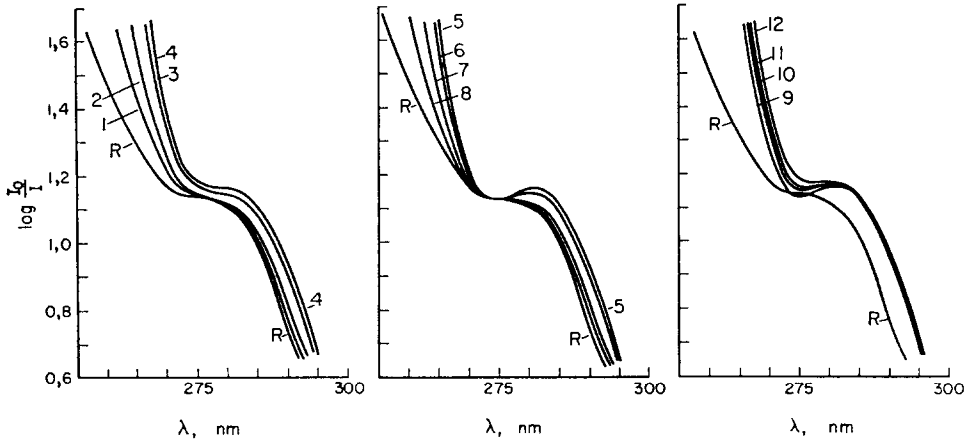
Zr gegeben μg/ml	Zr gefunden,* μg/ml								Zr gefunden,† μg/ml				Zr gefunden,‡ μg/ml	
	λ = 216,5 nm	Δ	λ = 242,5 nm	Δ	λ = 297 nm	Δ	Gebiet λ = 272,5 nm	Δ	λ = 215,2 nm	Δ	λ = 242,5 nm	Δ	λ = 297 nm	Δ
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
1,8$_2$	—	—	—	—	—	—	—	—	—	—	—	—	1,8	—
3,6$_4$	—	—	—	—	—	—	3,8	+0,2	—	—	—	—	—	—
9,1$_2$	8,8	−0,3	—	—	—	—	9,7	+0,5	9,3	+0,2	9,1	0	9,1	0
14,6	—	—	—	—	—	—	15,0	+0,4	—	—	—	—	—	—
18,2	18,2	0	17,9	−0,3	18,6	+0,4	—	—	18,2	0	17,7	−0,5	17,5	−0,7
27,4	26,6	−0,7	27,7	+0,3	26,6	−0,7	—	—	27,4	0	27,4	0	—	—
36,5	36,5	0	37,6	+1,1	35,9	−0,5	—	—	—	—	—	—	—	—

* Das Absortionskurvenverfahren mit Wasser als Bezugsflüssigkeit.
† Das Absortionskurvenverfahren mit Blindprobe als Bezugsflüssigkeit.
‡ Das Meßverfahren bei konstanter Wellenlänge.

TABELLE II.—SPEKTROPHOTOMETRISCHE BESTIMMUNG DES HAFNIUMS IN GEGENWART VON ZIRKONIUM

Hf gegeben, μg/ml	Hf gefunden,* μg/ml						Hf gefunden,† μg/ml				Hf gefunden,‡ μg/ml	
	λ = 218,2 nm	Δ	λ = 243,5 nm	Δ	λ = 298,5 nm	Δ	λ = 217,5 nm	Δ	λ = 243,5 nm	Δ	λ = 243 nm	Δ
1	2	3	4	5	6	7	8	9	10	11	12	13
3,5$_6$	—	—	—	—	—	—	—	—	—	—	3,3$_9$	−0,1$_7$
7,1$_8$	—	—	—	—	—	—		—	—	—	7,1$_8$	0
17,8	17,8	0	17,8	0	—	—	17,8	0	—	—	—	—
35,7	34,3	−1,4	35,7	0	34,3	−1,4	35,0	−0,7	35,0	−0,7	34,6	−1,1
53,5	52,1	−1,4	52,8	−0,7	53,5	0	53,5	0	51,8	−1,8	—	—
71,4	72,1	+0,7	70,7	−0,7	71,4	0	—	—	71,4	0	—	—

* Das Absortionskurvenverfahren mit Wasser als Bezugsflüssigkeit.
† Das Absortionskurvenverfahren mit Blindprobe als Bezugsflüssigkeit.
‡ Das Meßverfahren bei konstanter Wellenlänge.



(A) (B) (C)

ABB. 4.—Absorptionskurven der Systeme: Zr-ANDA (Diagramm A), Hf-ANDA (Diagramm B) und (Zr + Hf)-ANDA (Diagramm C).
Konstante Ligandkonzentration = $1{,}2 \cdot 10^{-3}M$. ZrO^{2+}-Konzentration: 0 (Kurve *R*), $1 \cdot 10^{-4}M$ (Kurve *1*), $2 \cdot 10^{-4}M$ (*2*), $4 \cdot 10^{-4}M$ (*3*), $5 \cdot 10^{-4}M$ (*4*). HfO^{2+}-Konzentration: 0 (Kurve *R*), $5 \cdot 10^{-4}M$ (Kurve *5*), $4 \cdot 10^{-4}M$ (*6*), $2 \cdot 10^{-4}M$ (*7*), $1 \cdot 10^{-4}M$ (*8*). Den Kurven *9*, *10*, *11*, *12* und *1*, *2*, *3*, *4* liegt die gleiche ZrO^{2+}-Konzentration zu Grunde. Die HfO^{2+}-Konzentration entspricht der der Kurven *5*, *6*, *7* und *8*. Bezugslösung: bidestilliertes Wasser. Schichtdicke: 10 mm.

der hohen Extinktion der Lösung in der Bezugsküvette und infolge des kleinen molaren Extinktionskoeffizienten der Systeme Zr– Hf–ANDA sind keine größeren Absorptionswerte zu erzielen. Aus denselben Gründen ist auch die Aufstellung der Kurven im Gebiet kleinerer Wellenlängen als 225 nm an größere Feher gebunden.

Meßverfahren bei konstantem λ

Die gleichzeitige Bestimmung von Zirkonium und Hafnium kann auch nur mit Hilfe eines nichtautomatischen Spektrophotometers durchgeführt werden. In diesem Falle sind aber nur Bestimmungen möglich, bei denen der Extinktionswert positiv ist. So kann man bei ungefähr 243 nm Hafnium bestimmen. Bei 297 nm kann man dagegen Zirkonium in Gegenwart von Hafnium erfassen, da sich die Absorptionskurven der Komplexe Zr-ANDA im Intervall zwischen diesen beiden Wellenlängen scheiden. Die Bestimmung des Zirkonium bei ungefähr 216 nm ist hier nicht möglich, weil die Messungen bei kleineren Wellenlängen als 220 nm zu ungenau sind.

Für die möglichen, obenangeführten Bestimmungen, zum Beispiel die Hf-Bestimmungen bei ungefähr 243 nm, wird wie folgt verfahren. Die Extinktion der Blindlösung (die alles, außer der Kationenlösung enthält) wird (bezogen auf Wasser) im Intervall von einigen nm um den, für den Komplex Zr-ANDA bekannten isosbestischen Punkt (aus Abb. 1), ermittelt. Für 2 bis 3 Proben, die den Komplex Zr-ANDA mit veränderlichen Zr-Mengen enthalten, wird die Extinktion bei denselben Wellenlängen gemessen. Ausgesucht wird die Wellenlänge, bei der die Extinktion aller Proben identisch und gleich der der Blindprobe ist. Bei dieser Wellenlänge nimmt man die Extinktion einer Eichserie für den Komplex Hf-ANDA (Kurve *6* aus Abb. 3B)

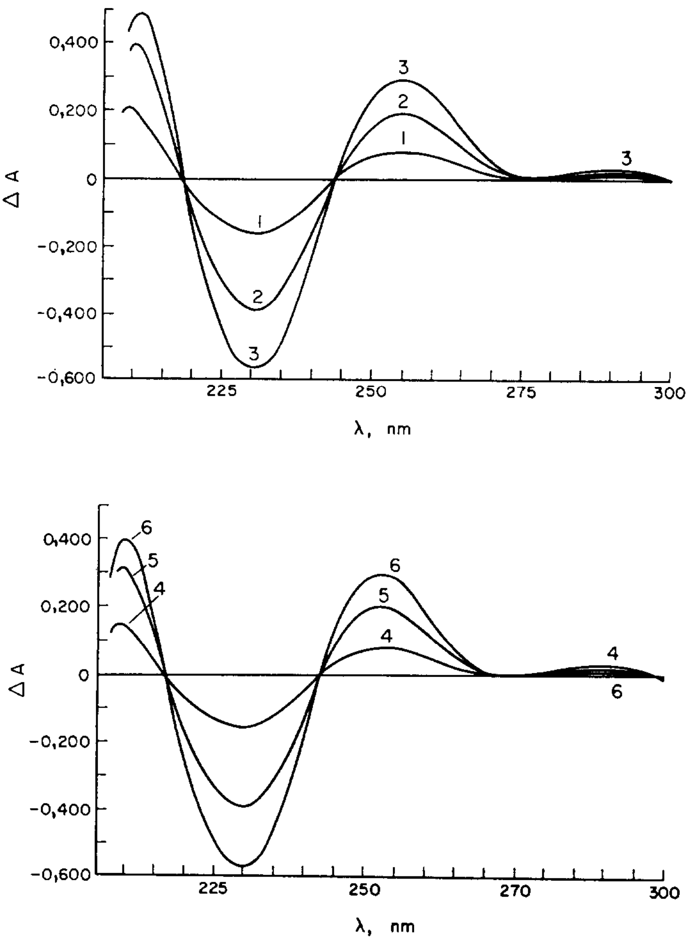


Abb. 5.—Absorptionskurven der Komplexe Zr-ANDA (Diagramm A) und Hf-ANDA (Diagramm B).
Konstante Ligandkonzentration = $0,4 \cdot 10^{-3}M$. ZrO^{2+}-Konzentration: $0,4 \cdot 10^{-4}M$ (Kurve *1*), $1 \cdot 10^{-4}M$ (*2*), $1,6 \cdot 10^{-4}M$ (*3*). HfO^{2+}-Konzentration: $0,4 \cdot 10^{-4}M$ (Kurve *4*), $1 \cdot 10^{-4}M$ (*5*), und $1,6 \cdot 10^{-4}M$ (*6*). Bezugslösung: Blindlösung. Schichtdicke 5 mm.

auf. Die anschließend gemessene Extinktion für ein Gemisch (Zr + Hf)-ANDA kann ausschließlich dem Komplex Hf-ANDA zugeschrieben werden. In Tabelle II zeigen die Spalten 12 und 13, daß bei Lösungen, in welchen ~2,5 % Hafnium im Vergleich zu Zirkonium enthalten sind, ein prozentualer Fehler von ~5 % auftritt. Für größere Zr-Gehalte liegt dieser aber bei $\leq 3\%$. Im Falle der Zr-Bestimmung bei der Wellenlänge von ungefähr 297 nm verfährt man analog. Erhalten wird so die Eichkurve *6* aus Abb. 3A. Beispiele für solche Bestimmungen sind in Tabelle I, Spalte 14, angegeben. Auch hier besteht die Möglichkeit gegen die Blindprobenlösung zu photometrieren. In diesem Fall kann die Extinktion aus den Eichdiagrammen (erhalten durch Differenzbildung: Extinktion der Versuchsprobe minus Extinktion der Blindprobe, beide bezogen auf Wasser) direkt abgelesen werden. Größere

Fehler, die bei der Messung sehr kleiner Extinktionen auftreten, machen das erste Verfahren vorteilhafter.

Im folgenden wird die spektrophotometrische Bestimmung des Zirkoniums und Hafniums bei den Wellenlängen $\lambda \sim 216$ bzw. 218 nm kurz beschrieben.

Zur Aufstellung der Eichkurven für das ZrO^{2+}-Ions werden vier Proben mit je 3 ml $10^{-4}M$ ANDA und 0,5–2,5 ml $5 . 10^{-3}N$ $ZrOCl_2$, gelöst in $10^{-1}M$ Perchlorsäure eingesetzt. Diese vier Kurven nebst der der Bezugsprobe *R* (Lösung sämtlicher Komponenten außer $ZrOCl_2$) bilden Diagramm A. Verfährt man analog für das Ion HfO^{2+}, so erhält man Diagramm B.

Aus Diagramm A wird bei $\lambda = 216,5$ nm die Differenz der Absorptionen zwischen jeder der Absorptionskurven und der Kurve *R* abgelesen und mit diesen Werten die Eichkurve der ZrO^{2+}-Ions aufgestellt. Aus Diagramm B wird bei $\lambda = 218$ nm analog die Eichkurve für HfO^{2+} erhalten.

Schließlich wird die Absorptionskurve einer Lösung, welche dieselbe Ligandmenge (3 ml $10^{-2}M$ ANDA und ein Gemisch von ZrO^{2+} und HfO^{2+}) enthält, aufgenommen. Die Summe von Zirkonium und Hafnium darf jedoch $1,25 . 10^{-5}$ Mol nicht überschreiten. In Diagramm C ist diese Absorptionskurve mit Bezugskurve *R* enthalten. Die Differenz beider Extinktionen bei der Wellenlänge $\lambda = 216,5$ nm entspricht dem Komplex Zr-ANDA. Die Konzentration des ZrO^{2+} hingegen wird aus der Eichkurve des Systems A entnommen. Die Extinktion bei der Wellenlänge $\lambda = 218$ nm entspricht dem Hf-ANDA-Komplex, die Konzentration des HfO^{2+} läßt sich dann aus der Eichkurve des Systems B ermitteln.

Summary—Zirconium may be determined in the presence of hafnium by ultraviolet spectrophotometry at the isosbestic wavelengths of 218·2, 243·3 or 298·8 nm, with anthranil-*N*,*N*,-diacetic acid in dilute acid solution. Hafnium may be determined in the presence of zirconium from measurements at 216·5, 242·5 or 297 nm. Concentrations in the range 2–36 μg/ml (Zr) and 3–70 μg/ml (Hf) may be determined, and in admixture, from 2·5 to 80% of Zr in Hf, and *vice versa*, with an error of 3–4%.

Résumé—On peut déterminer le zirconium en la présence de hafnium par spectrophotométrie ultra-violette aux longueurs d'ondes isosbestiques de 218,2, 243,5 ou 298,5 nm, avec l'acide anthranil *N*,*N*-diacétique en solution d'acide dilué. On peut déterminer le hafnium en la présence de zirconium des mesures à 216,5; 242,5 ou 297 nm. On peut déterminer des concentrations dans les domaines 2–36 μg/ml (Zr) et 3–70 μg/ml (Hf), et en mélange, de 2,5 à 80% de Zr dans Hf, et vice versa, avec une erreur de 3–4%.

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ANALYSIS BY PHASE TITRATION OF THREE-COMPONENT SYSTEMS CONTAINING TWO MUTUALLY IMMISCIBLE COMPONENTS

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Summary—A method, based on phase titration, for the analysis of ternary mixtures containing two mutually immiscible or partially miscible components is described. It can also be used for the determination of tie-lines. The method is illustrated by its application to the system consisting of benzene, cyclohexane and nitromethane.

THE PRINCIPLE of phase titrations has been used for many years to analyse binary solutions of components which are chemically similar but have different solubilities in water, by titrating the sample with water.[1] If the amount of water that was added is known, the composition of the binary system can be computed from the phase diagram. Siggia and Hanna[2] extended the technique to compute the composition of one-phase ternary systems containing two mutually immiscible components. In their method, one of the components was estimated by chemical or physical means. A separate sample was then titrated with one of the mutually immiscible components, until a turbidity appeared. The composition of the sample was then computed from the ternary phase diagram. More recently Rogers and co-workers[3] have done extensive work on phase titrations and have discussed the titration behaviour of ternary systems, on the basis of solubility relationships.

In the present communication, a method based on the principle of phase separation titration is described, which can be used to analyse a ternary mixture containing two mutually immiscible or partially miscible components, without separate determination of any component. The method can also be used to determine the tie-lines in such ternary systems and has several advantages over other methods. The time for the total analysis is considerably shortened and the errors involved in chemical determination of the components are avoided. The method can be used for systems where chemical analysis for any of its components is difficult.

Technique

The ternary phase diagram is first determined. This can be done easily by phase separation titration.[4] In order to get sharp turbidimetric end-points and to improve the accuracy of the determination, various solutions of the mutual solvent with each of the mutually immiscible components, richer in the latter, are prepared by weight and titrated with the other mutually immiscible component until a permanent turbidity appears. Such turbidimetric end-points can usually be obtained within a drop of titrant.[2]* The ternary mixture is then weighed to determine the weight of the

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* Dunnery and Atwood[5] preferred the clarification end-point to the turbidimetric end-point, the former being equally sharp over a wide composition range. The visibility of the end-point can be improved by the addition of colour contrast indicators, *e.g.*, iodine[6] and furfural.[7]

titrant added. The concentrations of the two sets of binary solutions are chosen so as to yield some overlapping points in the middle region of the curve on titration with the third component. This serves as an internal check on the determination and also illustrates the reproducibility of the technique.[8]

Consider a three-component system containing A, B and C, where A and B are mutually immiscible and C is miscible with both A and B. If to 1 g of the ternary solution having the composition represented by any point, **P**, on the binodal curve (Fig. 1), 1 ml (it is more practicable to add a known volume than a known weight) of component C is added, the composition of the resultant solution can now be represented by **Q**, a point on the line connecting **P**, representing the original composition and **C**, representing 100% C. On titration with B, the composition of this solution will move along the line **QB** and a permanent turbidity will appear when the composition reaches **R**, the point of intersection of the line **QB** with the binodal curve. The weight of component B required to produce permanent turbidity* thus depends upon the composition of the solution represented by **P** and **R** and is given by the expression:

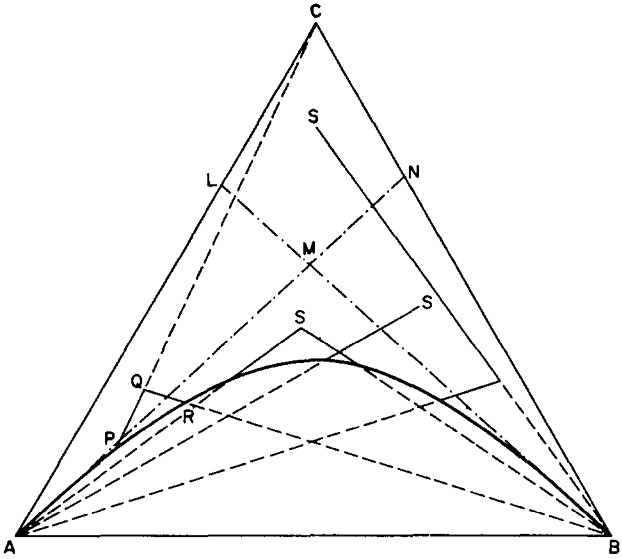

FIG. 1.—Ternary liquid–liquid miscibility diagram illustrating the analysis of the ternary mixture, S, by phase titrations.

$$W_B = \frac{X_{AP}}{X_{AR}} - (1 + W_C)$$

where W_C is the weight of component C added per g of the solution with composition **P**; W_B is the weight of titrant B required to titrate $(1 + W_C)$ g of solution from **Q** to **R**, *i.e.*, to the turbidimetric end-point, and X_{AP} and X_{AR} are the weight fractions of component A at compositions **P** and **R** respectively.

Once the binodal curve is determined, the amount of A or B required to produce a

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* Which non-con-solute component is selected as titrant depends upon the composition of the ternary to be titrated.[3]

turbidimetric end-point for a mixture of 1 g of a ternary composition lying on the binodal curve, and 1 ml of component *C*, for various amounts of *A* initially present can be calculated. Two calibration curves can then be plotted indicating the amount of *A* or *B* required to titrate such solutions, as a function of the amount of *A* or *B* in the initial ternary solution at **P**.

On addition of 1 ml of the component *C* to 1 g of a ternary composition lying on the binodal curve, if the composition of the resultant mixture lies outside **ALMNB**, the area defined by the tangents to the binodal curve, it will not yield any turbidimetric end-point on titration with either *A* or *B*. In such cases, for plotting the calibration curves the sample solution and component *C* are mixed in some other simple ratio such as 2 g/ml, 3 g/ml instead of 1 g/ml, and the amount of component *C* required to produce turbidity is calculated.

Determination of tie-lines

The composition of any ternary mixture lying on the binodal curve can be determined by adding 1 ml of *C* per g of the ternary mixture and titrating with *A* or *B*. From the amount required, the initial composition of the ternary can be computed from the calibration curves.

In order to determine the tie-lines, the composition of both the phases in equilibrium is computed as described above by running two sets of titrations for each phase, one with *A* and the other with *B*.

Analysis of ternary mixtures

To analyse a homogeneous mixture of *A*, *B* and *C*, having a composition represented by any point, S, other than on the binodal curve, two samples of known weight of the ternary are titrated with each of components *A* and *B* to bring the composition of the ternary on to the binodal curve. The solution is then weighed and the weight of *A* or *B* added is determined. The composition of this solution is then obtained as described above and hence the initial composition of the ternary is calculated.

If the composition of the ternary mixture lies somewhere in the area **CLMN**, a known weight of *A* or *B* is added to a known weight of the ternary, enough to bring the composition into either of the titratable regions **BNM** or **ANL**. The solution thus obtained is titrated with the other mutually immiscible component to the turbidimetric end-point and hence the composition of the ternary is determined. The amount of *A* or *B* sufficient to bring the composition of unit weight of the ternary into the titratable region can be calculated from the position of L and N (Fig. 1).

The method described is illustrated for the ternary system benzene, cyclohexane and nitromethane, the last two being partially miscible at ordinary temperatures.

EXPERIMENTAL

Procedure

The solvents were purified by established methods.[9,10] Their densities measured at 30° and 40° (±0·01°) are given in Table I, along with the literature values for comparison.[11]

The binodal curve was established at 40° as described earlier.[8] The technique and apparatus used were similar to those of Dunnery and Atwood.[5] The solutions and the solvents were kept in a thermostatic cabin before use, the temperature of the cabin during titrations being kept constant to within 0·1°. Enough solution was taken to give a titre of 10–20 ml. The results obtained are tabulated in Table II and are in good agreement with those obtained by Weck and Hunt[12] at 25° and by Suri *et al.*[8] at 20° and 30°.

Table I.—Densities of the solvents used

	Temp., °C	Present work, g/ml	Literature[11] g/ml
Benzene	30	0·8685	0·8685
	40	0·8575	0·8577
Cyclohexane	30	0·7694	0·7692
	40	0·7596	0·7594*
Nitromethane	30	1·1250	1·1245
	40	1·1108	—

* Value at 40·21°C.

Table II.—Composition at the binodal curve for the system C_6H_6—C_6H_{12}—CH_3NO_2 at 40°C

Cyclohexane, % w/w	Nitromethane, % w/w	Cyclohexane, % w/w	Nitromethane, % w/w
9·2	85·3	42·1	34·1
11·6	77·8	50·7	25·2
15·4	69·2	59·6	18·2
19·3	62·5	65·3	15·4
25·0	53·9	83·8	7·3
35·0	42·1	93·4	5·1

Since the addition of 1 ml of benzene to 1 g of the binodal curve ternary moved its composition outside the area ALMNB (Fig. 1) for most of the compositions, the two were mixed in the ratio 1 ml: 3 g for the system under study. The compositions of the resultant mixtures for various **P** values (Fig. 2) were calculated and are represented by **Q** values. The **Q** values were then joined with the apices corresponding to 100% cyclohexane and nitromethane, and from the composition of **R**, where one of these lines intersected the binodal curve, the amounts of cyclohexane or nitromethane required to produce a turbidimetric end-point were calculated. Two calibration curves were then drawn

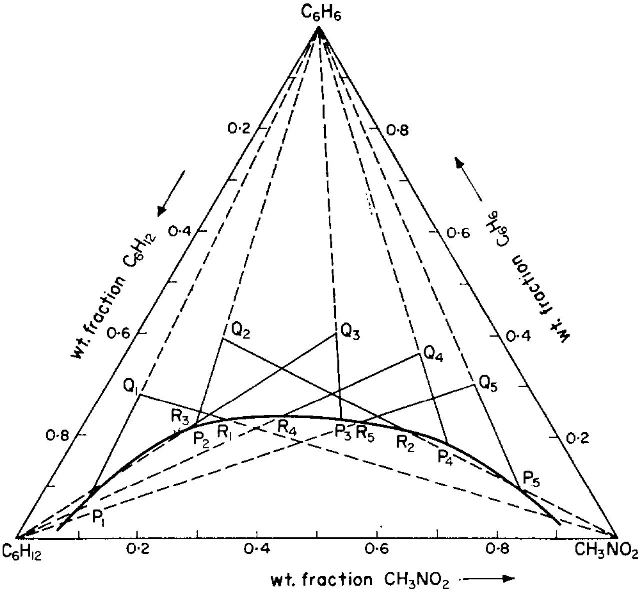

Fig. 2.—Determination of the amount of titrant required to construct the calibration curve for the ternary system benzene–cyclohexane–nitromethane at 40°C.

plotting the composition of the ternary at P *vs.* the amount of cyclohexane or nitromethane required to produce turbidity at the corresponding Q.

Results

Ten synthetic ternary mixtures were prepared by mixing different amounts of benzene, cyclohexane and nitromethane and were analysed by this method. The results obtained are compared with the actual values in Table III.

TABLE III.—COMPARISON OF THE ACTUAL AND THE ESTIMATED COMPOSITION OF THE TERNARY MIXTURE $C_6H_6 + C_6H_{12} + CH_3NO_2$

Sample	Cyclohexane, % *w/w*		Nitromethane, % *w/w*		Titrant
	Present	Estimated	Present	Estimated	
1	72·0	71·8	6·3	6·5	Nitromethane
2	50·8	49·9	12·2	12·4	Nitromethane
3	39·4	39·1	27·3	26·8	Cyclohexane
		39·6		26·4	Nitromethane
4	6·0	6·13	79·1	80·6	Cyclohexane
5	7·8	7·62	58·8	58·9	Cyclohexane
6	27·6	27·6	45·0	44·7	Cyclohexane
		28·2		45·8	Nitromethane
7	9·6	9·67	14·4	14·4	Cyclohexane
		10·1		14·8	Nitromethane
8	34·8	34·9	10·1	10·2	Cyclohexane
		35·3		10·4	Nitromethane
9	25·4	25·0	24·8	24·4	Cyclohexane
		25·2		25·7	Nitromethane
10	0·0	0·2	38·5	38·1	Cyclohexane
		0·1		38·3	Nitromethane

Samples 1 and 2 gave turbidimetric end-points with nitromethane, 4 and 5 with cyclohexane, 3 and 6 with both and 7–10 with neither. Two sets of each of samples 7–10 were diluted with about the same weight (because the position of L and M lies at ~0·5 weight-fraction) of nitromethane or cyclohexane and the resultant mixtures were titrated with cyclohexane or nitromethane respectively. The composition of the turbid solution obtained on titration with nitromethane or cyclohexane for all the samples was computed from the calibration curve by determining the amount of titrant required to titrate a mixture of 0·333 ml of benzene and 1 g of this solution to the turbidimetric end-point. The composition of the unknown ternary was then calculated.

DISCUSSION

It can be seen from Table III that the agreement between the actual and the determined values is satisfactory on the whole. The maximum difference is ~1·5% when cyclohexane is used and ~4% when nitromethane is used as titrant, indicating that the latter is a poor titrant for phase titrations. A similar observation was made earlier by Rogers and co-workers[13] for nitromethane. The agreement between the actual value and the two sets of determined values for samples 3, 6, and 7–10 is good.

Although the method described above is extremely useful when it is difficult to determine any of the components chemically, it is subject to certain limitations. If the refractive indices of the two phases produced are nearly the same, an opalescence instead of a turbidity will be observed near the end-point. The end-point will be invisible if the refractive indices are the same (iso-optic area). In such cases, addition of few drops of one of the three pure components to an aliquot of the sample is expected to help in locating the end-point. Various other sources of error are inadequate temperature control, evaporation losses during titration, errors involved in determining the phase diagram and lack of a sharp end-point in certain cases.

Zusammenfassung—Eine auf Phasentitration beruhende Methode zur Analyse ternärer Gemische wird beschrieben, die zwei nicht oder nur teilweise mischbare Komponenten enthalten. Sie kann auch zur Ermittlung von Konnoden dienen. Die Methode wird an ihrer Anwendung auf das System Benzol-Cyclohexan-Nitromethan erklärt.

Résumé—On décrit une méthode basée sur le titrage de phase pour l'analyse de mélanges ternaires contenant deux constituants mutuellement non miscibles ou partiellement miscibles. On peut aussi l'utiliser pour la détermination de lignes de jonction. La méthode est illustrée par son application au système consistant en benzène, cyclohexane et nitrométhane.

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DETERMINATION OF VANADIUM IN REFRACTORY METALS, STEEL, CAST IRON, ALLOYS AND SILICATES BY EXTRACTION OF AN NBPHA COMPLEX FROM A SULPHURIC–HYDROFLUORIC ACID MEDIUM

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Summary—A method for determining up to 0·15% of vanadium in high-purity niobium and tantalum metals, cast iron, steel, non-ferrous alloys and silicates is described. The proposed method is based on the extraction of a red vanadium(V)-*N*-benzoyl-*N*-phenylhydroxylamine complex into chloroform from a sulphuric–hydrofluoric acid medium containing excess of ammonium persulphate as oxidant. The molar absorptivity of the complex is 428 l.mole^{-1}.mm^{-1} at 475 nm, the wavelength of maximum absorption. Interference from chromium(VI) and cerium(IV) is eliminated by reduction with iron(II). Common ions, including large amounts of titanium, zirconium, molybdenum and tungsten, do not interfere.

NUMEROUS methods have been reported for the spectrophotometric determination of vanadium with *N*-benzoyl-*N*-phenylhydroxylamine (NBPHA).[1–12] In these methods, vanadium(V), as a purple 1:2 complex, is extracted into chloroform from a hydrochloric acid medium. Ryan[1] and Priyadarshini and Tandon[2] have stated that extraction of vanadium is quantitative under considerably different conditions of acid concentration, *i.e.*, from 5–9*M* and from 2·8–4·3*M* hydrochloric acid, respectively. However, other investigators[6,13] have found that extraction is not quantitative because of partial reduction of vanadium in relatively concentrated hydrochloric acid solutions. Because similar problems (low and erratic results), associated with the use of hydrochloric acid media, were encountered in this laboratory, an attempt was made to find a more suitable medium for extraction. Subsequently, it was established that the purple complex can be extracted readily from sulphuric acid (optimum concentration 3·0–3·5*M*)–sodium chloride (0·5–>2*M*) media containing excess of ammonium persulphate as oxidant, and that it has a higher molar absorptivity (498 l.mole^{-1}.mm^{-1} at 525 nm) than has been reported previously.[1–3]

In experiments testing the masking effect of fluoride on ions known to interfere with the extraction of the purple complex (*e.g.*, titanium, zirconium),[2,13,14] a change in colour of the extract to a reddish hue and a subsequent decrease in the wavelength of maximum absorption were observed. These changes were found to be more pronounced with increasing fluoride concentration and indicated the formation of a different complex in the presence of fluoride. Because of the beneficial complexing effect of fluoride, it was considered that a method based on extraction of the red vanadium complex from a fluoride medium would be more selective than one based on extraction of the purple complex from a chloride medium. Consequently, the conditions of formation and extraction of the red complex were investigated in the present work. The applicability of this extraction method to the determination of small amounts of vanadium in a variety of materials, including high-purity niobium and tantalum metals, is demonstrated.

EXPERIMENTAL

Apparatus

Funnels for filtering extract. Constructed from broken 10-ml pipettes by cutting the bulb in half.

Reagents

Standard vanadium solution. Dissolve 0·1785 g of vanadium pentoxide by heating in a 250-ml beaker with 40 ml of 12·5*M* sulphuric acid and 5 ml of concentrated nitric acid. Evaporate the resulting solution to fumes of sulphur trioxide, cool, and dilute to 500 ml with water. Prepare a working solution (1 ml ≡ 25 μg of vanadium) by appropriate dilution of this stock solution. (The vanadium pentoxide used was found to be pure by reduction and titration with permanganate.)

NBPHA solution. Prepare a 0·1% w/v solution-in chloroform and store in a brown bottle.

Iron(II) ammonium sulphate hexahydrate, 10% *solution, w/v.* Dissolve 5 g of the reagent in water, add 1 ml of 12·5*M* sulphuric acid and dilute to 50 ml with water. Prepare fresh as required.

Ammonium persulphate, 10% *solution, w/v.* Prepare fresh as required.

Sulphuric acid, 12·5*M.*

Hydrofluoric acid, 25*M.*

Chloroform (alcohol-free).[3]

Calibration curve

Add 8 ml of 12·5*M* sulphuric acid to each of seven 125-ml polypropylene separatory funnels (marked at 50 ml); then by burette, add to the last six funnels 1, 2, 3, 4, 5 and 6 ml, respectively, of standard 25 μg/ml vanadium solution. The first funnel contains the blank. Add to each funnel 8 ml of 25*M* hydrofluoric acid, 4 ml of 10% iron(II) ammonium sulphate solution, dilute to approximately 40 ml with water and mix. Then add 5 ml of 10% ammonium persulphate solution, dilute to the 50-ml mark with water and mix thoroughly. Add 10 ml of 0·1% NBPHA chloroform solution, stopper and shake for 2 min. Allow several min for the layers to separate, then filter the chloroform extract through a wad of cotton-wool into a dry 25-ml volumetric flask. Re-extract the solution three more times using, in succession, 5, 3 and 3 ml of NBPHA solution and shaking for 2 min each time. Combine these extracts with the first, wash the funnel with a few ml of chloroform and dilute to volume with chloroform. Determine the absorbance of each solution against chloroform as the reference solution, using 20-mm cells, at a wavelength of 475 nm. Correct the absorbance value obtained for each vanadium-NBPHA extract by subtracting that obtained for the blank. Plot μg of vanadium *vs.* absorbance.

Procedures

In the following procedures a reagent blank is carried along with the samples.

Niobium and tantalum metals. Transfer a suitable weight (0·1–0·5 g) of the powdered metal to a 250-ml Teflon beaker, add 5 ml of water, 8 ml of 12·5*M* sulphuric acid solution and 2 ml of hydrofluoric acid and cover the beaker with a Teflon cover. Add 4 ml of concentrated nitric acid, heat gently until all of the metal is in solution, then remove the cover and evaporate the solution to fumes of sulphur trioxide. After cooling, wash down the sides of the beaker with a small amount of water, add 1 ml of hydrofluoric acid and again evaporate to fumes to ensure complete removal of nitric acid. Cool, add 5 ml of water, allow to cool to room temperature and then, just before the extraction step, add 8 ml of 25*M* hydrofluoric acid solution (hydrofluoric acid volatilizes from the solution on prolonged standing at room temperature). Swirl the beaker to dissolve precipitated hydrates of niobium or tantalum, transfer the resulting solution to a 125-ml polypropylene separatory funnel and, after the addition of iron(II) ammonium sulphate and ammonium persulphate solutions, proceed with the extraction and determination of vanadium as described above.

Silicate rocks. Decompose a suitable weight of sample (0·1–0·5 g) depending on the expected vanadium content, by the method described for niobium and tantalum metals, using 5 ml of hydrofluoric acid instead of 2 ml (additional hydrofluoric and nitric acids may be required to obtain complete dissolution). After evaporating the resulting solution twice to fumes of sulphur trioxide, cool, add 5 ml of water and heat gently (if necessary) to clarify the solution. Add 8 ml of 25*M* hydrofluoric acid solution (calcium, in large amounts, is insoluble in this acid mixture but this does not impair the extraction of vanadium), transfer the resulting solution to a separatory funnel and proceed with the extraction and subsequent determination of vanadium.

Steel, cast iron and non-ferrous alloys (low chromium content). Decompose a 0·1–0·5-g sample containing not more than approximately 10 mg of chromium, by the method described for niobium and tantalum metals and determine vanadium as described above. With samples of cast iron, remove graphitic carbon before the extraction step, by filtering (plastic funnel) the resulting sulphuric–hydrofluoric acid solution into the separatory funnel.

Steel and non-ferrous alloys (high chromium content). Transfer a 0·1–0·5-g sample to a Teflon beaker and add 5 ml of water, 5 ml of concentrated perchloric acid, 4 ml of concentrated nitric acid, 2 ml of hydrofluoric acid and 5 ml of concentrated hydrochloric acid (if necessary). Cover and heat gently until all of the sample is in solution (additional nitric and hydrochloric acids may be required to obtain complete dissolution). Remove the cover, wash down the sides of the beaker with a small amount of water and evaporate to fumes of perchloric acid. Cool, add approximately 20 ml of water (heat, if necessary, to dissolve salts), transfer the solution to a mercury cathode cell and dilute to approximately 200 ml with water. Electrolyse the resulting solution for 45 min at approximately 10 A, then filter the electrolyte into a 400-ml Pyrex beaker and evaporate to dryness. Wash down the sides of the beaker with a small amount of water, add 8 ml of 12·5*M* sulphuric acid solution and evaporate to fumes of sulphur trioxide. Cool, add 5 ml of water, allow to cool to room temperature and then transfer the resulting solution to a separatory funnel. Add 8 ml of 25*M* hydrofluoric acid solution and proceed with the extraction and determination of vanadium.

RESULTS

Extraction and spectral characteristics of the red vanadium(V)–NBPHA complex

Figure 1 shows the difference between the absorption spectrum of the red complex extracted from a sulphuric acid–fluoride medium and that of the purple complex extracted from a sulphuric acid–chloride medium. The molar absorptivity of the red complex is 428 $\text{l.mole}^{-1}.\text{mm}^{-1}$ at 475 nm, the wavelength of maximum absorption.

Extraction of the red complex (and also the purple complex) was found to be quantitative after four separate batch extractions with 0·1% NBPHA-chloroform

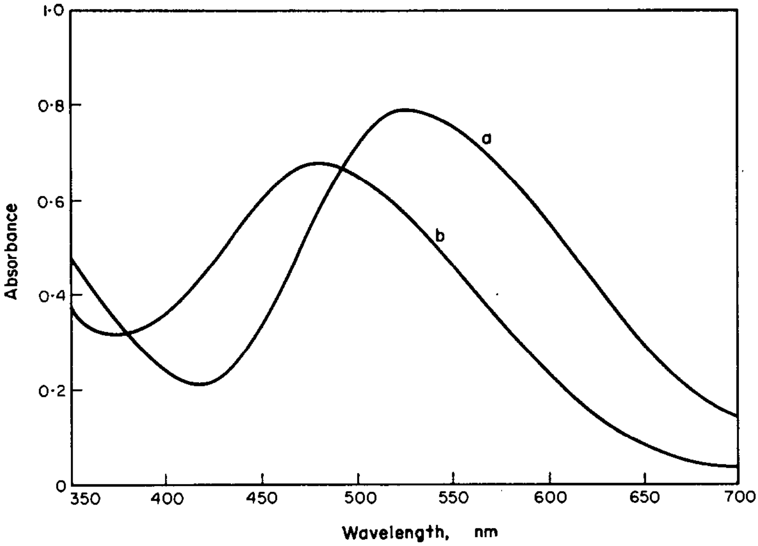

FIG. 1.—Absorption spectra of vanadium (V)–NBPHA complexes. (*a*) Vanadium (V) (100 μg) extracted from 3·25*M* sulphuric acid–1·0*M* sodium chloride medium. (*b*) Vanadium (V) (100 μg) extracted from 2*M* sulphuric acid–1·0*M* potassium fluoride (or hydrofluoric acid) medium. Spectra measured against a reagent blank in 20-mm cell.

solution when 2-min shaking periods were employed. The extracts were found to be stable for at least 24 hr.

Factors influencing formation and subsequent extraction of the red vanadium complex

Effect of oxidant. Potassium permanganate has been employed as oxidant in most methods involving the extraction of the purple vanadium(V)–NBPHA complex from a hydrochloric acid medium. However, the excess of permanganate must be destroyed before the extraction step because this reagent (and other strong oxidizing agents such as potassium dichromate and ceric sulphate) presumably oxidizes NBPHA, producing a yellow extract.[1,2] This destruction can be achieved by reduction with sodium nitrite and subsequent destruction of the excess of nitrite with urea,[1,8] or (with only a small excess) by the addition of the hydrochloric acid needed to maintain the acidity required for extraction.[1]

It has been found in this laboratory, and by other investigators,[6,13] that extraction of the purple complex under these conditions yields low results because some vanadium is reduced in relatively concentrated hydrochloric acid media. In the present work, a similar effect (low and erratic results) occurred when potassium permanganate was used as oxidant, in initial tests involving the extraction of the purple and red complexes respectively from sulphuric acid media containing sodium chloride or potassium fluoride. It was considered that this effect could be associated with the absence of excess of oxidant; consequently, an attempt was made to find an oxidant which could be used in excess, in relatively concentrated sulphuric acid solutions, without producing a yellow extract with NBPHA. Ammonium persulphate was found to fulfill these conditions and subsequent tests performed in both sulphuric acid–sodium chloride and sulphuric acid–potassium fluoride media with an excess of this reagent yielded consistent and reproducible results.

Effect of sulphuric acid concentration. Although the red vanadium(V)–NBPHA complex can be extracted from hydrofluoric acid media alone (0·5–2·5*M*), extraction from sulphuric acid–potassium fluoride (or hydrofluoric acid) solutions was considered more suitable for analytical purposes (*i.e.*, for dissolution procedures). Experiments showed (Table I) that in the presence of 2*M* potassium fluoride or hydrofluoric acid, the extraction of vanadium (as its red complex) is complete from solutions 1·5–5*M*

TABLE I.—EFFECT OF SULPHURIC ACID CONCENTRATION ON THE EXTRACTION OF THE RED VANADIUM COMPLEX

$[H_2SO_4]$, *M*	Absorbance	
	[KF], 2*M*	[HF], 2*M*
0·5	0·083	0·672
1·0	0·595	0·677
1·5	0·667	0·677
2·0	0·673	0·670
2·5	0·669	0·673
3·0	0·674	0·673
3·5	0·674	0·672
4·0	0·666	0·679
4·5	0·676	0·679
5·0	0·675	0·679

Vanadium taken, 100 μg.

or 0·5–5M in sulphuric acid, respectively. An intermediate concentration of 2M was chosen for subsequent work.

Effect of fluoride concentration. Tests carried out to determine the effect of fluoride concentration on the extraction of the red complex from solutions 2M in sulphuric acid showed that extraction is complete from solutions from 0·05 to at least 2M in potassium fluoride or 0·05–6·5M in hydrofluoric acid. Because potassium fluoride, in high concentrations, is insoluble in 2M sulphuric acid media and because tantalum forms an insoluble complex (potassium fluorotantalate) with this reagent, hydrofluoric acid was used in the proposed method. A concentration of 4M was found to be adequate for both extraction and masking purposes.

Effect of diverse ions

Recently, Vita *et al.*[13] have shown that, depending on acidity, various ions [titanium(IV), zirconium(IV), hafnium(IV), niobium(V), tantalum(V), chromium(VI), molybdenum(VI), tungsten(VI), technetium(VII), tin(IV), antimony(III) and antimony(V)] are completely or partially extracted (>50%) with an NBPHA-chloroform solution from hydrochloric acid media; other ions [manganese(II), iron(III), cobalt(II) and nickel(II)] are only slightly extracted (<15%). According to Shendrikar,[14] titanium, zirconium, molybdenum and tungsten are the principal interferents in the determination of vanadium by extraction of its purple NBPHA complex from a hydrochloric acid medium. However, other ions mentioned above (niobium, tantalum, tin, manganese and chromium) have been found to interfere also.[1–3] In the present work, involving extraction of vanadium from 2M sulphuric-4M hydrofluoric acid media, tests were carried out with 10-mg amounts of all of the ions mentioned above (except hafnium and technetium) and various other ions [copper(II) cadmium(II), zinc(II), arsenic(V), bismuth(III) and cerium(IV)]. The results of these tests showed that none of the ions tested, except chromium and cerium, interfered in the extraction and subsequent determination of vanadium. Additional tests performed with 500-mg amounts of niobium, tantalum, molybdenum, tungsten, titanium and zirconium showed that only molybdenum and tungsten interfered at this level by inhibiting the extraction of vanadium. However, up to 50 mg of these ions (present separately) do not interfere in the proposed method, and up to 100 mg can be tolerated if five batch extractions are performed. In these tests (and some of the previous tests) changes in the absorption spectra, detected between 340 and 425 nm, of extracts from niobium, tantalum, molybdenum and tungsten solutions suggested that some co-extraction of these ions occurs. Analysis (approximate) of the extracts confirmed this and showed that the amounts co-extracted, at the 500-mg level, did not exceed approximately 3 mg.

Interference from chromate and ceric ions is avoided in the proposed method by reduction of these ions to the tervalent state with iron(II).[1] Vanadium is also reduced by this reagent but is subsequently re-oxidized to the quinquevalent state with ammonium persulphate; chromium(III) and cerium(III) are not re-oxidized under these conditions (except possibly when silver is present).

Applications

The proposed method was applied to the analysis of a series of synthetic niobium and tantalum samples in which the added vanadium was varied from 0·001 to 0·10%.

TABLE II.—RECOVERY OF VANADIUM BY THE PROPOSED METHOD FROM SYNTHETIC NIOBIUM AND TANTALUM SAMPLES

Matrix	Total V present, %	V found, %
Nb	0·0014	0·0014
	0·0054	0·0055
	0·0104	0·0106
	0·0254	0·0257
	0·0504	0·0510
	0·1004	0·1022
Ta	0·0010	0·0010
	0·0050	0·0051
	0·0100	0·0100
	0·0250	0·0251
	0·0500	0·0502
	0·1000	0·1003

Duplicate determinations of vanadium in the Nb and Ta metals by the proposed method gave average results of 0·0004% and none detected, respectively.

TABLE III.—DETERMINATION OF VANADIUM IN N.B.S. STEEL, CAST IRON AND NON-FERROUS ALLOY SAMPLES

Sample	Nominal composition, %	Certified value and range % V	V found, %
6F Cast iron	0·4 Cr, 0·1 Ti, 0·5 Mn	0·032 (0·027–0·038)	0·031
19G Acid open-hearth steel	0·4 Cr, 0·6 Mn	0·012	0·012
30E Chromium–vanadium steel	0·9 Cr, 0·8 Mn	0·149 (0·146–0·152)	0·146
32E Nickel-chromium steel	0·7 Cr, 1·2 Ni, 0·8 Mn	0·002 (0·001–0·004)	0·0013
36A Chromium–molybdenum steel	2·4 Cr, 0·9 Mo, 0·4 Mn	0·006 (0·005–0·007)	0·0041, 0·0040*
85B Aluminium alloy	0·2 Cr, 4·0 Cu, 1·5 Mg, 0·6 Mn	0·006	0·0069
87A Silicon–aluminium alloy	6·2 Si, 0·2 Ti, 0·1 Cr	<0·01	0·0080
100A Manganese steel	1·7 Mn	0·003	0·0019
101E Chromium–nickel steel	18·0 Cr, 9·5 Ni, 1·8 Mn	0·043 (0·038–0·045)	0·039*, 0·039*
106B Chromium–molybdenum–aluminium–steel	1·2 Cr, 0·2 Mo, 1·1 Al, 0·5 Mn	0·003 (0·002–0·005)	0·0030
111A Nickel–molybdenum steel	1·7 Ni, 0·2 Mo, 0·2 Cr, 0·7 Mn	0·002	0·0020
133 Chromium–molybdenum steel	13·6 Cr, 0·6 Mo, 0·8 Mn	0·020 (0·014–0·025)	0·018*
139 Chromium–nickel–molybdenum steel	0·5 Cr, 0·6 Ni, 0·2 Mo, 0·9 Mn	0·002	0·0016
155 Chromium–tungsten steel	0·5 Cr, 0·5 W, 1·2 Mn	0·014 (0·010–0·022)	0·012
159 Chromium–molybdenum–silver steel	1·0 Cr, 0·4 Mo, 0·1 Ag, 0·8 Mn	0·054 (0·046–0·06)	0·053
160A Chromium–nickel–molybdenum steel	18·8 Cr, 14·1 Ni, 2·8 Mo, 1·6 Mn	0·052	0·050*
161 Nickel–chromium casting alloy	64·3 Ni, 16·9 Cr, 15·0 Fe, 0·5 Co, 1·3 Mn	0·029 (0·023–0·034)	0·029*

* Mercury cathode separation of chromium.

The standard vanadium solution was added directly to the powdered metal samples. It was also applied to cast iron, steel, non-ferrous alloys and standard silicate rocks. The chemical compositions of six of these rocks (G-2–BCR-1), which were obtained from the United States Geological Survey, have not been fully established. The results of these analyses are given in Tables II, III and IV.

TABLE IV.—DETERMINATION OF VANADIUM IN U.S.G.S. STANDARD SILICATE ROCKS

Sample	Vanadium, *ppm*			
	Reported value and range	Average value (Peck‡)	Average value (Suhr§)	This work
G-1 (granite)	16 (10–21)*	15 ± 1	—	16·0
W-1 (diabase)	240 (213–360)*	276 ± 7	—	272, 274
G-2 (granite)	37 (26–60)†	35	39	35·5, 35·5
GSP-1 (granodiorite)	52 (38–67)†	53	53	52·5, 52·5
AGV-1 (andesite)	121 (70–171)†	124	125	121, 122
PCC-1 (peridotite)	31·2 (21–55)†	29	28	22·0, 23·0
DTS-1 (dunite)	18·9 (6–52)†	11	<5	6·0, 6·5
BCR-1 (basalt)	384 (120–700)†	426	420	420, 424

* Fleischer.[15]

† Flanagan.[16]

‡ Average values (spectrophotometric) by L. C. Peck (U.S. Geological Survey, Denver, Colorado reported by Fleischer and Flanagan.

§ Average values (optical spectrography) by N. H. Suhr (Pennsylvania State University, University Park, Pennsylvania) reported by Flanagan.

DISCUSSION

Table II shows that the results obtained for the synthetic niobium and tantalum samples agree favourably with the total calculated amount present. The results obtained (Table III) for National Bureau of Standards samples of cast iron, aluminium and nickel-chromium alloys and different types of steel are in excellent agreement with certificate values. Although not all of the results obtained (Table IV) for the silicate rocks agree with the values reported by Fleischer[15] and Flanagan,[16] they are in reasonably good agreement with all of the average results obtained by Peck and Suhr. Flanagan's values for samples G-2–BCR-1 are the result of the first compilation of data on these rocks and represent the arithmetic mean (of approximately 17–22 values) of widely varying values obtained by different investigators using various methods (optical spectrography, X-ray fluorescence, spectrophotometry). Because of the distribution of these data either above or below Flanagan's reported values, his arithmetic mean values for PCC-1 and DTS-1 may be high, while that for BCR-1 may be low. For example, for DTS-1, 15 results out of 20 are in the range <5–18·9 ppm (mean value), while 10 out of 20 are 11 ppm and lower. Similarly, for PCC-1, 14 results out of 20 are in the range 20–31·2 ppm (mean value). Conversely, for BCR-1, 14 results out of 22 are 384 ppm and higher.

Recently, Dražić-Antonijević *et al.*[17] have suggested that the purple complex extracted from relatively concentrated hydrochloric acid media is a vanadium(V)-NBPHA complex with one co-ordinated chloride ion. Montequi[18] and Majumdar *et al.*[19] have also isolated the compounds $[(C_{13}H_{10}O_2N)_2VO_2H.HCl]$ and $VO(NBPHA)_2Cl$, respectively. Consequently, it is reasonable to assume that the red complex extracted from fluoride media is a corresponding vanadium(V)–NBPHA–fluoride complex. The differences in the absorption spectra, *i.e.*, absorption maxima and molar absorptivities, of the two complexes (Fig. 1) indicate strongly that chloride and fluoride ions react in these systems by co-ordination, not by ion-association. It is probable that vanadium forms similar red fluoro-complexes with other substituted hydroxylamines because the purple complexes, extracted from hydrochloric acid media with chloroform solutions of these reagents, appear to resemble the vanadium–NBPHA–chloride complex; their absorption maxima and molar absorptivities do not differ very greatly.[20–23]

In the initial work involving the extraction of the purple vanadium(V)–NBPHA complex from sulphuric acid–sodium chloride media, extractions were carried out at about 5–15° because it was observed that ammonium persulphate oxidizes chloride ion to chlorine at room temperature. A similar effect cannot occur with fluoride.

In the proposed method, the amount of iron(II) used is sufficient to reduce approximately 10 mg of chromium(VI). A mercury cathode separation in perchloric acid medium is recommended for samples containing larger amounts of chromium, because of the insolubility of chromium(II) salts in sulphuric acid alone and in the sulphuric–hydrofluoric acid medium used for extraction.

The method for niobium and tantalum metals is suitable, without modification, for the determination of small amounts of vanadium in titanium and zirconium metals. It has been employed to determine trace amounts of vanadium in cobalt and nickel arsenides, but, to obtain complete extraction, it was found necessary to increase the concentration of ammonium persulphate. It can also be applied to molybdenum and tungsten metals, if not more than 100 mg of sample are taken and five batch extractions are performed. Tungsten forms the insoluble hydrated trioxide when the recommended dissolution procedure is employed. However, satisfactory solutions can be prepared by using less sulphuric acid and evaporating to near dryness, followed by dissolution of the tungsten trioxide residue in potassium hydroxide solution and addition of the requisite amounts of sulphuric (including that required to neutralize the excess of potassium hydroxide) and hydrofluoric acids.

Priyadarshini and Tandon[2] state that the colour system resulting from the extraction of the purple vanadium(V)–NBPHA complex from hydrochloric acid media obeys Beer's law between the limits of 0·7 and at least 12 ppm of vanadium (17·5–300 μg; 25-ml volume; 10-mm cells). In the present method Beer's law is obeyed for 1–150 μg of vanadium and the calibration curve passes through the origin. Larger amounts were not tested because of the high absorbance of the extract when 20-mm cells are used for measurement. Although the proposed method is slightly less sensitive than methods involving extraction of the purple complex, it is considerably more selective and reasonably specific as far as common ions are concerned.

The method presented in this paper is suitable for samples containing up to 0·15% of vanadium, but material containing larger amounts can also be analysed if smaller samples or suitable aliquots (with the exception of niobium and tantalum metals) of a sulphuric acid solution of the sample are taken.

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Zusammenfassung—Ein Verfahren zur Bestimmung von bis zu 0,15% Vanadium in hochreinem metallischem Niob und Tantal, Gußeisen, Stahl, Nichteisenlegierungen und Silikaten wird beschrieben. Es beruht auf der Extraktion eines roten Komplexes von Vanadium(V) mit

N-Benzoyl-*N*-phenylhydroxylamin in Chloroform aus einem schwefel- und flußsauren Medium, das überschüssiges Ammonpersulfat als Oxidationsmittel enthält. Der molare Extinktionskoeffizient des Komplexes beträgt bei 475 nm, dem Absorptionsmaximum, 428 $l\ mol^{-1}\ mm^{-1}$. Die Störung durch Chrom(VI) und Cer(IV) wird durch Reduktion mit Eisen(II) beseitigt. Häufig vorkommende Ionen, auch große Mengen Titan, Zirkonium, Molybdän und Wolfram stören nicht.

Résumé—On décrit une méthode pour doser jusqu'à 0,15 per cent de vanadium dans les niobium et tantale métalliques de haute pureté, la fonte, l'acier, des alliages non ferreux et des silicates. La méthode proposée est basée sur l'extraction d'un complexe rouge vanadium(V)-*N*-benzoyl *N*-phénylhydroxylamine en chloroforme d'un milieu acide sulfurique-acide fluorhydrique contenant un excès de persulfate d'ammonium comme oxydant. Le coefficient d'absorption moléculaire du complexe est 428 $l.mole^{-1}.mm^{-1}$ à 475 nm, la longueur d'onde du maximum d'absorption. On élimine l'interférence du chrome(VI) et du cérium(IV) par réduction au fer(II). Les ions communs, y compris de grandes quantités de titane, zirconium, molybdène et tungstène ne gênent pas.

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RELATIVE SENSITIVITY OF RARE EARTH ELEMENTS IN SPARK-SOURCE MASS SPECTROMETRY*

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Summary—A method for calculating the relative sensitivity factors for the rare earth elements in geological material is outlined. A close correlation is found between the relative sensitivity factors calculated and isotopic mass and the first ionization potential for the elements. The points are grouped in the vicinity of a regression line, which may be used to determine the relative sensitivity factors for all the rare earth elements.

THE SENSITIVITY factors of rare earth elements relative to rhenium given by Nicholls *et al.*[2] vary between 14·0 and 28·0. The variation of these relative sensitivity factors has no straightforward relation to mass number.

In the present work the relative sensitivity factors of the rare earth elements were studied in more detail in two standard rocks, W-1 and ASK Larvikite, and two quaternary clays from Åserum and Rødberg, Norway. The rare earth concentrations were also determined by neutron-activation analysis.[3–5] The relative sensitivity factors for the lanthanide elements and yttrium are calculated on the basis of mass spectrometric and neutron-activation analysis.

EXPERIMENTAL

The mass spectrometer was a GEC/AEI MS 702 fitted with Norbeck sample holders. The powdered samples were mixed with equal amounts of Ringsdorffwerke RWO graphite, pressed, and the electrodes evacuated to <1 μbar. Working pressures in the analyser region and in the source region were 53 pbar and 5·9 nbar respectively. The exposure conditions have been described by Taylor.[6] The data used were similar to those applied by Nicholls *et al.*[2] The densities of each line were measured by a modified Joyce-Loebl recording microdensitometer.

Rhenium satisfies the criteria for an internal standard element listed by Taylor[6] and Nicholls *et al.*[2] A solution of rhenium (Johnson Matthey "Specpure" potassium perrhenate) was added to the powdered sample at ppm level. This method is satisfactory for the fine-grained clay samples, though generally not for powdered rock samples.

RESULTS

The rare earth concentrations in W-1, ASK Larvikite, Åserum and Rødberg clay, determined by neutron-activation analysis, are listed in Table I. The data for W-1 and ASK Larvikite represent average values (La, Ce, Nd, Sm, Eu, Tb and Lu) of 10 and 6 replicate analyses respectively and (Gd, Dy, Ho and Tm) of 4 replicate analyses. The relative standard deviations for the concentrations of Nd, Tb, Ho, Yb and Lu are 10–30% and are larger for Gd. The data for Åserum clay represent one analysis while the data for Rødberg clay represent the mean of two analyses. Duplicate analyses agreed within 10% for La, Ce, Sm and Eu and within 15% for Nd, Gd and Tb.

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* Contribution to the Numedal project.[1]

TABLE I.—CONCENTRATIONS (*ppm*) OF RARE EARTH ELEMENTS IN W-1, ASK LARVIKITE, ÅSERUM AND RØDBERG CLAYS

	W-1[4]	ASK Larvikite[4]	Åserum clay[3]	Rødberg clay[5]	Isotope used[5]	Isotopic abundance[7], %	Ionization energy[7] *eV*
Y	24[8]		40		89	100	6·38
La	10·9	120	53	97	139	99·91	5·61
Ce	27·4	229	143	190	140	88·48	5·60
Nd	16·4	70	88	18·1	143	12·17	5·51
Sm	3·36	13·1	11	9·4	149	13·83	5·60
Eu	1·1	5·5	1·44	1·75	153	52·18	
Gd	4·3	15	11	8·4	158	24·87	6·16
Tb	0·7	2·0	1·44	0·93	159	100	5·98
Dy	4·4	10·6	7·0		161	18·88	6·8
Ho	1·0	2·7	1·48		165	100	
Er			4·1		166	33·41	6·08
Tm	0·7	0·97	0·56		169	100	
Yb	2·4	4·13	4·0		174	31·84	6·2
Lu	0·4	0·60	0·6		175	97·41	
Re					187	62·93	7·87

The literature data for the ionization energies for the rare earth elements vary. The relative sensitivity factors were determined from equation (1):

$$C_E = C_S \times \frac{Exp_S}{Exp_E} \times \frac{I_S}{I_E} \times \frac{1}{R} \tag{1}$$

C_E = content of element E in electrode analysed (in ppm).

C_S = content of a second element S, the internal standard element (in ppm).

Exp_S = exposure (in ncb) required to give a line of chosen density for a chosen isotope of element S on a photographic plate.

Exp_E = exposure in the same units required to give a line of the same chosen density for a chosen isotope of element E on the same photographic plate.

I_S = isotopic abundance of the chosen isotope of S.

I_E = isotopic abundance of the chosen isotope of E.

R = the relative sensitivity factor, introduced as a measure of sensitivity of total recording procedure for line of element E used compared with sensitivity for line of element S used.

In Table II the calculated *R*-factors are tabulated together with the data obtained by Nicholls *et al.*[2] The *R*-factors for Eu are remarkably high. Interference with ^{153}Eu results from ^{137}BaO$^+$ with mass 153.

Multiple carbon atoms interfere at line 169 and make it impossible to determine R_{Tm} by this method. The neutron-activation results for the Gd content in the standard rocks show great variations. *R*-factors based on these values were not calculated. The intensities of the mass spectral lines for Lu were too weak to give reliable calibration curves for this element.

When the relative sensitivity factors calculated are plotted *vs.* isotopic mass and *vs.* the first ionization potential the points are grouped near a regression line, as illustrated in Figs. 1 and 2. The data for W-1 and Åserum clay are the most complete. The values for europium are not incorporated in the calculations.

The regression lines were calculated by least-squares, and a close correlation was found in both cases, as shown in Table III.

TABLE II.—THE RELATIVE SENSITIVITY FACTORS FOR THE RARE EARTH ELEMENTS

	W-1	ASK Larvikite	Åserum clay	Rødberg clay	Obtained by Nicholls *et al.*[a]
R_{Y}	8·7		7·0		14·0
R_{La}	10·4	8·5	9·2	8·2	18·0
R_{Ce}	7·6	9·0	7·7	8·1	
R_{Nd}	10·5		10·4	11·7	24·1
R_{Sm}	10·2	10·1	8·3	9·7	
R_{Eu}	24·4	25·0	16·2	10·5	28·0
R_{Gd}			7·9	8·5	26·4
R_{Tb}	10·5	7·7	6·2	7·6	15·5
R_{Dy}	7·1	3·0	8·2		22·6
R_{Ho}	4·8	3·5	4·4		15·5
R_{Er}			6·0		14·0
R_{Yb}	6·2	4·7	5·25		
R_{Lu}					16·4
R_{Re}	1·0	1·0	1·0	1·0	1·0

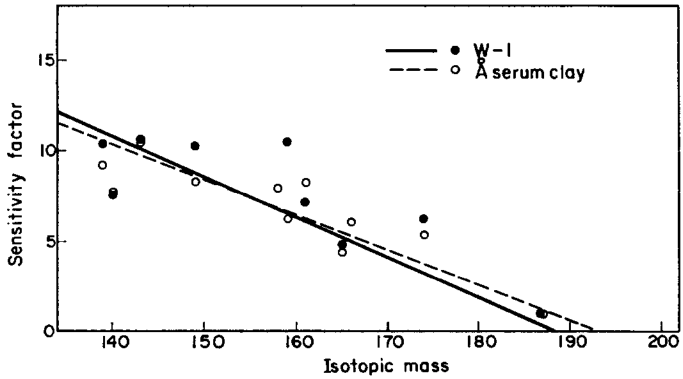

FIG. 1.—Variation of sensitivity factor with isotopic mass.

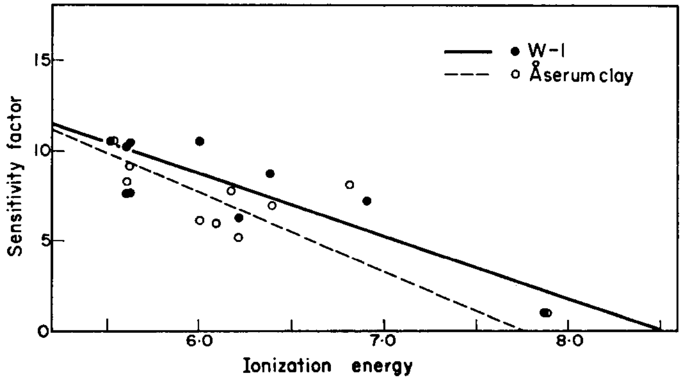

FIG. 2.—Variation of sensitivity factor with ionization energy.

TABLE III.—THE REGRESSION LINES $Y = AX + B$

		A	B	Std. devn. of X	Std. devn. of Y	Correlation coefficient
W-1	1	−4·14	188·9	$4{\cdot}1 \times 10^{-9}$	97·96	−0·8247
	2	−3·54	29·9	$-1{\cdot}2 \times 10^{-9}$	2·44	−0·8818
Åserum	1	−5·05	192·5	0	53·93	−0·8834
clay	2	−2·91	24·9	0	2·35	−0·8097

1. For the relative sensitivity factor *vs.* isotopic mass.
2. For relative sensitivity factor *vs.* ionization energy.

The relative sensitivity factors for all the lanthanide elements are determined from the regression line provided that the R-factors are on this line.

Correction for interference of $^{137}BaO^+$ with ^{153}Eu is made by using the intensity of line 154, which results from ^{154}Sm, ^{154}Gd and $^{138}BaO^+$, combined with the isotopic abundances of the Ba, Sm and Gd isotopes.[7]

If the intensities of lines 153 and 154 were caused by monoisotopic elements, the concentrations of these elements in the sample, C_{153} and C_{154}, would be:

$$C_{153} = C_S \times \frac{Exp_S}{Exp_{153}} \times \frac{I_S}{100} \times \frac{1}{R_{153}} \qquad (2)$$

and

$$C_{154} = C_S \times \frac{Exp_S}{Exp_{154}} \times \frac{I_S}{100} \times \frac{1}{R_{154}} \qquad (3)$$

where R_{153} and R_{154} are the relative sensitivity factors for isotopes with masses 153 and 154. The R-factors are taken from the regression line. The intensity of line 153 results from $^{137}BaO^+$ and ^{153}Eu:

$$C_{153} = C_{^{137}\mathrm{BaO}^+} + C_{^{153}\mathrm{Eu}} \times (52.18/100) \qquad (4)$$

and the intensity of line 154 results from Sm and Gd in addition to barium oxide:

$$C_{154} = C_{^{138}\mathrm{BaO}^+} + C_{^{154}\mathrm{Sm}} \times (22.71/100) + C_{^{154}\mathrm{Gd}} \times (2{\cdot}15/100) \qquad (5)$$

The amount of interfering $^{137}BaO^+$ is calculated by using the isotopic abundance of Ba and the amount of $^{138}BaO^+$ [which is calculated from equation (5)]:

$$C_{^{137}\mathrm{BaO}^+} = C_{^{138}\mathrm{BaO}^+} \times (11{\cdot}32/77{\cdot}66) \qquad (6)$$

The equations are combined in an expression for the europium concentration, C_{Eu}:

$$C_{\mathrm{Eu}} = \{C_{153} - [C_{154} - (C_{\mathrm{Sm}} \times 22{\cdot}71 + C_{\mathrm{Gd}} \times 2{\cdot}15)/100] \times 11{\cdot}32/77{\cdot}60\} \times 100/52{\cdot}18 \qquad (7)$$

To get better evidence for the relation between the relative sensitivity factors and isotopic mass, the polyisotopic lanthanides were studied. Solutions of Sm, Dy and Gd, were added to graphite, dried and analysed. The relative sensitivity factors calculated for the different isotopes of a particular element decreased as the isotopic mass increased.

DISCUSSION

Yttrium is chemically similar to the lanthanide elements. The calculated sensitivity factor for yttrium is near those for dysprosium and holmium. This indicates that the sensitivity factors are not primarily a function of isotopic mass. Either the ionization energy, or the ionization potential, is the dominating factor. However, the literature values for the ionisation energies of the lanthanides are unreliable. The dependence on ionization potential has been mentioned by Taylor.[6] Elements with low ionization potentials give the highest sensitivity while elements with high ionization potentials give poorer sensitivity. The ionization energies increase from lanthanum to lutetium.

The Saha-Langmuir equation in its modified form, when the ionization potential of the evaporating atoms exceeds the maximum electronic work function of the polycrystalline surface, gives the total positive ion current I^+ from the surface as[9]

$$I^+ = eA^* \exp\,(e/kT)(\phi^* + \psi - \mathrm{I})$$

where

$$A = An_0 \sum_n F_n \exp\,(e/kT)(\phi_n - \phi^*)$$

where e is the charge of the electron; A is a constant which includes the statistical weights, the reflection coefficients of the ions and neutral atoms and the transmission constant of the lens system of the ion source; n_0 is the number of neutral particles incident per cm^2 of the n-th fraction of the surface of area F_n and work function ϕ_n per sec; ϕ^* is the effective work function of the surface, its value lying between the maximum and minimum values of work function of the polycrystalline surface; k is the Boltzmann constant; T is the absolute temperature of the surface; I is the ionization potential of evaporating atoms and ψ is a function of the electric field strength at the surface.

From the constant A in the Saha-Langmuir equation it is evident that the ionization potential of an isotope is a function of its mass. Most of the parameters in the equation are unknown variables. Until these factors are known it is impossible to determine the ionization potentials with the desired accuracy. When the ionization energies are accurately determined they can be used to calculate the relative sensitivity factors for trace elements.

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Zusammenfassung—Eine Methode zur Berechnung der relativen Empfindlichkeitsfaktoren der seltenen Erdelemente in geologischem Material wird skizziert. Es wird eine enge Beziehung zwischen den berechneten Empfindlichkeitsfaktoren und der Nuklidmasse und dem ersten Ionisationspotential der Elemente gefunden. Die Punkte gruppieren sich in der Nähe einer Regressionslinie, die zur Ermittlung der relativen Empfindlichkeitsfaktoren aller seltenen Erdelemente dienen kann.

Résumé—On indique une méthode pour calculer les facteurs de sensibilité relatifs pour les éléments des terres rares dans des matières géologiques. On trouve une relation étroite entre les facteurs de sensibilité relatifs calculés et la masse isotopique et le premier potentiel d'ionisation pour les éléments. Les points sont groupés au voisinage d'une ligne de régression, que l'on peut utiliser pour déterminer les facteurs de sensibilité relatifs pour tous les éléments des terres rares.

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INDIRECT DETERMINATION OF FLUORIDES BY THE EDTA TITRATION OF SAMARIUM

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Summary—Fluorides are determined by the back-titration of excess of samarium with EDTA to the canary yellow end-point of Methylthymol Blue. The fluoride is precipitated and digested in a solution buffered at pH 2·5–3·0 with monochloroacetate buffer. After digestion, the pH is adjusted to 5·6–5·8 with pyridine and the excess of samarium is back-titrated in the presence of the precipitate, for samples with small quantities of fluoride. The procedure was used to analyse simple fluorides, fluoroborates and some other fluoro-complexes.

The need to determine the total fluoride in fluoride–fluoroborate mixtures ranging from moderately concentrated to very dilute solutions required study of the system. Unsatisfactory analytical results were obtained with different procedures such as the titration with thorium nitrate,[1] the pyrolytic-cerium technique,[2] the Winter and Willard distillation method,[3] and the gravimetric lanthanum fluoride method[4] because of boron complex interference. In addition, in the pyrolytic-cerium technique,[2] the end-point colour change for the arsenazo-Cresol Red indicator, from pale red to yellow-orange, was quite inconclusive. Precipitation of the fluoride as calcium fluoride was not used, because of the gelatinous nature of the precipitate and difficulties previously experienced with filtering.

It was found possible to precipitate relatively small quantities of the very insoluble samarium fluoride as a granular easily filterable precipitate. Larger quantities of fluoride produced the expected gelatinous precipitate[5] unless precipitated carefully and digested for periods of one or more hours. This precipitate was found to be essentially insoluble in low concentrations of EDTA. A back-titration procedure for small quantities of total fluoride was therefore developed; the fluoride is precipitated as samarium fluoride (SmF_3) and the excess of samarium ion is titrated with EDTA by using Methylthymol Blue as the indicator. The back-titration is performed in the presence of the precipitate unless the latter is large. Fluoroborates and fluorosilicates are analysed in the same manner. For fluorostannates, thioglycollic acid was used to complex the tin.

EXPERIMENTAL

Reagents

EDTA solution, 0·010*M*. Standardized against standard yttrium solution.

Methylthymol Blue indicator solution, 0·05% *w/v*.

Yttrium stock solution, 10·00 *mg/ml*. Dissolve 2·5398 g of yttrium oxide (Y_2O_3, 99·9999% pure, ignited to constant weight) in 35 ml of hydrochloric acid (1 + 1) and dilute to 200 ml. For standard working solution, 0·500 mg/ml, dilute 10·00 ml of the stock solution to 200·0 ml with 1*M* hydrochloric acid.

Samarium chloride stock solution. Dissolve approximately 10·5 g of samarium trichloride in 0·1*M* hydrochloric acid and dilute to 250 ml with the same acid; 1 ml is equivalent to about 6 mg of fluoride. For lower amounts of fluoride, dilute the stock solution 20-fold with 0·2*M* hydrochloric acid. Standardize these solutions against the standard EDTA solution. Samarium oxide, ignited, and then dissolved in hydrochloric acid (1 + 1), can be used in place of the Y_2O_3 and $SmCl_3$.

Pyridine solution, 50% *v/v*. Prepared from analytical-grade pyridine and demineralized water.

Monochloroacetate buffer. Dissolve 47·2 g of monochloroacetic acid and 10 g of sodium hydroxide in water and dilute to nearly 500 ml. If the pH is not between 2·5 and 3·0, adjust with a little of the solid acid or alkali, as needed.

Apparatus

Semimicro burettes, 5 and 10 ml, were used; stainless steel No. 24 hypodermic needles were used as tips for the EDTA titration. Platinum tips were used for measuring the acidic samarium solutions.

Procedure

Samples analysed by this procedure were received in solution, or as solids which dissolved in water or dilute hydrochloric acid.

To the dissolved sample or an aliquot, slowly add an excess of standard samarium chloride solution, approximately 1·5–2 times the expected stoichiometric amount. Adjust the pH to 2·5–3·0 with 0·2*M* hydrochloric acid or 4*M* ammonia. Should the solution be strongly acidic, dilute sodium hydroxide solution may be used in the initial phase of the pH adjustment. Add 10 ml of the monochloroacetic buffer. Digest on a sand-bath at approximately 90° for 30 min or more, then cool to room temperature. The time for digestion will depend on the amount of precipitate. Adjust the pH to 5·6–5·8 with the pyridine solution, added dropwise as the desired pH is approached. Pyridine is used since rare earth fluorides are slightly soluble in ammonium salt solutions. Add 1 ml of Methylthymol Blue indicator and back-titrate the excess of samarium with standard EDTA solution to the yellow end-point colour.

Filtering is not necessary for samples containing low quantities of fluoride; the back-titration is carried out in the presence of the precipitate. The precipitate from larger samples interferes with the visibility of the end-point colour change. Samples containing 20 mg or more fluoride should be diluted to a specific volume and aliquots taken for the precipitation and subsequent titration. Alternatively, all the fluoride can be precipitated, and digested, then the precipitate be permitted to settle after diluting to volume; after this aliquots of the clear solution are taken for the back-titration.

RESULTS AND DISCUSSION

Indicator

For the samarium–EDTA titration, Methylthymol Blue yields a sharp colour change from blue to canary yellow at the end point. Two or three drops (1 drop = 0·01 ml) of 0·01*M* EDTA produces the colour change. This end-point is far superior to that for indicators such as arsenazo-Cresol Red or Eriochrome Black T. In the presence of the samarium fluoride precipitate, a short warning of the approaching end-point is indicated by a colour change from blue to gray, which is followed by the yellow. About two drops of 0·01*M* titrant are needed for each change in colour. When 0·1*M* EDTA is used, the intermediate gray is not observed. The curve for spectrophotometric titration with samarium fluoride present did not indicate the change to gray; apparently this change is due to the light-scattering effect of the precipitate.

The spectrophotometric titration showed sharp deflections in the titration curves for 0·1 and 0·01*M* EDTA but a gradual change for the titration with 0·001*M* EDTA. The last is not satisfactory for visual titrations because the end-point is not well defined.

Traces of iron interfere with the titration, giving a change from blue to a reddish colour. The iron forms a more stable complex with the indicator than with EDTA.

Range and reproducibility

Visual titrations were carried out in the range from 1 to 6 mg of fluoride from sodium fluoride and sodium fluoroborate. Various mixtures totalling from 3 to 4 mg of fluoride were also titrated. At the 1-mg fluoride level, based on 14 samples, the standard deviation was approximately 16 μg and the average relative error was $-3{\cdot}0\%$. At the 2, 4 and 6-mg quantities, based on 12 samples, the standard deviations and relative errors were approximately 17, 7 and 9 μg, and $-9{\cdot}0\%$, $-0{\cdot}1_5\%$, and

$-0{\cdot}1_2\,\%$, respectively. For 20 mixed samples the standard deviation was 9 μg and the relative error was $-0{\cdot}3_4\,\%$. The individual results for this sample range are shown in Table I. Results for quantities in the range of 100–200 mg of fluoride are given later, in Table IV.

TABLE I.—RANGE AND REPRODUCIBILITY*

Number of titrations	Sample, *mg* F, taken as			Time of digestion, *min*	F found, *mg*	Relative error, %	Std. devn., μg
	NaF	$NaBF_4$	Total				
6	$0{\cdot}994_5$			30	0·958	−3·6	34
4	1·989			30	1·959	−1·5	13
4	3·978			30	3·970	−0·2	7
4	5·967			30	5·950	−0·3	14
4	$0{\cdot}994_5$			60	0·969	−2·5	5
4	1·989			60	0·976	−0·7	16
4	3·978			60	3·974	−0·1	8
4	5·967			60	5·982	+0·3	6
4		$0{\cdot}929_7$		30	0·904	−2·9	8
4		1·859		30	1·849	−0·5	21
4		3·719		30	3·714	−0·1	7
4		5·578		30	5·556	−0·3	9
4	$0{\cdot}994_5$	1·859	2·854	30	2·838	−0·6	8
4	1·989	1·859	3·848	30	3·866	+0·5	7
4	1·989	$0{\cdot}929_7$	2·919	30	2·901	−0·6	6
4	2·984	$0{\cdot}929_7$	3·914	30	3·898	−0·4	12
4	$0{\cdot}994_5$	2·790	3·785	30	3·764	−0·6	11

* 0·01*M* EDTA, visual titrations.

The results for sodium fluoroborate and various ratios of sodium fluoride and sodium fluoroborate indicate that the precipitation of samarium trifluoride quantitatively breaks up the fluoroborate complex.

It is to be noted that the relative errors are generally negative. Since the EDTA was standardized directly against yttrium oxide this indicates that the negative values are due to slight solubility of the precipitate (assuming titration to the correct end-point). In some experiments in which the samples were permitted to stand after titration, the blue colour would begin to return in a half-hour or so, indicating some solubility of the precipitate in the slight excess of EDTA. Indirect standardization of the EDTA against 1–2 mg of fluoride, precipitated as samarium fluoride, would reduce the relative error in this concentration range.

Digestion time

A 30-minute digestion was used in obtaining most of the results included in the tables. In a brief study to determine the effect of time on completeness of precipitation and crystal growth with sodium fluoride and sodium fluoroborate, the difference for 30- and 60-min digestion periods was found to be insignificant. However, for some of the more stable complexes and precipitates, or larger samples, long digestion times were necessary.

Delayed back-titration

Samarium fluoride, precipitated from sodium fluoride samples, after digestion was left remaining in the buffered solution at pH 2·5–3·0 for 0–20 hr before titration. There was no significant change in the relative errors.

Effect of pH

A pH range of 2·5–3·0 was found satisfactory for the precipitation of samarium fluoride from the solution containing fluorides and fluoro-complexes. There was little variation in error with pH changes from 2·5 to 3·5 for sodium fluoride, but the error is relatively large at pH 3·5 for the fluoroborate, Table II. The rapidly increasing positive error associated with pH increase results from the hydrolysis of the samarium ion and its subsequent precipitation as the hydroxide. The negative error increased rapidly with an increase in acidity, Table II. For acid samples, the errors were more negative if the precipitate was permitted to stand before titration. This increasing error is thought to be due to the formation and possible loss of the weak hydrofluoric acid ($K_a = 7{\cdot}2 \times 10^{-4}$) in the presence of the strong hydrochloric acid. In simple experiments to detect evolution of hydrogen fluoride, slight etching was found on the watch-glass covers.

TABLE II.—EFFECT OF pH ON PRECIPITATION OF SmF_3

pH 6	NaF*			NaBF$_4$†		
	F found, *mg*	Error *mg*	Error % Rel.	F found, *mg*	Error *mg*	Error % Rel.
1·75	3·811	−0·167	−4·2	3·781	+0·062	+1·7
2·00	3·830	−0·148	−3·7	3·740	+0·021	+0·6
2·25	3·884	−0·094	−2·4	3·727	−0·008	+0·2
2·50	3·974	−0·004	−0·1	3·714	−0·005	−0·1
2·75	3·975	−0·003	−0·1			
3·00	3·977	−0·001	−0·0	3·721	+0·002	+0·1
3·25	3·965	−0·013	−0·3			
3·50	3·968	−0·010	−0·3	3·674	−0·045	−1·2
4·00	4·004	+0·026	+0·7	3·563	−0·156	−4·2
4·50	4·089	+0·111	+2·8	3·537	−0·182	−4·9
5·00	4·116	+0·138	+3·5	3·225	−0·494	−13·3
5·60	4·154	+0·176	+4·4	3·105	−0·614	−16·5

* 3·978 mg of F taken as NaF.
† 3·719 mg of F taken as NaBF$_4$.

There was little error when the samarium fluoride was precipitated from sodium fluoroborate solution at pH 2·5–3·0, Table II. However, for the more acidic solutions the error was positive, not negative as observed for the sodium fluoride solutions. As the acidity decreased the negative error increased very rapidly, which is in contrast to the pattern observed for the sodium fluoride solutions. The pH range 2·5–3·0 was found to be satisfactory for the digestion of other fluoro-compounds such as fluorosilicate and fluorostannate.

The samarium fluoride obtained from low concentrations of fluoride ion at the proper pH was a granular precipitate which could be filtered off easily. With higher concentrations and more rapid precipitation, the precipitate was colliodal in nature and required more digestion time.

Additional fluoride compounds

The analytical results for some additional fluoro compounds and larger samples (treated solution aliquots) are summarized in Table III. Thioglycollic acid was used to complex the tin.

TABLE III.—ADDITIONAL COMPLEX FLUORIDES

Number of aliquots	Compound	Sample, *mg*		Digestion, *min*	Error		Std. devn., *μg*	Comments
		Taken	Found		*mg*	% Rel.		
4	NaF	9·945	9·950	90	+0·005	+0·05	7	
4	$NaBF_4$	9·298	9·294	90	−0·004	−0·05	5	
4	SnF_2	4·000	3·998	30	−0·002	−0·05	8	15 drops thioglycollic acid before digestion
4	SnF_2	10·000	9·994	60	−0·006	−0·06	4	15 drops thioglycollic acid before digestion
6	Na_2SiF_6	4·000	3·991	30	−0·009	−0·22	6	
4	Na_2SiF_6	9·970	9·941	90	−0·029	−0·29	10	filtered off ppte. before titration
4	K_2SnF_6	4·290	4·286	90	−0·004	−0·09	13	15 drops thioglycollic acid before digestion
4	K_2SnF_6	6·890	6·895	90	+0·005	+0·07	11	

TABLE IV.—INDIVIDUAL SOLID FLUORIDES

Compound	Number of samples	Range of sample weight, *mg*	Mean % fluoride		% Error		Std. devn, %	Comments
			Theory	Found	Abs.	Rel.		
NaF	4	47·5–68·8	45·25	45·1$_7$	−0·0$_8$	−0·2	0·11	
KF	4	435·0–558·2	32·70	32·7$_8$	+0·0$_8$	+0·3	0·33	
Na_2SiF_6	8	132·2–323·7	60·62	60·4$_6$	−0·1$_6$	−0·3	0·02	
K_2SnF_6	8	172·5–415·2	35·75	35·7$_2$	−0·0$_3$	−0·1	0·02	Add thioglycollic acid to complex Sn
SnF_2	8	231·4–415·2	24·35	24·2$_5$	−0·1$_0$	−0·4	0·00$_6$	
CaF_2	4	44·0–68·7	48·67	48·6$_9$	+0·0$_2$	+0·0	0·07	Dissolve with 2 ml of 5% H_3BO_3 and 10 ml of 0·5*M* HCl at 90°. Then digest ppte. 90 min.
MgF_2	4	33·0–68·7	60·98	61·0$_3$	+0·0$_5$	+0·1	0·09	
TiF_4	8	102·5–358·0	61·34	61·3$_8$	+0·0$_4$	+0·1	0·06	Treat fluoride solutions of Fe, Co, Ni, Ti with 40% NaOH to precipitate cation as hydroxide, filter, then treat sample as NaF.
CoF_3	4	98·4–220·3	49·17	46·0$_0$	−3·1$_7$	−6·5	0·00$_5$	
CoF_3*	4	58·5	49·17	48·9$_4$	−0·1$_3$	−0·3	0·02	
FeF_3	8	68·3–163·3	50·51	32·1$_3$	−18·4	−36	0·02	
FeF_3*	4	50·0	50·51	50·4$_5$	−0·0$_6$	−0·1	0·07	
SbF_3	6	159·6–451·4	31·89	30·3$_9$	−1·50	−5·0	0·02	
$AgBF_4$	6	235·7–316·2	39·03	37·1$_2$	−1·91	−4·9	0·11	Ag separated as AgCl
$AgBF_4$*		100·0	39·03	38·9$_7$	−0·06	−0·2	0·08	
$NaAsF_6$†					Very low			

* Solutions containing the elements in stoichiometric ratio corresponding to the nominal compound. Used to determine probability of correct results being obtained for commercial compounds FeF_3, CoF_3, and $AgBF_4$ if these were pure.

† As(III) did not interfere, but reduction of As(V) to As(III) was incomplete.

The analyses of a number of relatively large individual solid samples of different fluoro compounds are summarized in Table IV. Several of these compounds are highly deliquescent or unstable in the presence of moisture and were handled in a dry-box.

When stable fluorides such as calcium and magnesium fluorides were dissolved in dilute hydrochloric acid low results were obtained. It was found that the addition of boric acid, which apparently formed the fluoroborate, prevented the loss of the fluoride as hydrogen fluoride. It was possible to dissolve calcium and magnesium fluorides in samarium solution at pH 2·5 but long digestion periods were required, of the order of 16–24 hr, and the results were slightly low. The use of fusion with sodium carbonate–potassium carbonate mixture (1:1) resulted in fluoride values from 2% to 5% low.

The low results but reasonably good precision for the compounds cobalt(III) fluoride, iron(III) fluoride, antimony fluorides, and silver fluoroborate indicated the compounds were not pure. This finding was confirmed when solutions with the stoichiometric ratio of fluoride ion to cation were prepared and permitted to stand before analysis.

Arsenic(III) did not cause interference, but with the fluooarsenate ion the need to use strong reducing agents made the analysis impossible.

Stable organic fluorides can be analysed after hydrolysis in concentrated sodium hydroxide solution or decomposition by fusion with sodium. It was also found that fluorophosphate compounds required treatment with alcoholic potassium hydroxide.[5]

Diverse ions

The addition of elements that complex with EDTA only in a relatively basic solution, Mg, Ca, Sr and Ba, has no interference effect on the procedure. Elements such as Fe, Co, Ni, Cu, Pb and Zn that react with EDTA at pH 5·6 will interfere and so will those that form strong fluoride complexes, *e.g.*, Fe, Al, Sn, Zr. Iron, cobalt and nickel were separated as the hydroxide. Tin was complexed with thioglycollic acid and prevented interference. However, sulphanilic acid did not release the fluoride from the aluminium fluoride complex.

Bismuth, antimony and arsenic(III) do not cause interference. However, more precise results were obtained when the heavy white precipitate from hydrolysis was removed by filtering.

Most simple anions do not interfere, but phosphates and sulphates will interfere by complexing with the samarium.

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Zusammenfassung—Flouride werden durch Rücktitration von überschüssigem Samarium mit EDTA bis zum kanariengelben Endpunkt von Methylthymolblau bestimmt. Das Fluorid wird aus einer mit Monochloracetatpuffer auf pH 2,3–3,0 gepufferten Lösung gefällt und digeriert. Nach dem Digerieren wird der pH mit Pyridin auf 5,6–5,8 gebracht und das überschüssige Samarium bei kleinen Fluoridmengen in Gegenwart des Niederschlags zurücktitriert. Die Vorschrift wurde zur Analyse von einfachen Fluoriden, Fluoroboraten und einigen anderen Fluorokomplexen verwendet.

Résumé—On dose les fluorures par le titrage en retour d'un excès de samarium avec l'EDTA jusqu'au point de virage jaune canari du bleu de méthylthymol. Le fluorure est précipité et digéré dans une solution tamponnée à pH 2,5–3,0 avec un tampon monochloracétate. Après digestion, on ajuste le pH à 5,6–5,8 avec la pyridine et l'excès de samarium est titré en retour en la présence du précipité pour des échantillons avec de faibles quantités de fluorure. La méthode a été utilisée pour analyse des fluorures simples, des fluoborates et quelques autres fluorocomplexes.

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INFLUENCE OF pH IN FLUORESCENCE AND PHOSPHORESCENCE SPECTROMETRIC ANALYSIS*

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Summary—An account is given of the theory of the effect of pH changes on fluorescence and phosphorescence of organic species which exhibit acid–base properties, and of the practical applications of the effect.

THE USE of fluorimetry and phosphorimetry in organic analytical and bioanalytical procedures has increased considerably in recent years.[1] Because many organic molecules have one or more prototropically dissociable groups, the pH of the solution in which luminescence is observed will influence the characteristics of the luminescence.[2] In fact, both the frequency and the intensity of luminescence from organic acids and bases are pH-dependent.

The frequency shift of molecular luminescence, observed when pH is varied, is due to the conversion of the organic acid into its conjugate base in both the ground and excited states, and the difference between the dissociation constants of the organic acid in the ground state and in the excited states from which luminescence originates. The relationship between the dissociation constants is given, approximately, by the Förster equation[3]:

$$\mathrm{p}K - \mathrm{p}K^* = \frac{hc}{2{\cdot}303kT}(\bar{\nu}_\mathrm{a} - \bar{\nu}_\mathrm{b}); \qquad (1)$$

where pK and pK^* are the logarithms of the reciprocals of the dissociation constants of the organic acid in its ground state and in the excited state from which luminescence originates (the lowest excited singlet state in the case of fluorescence and the lowest excited triplet state for phosphorescence), respectively; h is Planck's constant, k is the Boltzmann constant; c is the velocity of light and $\bar{\nu}_\mathrm{a}$ and $\bar{\nu}_\mathrm{b}$ are the frequencies (in cm^{-1}) of the 0—0 vibronic band in the luminescence spectra of acid and its conjugate base (if both species are luminescent), respectively.

pH DEPENDENCE OF FLUORESCENCE

In analytical applications, fluorescence is most often observed in fluid solution (aqueous or non-aqueous solutions at room temperature), in which case the rates of association and dissociation in the lowest excited singlet state are usually greater than or comparable to the rate of fluorescence of the excited species ($\sim 10^8$ sec^{-1}). In this case, prototropic equilibrium is at least partially established within the lifetimes of the lowest excited singlet states of acid and conjugate base.[4] Owing to the large difference in electronic dipole moment between a molecule in its ground and lowest excited singlet state, the pK^* for the lowest excited singlet state is usually quite different

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from the pK of the ground state. For phenols, aromatic amines and aromatic mercaptans, the lowest excited singlet state is several orders of magnitude more acidic than the ground state of the same molecule. For carboxylic acids, aromatic aldehydes and ketones and aromatic ring heteroatoms, the lowest excited singlet state is considerably more basic than the ground state.[2] As a result, the shifting of the frequency of fluorescence, due to conversion of the excited acid into excited conjugate base, generally occurs at a pH (or Hammett acidity function, H_0) very different from that at which the shifting of the absorption spectrum (due to conversion of the ground state acid into ground state conjugate base) occurs. Consequently, it is possible to excite a solution which has a pH such that only the acid or its conjugate base is present and therefore only one species can absorb the exciting radiation, and yet observe the fluorescence from both the excited acid and its conjugate base. Conversely, it is possible to excite the solution with pH $\sim$ pK so that the acid and its conjugate base are both excited and then observe fluorescence from only one excited species. On the other hand, if only one member of the conjugate excited pair is fluorescent, it would be possible to excite only the ground state of that species and yet observe no fluorescence, or only part of the maximum obtainable fluorescence intensity, owing to dissociation in the lowest excited singlet state to the non-fluorescent species.

The relationship between fluorescence radiant flux and analyte concentration (for low analyte concentration) forms the basis of quantitative fluorimetry and is given by:

$$P_{f\lambda'} = 2{\cdot}3\phi_{f\lambda'}P_{0\lambda}\varepsilon_{\lambda}Cb; \tag{2}$$

where $\phi_{f\lambda'}$ is the quantum yield of fluorescence at the emission wavelength λ' ($\phi_{f\lambda'}$ is the spectral quantum yield at λ' times the emission monochromator spectral bandwidth *i.e.*, quantum yield per wavelength interval times the wavelength interval measured), ε_{λ} is the molar absorptivity at the absorption wavelength λ of the analyte, C is the analyte concentration and b is the pathlength of exciting radiation through the sample. $P_{f\lambda'}$ and $P_{0\lambda}$ are, respectively, the radiant flux of fluorescence falling on the detector at λ' and the radiant flux of exciting radiation incident upon the sample at an absorption wavelength of λ. It is assumed that excitation and emission monochromators are used to select small wavelength intervals at λ' in luminescence. Ordinarily, the product $\phi_{f\lambda'}P_{0\lambda}\varepsilon_{\lambda}b$ is not evaluated. Rather, the radiant flux of fluorescence of a sample (actually it is usually the signal due to the flux, but the instrumental signal is proportional to the flux reaching the spectrometric system) of known concentration is compared with that of the unknown, according to:

$$\frac{P_{fu\lambda'}}{P_{fs\lambda'}} = \frac{C_u}{C_s}; \tag{3}$$

where $P_{fu\lambda'}$ and $P_{fs\lambda'}$ are the radiant fluxes of fluorescence and C_u and C_s are the analyte concentrations in unknown and standard samples, respectively. Equation (3) is, of course, valid only if $\phi_{f\lambda'}P_{0\lambda}\varepsilon_{\lambda}b$ is identical for unknown and standard samples—if the analyte is in the same chemical form in the unknown as in the standard sample. The latter condition may not be valid if the analyte has dissociable groups and the pH of the unknown and standard solutions are slightly different—especially if pH $\sim$ pK. Such a situation may arise from simple errors in solution preparation or from absorption of atmospheric carbon dioxide but may be eliminated as a source of error by making the solutions sufficiently acidic or basic so that only one species (the acid or conjugate base) absorbs. Control of instrumental variables can fix $P_{0\lambda}$ and b while for a particular absorbing species at a given wavelength of excitation and temperature and in a given solvent ε_λ is constant. For a fluorescing species not participating in chemical reactions in the electronically excited state, $\phi_{f\lambda'}$ is a constant at the emission wavelength λ' and in a given solvent at a given temperature.

If the luminescing species contains dissociable groups and the pH of the solution is such that pH $\sim$ pK^*, then $\phi_{f\lambda'}$ will show a pH dependence[2] given by:

$$\frac{\phi_{f\lambda'}}{\phi^0_{f\lambda'}} = (1 - W) + W\left[\frac{(1 + \overleftarrow{k}\tau_0'[\mathrm{H}^+])}{(1 + \overrightarrow{k}\tau_0 + \overleftarrow{k}\tau_0'[\mathrm{H}^+])}\right] \tag{4}$$

where $\phi^0_{\lambda f'}$ is the quantum yield of fluorescence of the excited acid at the emission wavelength λ' when pH $\ll$ pK^*, W is the fraction of excited acid molecules which enter into the equilibrium process in the lowest excited singlet state and is an exponential function of [H$^+$] [(1 − W) is thus the fraction of excited acid molecules which fluoresce without dissociation], $\overrightarrow{k}$ and $\overleftarrow{k}$ are the rate constants for the unimolecular and bimolecular protonation reactions in the excited state, respectively, τ_0 and τ_0' are the mean radiative lifetimes of the excited acid and base, respectively and [H$^+$] is the protonated solvent concentration (in strongly acidic or basic solutions [H$^+$] may be replaced by the Hammett acidity function H_0). If the conjugate base is also fluorescent, the quantum yield of fluorescence $\phi'_{f\lambda'}$ at the emission wavelength λ' in the region pH $\sim$ pK^*, assuming the acid is excited, will show the pH dependence:

$$\frac{\phi'_{f\lambda'}}{\phi^{0'}_{f\lambda'}} = W\left[\frac{\overrightarrow{k}\tau_0}{(1 + \overrightarrow{k}\tau_0 + \overleftarrow{k}\tau_0'[\mathrm{H}^+])}\right] \tag{5}$$

where $\phi^{0'}_{f\lambda'}$ is the quantum yield of fluorescence of the excited conjugate base when pH $\gg$ pK^* and all other symbols have the same meaning as in equation (4). If prototropic equilibrium is essentially complete within the lifetimes of the lowest excited singlet states of acid and conjugate base, then $W \rightarrow 1$, and equations (4) and (5) reduce to:

$$\frac{\phi_{f\lambda'}}{\phi^0_{f\lambda'}} = \frac{1 + \overleftarrow{k}\tau_0'[\mathrm{H}^+]}{1 + \overrightarrow{k}\tau_0 + \overleftarrow{k}\tau_0'[\mathrm{H}^+]} \tag{6}$$

and

$$\frac{\phi'_{f\lambda'}}{\phi^{0'}_{f\lambda'}} = \frac{\overrightarrow{k}\tau_0}{1 + \overrightarrow{k}\tau_0 + \overleftarrow{k}\tau_0'[\mathrm{H}^+]}\,. \tag{7}$$

Substitution of equation (4) into equation (2), for an organic acid, yields:

$$P_{f\lambda'} = P^0_{f\lambda'}\left[(1 - W) + \frac{W(1 + \overleftarrow{k}\tau_0[\mathrm{H}^+])}{(1 + \overrightarrow{k}\tau_0 + \overleftarrow{k}\tau_0'[\mathrm{H}^+])}\right] \tag{8}$$

while for the excited conjugate base formed as a result of excitation of the acid

$$P_{\mathrm{f}\lambda}' = P^{0}_{\mathrm{f}\lambda'}\left[\frac{W\overrightarrow{k}\tau_0}{(1+\overrightarrow{k}\tau_0+\overleftarrow{k}\tau_0'[\mathrm{H}^+])}\right] \tag{9}$$

where $P_{\mathrm{f}\lambda'}$ and $P^{0}{}_{\mathrm{f}\lambda'}$ are the radiant fluxes of fluorescence of the excited acid and its conjugate base, respectively, at the emission wavelengths λ' (however, the emission wavelengths, λ', need not be the same for the acid and base species), and $P\,{}^{0}_{\mathrm{f}\lambda'} = 2{\cdot}3\,\phi^{0}_{\mathrm{f}\lambda'}P_{0\lambda}\varepsilon_\lambda Cb$ and $P^{0'}_{\mathrm{f}\lambda'} = 2{\cdot}3\,\phi^{0'}_{\mathrm{f}\lambda'}P_{0\lambda}\varepsilon_\lambda Cb$ are the radiant fluxes of fluorescence of excited acid when pH $\ll$ pK^* and excited base when pH $\gg$ pK^*, respectively. The pH dependence of the total radiant flux of fluorescence $P_{\mathrm{t}\lambda'}$ at the analytical emission wavelength is finally given by the sum of equations (8) and (9):

$$P_{\mathrm{t}\lambda'} = P^{0}_{\mathrm{f}\lambda'}(1-W) + \frac{P^{0}_{\mathrm{f}\lambda'}W(1+\overleftarrow{k}\tau_0'[\mathrm{H}^+]) + P^{0'}_{\mathrm{f}\lambda'}W\overrightarrow{k}\tau_0}{(1+\overrightarrow{k}\tau_0+\overleftarrow{k}\tau_0[\mathrm{H}^+])}. \tag{10}$$

Alternatively, it can be shown that if the ground state of the basic species is excited, the radiant power of fluorescence is

$$P_{\mathrm{t}\lambda'} = P^{0'}_{\mathrm{f}\lambda'}(1-V) + \frac{P^{0}_{\mathrm{f}\lambda'}V(1+\overleftarrow{k}\tau_0'[\mathrm{H}^+]) + P^{0'}_{\mathrm{f}\lambda'}V\overrightarrow{k}\tau_0}{(1+\overrightarrow{k}\tau_0+\overleftarrow{k}\tau_0'[\mathrm{H}^+])}, \tag{11}$$

where V is similar to W but is the fraction of excited base molecules which enter into the equilibrium in the lowest excited singlet state and the ε_λ contained in $P^{0}_{\mathrm{f}\lambda'}$ and $P^{0'}_{\mathrm{f}\lambda'}$ is now that of the long wavelength band in the absorption spectrum of the basic species.

The dependence of the radiant flux of fluorescence upon prototropic equilibrium in the lowest excited singlet states of acids and bases can be useful to the analytical chemist. It is possible, by careful adjustment of pH, to determine small amounts of certain substances in the presence of large amounts of interfering substances even though their fluorescence bands strongly overlap, provided that their pK^* values are appreciably different. For example, in the bromination of 8-quinolinol, it is possible to determine[5] the unreacted 8-quinolinol (p$K^* = -6{\cdot}5$) in the presence of the large excess of 5-bromo-8-quinolinol (p$K^* = -7{\cdot}8$), by adjusting the Hammett acidity of the solution to $H_0 = -6$ with perchloric acid so that the 8-quinolinol cation fluoresces while the 5-bromo derivative does not. This selectivity is not possible with absorption spectrophotometry and would not be possible with fluorimetry if it were not feasible to take advantage of the difference in pK^* between these compounds.

On the other hand, the pH dependence of the radiant flux of fluorescence can be a hindrance to the analytical chemist. Adjustment of the pH of the test and standard solutions so that only one species is absorbing the exciting radiation can leave the solutions in a pH region where the radiant flux of luminescence, at the wavelength at which fluorescence is observed, varies appreciably with pH. In this case, the radiant flux of fluorescence may also not be the maximum obtainable, so that some sensitivity may be lost. Even worse, if the standard and unknown solutions are at slightly different pH in the region pH $\sim$ pK^*, the analytical utility of equation (3) will be invalid, owing to the differences in $\phi_{f\lambda'}$ between the standard and unknown solutions. These problems are especially likely to occur in solutions of acids having small values of $\overrightarrow{k}\tau_0$ and bases having small values of $\overleftarrow{k}\tau_0'$, in solutions of high pH, in which case the region of strong pH dependence of $P_{t\lambda'}$ is spread over several pH units. Occasionally, this problem can be eliminated by the obvious method of making the solution sufficiently acidic or basic to be well removed from the pH $\sim$ pK^* region. If this is successful the solution will be in a region where $P_{t\lambda'}$ is not strongly pH-dependent and routine analysis can be performed. However, because pK and pK^* are often different by six or more units, the adjustment of pH to a region where only one species luminesces may leave the solution so strongly acidic or basic that side-reactions may occur (condensation, hydrolysis, rearrangement, *etc*), further complicating analysis.

USE OF THE ISOEMISSIVE POINT FOR ANALYSIS TO MINIMIZE ERRORS DUE TO DISSOCIABLE PROTONS

Analytical problems in fluorimetry, due to the different pH regions in which corresponding ground and excited state equilibria occur, can be minimized for certain acid–conjugate base pairs, provided that both are fluorescent, if an emission wavelength can be found such that $P_{t\lambda'}$ is independent of pH (or [H$^+$]). Such a wavelength is analogous to an isosbestic point in the absorption spectrum of an acid–conjugate base pair, and will hereafter be referred to as an "isoemissive point". Like an isosbestic point, the existence of an isoemissive point is dependent on the presence of only two species derived from the same compound in equilibrium with one another at the pH of the solution. A further stipulation for the existence of an isoemissive point is derived from the invariance of the radiative power of fluorescence with [H$^+$]. Differentiation of equation (10) with respect to [H$^+$] yields

$$\frac{\partial P_{t\lambda'}}{\partial[\mathrm{H}^+]} = \frac{\overrightarrow{k}\tau_0}{(1+\overrightarrow{k}\tau_0+\overleftarrow{k}\tau_0'[\mathrm{H}^+])} \times \left[(P^{0'}_{f\lambda}-P_{f\lambda}{}^0)\frac{\partial W}{\partial[\mathrm{H}^+]} + \frac{\overleftarrow{k}\tau_0'}{(1+\overrightarrow{k}\tau_0+\overleftarrow{k}\tau_0'[\mathrm{H}^+])}(P_{f\lambda}{}^0-P_{f\lambda}{}^{0'})W\right]. \qquad (12)$$

With the condition that at the isoemissive point $\partial P_{t\lambda'}/\partial[\mathrm{H}^+] = 0$, we get

$$P_{f\lambda}{}^{0'} = P_{f\lambda}{}^0 \qquad (13)$$

or

$$\phi^{0'}_{f\lambda'} = \phi_{f\lambda}{}^0. \qquad (14)$$

Thus the isoemissive point corresponds to that emission (luminescence) wavelength at which the fluorescence quantum yields of excited acid and conjugate base are equal, when only unimolecular deactivating processes are competing with fluorescence and the dissociation process for depopulation of the lowest excited singlet state. Anderson and Weber[6] have observed the occurrence of an isoemissive point in the fluorescence study of the binding of reduced 3-acetylpyridine-adenine dinucleotide by lactic dehydrogenase and have used it to establish that the quantum yields of bound and unbound lactic dehydrogenase were identical *i.e.*, binding did not result in preferential quenching of one form of the enzyme fluorescence.

The fluorescence spectra of 2-naphthol and 1-amino-2-naphthol-4-sulphonic acid at different pH values are shown in Figs. 1 and 2, respectively. These spectra were taken on an Aminco Bowman Spectrophotofluorimeter, with a 150-W xenon lamp as the excitation source and an RCA 1P28 multiplier phototube as the detector. An isoemissive point is clearly discernible for 2-naphthol over the entire pH range while for 1-amino-2-naphthol-4-sulphonic acid an isoemissive point is present in the Hammett range from 0·94 to −1·18. Owing to the polyacidity of the latter compound, more than two species are present in prototropic equilibrium with one another over most of the acidity range, resulting in the absence of isoemissive points at higher and lower Hammett acidity values.

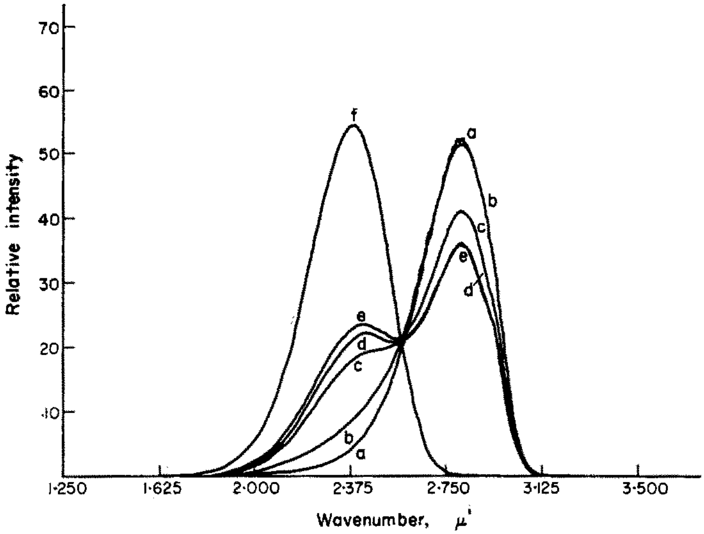

FIG. 1.—Fluorescence spectra of 2-naphthol at several acidities.
a—2·30 × $10^{-1}M$ $HClO_4$; *b*—2·30 × $10^{-2}M$ $HClO_4$; *c*—2·30 × $10^{-3}M$ $HClO_4$ *d*—2·30 × $10^{-4}M$ $HClO_4$; *e*—2·30 × $10^{-5}M$ $HClO_4$; *f*—1·0 × $10^{-4}M$ NaOH.

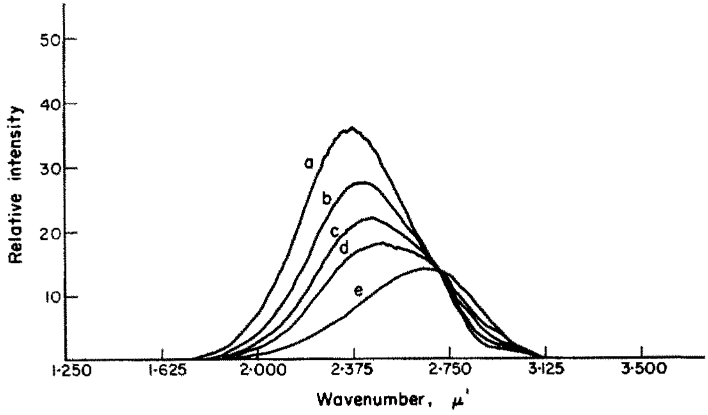

FIG. 2.—Fluorescence spectra of 1-amino-2-naphthol-4-sulphonic acid at several acidities.
a—0·115*M* $HClO_4$; *b*—0·345*M* $HClO_4$; *c*—0·690*M* $HClO_4$; *d*—1·15*M* $HClO_4$; *e*—2·88*M* $HClO_4$.

Another possible use of the isoemissive point in analysis is to increase precision of measurement. If an isoemissive point is present, it is possible to use scale expansion techniques to enhance precision by setting the emission wavelength at the isoemissive point. By use of dual emission wavelengths—one wavelength set at the isoemissive point and one wavelength set at some other value—it should also be possible to increase the sensitivity of the measurement.

THE pH DEPENDENCE OF PHOSPHORESCENCE

Because of the differences in electronic repulsions in singlet and triplet states, the electronic dipole moment changes accompanying singlet–triplet transitions are usually much smaller than those accompanying singlet–singlet transitions. As a result, the pK^* values of the lowest triplet states of organic acids and bases are usually much closer to the ground state values than are those of the lowest excited singlet states.[7] From equation (1), it is evident that the frequency shift of the phosphorescence emission of an organic acid or base with changing pH will be generally smaller than that for fluorescence from the same compound.

Owing to the long lifetimes of excited triplet states, collisional deactivation in fluid solution competes seriously with phosphorescence as a mode of depopulation of excited triplet states. Consequently, phosphorescence is almost never observed in fluid solution (solvents at room temperature) and must be studied in rigid glasses (solvents at low temperature, *e.g.*, 77K). In rigid media, the mobility of the solvated proton is very low so that proton exchange between an organic acid and the solvent does not occur appreciably within the lifetime of the excited triplet state. As a result, the excited species in phosphorescence generally corresponds to the ground state species which absorbed the exciting radiation. Thus if the pH of the solution is adjusted prior to freezing, to a region where only one ground state species is present, phosphorescence should be observed from only one species.

The excited species (whether the neutral or dissociated form of an organic acid or the neutral or protonated form of an organic base, the phosphorescence of which is employed for analytical purposes) can frequently make a considerable difference in the intensity of phosphorescence, and hence in the sensitivity of the analysis. The radiant flux of phosphorescence $P_{p\lambda'}$ is given by

$$P_{p\lambda'} = \left[\frac{k_{st}}{k_{st} + k_f + \sum\limits_{i} k_i}\right] \phi_{p\lambda'} P_{0\lambda} \varepsilon_\lambda Cb = k_{st} \tau_f \phi_{p\lambda'} P_{0\lambda} \varepsilon_\lambda Cb \tag{15}$$

where $P_{0\lambda}$, ε_λ, C and b have the same significance as in equation (2), k_{st} and k_f are the probabilities of intersystem crossing from the lowest excited singlet state and that of fluorescence, respectively, $\sum\limits_{i} k_i$ is the total probability of all other first-order and pseudo first-order processes deactivating the lowest excited singlet state, τ_f is the radiative lifetime of the lowest excited singlet state, and $\phi_{p\lambda'}$ is the relative quantum yield of phosphorescence at the emission wavelength λ' and is given by:

$$\phi_{p\lambda'} = \left[\frac{k_p}{k_p + \sum\limits_{i} k_i'}\right] = k_p \tau_p \tag{16}$$

where k_p is the probability of phosphorescence, $\sum\limits_{i} k_i'$ is the total probability of all non-radiative first- and pseudo first-order processes deactivating the lowest excited triplet state and τ_p is the radiative lifetime of the lowest excited triplet state.

In general, intense phosphoresence is favoured by large values of k_{st}, k_p, τ_f and τ_p. All processes, other than intersystem crossing, in the lowest excited singlet state decrease the term $k_{st}\tau_f$ in equation (15) and thereby decrease the radiant flux of phosphorescence. Similarly, all processes other than phosphorescence from the lowest excited triplet state decrease $\phi_{p\lambda'}$ and thus the intensity of phosphorescence. The values of k_{st}, k_p, τ_f and τ_p for a phosphorescence are determined by the electronic structure of the molecule as well as its solvent cage and the presence of quenching species in solution.

The inter-relationships between k_{st}, k_p, τ_f and τ_p determine the luminescence flux. For example, aromatic molecules having non-bonded electron pairs on ring heteroatoms (bases) often show the lowest frequency transition in their singlet–singlet absorption spectrum to be of $^1(n \rightarrow \pi^*)$ nature.[8] The $^1(n \rightarrow \pi^*)$ transition is said to be "symmetry-forbidden" [as is the $^1(n \leftarrow \pi^*)$ transition] because of the poor overlap between the non-bonded orbital and the usually orthogonal π^* orbital. As a result, τ_f for an n–π^* lowest excited singlet state is ~100 times greater than that for a π–π^* lowest excited singlet state in the same molecule. Also, the presence of a heteroatom may somewhat enhance spin-orbital coupling in the molecule and result in a greater value of k_{st} than would be encountered in the analogous purely carboxyclic molecule. Consequently, molecules showing low energy $^1(n \rightarrow \pi^*)$ absorptions usually phosphoresce well. If a highly phosphorescent molecule having a non-bonded electron pair is put into a polar solvent, the non-bonded pair may have some σ-bond character induced in it by electrostatic interaction with the positive end of the solvent dipole. In this case, the n–π^* nature of the lowest excited singlet transition may be partially lost so that τ_f decreases and with it the intensity of phosphorescence. If the solution contains acidic species, the non-bonded pair may be completely converted into a σ-bond by co-ordinate covalent bonding (*e.g.*, protonation) in which case the lowest excited singlet state of the molecule will be $^1(\pi$–$\pi^*)$ with an attendant lower value of τ_f and possibly weaker phosphorescence. Examples of the latter phenomena are represented by the fluorescence and phosphorescence of quinoline in polar solvents but only phosphorescence in non-polar ones[9,10] and by the much stronger phosphorescences of the neutral forms of quinoline and acridine than of the protonated forms.[7]

The quenching of the luminescence arising from electronically excited states of aromatic molecules may be due to any of a number of processes occurring between the potential luminescer and the quenching species, *e.g.*, resonance energy transfer and photochemical reaction. There are at least two distinct ways in which pH can affect quenching processes. First, the solvated proton (or hydroxide ion) can react with the phosphorescing species to form the conjugate acid (or base). The conjugate species may be weakly phosphorescent or non-phosphorescent by virtue of its own molecular electronic structure, *i.e.*, the rate of internal conversion in the lowest singlet and/or triplet excited states of the acid may be very different from that in the conjugate base. Table I shows the limits of detection, as determined on the Aminco-Bowman SPF, of the three isomeric mononitrophenols by phosphorimetry, in both neutral and dissociated forms. The neutral form was studied in absolute ethanol containing 1% v/v of 18*M* sulphuric acid, while the dissociated form was studied in absolute ethanol containing 1% v/v of saturated sodium hydroxide solution. The tremendous difference in sensitivity between the neutral and dissociated forms of the *para* isomer is apparent. It is also interesting that the limit of detection of the *p*-nitrophenolate anion is much lower than any of the other species, and that for the *ortho* isomer the limit of detection of the neutral species is actually somewhat lower than that for its conjugate base.

TABLE I.—LIMITS OF DETECTION FOR THE MONONITROPHENOLS AND THEIR ANIONS, BY PHOSPHORIMETRY

p-Nitrophenol		*m*-Nitrophenol		*o*-Nitrophenol	
neutral	anion	neutral	anion	neutral	anion
$1\cdot5 \times 10^{-7}M$	$1\cdot5 \times 10^{-10}M$	$5\cdot2 \times 10^{-8}M$	$6\cdot7 \times 10^{-8}M$	$6\cdot5 \times 10^{-8}M$	$3\cdot0 \times 10^{-7}M$

The second way in which pH affects the quenching of phosphorescence derives from the fact that quenching is a highly specific process. It is possible for the luminescence from a given species to be quenched by some extraneous species and yet the luminescence from the conjugate base (or acid) to be unaffected by the quencher. For example oxygen has a greater tendency to quench some anionic species than their conjugate acids.[11]

For the most part, phosphorimetry has been confined to a few solvent media (EPA*, ethanol, alkyl halides) because of their ability to form clear glasses when frozen. Recently, the ability to use "snowed" solvents[12] has been demonstrated as a result of the development of a rotating sample tube.[13] Thus liquid alkanes are now potential phosphorimetric solvents. However, only the protic solvents (ethanol, EPA, *etc*) allow the advantage of being able to select the prototropic species, derived from the analyte, with the lowest limit of detection, by permitting the variation of pH. Because it is at present impossible to predict accurately, *a priori*, whether the phosphorescence from a neutral species or from its charged conjugate acid or base will be more intense and will therefore yield lower limits of detection, it is prudent to keep in mind that the variation of the pH of the test solution in a protic solvent can be a powerful tool in the analytical application of phosphorescence.[14]

Zusammenfassung—Die Theorie des pH-Einflusses auf Fluoreszenz und Phosphoreszenz organischer Spezies mit Säure-Basen-Eigenschaften wird dargelegt und praktische Anwendungen davon angegeben.

Résumé—On donne un compte-rendu de la théorie de l'influence des variations de pH sur la fluorescence et la phosphorescence d'espèces organiques qui présentent des propriétés acide-base, et des applications pratiques de l'influence.

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* Diethyl ether, isopentane and ethanol; 5:5:2 v/v.

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DETERMINATION OF IRIDIUM IN MAFIC ROCKS BY ATOMIC ABSORPTION*

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Summary—Iridium is determined in mineralized mafic rocks by atomic absorption after fire-assay concentration into a gold bead. Inter-element interferences in the atomic-absorption determination are removed and Ir sensitivity is increased by buffering the solutions with a mixture of copper and sodium sulphates. Substantial amounts of Ag, Al, Au, Bi, Ca, Cd, Co, Cr, Fe, Ho, Hg, K, La, Mg, Mn, Mo, Ni, Pb, Te, Ti, V, Y, Zn and platinum metals can be tolerated in the atomic-absorption determination. The sensitivity and detection limits are 3·2 and 0·25 ppm of Ir, respectively.

A MAJOR advance in the atomic-absorption determination of iridium was made by Van Loon[1] who found that the presence of at least 500 ppm of copper and 1000 ppm of sodium in solution minimizes interferences from base and noble metals. Some problems remained, however. For example, we found Van Loon's procedure to be disturbed excessively by sulphate ion and appreciably by variation in the concentration of copper, sodium, and other metals. Furthermore, because no provision was made for the preconcentration of iridium, the procedure is directly applicable only to samples containing iridium as a major constituent.

This paper presents a procedure for the atomic-absorption determination of iridium based on preconcentration of iridium in a gold bead resulting from fire-assay fusion and cupellation. It is directly applicable to mineralized mafic rocks containing at least 2·5 ppm of iridium. To minimize interference and maximize sensitivity, atomic-absorption measurements are made on solutions buffered with copper and sodium sulphates with copper and sodium concentrations maintained at approximately 0·7% and 0·3% respectively. The detection limit (twice the standard deviation) is 0·25 ppm Ir and the sensitivity 3·2 ppm Ir for 1% absorption.

Fire assay is not a generally recommended procedure for the concentration of iridium. For example, Beamish[2] cites losses of as much as 5% in cupellation with silver as a collector, and severe losses to basic or subsilicate slags. We have observed no losses for mafic rocks when sufficient gold is used as a collector and the slag ranges from monosilicate (orthosilicate) to bisilicate (metasilicate) in composition.

EXPERIMENTAL

Reagents and apparatus

Gold wire. For fire-assay, 99·999% pure.

Copper sulphate solution, 7% w/v copper. Dissolve 27·5 g of copper sulphate pentahydrate in water and dilute to 100 ml.

Mixed copper–sodium solution. Dissolve 13·75 g of copper sulphate pentahydrate and 4·64 g of sodium sulphate in 50 ml of hydrochloric acid and make up to 100 ml with water.

Standard solutions of iridium. Prepare from ammonium hexachloroiridate a stock solution containing 1·000 mg of iridium per ml in 2% v/v hydrochloric acid. Prepare other solutions by dilution with 2% v/v hydrochloric acid.

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Cylindrical alumina crucibles, 2 ml capacity, for sodium peroxide fusions. Coors AD-999 alumina ceramic crucibles available from Coors Porcelain Company, Golden, Colorado.

Synthetic standards. Two synthetic standards were prepared, using U.S.G.S. dunite DTS-1 as a base. Analyses cited by Flanagan[3] show it to contain negligible amounts of platinum metals. The first standard was made to contain 10 ppm each of Ir and Rh, and the second 10 ppm each of Ir, Os, Pd, Pt, Rh and Ru. Iridium contents were verified by activation analysis while Pd, Pt and Rh contents were verified by fire-assay/atomic-absorption procedures.[4,5] The fate of Os and Ru was not ascertained. The standards are prepared as follows. To weighed samples of dunite finer than 200 mesh in porcelain casseroles, add water to form a slurry. Add the required amounts of standard solutions of the appropriate platinum metals and mix. Evaporate the solutions on a steam-bath, stirring the slurries frequently. Dry the residues in an oven at 110° and then heat in a furnace at 450° for approximately 30 min. Roll the samples in a ceramic jar mill with alumina balls for 3 hours. Mix and bottle.

Instrument parameters and settings

A Perkin–Elmer Intensitron hollow-cathode tube with a Perkin–Elmer Model 303 instrument was used in the experiments. The conditions were as follows.

Wavelength	263·97 nm
Slit	0·3 mm
Hollow-cathode current	30 mA
Fuel, acetylene pressure	69 kN/m^2 (10 psi)
flow-meter setting	8·5
Oxidizer, air pressure	190 kN/m^2 (28 psi)
flow-meter setting	7·5
Flame	oxidizing
Burner	standard head
Aspirator	adjusted for uptake of ~3 ml/min

Conditions for other instruments must be found by trial and error.

Procedure

The fire-assay fusion and cupellation procedures used here follow generally accepted practices as described by Bugbee.[6] A bisilicate slag composition is to be preferred. For a 20-g sample of dunite, a flux consisting of 50 g of lead (II) oxide, 35 g of sodium carbonate, 15 g of silica, 19 g of sodium tetraborate and 4 g of flour will yield both a satisfactory lead button and a bisilicate slag. The fusion is made in the presence of 50 mg of added gold for the quantitative collection of Ir, Pd, Pt, and Rh.

Transfer the gold bead obtained on cupellation to a small beaker. Add 5 ml of *aqua regia*, cover and allow the mixture to react at room temperature for approximately 1 hr. Heat on a steam-bath for several hr more. Add 3 ml of water and a small amount of paper pulp, mix and filter through a 42·5-mm medium porosity filter paper. Wash the iridium residue with water. Reserve the filtrate for the determination of Pd, Pt, and Rh. Ignite the residue in a 2-ml alumina crucible at 600° starting with a cold furnace. Add 100 ± 10 mg of sodium peroxide by calibrated dipper and carefully fuse the residue. Heat for 5 min more, maintaining in the molten state. Cool. Add 1·5 ml of water, cover and allow to stand at room temperature for approximately 15 min. Warm the mixture until the melt disintegrates, and transfer the solution to a 25-ml beaker by several alternating washes with 1-ml portions of concentrated hydrochloric acid, nitric acid and water. Add 0·15 ml of sulphuric acid (1 + 1) by pipette to convert sodium salts into sulphate and evaporate the solution on a steam-bath. Add 2 ml of hydrochloric acid (1 + 1), warm briefly to dissolve salts and transfer the solution to a 10-ml volumetric flask with water. Dilute to volume with water and mix. Transfer a 5-ml aliquot of the solution to another 10-ml volumetric flask, and reserve the remainder for the determination of Pd, Pt and Rh. Add 1 ml of hydrochloric acid (1 + 1) and 1 ml of copper sulphate solution. Adjust to volume with water and mix. Prepare iridium standards and a blank, each containing 1 ml of mixed copper-sodium solution in a 5-ml volume. Determine iridium in all solutions by atomic absorption.

RESULTS

Buffering agents

The interference of sulphate in Van Loon's procedure has been noted in the introduction. For example, the absorbance of 200 ppm of iridium in a solution also containing 500 ppm of copper and 1000 ppm of sodium as chlorides increases approximately 10 and 40% in the presence of 10 and 100 ppm of sulphate respectively.

Similarly, when the sulphates of sodium and copper are substituted, maintaining the same metal concentrations, the absorbance of 200 ppm of iridium increases approximately 200%. From these results a sulphate system would seem to be advantageous.

The potential of various sulphates for minimizing interference of other noble metals was determined on test solutions containing 200 ppm of Ir and from 100 to 500 ppm each of the various noble metals. Of the many salts tried, copper, sodium and cadmium sulphates individually or together in binary and ternary mixtures all showed excellent reduction of interference. While a given salt or salt mixture would prove superior in the reduction of interference of a specific noble metal, best results for all noble metals were obtained with a mixture of 7 parts of copper and 3 parts of sodium at a total metal concentration of 10000 ppm. These conditions were adopted.

The greater effectiveness of the 7:3 copper–sodium mixture over that of sodium or copper alone in overcoming the depressive interference of 300 ppm of rhodium on 200 ppm of iridium is illustrated in Fig. 1. It is also apparent that the copper-sodium sulphate system is insensitive to changes in total metal concentration as long as the final total metal concentration is in the range 0·75–1·5%.

Figure 2 shows that a concentration of 500 ppm of rhodium produces a 5% relative error in the determination of 200 ppm of iridium. The magnitude of this error is independent of the weight ratio of copper to sodium in the range 1·5–4.

Effect of hydrochloric acid concentration

The absorbance of iridium decreases approximately 4% for each 10% by volume increase of hydrochloric acid concentration. A 10% v/v hydrochloric acid concentration was adopted.

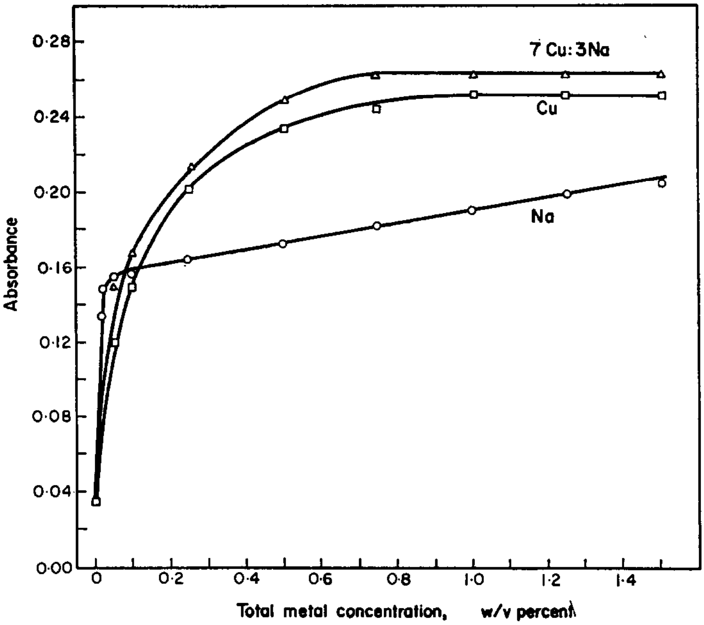

FIG. 1.—Effect of concentration of various sulphates on the absorbance of 200 ppm of Ir in the presence of 300 ppm of Rh in 10% v/v hydrochloric acid.

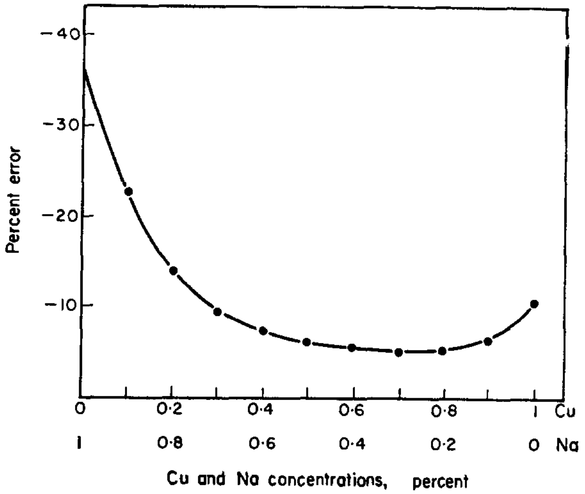

FIG. 2.—Errors in the absorbance of 200 ppm of Ir caused by 500 ppm of Rh, as a function of copper–sodium ratio.

Tolerances for other elements

In atomic-absorption determination of 20 or 200 ppm of iridium, the copper–sodium system tolerates separately (error less than 2%) 1000 ppm each of Al, Bi, Ca, Cd, Co, Cr, Fe, Hg, Ho, K, La, Mg, Mn, Mo, Ni, Pb, V, Y or Zn, 500 ppm each of Au, Pd, Pt, Os and Ru and 20 ppm of Ag, the maximum amount of each element tested. Rhodium should be restricted to 300 ppm. At the 20-ppm level of iridium 1000 ppm each of Te and Ti do not interfere, but only half these concentrations can be tolerated at 200 ppm of iridium. No interference was observed in the determination of 20 or 200 ppm of iridium in solutions also containing mixtures of 200 ppm each of Au, Pd, Pt, Os, Rh and Ru. When the total procedure is considered, substantially larger amounts of these elements can be tolerated inasmuch as they are largely separated from iridium during the dissolution of the gold bead following cupellation.

Standard curve

A plot of net absorbance *vs.* iridium concentration at 264 nm yields a straight line up to a concentration of 200 ppm of iridium, the maximum tested. The sensitivity is 3·2 ppm of Ir for 1% net absorption. The detection limit (at twice the standard deviation) is 0·25 ppm.

The fire assay

With 20-g samples of each of the prepared iridium-dunite standards, at least 95% of the iridium was collected when 30 mg or more of gold were used as a carrier in the cupellation. With 10 mg of gold, iridium recoveries averaged only 87%. A 50-mg gold bead was adopted for the recommended procedure. It was also observed that a single fire-assay fusion sufficed for the quantitative recovery of Ir, Pd, Pt and Rh, with slags varying from monosilicate to bisilicate in composition.

In the parting of the gold bead with *aqua regia*, iridium was invariably completely insoluble while gold, palladium and platinum were completely soluble. The fate of rhodium depended on the amount of gold used. With 50 mg of gold approximately 91% of the rhodium dissolved; with 30 mg of gold 73% of the rhodium was soluble, and with 10 mg of gold only 40% of the rhodium dissolved.

Test of total procedure

Fifteen dunite standards containing 10 ppm each of Ir and Rh and fifteen containing 10 ppm each of all six platinum metals were taken through the total procedure. Inasmuch as the results obtained on each set did not differ significantly, all results were lumped together. The average recovery of iridium was found to be 98·2% with a standard deviation of 2·1%, assuming the iridium content of the samples to be exactly 10 ppm. The overall average obtained on 8 samples by Paul Greenland of this laboratory by triple coincidence counting of ^{192}Ir after neutron activation amounted to 10·2 ppm with a standard deviation of 0·5 ppm.

To exclude the possibility that the other platinum metals in the samples were necessary carriers for Ir during the fire assay, four 20-g samples of dunite containing 10 ppm of iridium alone were also processed. No significant differences were found in the recovery of iridium from these and the previous samples. Finally there remained the question of how small an amount of iridium can be determined without loss in the procedure. Accordingly 20-g samples salted to contain from 50 to 200 μg of Ir were taken for analysis. Again no noticeable differences in recoveries were obtained. Thus the procedure should be applicable to samples containing as little as 2·5 ppm of Ir.

Zusammenfassung—Iridium wird in mineralisierten Magnesium-Eisen-Gesteinen nach Schmelzanreicherung in der Goldperle durch Atomabsorption bestimmt. Durch Puffern der Lösungen mit einer Mischung von Natrium- und Kupfersulfat werden gegenseitige Störungen der Elemente beseitigt und die Iridium-Empfindlichkeit erhöht. Die Anwesenheit erheblicher Mengen Ag, Al, Au, Bi, Ca, Cd, Co, Cr, Fe, Ho, Hg, K, La, Mg, Mn, Mo, Ni, Pb, Te, Ti, V, Y, Zn und der Platinmetalle ist bei der Atomabsorptionsbestimmung zulässig. Empfindlichkeit und Nachweisgrenze betragen 3,2 bzw. 0,25 ppm Ir.

Résumé—On dose l'iridium dans les roches "mafiques" (d'origine ferromagnésienne) minéralisées par absorption atomique après concentration par voie sèche dans une perle d'or. Les interférences inter-éléments dans le dosage par absorption atomique sont éliminées et la sensibilité pour Ir est accrue en tamponnant les solutions avec un mélange de sulfates de cuivre et de sodium. Des quantités importantes de Ag, Al, Au, Bi, Ca, Cd, Co, Cr, Fe, Ho, Hg, K, La, Mg, Mn, Mo, Ni, Pb, Te, Ti, V, Y, Zn et métaux du platine peuvent être tolérées dans la détermination par absorption atomique. Les limites de sensibilité et de détection sont de 3,2 et 0,25 ppm d'Ir, respectivement.

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STUDIES ON NUCLEATION FROM SOLUTION OF SOME ANALYTICALLY IMPORTANT METAL CHELATES

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Summary—The combination of precipitation from homogeneous solution and Vonnegut's droplet technique is employed in the study of nucleation from solution of bis(1,2-cyclohexanedionedioximato)-Ni(II), bis(1,2-cycloheptanedionedioximato)Ni(II), bis(1,2-cyclohexanedionedioximato)Pd(II) and bis(1,2-cycloheptanedionedioximato)-Pd(II). Values of the kinetic constant, surface energy, critical radius and the number of molecules per critical nucleus are calculated and discussed in terms of the limitations of the classical theory of nucleation when applied to crystal nucleation from aqueous solutions of electrolytes.

IN PREVIOUS communications[1,2] it was suggested that a combination of precipitation from homogeneous solution[3] and Vonnegut's droplet technique[4] could be used to study homogeneous nucleation from solution. This combination utilizes both the controlled build-up of supersaturation and the sequestering of motes within the system, the respective advantages offered by the two techniques. Consequently, the data required for investigation of the nucleation of compounds of interest, namely the rate of homogeneous nucleation as a function of the supersaturation attained by the system, can be obtained experimentally.

The purpose of this communication is to report and discuss the results of nucleation studies on four analytically important metal chelates: bis(1,2-cyclohexanedionedioximato)nickel(II), bis(1,2-cycloheptanedionedioximato)nickel(II), bis(1,2-cyclohexanedionedioximato)palladium(II) and bis(1,2-cycloheptanedionedioximato)palladium(II).

EXPERIMENTAL

The reaction between a suitable α-diketone and hydroxylamine in the presence of the metal ion of interest was used to generate, *in situ*, the metal chelate under study. Aqueous solutions containing the reactants were dispersed in light mineral oil and then photomicrographs were taken to record the result of crystal nucleation within the droplets.

Apparatus

The dispersions were prepared with the aid of a microhomogenizer, then placed in cups (diameter 32 mm, height 25 mm) made from Nessler tubes, and were then centrifuged.

The droplets were examined with a polarizing microscope (crossed polarizers, 40× magnification) provided with high intensity illumination from a 600-W projector lamp.

The photographs were taken with a microscope camera at a shutter speed of 0·5 sec. The 35-mm slides were projected onto a calibrated screen so that accurate drop diameter measurements could be made.

Procedure

A typical nucleation study involved three separate experiments: a droplet experiment, a kinetic experiment and a solubility determination. Immediately before a droplet experiment on a given system, two stock solutions were prepared for that system. The two stock solutions were mixed so as to yield the optimum solution conditions for the nucleation study (see Table I). After mixing, a

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small drop (0·01–0·02 ml) of the reaction solution was added to 6 ml of light mineral oil contained in a micro-homogenizer flask and stirred for 15 sec at about 15000 rpm. The resulting dispersion was transferred to a Nessler cup and centrifuged for 15 sec. Then the main part of the dispersion was decanted. The part remaining in the cup was centrifuged again for 30 sec. Photomicrographs of the dispersion were taken at 30-sec intervals.

The kinetic experiment was carried out by mixing the stock solutions in the same proportions used for the droplet experiment and then determining the weight of precipitate formed per unit volume, as a function of time.

In order to determine the solubility of the metal chelate, a medium containing all the components of the reaction solution, except the metal ion and the diketone (see Table I) was saturated with the chelate. After equilibration, organic matter in the solution was destroyed by wet-ashing. The concentration of the metal ion in solution was determined by EDTA titration.[5,6]

TABLE I.—INITIAL SOLUTION CONDITIONS FOR THE NUCLEATION STUDIES

System	M^{+2}, [*M*]	HCl, [*M*]	$NH_2OH \cdot HCl$, [*M*]	α-Diketone, [*M*]
$Ni(C_6H_9N_2O_2)_2$*	0·2	0·03	1	0·4
$Ni(C_7H_{11}N_2O_2)_2$†	0·1	—	0·2	0·2
$Pd(C_6H_9N_2O_2)_2$	0·1	1	0·7	0·2
$Pd(C_7H_{11}N_2O_2)_2$	0·03	6	0·2	0·3

Added conditions:

* Urea (2*M*).

† Phosphoric acid (0·3*M*) ammonium acetate (0·4*M*).

RESULTS

From the photomicrographs, the number and diameters of the droplets containing one crystal were recorded as a function of the lapsed time between mixing of the reagents and the appearance of a crystal within the droplet. An analysis of the data indicated that there was a correlation between the median crystallization time and the logarithm of the droplet diameter. Figure 1 shows the correlation. This was used to

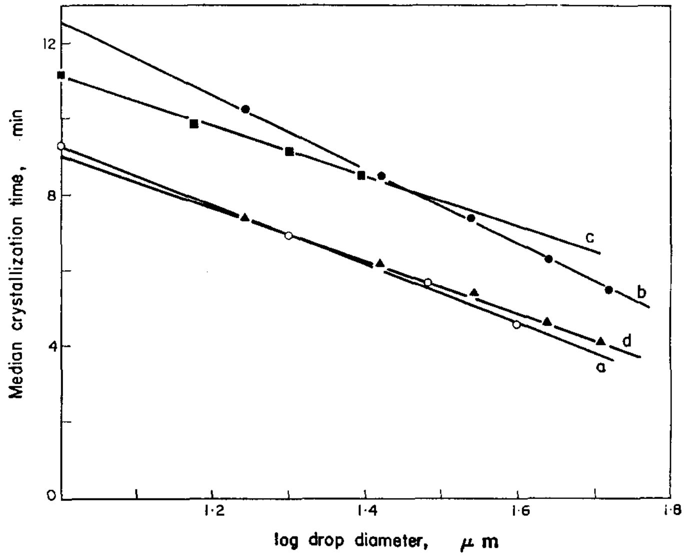
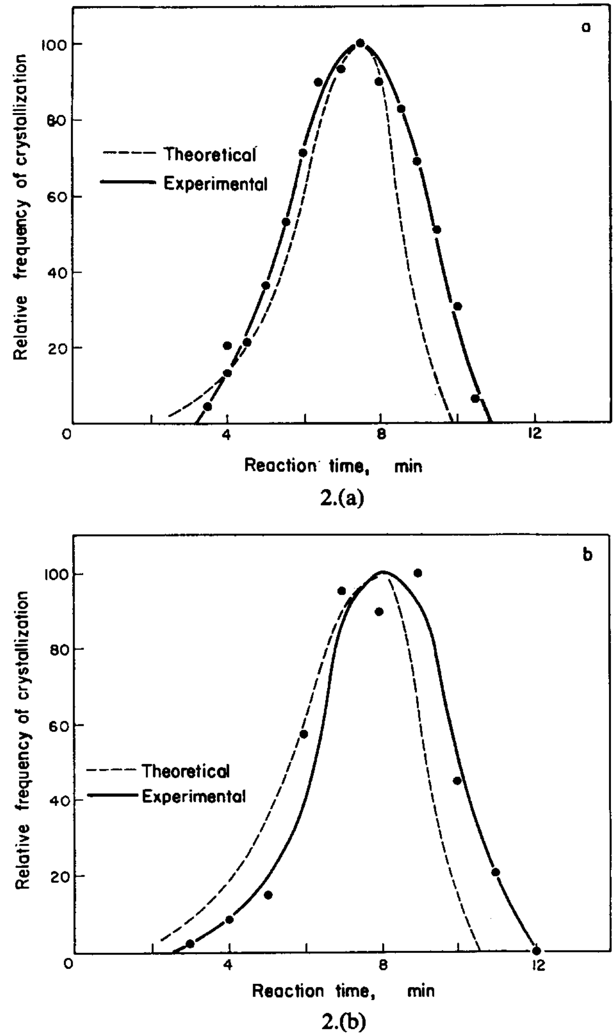


FIG. 1.—Median crystallization time *vs.* log drop diameter for the Ni(II) and Pd(II) chelates. *a*, $Ni(C_6H_9N_2O_2)_2$; *b*, $Ni(C_7H_{11}N_2O_2)_2$; *c*, $Pd(C_6H_9N_2O_2)_2$; *d*, $Pd(C_7H_{11}N_2O_2)_2$.

reduce the crystallization time of any droplet to that of a standard sized droplet. The results of these calculations are presented in Fig. 2 as plots of the relative frequency of crystallization of a standard droplet *vs.* crystallization time.

The probability of crystallization within a standard droplet as a function of crystallization time was calculated from the plots shown in Fig. 2. The results are shown as the solid lines of Fig. 3.

The dependence of the rate of nucleation, *J*, on the supersaturation, *S*, of the solute within the droplets was calculated from the slopes[7] of the curves shown in Fig. 3,

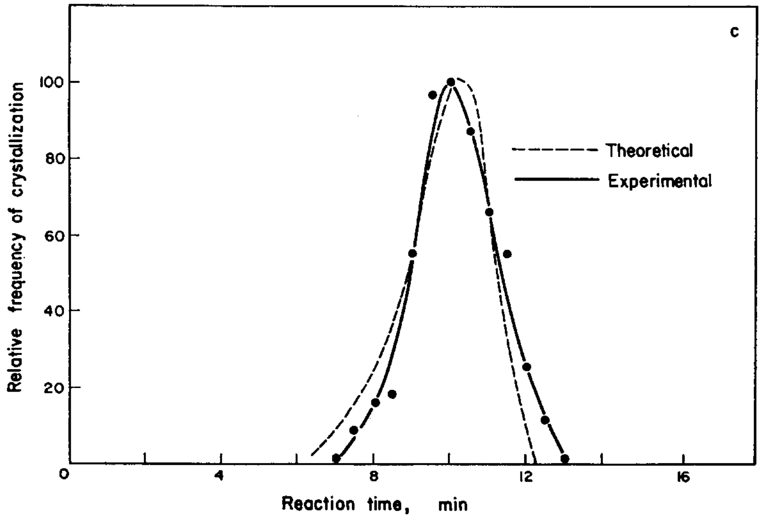


2.(a)

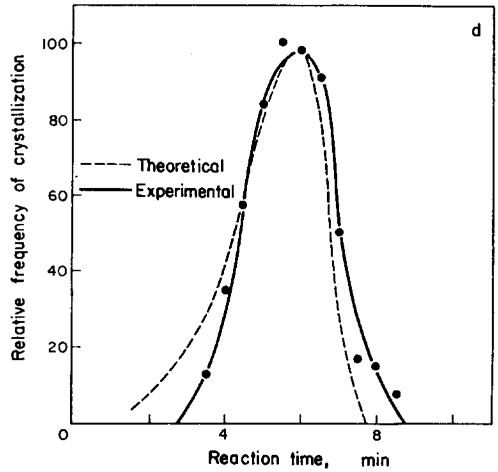
2.(b)

FIG. 2.—Relative frequency of crystallization *vs.* reaction time for the Ni(II) and Pd(II) chelates.

Compound	Standard droplet diameter *μm*
a Ni($C_6H_9N_2O_2$)$_2$	20
b Ni($C_7H_{11}N_2O_2$)$_2$	35
c Pd($C_6H_9N_2O_2$)$_2$	15
d Pd($C_7H_{11}N_2O_2$)$_2$	35



2.(c)



2.(d)

combined with the results of the kinetic experiments shown in Fig. 4. The results of these calculations are shown in Fig. 5.

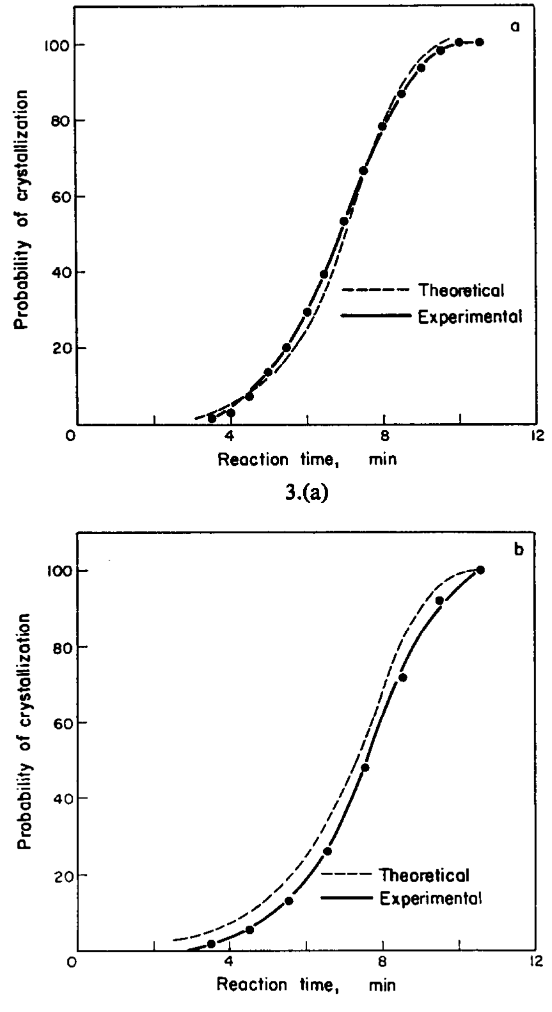
The kinetic constant, A, of the classical nucleation rate equation[8] for each chelate studied was evaluated from the intercepts of the curves in Fig. 5. These are collected in Table II. Various other parameters of importance in classical nucleation theory were calculated[9] from the values of J and S at the point of maximum crystallization frequency. Table II also shows these results for each of the chelates.

DISCUSSION AND CONCLUSIONS

A linear relationship between the median freezing temperature and the logarithm of the droplet diameter was observed by Bigg[11] in his studies on the supercooling of water droplets. To interpret his data, Bigg derived a relationship between freezing temperature, droplet volume and duration of supercooling. Equation (1), analogous to Bigg's equation, has been used to interpret the data found in the present studies.

$$\ln(1-P) = -\int_0^t Vf(S)\,\mathrm{d}t \qquad (1)$$

where P = probability of crystallization, t = crystallization time, V = droplet volume, $f(S)$ = some function of the supersaturation.

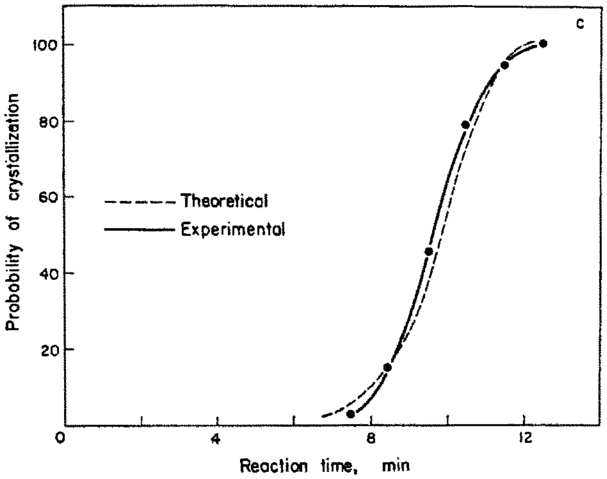


3.(a)

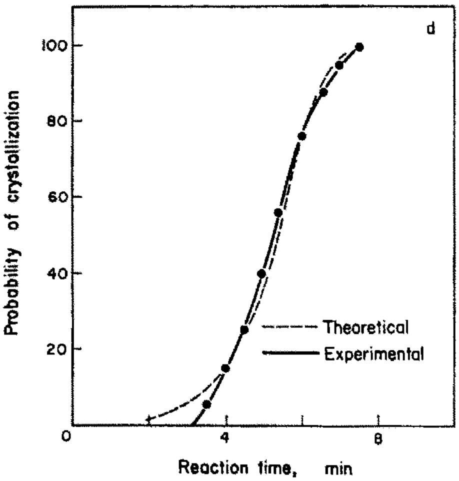
3.(b)

FIG. 3.—Probability of crystallization *vs.* reaction time for the Ni(II) and Pd(II) chelates.

Compound	Standard droplet diameter μm
a $Ni(C_6H_9N_2O_2)_2$	20
b $Ni(C_7H_{11}N_2O_2)_2$	35
c $Pd(C_6H_9N_2O_2)_2$	15
d $Pd(C_7H_{11}N_2O_2)_2$	35



3.(c)



3.(d)

In order to apply equation (1), it was necessary to transform the relationships of Fig. 1 from

$$\bar{t} = m \log d + c \tag{2}$$

into

$$\ln V = a\bar{t} + b \tag{3}$$

where $a = 6{\cdot}9/m$, and $b = -(6{\cdot}9c/m + 0{\cdot}65)$, m = slope from Fig. 1, c = intercept from Fig. 1, $\bar{t}$ = median crystallization time, d = droplet diameter.

At any given time, t, during a droplet experiment there will be a certain droplet volume for which $P = 0{\cdot}5$. From this and equations (1) and (3), it follows that

$$\int_0^t f(S)\,\mathrm{d}t = 0{\cdot}693 \exp(-b)\,[\exp(-at) - 1]. \tag{4}$$

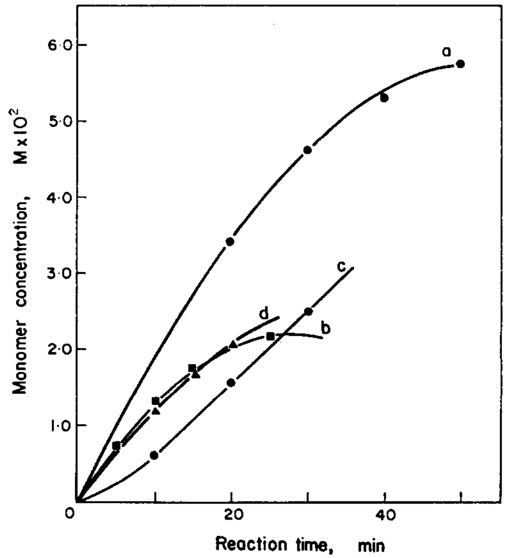


FIG. 4.—Monomer concentration *vs.* reaction time for the Ni(II) and Pd(II) chelates *a*, $Ni(C_8H_9N_2O_2)_2$; *b*, $Ni(C_7H_{11}N_2O_2)_2$; *c*, $Pd(C_8H_9N_2O_2)_2$; *d*, $Pd(C_7H_{11}N_2O_2)_2$.

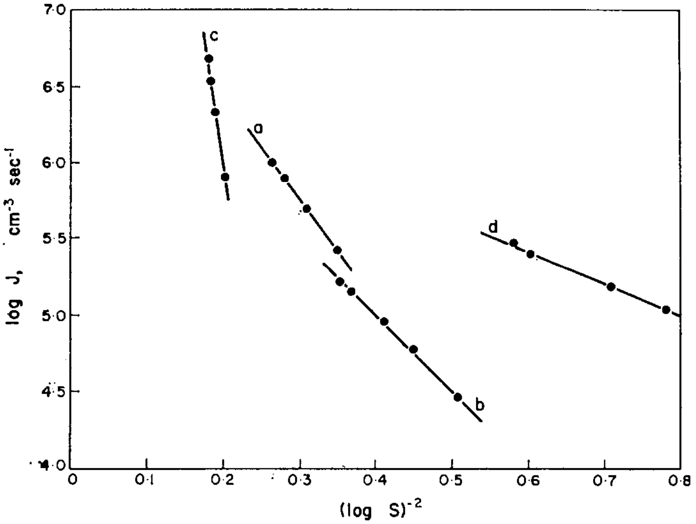


FIG. 5.—Log J *vs.* (Log $S)^{-2}$ for the Ni(II) and Pd(II) chelates *a*, $Ni(C_8H_9N_2O_2)_2$; *b*, $Ni(C_7H_{11}N_2O_2)_2$; *c*, $Pd(C_8H_9N_2O_2)_2$; *d*, $Pd(C_7H_{11}N_2O_2)_2$.

Further, at any given time the value of $\int_0^t f(S)\,dt$ is the same for all droplets. Consequently, equations (1) and (4) can be used to calculate the value of P for droplets of any standard size, V_s. The results of such calculations are shown as broken lines on Fig. 3. Since $(\partial P/\partial t)V_s$ is proportional to the crystallization frequency, equation (5) was used to calculate the frequency as a function of time.

$$-\left(\frac{\partial P}{\partial t}\right) = K\exp(-at)(1 - P) \qquad (5)$$

TABLE II.—VALUES OF VARIOUS NUCLEATION PARAMETERS FOR THE Ni(II) AND Pd(II) CHELATES

Compound	Solubility *M*	*A* *cm*$^{-3}$ · *sec*$^{-1}$	*S*	Surface energy, *erg* · *cm*$^{-2}$ (σ)	Critical radius Å (r^*)	Molecules/ nucleus (n^*)
$Ni(C_6H_9N_2O_2)_2$	$1{\cdot}7 \times 10^{-4}$	1×10^8	88	34	12	25
$Ni(C_7H_{11}N_2O_2)_2$	$2{\cdot}4 \times 10^{-4}$	2×10^2	49	29	14	30
$Pd(C_6H_9N_2O_2)_2$	$2{\cdot}3 \times 10^{-5}$	1×10^{12}	$2{\cdot}5 \times 10^2$	36	12	19
Pd $(C_7H_{11}N_2O_2)$	$3{\cdot}5 \times 10^{-4}$	5×10^6	21	23	16	38

* See Table I for solution conditions. The non-S.I. units previously used have been retained to facilitate comparison. In a short communication[10] on the nucleation of $Pd(C_6H_9N_2O_2)_2$, the values given for *S*, σ and r^* were different from the present values. The values above are based on improved methods of analysis.

where $K = [aV_s]\,[0{\cdot}693 \exp(-b)]$. The results are shown as broken lines on Fig. 2. The discrepancy between the experimental and calculated curves of Figs. 2 and 3 is thought to be due to experimental error.

The usual value[12,13] of the kinetic constant, *A*, computed by Turnbull and Vonnegut[14] for the homogeneous nucleation of crystals from melts, was used to calculate the various nucleation parameters shown in Table II. The experimental values of *A*, however, were found to differ by many orders of magnitude from 10^{30} cm^{-3}. sec^{-1} (see Table II). This may be attributed partially to the large entropy changes which accompany crystallization of compounds of some structural complexity, *i.e.*, the activation of the molecules for interface transfer must be accompanied by a large entropy decrease. As Dunning[15,16] points out, the entropy change which occurs during phase transformations is neglected in the Becker-Döring theory. Similar discrepancies between the theoretical and experimental values of *A* have been reported[8,15,16] and discussed[15,16] previously by other investigators.

Another explanation for the discrepancy between the observed and calculated values of the kinetic constant can also be found in the classical theory. The validity of the functional relationships predicted by equation (6) when applied to nucleation of liquid drops from the vapour is being debated at the present time.[17,18]

$$J = A \exp\left(-\frac{16\pi v^2 \sigma^3}{3(kT)^3 (2{\cdot}303 \log S)^2}\right) \tag{6}$$

where k = Boltzmann's constant, T = absolute temperature. With the added complication of the ionic nature of the species present in solutions of electrolytes and the significant solvation and entropy effects which are known to accompany nucleation in such solutions, it is doubtful if agreement between predicted and calculated values of *A* should be expected.

Acknowledgement—The authors acknowledge the financial assistance provided by the National Research Council of Canada and the Department of University Affairs, Province of Ontario, Canada.

Zusammenfassung—Die Kombination der Fällung aus homogener Lösung und der Tröpfchenmethode nach Vonnegut wurde bei der Untersuchung der Keimbildung aus Lösungen von Bis(1,2-cyclohexandiondioximato)Ni(II), Bis(1,2-cycloheptandiondioximato)-Ni(II), Bis(1,2-cyclohexandiondioximato)Pd(II) und Bis(1,2-cycloheptandiondioximato)Pd(II) verwendet. Werte für die kinetische Konstante, die

Oberflächenenergie, für den kritischen Radius und die Anzahl von Molekülen pro kritischem Keim werden berechnet und diskutiert im Hinblick auf die Grenzen der klassischen Keimbildungstheorie bei der Anwendung auf Kristallkeimbildung aus wäßrigen Elektrolytzlösungen.

Résumé—On emploie la combinaison de la précipitation à partir d'une solution homogène et de la technique de gouttelette de Vonnegut dans l'étude de la nucléation à partir d'une solution de bis(1,2-cyclohexanedione dioxamato) Ni(II), bis(1,2-cycloheptanedione dioxamato) Ni(II), bis(1,2-cyclohexanedione dioxamato) Pd(II) et bis(1,2-cycloheptanedione dioxamato) Pd(II). On calcule les valeurs de la constante cinétique, de l'énergie de surface, du rayon critique, et le nombre de molécules par noyau critique et en discute par rapport aux limitations de la théorie classique d'amorçage lorsqu'on l'applique à l'amosçage du cristal à partir de solutions aqueuses d'électrolytes.

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SHORT COMMUNICATIONS

Determination of carbon monoxide in metal carbonyl complexes—II
Development of a volumetric finish

(*Received* 4 *December* 1969. *Accepted* 17 *December* 1969)

IN AN EARLIER paper[1] a method was described for the determination of carbon monoxide in metal carbonyl complexes. Carbon monoxide is displaced from the complex by an oxidative technique and oxidized by the Schütze reagent to carbon dioxide which is determined gravimetrically by absorption on soda asbestos in a conventional Pregl-type absorption tube. A modification is now described in which the carbon monoxide is estimated titrimetrically. This is more suitable for normal laboratory conditions and avoids the stringent analytical conditions required for an accurate gravimetric finish. It also permits the use of a smaller sample size without loss in accuracy.

The recommended titrimetric procedure utilizes the method adopted by Unterzaucher[2] for the determination of oxygen in organic compounds. The carbon monoxide is displaced as before by an oxidative procedure and reacted with anhydro-iodic acid at 120°. Iodine, which is quantitatively released at this temperature, is absorbed in aqueous sodium hydroxide and estimated by the six-fold amplification technique of Leipert as modified by Fildes and Macdonald.[3]

EXPERIMENTAL

Apparatus

The apparatus described in the previous publication has been modified (see Fig. 1) to permit the use of anhydro-iodic acid at 120°. The decomposition and purification sections *A–F* as previously described are retained.[1] The new oxidation tube *G* of 12 mm bore is 0·25 m long. It contains a 100-mm section of anhydro-iodic acid *H*, held in place by 3-mm pads of glass-wool and heated to 120° by the furnace *I* (Hösli electrical furnace operated from a 36-V constant voltage transformer). A ball joint connects the oxidation tube to the absorption tube *J* of 12 mm bore. This 0·25-m long tube has indentations along about 0·15 m of its length and the end near the ball joint is heated by the 50-mm long aluminium heating block *K*. A glass tube insert of 7 mm outside diameter and 70 mm length, held in the oxidation tube by a tightly fitting O-ring, ensures that iodine sublimes well into the absorption tube, avoiding loss through the ball joint. The gas flow may be checked by a flow-meter *L* connected to the exit end of the absorption tube.

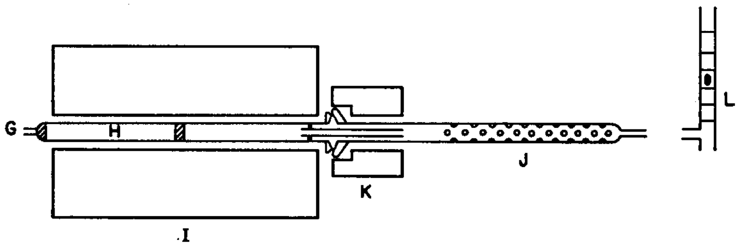

FIG. 1

Reagents

The following reagents are necessary in addition to those previously listed.

Anhydro-iodic acid. Prepared according to the method of Unterzaucher.[4] It is essential that this reagent be prepared and stored in subdued light. The product must remain white at the operating temperature.

Sodium hydroxide, 5*M* and 1*M*.

Phosphoric acid, 3*M*.

Bromine water. Saturated aqueous solution.

Formic acid, 90%. Analytical reagent grade.

Method

Assemble the apparatus and tube packings as described. Adjust the sample flask heating block to 60–70°, the oxidation tube furnace to 120°, the absorption tube heating block *K* to about 120° and the nitrogen carrier-gas flow to 5–10 ml/min. Allow the nitrogen carrier-gas to purge the apparatus for at least 12 hr and then activate the anhydro-iodic acid by decomposing about 10 mg of sodium formate in the sample flask. Cool the condenser with tap water and immerse the cold trap in solid carbon dioxide and acetone.

To charge the absorber draw 5*M* sodium hydroxide into the tube and allow the reagent to drain. Weigh the sample (3–5 mg) into the reaction vessel, add about 30–50 mg of pyridine hydrobromide perbromide and immediately connect the flask to the apparatus. Add 3 ml of dichloromethane from the dropping funnel *B* under nitrogen flow and continue the nitrogen flow at 5–10 ml/min while the flask is heated to 70° for about 20 min. Disconnect the absorption tube and rinse the contents into a 250-ml conical flask with distilled water followed by 4 ml of 1*M* sodium hydroxide and further distilled water. Acidify the resulting solution by the addition of 2 ml of 3*M* phosphoric acid, add 5 ml of bromine water, and set aside for 5 min. Destroy the free bromine by the dropwise addition of formic acid and after cooling the solution for 15 min in ice water add 2 ml of 4*M* sulphuric acid and a few crystals (about 50 mg) of potassium iodide. Titrate the liberated iodine with 0·02*M* sodium thiosulphate.

$$1 \text{ ml of } 0{\cdot}02M \text{ sodium thiosulphate} \equiv 0{\cdot}2334 \text{ mg of CO.}$$

RESULTS AND DISCUSSION

The results obtained for a range of compounds are given in Table I. These compounds, which were either available commercially or obtained from research projects, all give satisfactory analytical figures for carbon on combustion analysis. It is apparent that an acceptable order of accuracy has been retained with a 3–5-mg sample, which is smaller than that previously recommended.

TABLE I.—DETERMINATION OF CARBON MONOXIDE IN METAL CARBONYL COMPLEXES

Sample*	Carbon monoxide, %	
	Theory	Found
$Mo(CO)_3(P\phi_3)_2Cl_2$	10·81	10·8
$Mo(CO)_4$·phen	28·87	28·9
$Mo(CO)_6$	63·63	64·0
$W(CO)_6$	47·73	48·3
$W(CO)_3$·phen·I_2	11·97	11·6
$[Co(CO)_4CF_2]_2$	50·68	50·7
$W(CO)_3(As\phi_3)_2I_2$	7·41	7·2
$W(CO)_3(Sb\phi_3)_2Br_2$	9·31	8·5
$W(CO)_3(Sb\phi_3)_2I_2$	6·85	6·4

* $\phi = C_6H_5$; phen = 1,10-phenanthroline.

The main difficulty with this modification concerns the quality and reactivity of the anhydro-iodic acid reagent. We find that the reagent functions satisfactorily provided it is prepared strictly in accordance with the conditions set down by Unterzaucher,[4] and that the temperature of the reagent in the furnace is not allowed to rise above 120°. (Higher temperatures up to 135° were found to cause decomposition of this reagent, resulting in high blanks.) All of four batches prepared were active for the oxidation of carbon monoxide to carbon dioxide, and give blank values around 0·03–0·05 ml of 0·02*M* sodium thiosulphate. In our experience, commercially available iodine pentoxide is quite unreliable for this oxidation, although it has been reported that iodine pentoxide is more active in oxidizing carbon monoxide than is anhydro-iodic acid.[5]

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Summary—The method previously described for the determination of carbon monoxide in metal carbonyl complexes has been modified to provide an accurate volumetric finish.

Zusammenfassung—Die früher beschriebene Methode zur Bestimmung von Kohlenmonoxid in Metallcarbonylkomplexen wurde abgeändert und bietet jetzt einen genauen volumetrischen Abschluß.

Résumé—La méthode antérieurement décrite pour le dosage de l'oxyde de carbone dans les complexes métal-carbonyle a été modifiée pour fournir une fin de dosage volumétrique précise.

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Contributions to the analytical chemistry of osmium and ruthenium—IX

The dimercapto derivatives of asymmetric triazine as colour reagents for osmium*

(*Received* 3 *November* 1969. *Accepted* 22 *December* 1969)

SPECTROPHOTOMETRIC determinations of osmium have been based upon its colour reactions with both inorganic and organic reagents. Whereas the number of inorganic reagents used for this purpose is relatively limited, the number of organic reagents is great. Among them the derivatives of thiourea,[1] thiosemicarbazide[2,3] and thiosemicarbazone[4–6] hold a prominent place.

Recently, by the substitution of selenium for the sulphur atom in the molecule of the organic reagent, new derivatives, which give coloured compounds with osmium, were obtained.[7,8] The sensitivity of these colour reactions does not differ too much from that of the reactions of the similar sulphur derivatives.

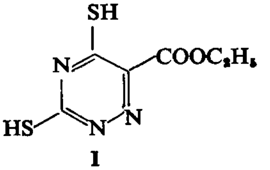
Concomitantly with aliphatic mercapto derivatives some heterocyclic mercapto derivatives such as 2-mercaptobenzimidazole[9] and asymmetric mercaptotriazines have begun to be used for the spectrophotometric determination of osmium.

In previous papers[8,10–12] the colour reactions of osmium with some mercapto derivatives of the asymmetric triazine class were reported. They may be classified in the three groups shown in Table I, from which it can be seen that for each group of reagents the substituents in the positions 3 and 5 of the triazine ring are the same, while the substituent in position 6 can be any radical.

Table I summarizes the radicals attached in position 6 to the three main rings, and also shows 2-methyl-3,5-dihydroxy-6-mercapto-1,2,4-triazine in group *C*.

The location of this compound in reagent group *C* is justified by the fact that it is derived from one of the tautomeric forms of *C*.

The present paper reports the results of a study of the colour reaction of osmium with a new triazine derivative, namely 3,5-dimercapto-6-(ethylcarboxyl)-1,2,4-triazine (I),[13] which may be regarded as a member of a fourth group of 6-substituted triazine derivatives (II), the colour reactions of which with osmium are going to be studied.



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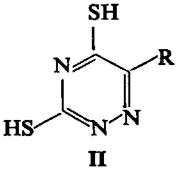

II

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* Paper presented at the National Conference of Analytical Chemistry, Mamaia 1969 (Romania).

Zusammenfassung—Die früher beschriebene Methode zur Bestimmung von Kohlenmonoxid in Metallcarbonylkomplexen wurde abgeändert und bietet jetzt einen genauen volumetrischen Abschluß.

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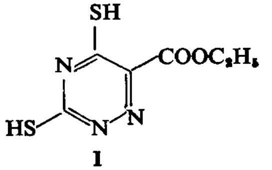

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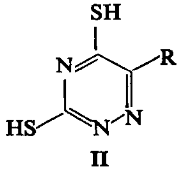

II

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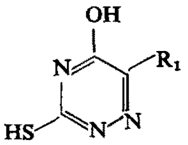
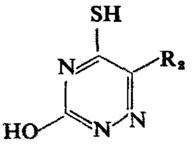
* Paper presented at the National Conference of Analytical Chemistry, Mamaia 1969 (Romania).

TABLE I.—REAGENTS FOR OSMIUM

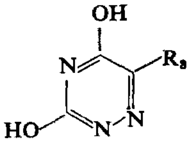
Group *A*

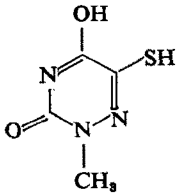


Group *B*



Group *C*



No.	R_1	R_2	R_3
1	H	H	H
2	CH_3	SCH_3	SCH_3
3	$(CH_3)_2$	SC_2H_5	SC_4H_9
4	COOH	SC_4H_9	$SCH_2CH{=}CH_2$
5	$COOC_2H_5$	$SCH_2C_6H_5$	SH
6	CH_2COOH	C_6H_5	
7	$CH_2COOC_2H_5$	$(CH_2)_5CH_3$	
8	$CH_2SCH_2C_6H_5$	$N(CH_2)_4O$	

EXPERIMENTAL

Reagents

Osmium solution, 2990 ppm. Prepared by dissolving osmium tetroxide in 0·2M sodium hydroxide, and standardized by Klobbie's method.[14] Test solutions of various concentrations were obtained by dilution with 0·2M sodium hydroxide.

Reagent solution, 0·1%. Prepared in 0·2M sodium hydroxide.

Metal ion solution. Aqueous solutions of commercially obtained $RuCl_3$, $PdCl_2$, H_2PtCl_6, $AuCl_3$, and $UO_2(NO_3)_2{\cdot}6H_2O$.

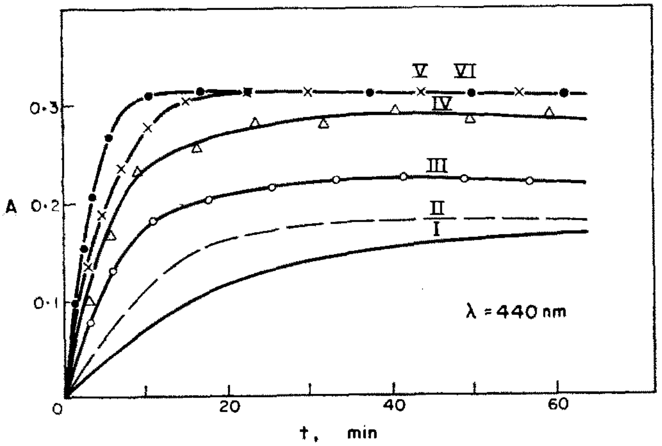


FIG. 1.—Effect of sulphuric acid concentration on rate of colour development. I—$10^{-2}M$; II—1M; III—2M; IV—3M; V—4M; VI—5M; 2 ml added per 25 ml total volume.

Procedures

To 25-ml graduated flasks osmium, reagent and sulphuric acid solutions were added in that order and the mixture was made up to the mark with distilled water.

For study of the effect of reagent concentration the mixtures contained 150 μg of osmium, 2 ml of 5*M* sulphuric acid and various amounts of 0·1% reagent solution. For study of the effect of acid concentration the solutions contained 150 μg of osmium, 3 ml of 0·1% reagent solution and 2 ml of sulphuric acid of various concentrations.

The absorption spectrum of the resulting coloured compound was measured against a blank solution on a sample containing 150 μg of osmium, 3 ml of 0·1% reagent solution and 2 ml of 5*M* sulphuric acid, made up to 25 ml with distilled water. The absorption spectrum of the blank (the reagent under the conditions of the reaction) was measured against water.

The effect of osmium concentration was studied by taking various amounts of osmium, 3 ml of 0·1% reagent solution and 2 ml of 5*M* sulphuric acid in 25 ml total volume.

RESULTS AND DISCUSSION

A volume of 3 ml of 0·1% reagent solution was found sufficient for complete reaction over the range of osmium concentration studied.

The results of some of the experiments to determine the effect of acidity are shown in Fig. 1, which shows that with rise in acid concentration in the sample, the rate of reaction and the intensity of colour both increase. The time needed for full colour development is reduced to less than 10 min when the concentration of the acid added is higher than 4*M*. The addition of acid more concentrated than 4*M* does not substantially change the maximum value of absorbance. It was therefore decided to add 2 ml of 5*M* sulphuric acid per 25 ml total volume.

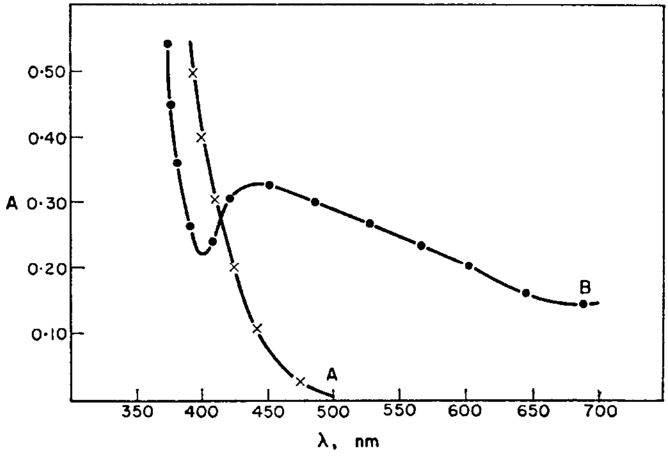


Fig. 2.—Absorption spectra.
A—Reagent *vs.* water.
B—Coloured compound *vs.* blank.

Absorption spectra

Figure 2 shows the absorption spectrum of the reagent *vs.* water under the conditions of the reaction (curve A), and of the resultant coloured compound against the blank (curve B).

This plot shows that the sensitivity is maximal between about 440 and 550 nm. We selected 440 nm as the wavelength for measurements.

On comparing the colour reaction of osmium with this derivative and the previously studied reaction with the similar compound of group *A*,[10] which contained the —OH group instead of the —SH group in position 5 of the triazine ring, it may be concluded that this change of group does not substantially change the position and the number of absorption bands.

Beer's law is obeyed over the range 0·5–18·0 ppm osmium at 440 nm and 0·7–18·0 ppm at 560 nm respectively, the corresponding absorbance for concentrations of 18·0 ppm being 0·97 and 0·73.

Comparison of the sensitivity of this reaction and that of the reaction using the similar reagent of the triazine group *A* shows that the substitution of the —SH group for the —OH group substantially increases the sensitivity, the lower concentration limit falling from 1·5 to 0·5 ppm.

Interferences

The study of the effect of the ions UO_2^{2+}, Pd^{2+}, Pt^{4+}, Ru^{3+}, Au^{3+} on the colour reaction of osmium with the reagent showed the following: the ions UO_2^{2+}, Ru^{3+} and Au^{3+} do not form a similarly coloured complex but inhibit the determination; Pd^{2+} interferes by forming a precipitate; Pt^{4+} can be tolerated up to Os:Pt ratios of 1:6.

The composition of the compound

The method of continuous variations[15] and the method of spectrophotometric titration[16] both suggested that the ratio Os:R is 1:2.

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Summary—The parameters of the reaction of osmium with 3,5-dimercapto-6-(ethylcarboxy)-1,2,4-triazine have been studied and the optimum conditions for the spectrophotometric determination of osmium over the range 0·5–18·0 ppm determined. The coloured product contains the components in the ratio 1:2 metal:ligand.

Zusammenfassung—Die Parameter der Reaktion von Osmium mit 3,5-Dimercapto-6-äthylcarboxy-1,2,4-triazin wurden untersucht und die optimalen Bedingungen zur spektrophotometrischen Bestimmung von Osmium im Bereich 0,5–18,0 ppm ermittelt. Die farbige Verbindung enthält die Komponenten im Verhältnis Metall:Ligand = 1 : 2.

Résumé—On a étudié les paramètres de la réaction de l'osmium avec la 3,5–dimercapto 6–(éthylcarboxy) 1,2,4–triazine et déterminé les conditions optimales pour le dosage spectrophotométrique de l'osmium dans le domaine 0,5–18,0 p.p.m. Le produit coloré renferme les composants dans le rapport 1:2, métal:ligand.

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Submicro determination of aluminium, bismuth and copper in organometallic compounds*

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THE RANGE of organometallic materials analysed on the submicro scale has now been extended to those containing aluminium, bismuth and copper.

For reasons discussed earlier,[1] photometric titration of the metals after digestion of organic materials was not pursued, suitable spectrophotometric procedures being available, but both open and closed tube digestion procedures were attempted.

EXPERIMENTAL

Spectrophotometric methods

Aluminium. From previous experience, it was considered that methods involving lake formation and stabilizing agents[2,3] would not be suitable, and the most promising alternative appeared to be extraction of the 8-hydroxyquinoline (oxine) complex.[3] A single extraction from a solution at pH 5·2 gave consistent results over the range 1·5–10·5 μg of metal provided that the shaking time during extraction was controlled. Particular attention had to be paid to cleanliness of apparatus to retain the required repeatability of results. Separatory funnels and cuvettes were washed successively with chloroform, distilled water, concentrated nitric acid, distilled water and acetone.

Bismuth. The thiourea and iodide methods of Lisicki and Boltz[4] were examined. Volumes of reagents and final solutions were halved and absorbances measured in 40-mm cells in order to approach the required sensitivity. The thiourea method was not successful; on the other hand, although sensitivity was not very high, the iodide method gave results of sufficient consistency to warrant its adoption. To prevent hydrolysis and to bring the acid concentration up to that recommended for the final solution, 10 ml of 5*N* sulphuric acid were used to rinse out the digestion tubes into the volumetric flasks.

Copper. Three extraction techniques were considered. Use of diethyldithiocarbamate[5] was not very successful; 2,2-diquinolyl[6] was too insensitive for present purposes but a modification of the technique described by Tuck and Osborn,[6] using neocuproine, was successfully developed. It was found, however, that use of bis-cyclohexanone oxalyldihydrazone,[7] which required no extraction, was not only simpler but more sensitive and repeatable when the buffer recommended by Somers and Garraway[8] was used.

Mineralization procedures

Open-tube digestion with perchloric/sulphuric acid mixture gave satisfactory results for the bismuth compounds but low and variable results for the copper and aluminium compounds, particularly the latter. Sealed-tube digestion with nitric/sulphuric acid mixture, however, gave satisfactory results for all the compounds.

Recommended procedures

Mineralization. Digest the samples, containing 4–20 μg of metal for bismuth or copper compounds or 1·5–10·5 μg of aluminium, in sealed tubes by the procedure described elsewhere.[9,10]

Determination of aluminium. Transfer the residue from the digestion tube into a 50-ml separatory funnel with about 10 ml of water. Add 5 ml of buffer solution (30 g of sodium acetate trihydrate in 420 ml of water plus 60 ml of 0·5*M* acetic acid). By pipette add 10 ml of a 0·25% chloroform solution of oxine to the funnel, stopper and shake it for 3 min. Allow the layers to separate and allow the organic layer to flow into a 30-mm stoppered spectrophotometer cuvette through a plug of cotton wool in the stem of the funnel. Measure the absorbance at 395 nm against a reference blank solution taken through the whole procedure. Prepare a calibration curve by applying the colour development procedure to a standard aluminium solution.

Determination of bismuth. Transfer the residue from the digestion tube into a 25-ml volumetric flask with 10 ml of 5*N* sulphuric acid. Add 10 ml of iodide–ascorbic acid reagent (140 g of potassium iodide and 10 g of ascorbic acid dissolved in water and diluted to 1 litre). Dilute to the mark and

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measure the absorbance at 337 nm in a 40-mm cuvette against a reference blank solution taken through the whole procedure. Prepare a calibration curve by applying the colour development procedure to portions of standardized[11] bismuth solution.

Determination of copper. Transfer the residue from the digestion tube into a 25-ml volumetric flask with about 10 ml of water. Add, in quick succession, 0·2 ml of 10% ammonium citrate solution, one drop of 0·02% aqueous Neutral Red solution, 3*M* sodium hydroxide dropwise until the indicator changes colour, 5 ml of buffer solution (400 ml of 0·5*M* boric acid and 60 ml of 0·5*M* sodium hydroxide) and, finally, 1 ml of 0·2% bis-cyclohexanone oxalyldihydrazone solution in 50% ethanol. After 20 min, dilute to the mark and measure the absorbance at 595 nm in a 40-mm cuvette against a reference blank solution taken through the whole procedure. Prepare a calibration curve by applying the colour development procedure to a standard copper solution.

RESULTS AND DISCUSSION

The results of the analysis of a number of organometallic compounds by the recommended methods are summarized in Table I. Two of the 44 determinations done fell just outside the normally accepted limits, of ±0·3% absolute, for microanalysis of organic compounds.

TABLE I.—ANALYSIS OF ORGANOMETALLIC COMPOUNDS

Compound	Range of weight, μg	Metal, % Calc.	Metal, % Found, mean*	Range of errors, % absolute
Al acetylacetonate	78·3–95·9	8·31	$8{\cdot}3_4$	$-0{\cdot}0_9$ to $+0{\cdot}1_6$
Al *N*-benzoyl-*N*-phenylhydroxylaminate	90·8–103·2	4·06	$3{\cdot}9_9$	$-0{\cdot}1_6$ to $+0{\cdot}0_1$
Al oxinate	72·0–107·3	5·87	$5{\cdot}9_3$	$-0{\cdot}0_3$ to $+0{\cdot}1_7$
Bi 7,8-benzoquinoline iodide	39·9–77·8	23·30	$23{\cdot}2_2$	$-0{\cdot}1_5$ to $-0{\cdot}0_3$
Bi mercaptobenzothiazole	38·9–55·3	29·53	$29{\cdot}5_8$	$-0{\cdot}3_1$ to $+0{\cdot}3_2$
Bi oxinate	50·4–70·7	31·69	$31{\cdot}6_9$	$-0{\cdot}0_8$ to $+0{\cdot}0_8$
Cu acetylacetonate	52·2–85·8	24·27	$24{\cdot}2_5$	$-0{\cdot}2_7$ to $+0{\cdot}2_9$
Cu *N*-benzoyl-*N*-phenylhydroxylaminate	59·7–77·9	13·02	$13{\cdot}0_0$	$-0{\cdot}1_8$ to $+0{\cdot}2_8$
Cu pyridinethiocyanate	82·4–100·6	18·80	$18{\cdot}7_6$	$-0{\cdot}2_6$ to $+0{\cdot}1_6$
Cu quinaldinate	70·6–77·5	14·92	$14{\cdot}8_9$	$-0{\cdot}2_8$ to $+0{\cdot}2_3$
Cu salicylaldoximate	72·6–86·6	18·92	$18{\cdot}8_5$	$-0{\cdot}1_3$ to $-0{\cdot}0_1$

* Of 4 results.

Although good results were obtained for the analysis of bismuth compounds after open-tube digestion with perchloric/sulphuric acid mixture, those for the copper compounds tended to be low (average recovery 98·6%) whilst those for aluminium compounds were very low and erratic. Open-tube digestion is, however, manipulatively simpler and more rapid than the sealed-tube technique; attempts are being made to modify the procedure so far employed, so as to produce a generally applicable method.

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Summary—Methods for the determination of aluminium, bismuth or copper in samples of organometallic compounds weighing 40–110 μg have been developed. Spectrophotometric determination following digestion with nitric and sulphuric acids in a sealed tube is recommended, all results obtained from the analysis of standard compounds being within ±0·3% absolute error. Digestion in an open tube with perchloric and sulphuric acids gives satisfactory results for bismuth compounds but erratic and often low results for aluminium and copper compounds.

Zusammenfassung—Zur Bestimmung von Aluminium, Wismut oder Kupfer in Proben metallorganischer Verbindungen, die 40–110 μg wiegen, wurden Verfahren entwickelt. Es wird empfohlen, an einen Aufschluß mit Salpeter- und Schwefelsäure im verschlossenen Rohr eine spektrophotometrische Bestimmung anzuschließen; alle Ergebnisse der Analyse von Standardverbindungen lagen innerhalb ±0,3 prozent absolutem Fehler. Aufschluß mit Perchlorsäure im offenen Rohr gibt bei Wismutverbindungen zufriedenstellende, bei Aluminium- und Kupferverbindungen jedoch stark streuende und oft zu niedrige Ergebnisse.

Résumé—On a élaboré des méthodes pour la détermination d'aluminium, bismuth ou cuivre dans des échantillons de composés organométalliques pesant 40–110 μg. On recommande la détermination spectrophotométrique suivant la digestion avec les acides nitrique et sulfurique en tube scellé, tous les résultats obtenus de l'analyse de composés étalons étant d'erreur absolue comprise dans les limites ±0,3%. La digestion dans un tube ouvert avec les acides perchlorique et sulfurique donne des résultats satisfaisants pour les composés du bismuth mais des résultats variables et souvent faibles pour les composés de l'aluminium et du cuivre.

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Fällung des Wismuts als Bis(triphenylselenonium)-Pentachlorobismutat (III)

(*Eingegangen am* 12 *Dezember* 1969. *Angenommen am* 31 *Januar* 1970)

INNERHALB verschiedener wasserlöslicher Komplexe (Gutbier und Müller[1]): $[BiCl_4]^-$, $[BiCl_5]^{2-}$, $[BiCl_6]^{3-}$ und verschiedener mehrkerniger Ionen schreiben Remy und Pellens[2] dem Pentachlorobismutat die größte Stabilität zu. Mit aliphatisch substituierten Ammoniumsalzen wird das Wismut aus salzsauren Lösungen als Tetrachlorokomplex gefällt und kann zu extraktiv-photometrischen

Summary—Methods for the determination of aluminium, bismuth or copper in samples of organometallic compounds weighing 40–110 μg have been developed. Spectrophotometric determination following digestion with nitric and sulphuric acids in a sealed tube is recommended, all results obtained from the analysis of standard compounds being within ±0·3% absolute error. Digestion in an open tube with perchloric and sulphuric acids gives satisfactory results for bismuth compounds but erratic and often low results for aluminium and copper compounds.

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Bestimmungen[3] in dieser Form separiert werden ($[HN(C_4H_9)_3]$ $[BiCl_4]$, $\lambda_{max}/CH_2Cl_2 = 330$ nm), Triphenylselenoniumionen scheiden jedoch das, eutspechend, extrahierbare Pentachloroanion ab. $[(C_6H_5)_3Se]_2$: $[BiCl_5]$, $\lambda_{max}/CH_2Cl_2 = 340$ nm.

Unter den Triphenylselenoniumsalzen anderer komplexer Halogenometallsäuren (Tabelle I) weist die Mehrzahl in wäßrigen Medien deutlich hervortretende Löslichkeiten auf. Aus 10%-ig Kalium- bzw. Natriumchlorid-haltigen Lösungen beginnt die Fällbarkeit des Kupfers, Kobalts, Zinks und Cadmiums erst bei Metallgehalten ab 2%. Leichter fällbar sind die entsprechenden Salze von Halogenosäuren dreiwertiger Metalle. In Citrat-haltigen, schwach sauren Medien sind jedoch alle leicht komplex löslich außer $[(C_6H_5)_3Se]_2$ $[BiCl_5]$ und $[(C_6H_5)_3Se]_2$ $[BiBr_5]$. Im ammoniakalischen Bereich werden auch diese durch Citrat leicht gelöst.

TABELLE I.

Metall	Verbindung	Farbe	Schmelzpunkt, °C
Kupfer	$[(C_6H_5)_3Se]_2[CuCl_4]$	gelb	214–216 (Zers.)
	$[(C_6H_5)_3Se]_2[CuBr_4]$	schwarz-violett	197–199
Kobalt	$[(C_6H_5)_3Se]_2[CoCl_4]$	blau	276–278
	$[(C_6H_5)_3Se]_2[CoBr_4]$	grün	259–260
Zink	$[(C_6H_5)_3Se]_2[ZnCl_4]$	farblos	287–289
	$[(C_6H_5)_3Se]_2[ZnBr_4]$	farblos	261–263
Cadmium	$[(C_6H_5)_3Se]_2[CdCl_4]$	farblos	278–279
	$[(C_6H_5)_3Se]_2[CdBr_4]$	farblos	248–249
Blei	$[(C_6H_5)_3Se]_2[PbCl_4]$	farblos	215–216
Mangan(III)	$[(C_6H_5)_3Se]_2[MnCl_5]$	grün	—
Eisen(III)	$[(C_6H_5)_3Se][FeCl_4]$	gelb	—
	$[(C_6H_5)_3Se][FeBr_4]$	dunkelbraun	134–135
Antimon(III)	$[(C_6H_5)_3Se]_2[SbCl_5]$	farblos	—
Wismut	$[(C_6H_5)_3Se]_2[BiCl_5]$	farblos	278–280
	$[(C_6H_5)_3Se]_2[BiBr_5]$	blaßgelb	259–260

Eine von Burkhalter und Solarek[4] ausgearbeitete Bestimmungsmethode für Wismut als Trimethylphenylammonium-Tetrajodobismutat(III) $[(CH_3)_3(C_6H_5)N]$ $[BiJ_4]$ H_2O bietet keine Trennungsmöglichkeiten von Übergangsmetallionen, außerdem stört die Anwesenheit anderer Halogenionen.

EXPERIMENTELLER TEIL

Reagentien

Triphenylselenoniumchlorid, 20%ig *wässrige Lösung.* Sie wird unter gelegentlichem Umrühren 2–3 Stunden mit Aktivkohle auf dem Wasserbad erwärmt. Die filtrierte, wasserhelle Lösung ist mindestens 3 Monate haltbar. Zur Fällung des Wismuts verdünnt man sie mit 1*M* Salzsäure im Verhaltnis 1:1.

Zitronensäure bzw. *Trinatriumcitrat.*

Ammoniumchlorid, 15%ig *wässrige Lösung.*

Waschlösung. Triphenylselenoniumchlorid (2g) und Zitronensäure (0,5 g) in 100 ml 0,2*M* Salzsäure.

Salzsäure, 0,2*M*.

Wismut-Standardlösung. Die erforderliche Menge Wismut *p.a.* (z.B. Baker 99,95% bezw. 99,999% Bi) wird mit konz. Salpetersäure gelöst. Man dampft bis zur beginnenden Trockne ein, und nimmt mit dem gewünschten Volumen 0,7*M* Salpetersäure auf.

Aus Wismutnitrat mit verd. Salpetersäure bereitete lösungen werden komplexometrisch eingestellt, unter Gebrauch von Brenzkatechinviolett als Indikator. Dieses Verfahren setzt die Abwesenheit von Chloridionen voraus.

Arbeitsvorschrift

Die salpeter-, oder salzsaure Probelösung, die 15–60 mg Wismut(III) enthalten mag, und deren Acidität zwischen 0,2 und 1*N* liegt, wird im Becherglas von 400–600 ml Inhalt bei Aciditäten $<0{,}5N$ mit 4 g Citronensäure und beim Vorliegen solcher $>0{,}5N$, mit 5 g Trinatriumcitrat versetzt. Nach deren Auflösung verdünnt man mit Wasser unter Rühren auf etwa 150 ml und fügt ebenfalls unter Rühren 20 ml Ammoniumchlorid-Lösung hinzu.

Die Fällung des Wismuts erfolgt bei Raumtemperatur durch langsames Zutropfen von 15 ml 0,5*M* salzsaurer Lösung des Triphenylselenoniumchlorids unter Umrühren. Der anfänglich flockig-voluminöse Niederschlag wird gegen Ende der Reagenzzugabe feinkristallin. Man rührt mehrmal, um, und beläßt eine Stunde bei Raumtemperatur. Nach dieser Zeit ist die überstehende Lösung klars der Niederschlag hat sich gut abgesetzt.

Man filtriert nun den aufgewirbelten Niederschlag durch einen bei *110°* zur Gewichtskonstanz getrockneten Filtertiegel der Frittendichte G4, und benutzt zum vollständigen Überführen und Waschen 50 ml Waschlösung. Durch nur mässig starkes Trockensaugenwird Rissbildung in der Niederschlags-schichte vermieden. Man wäscht zweimal mit je 5 ml 0,2*M* Salzsäure und saugt dann scharf ab.

Der Niederschlag wird im (belüfteten) Trockenschrank bei 110° in 60 min bis zur Gewichtskonstanz getrocknet. Umrechnungsfaktor für Wismut beträgt 0,2077. Zur Säuberung der Fritten eignet sich raschlösende ammoniakalische Citratlösung, nicht Chromschwefelsäure.

Der mittlere Fehler für die Bestimmung des Metalls aus reinen Lösungen liegt bei 0,3 %.

Spezifität und Vorteile der Methode

Unter genannten Arbeitsbedingungen wird Wismut bereits aus 5 × 10^{-3}%-igen Lösungen quantitativ abgeschieden. Dabei sind Schwankungen der Salzsaurekonzentration zwischen 0,1 und 1*M* tragbar. Citrat hält in noch schwächer sauren oder alkalischen Lösungen (nach Aufschlüssen mit

TABELLE II.

Wismut, *mg*		Fehler			Verhältnis
gegeben	gefunden	%	Fremdion, *mg*		Fremdion:Bi^{3+}
29,0	29,3$_5$	+1,2	Chlorid	10000	350
29,0	28,8	−0,7	Nitrat	2900	100
30,0	29,6	−1,3	Sulfat	1500	50
30,0	29,8	−0,7	Phosphat	1500	50
20,0	20,2	+0,8	Citrat	2000	100
20,0	20,1	+0,7	Citrat	4000	200
48,4	48,2$_5$	−0,3	Tartrat	4000	80
40,0	40,2$_5$	+0,6	Co^{2+}	40	1
29,0	28,8$_5$	−0,5		145	5
20,0	19,8$_5$	−0,8		200	10
29,0	29,3	+1	Ni^{2+}	145	5
20,0	19,8$_5$	−0,8		200	10
40,0	40,3	+0,8	Mn^{2+}	40	1
29,0	28,8	−0,8		290	10
38,7	39,0	+0,8	Al^{3+}	200	5
30,0	29,8	−0,7		300	10
19,3$_5$	19,5	+0,8		400	20
50,0	49,7	−0,6	Fe^{3+}	50	1
20,0	19,8$_5$	−0,9		100	5
20,0	20,1$_5$	+0,8		200	10
20,0	20,1$_5$	+0,8	Cr^{3+}	100	5
30,0	29,8$_5$	−0,5		3000	10
39,0	38,9$_5$	−0,2	Cu^{2+}	39	1
30,0	30,2$_5$	+0,8		150	5
20,0	20,2	+1		200	10
20,0	20,2	+1	Pb^{2+}	20	1
40,0	40,8	+2		80	2
50,0	49,7	−0,6	As(III)	50	1
29,0	28,9$_5$	−0,2		145	5
20,0	20,0$_5$	+0,4	Sb^{3+}	20	1
39,0	39,6	+1,6		80	2
30,0	30,1$_5$	+0,6	Te(IV)	60	2
40,0	39,8	−0,5	Th^{4+}	40	1
19,3$_5$	19,5$_5$	+1,1		100	5
39,0	39,1	+0,3	Mo(VI)	40	1

Natriumhydroxid) Wismut in Lösung, ohne Störungen zu verursachen. Da die Anionen der Mineralsäuren nicht stören (Tabelle II), können diese nach schließlichem Zusatz von Citrat mit Natriumhydroxidlösung bis in den pH-Bereich 0,5–1 abgestumpft werden. Bemerkenswert gering ist hierbei der Störeinfluß von Phosphat, sowie Eisen(III) und Chrom(III). Zink, Cadmium und Quecksilber(II) verursachen bei Verhältnissen Bi^{3+}:Fremdion = 1:1 Überbefunde, und man trennt dann das Wismut durch Vorfällung mit Ammoniak von den Ionen Zn^{2+} und Cd^{2+} ab. Größere Mengen Ble über das Verhältnis Bi:Pb = 1:1 hinausgehend trennt man am günstigsten durch den Aufschluß mit konz. Schwefelsäure ab. Das Verfahren eignet sich zur Analyse von Materialien mit Wismut-Gehalten ab etwa 5% Bi (Tabelle III).

Tabelle III.—Wismutbestimmung in technischen Produkten

Katalysator (Knappsack)		Weichlot	
SiO_2	51,8%	Pb	49,5%
MoO_3	17,0%	Sn	40,1%
Fe_2O_3	7,0%	Sb	0,42%
P_2O_5	1,04%	Cu	0,03%
Bi_2O_3	19,0%	Bi	9,8%
Bi_2O_3 gefunden	$19{,}0_5$%	Wismut gefunden	9,9%

Der Deutschen Forschungsgemeinschaft und dem Fonds der Chemischen Industrie danken wir für die Unterstützung der Arbeit.

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Zusammenfassung—Die Fällung des Wismuts als $[(C_6H_5)_3Se]_2[BiCl_5]$ ermöglicht bei Gegenwart von Citrat die gravimetrische Bestimmung von 15–50 mg Wismut und deren Trennung von mittleren Mengen zwei- und dreiwertiger Übergangsmetalle, sowie von Phosphat. Es wird der Aufbau verschiedener Triphenylselenonium Halogenokomplexe solcher Metalle ausgewiesen.

Summary—By precipitation as $[(C_6H_5)_3Se]_2[BiCl_5]$ in the presence of citrate, 15–50 mg of bismuth can be determined gravimetrically, and separated from moderate amounts of bi- and tervalent metals and from phosphate. Such metals are characterized by the formation of the triphenylselenonium salts of their various halide complexes.

Résumé—Par précipitation à l'état de $[(C_6H_5)_3Se]_2[BiCl_5]$ en la présence de citrate, on peut doser gravimétriquement 15–50 mg de bismuth et le séparer de quantités peu élevées de métaux di- et trivalents et de phosphate. Tels métaux sout characterisés par la formation des sels de triphénylsélénium de leurs divers complexes halogénés.

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Two new spectrophotometric reagents for copper

(*Received* 10 *November* 1969. *Accepted* 15 *January* 1970)

It has been known for many years that chromogens containing the methine or ferroin group may be transformed into reagents specific for copper(I) by alkyl, aryl, or amino substitution on the carbon

Natriumhydroxid) Wismut in Lösung, ohne Störungen zu verursachen. Da die Anionen der Mineralsäuren nicht stören (Tabelle II), können diese nach schließlichem Zusatz von Citrat mit Natriumhydroxidlösung bis in den pH-Bereich 0,5–1 abgestumpft werden. Bemerkenswert gering ist hierbei der Störeinfluß von Phosphat, sowie Eisen(III) und Chrom(III). Zink, Cadmium und Quecksilber(II) verursachen bei Verhältnissen Bi^{3+}:Fremdion = 1:1 Überbefunde, und man trennt dann das Wismut durch Vorfällung mit Ammoniak von den Ionen Zn^{2+} und Cd^{2+} ab. Größere Mengen Blei über das Verhältnis Bi:Pb = 1:1 hinausgehend trennt man am günstigsten durch den Aufschluß mit konz. Schwefelsäure ab. Das Verfahren eignet sich zur Analyse von Materialien mit Wismut-Gehalten ab etwa 5% Bi (Tabelle III).

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IT HAS been known for many years that chromogens containing the methine or ferroin group may be transformed into reagents specific for copper(I) by alkyl, aryl, or amino substitution on the carbon atoms immediately contiguous to the chelating nitrogen atoms.[1-3] This effect has been attributed to steric hindrance which prevents octahedral co-ordination around iron(II) but allows tetrahedral co-ordination around copper(I).[1,2] Two more compounds have been prepared which exhibit this property: 6-methyl-2-pyridylhydrazidine and the hitherto unknown 3-(6-methyl-2-pyridyl)-5,6-diphenyl-1,2,4-triazine, hereafter referred to as MPH and MPTZ respectively. MPH reacts with copper(I) to give a fairly stable yellow compound ($\varepsilon = 700$ l.mole^{-1}.mm^{-1}; λ_{max} 426 nm) and MPTZ reacts to form a stable red-orange compound ($\varepsilon = 955$ l.mole^{-1}.mm^{-1}; λ_{max} 492 nm).

EXPERIMENTAL

Reagents

Preparation of MPH. MPH has been previously reported by van der Burg,[4] but in the present work, the method of Case[5] was used with the following modifications: 97% hydrazine and anhydrous isopropanol were employed in place of 95% hydrazine and 95% ethanol, and anhydrous magnesium sulphate was added to the reaction mixture. The crude product was recrystallized three times from boiling isopropanol. White plates were obtained, in 82% yield, m.p. 115°, in agreement with that reported by van der Burg. Calculated for $C_7H_{10}N_4$: C, 55·98%; H, 6·71%; N, 37·31%; found: C, 55·8%; H, 6·7%; N, 37·0%.

TABLE I.—DETERMINATION OF COPPER IN IRON-CONTAINING BOILER WATER

	Copper in sample, *ppm*	Copper added, *ppm*	Iron added, *ppm*	Copper found, *ppm*
By extraction of $Cu(MPTZ)_2^+$ into isopentanol	?	0	0	0·34
	0·34	0·50	0	0·85
	0·34	1·00	0	1·34
	0·34	1·50	0	1·86
	0·34	0	1·00	0·34
	0·34	0	10·0	0·35
	0·34	0	100·0	0·34
By $Cu(MPH)_2^+$ in aqueous solution	?	0	0	0·17
	0·17	0·50	0	0·68
	0·17	1·00	0	1·15
	0·17	1·50	0	1·69
	0·17	0	1·00	0·18
	0·17	0	10·0	0·17
	0·17	0	100·0	0·18
By extraction of $Cu(MPH)_2^+$ into isopentanol	?	0	0	0·17
	0·17	0·50	0	0·67
	0·17	1·00	0	1·15
	0·17	1·50	0	1·65
	0·17	0	1·00	0·16
	0·17	0	10·0	0·18
	0·17	0	100·0	0·17

All analyses were performed in triplicate on the same sample of boiler effluent. The sample was diluted 1:1 with standard copper and iron solutions or demineralized water for the determinations with MPH.

Preparation of MPTZ. The method of Case[6] was used with the following modifications: isopropanol was used as the solvent for the MPH and a mixture of 1:5 methanol–isopropanol was used as the solvent for the benzil. The crude yellow product was recrystallized three times from boiling benzene. Slightly yellow crystals were obtained, in 68% yield, m.p. 179°. Calculated for $C_{21}H_{16}N_4 \cdot H_2O$: C, 73·69%; H, 5·27%; N, 16·31%; found: C, 73·6%; H, 5·4%; N, 16·1%.

MPH reagent solution, 0·02*M*. Dissolve 0·30 g of MPH in 50 ml of isopropanol and dilute to 100 ml with copper-free water.

MPTZ reagent solution, 0·02*M*. Dissolve 0·65 g of MPTZ in 90 ml of boiling methanol. Cool to room temperature and dilute to 100 ml with methanol.

Phosphate buffer solution, pH 6·5, copper-free. Dissolve 10 g each of potassium dihydrogen phosphate and dipotassium hydrogen phosphate in water and dilute to 100 ml. Purify as below.

Phosphate buffer solution, pH 10, copper-free. Dissolve 10 g of dipotassium hydrogen phosphate in 50 ml of water, add 12·5 ml of 0·10*M* sodium hydroxide, dilute to 100 ml, and purify as below.

Hydroxylammonium chloride solution 10%, copper-free. Purified as below.

Sodium hydroxide solution, 5M.

Copper-free water. To 1 litre of distilled water, add 1 ml of MPTZ reagent solution, 1 ml of 10% hydroxylammonium chloride solution and 10 ml of pH 6·5 buffer solution. Extract with 50 ml of isopentanol. Discard the alcoholic phase.

Buffer and other aqueous solutions were purified by a similar procedure.

Standard copper solutions, 1000 ppm. Prepared from electrolytic grade copper, and freed from nitrate by fuming with sulphuric acid.

Procedures

Preparation of sample. Both MPH and $Cu(MPH)_2^+$ are soluble in water. $Cu(MPTZ)_2^+$ is somewhat soluble in water, but MPTZ itself is not water-soluble over the pH range of colour development. The nitrates and perchlorates of both complexes are insoluble in water, and those of $Cu(MPH)_2^+$ are extractable, whereas the extraction of $Cu(MPTZ)_2^+$ is independent of presence of perchlorate. Thus, when copper is to be determined in aqueous solution with MPH the dissolution procedure must avoid perchloric acid and nitrate ions must be removed if nitric acid is used. When the solvent extraction procedures are used, it is best to dissolve samples in nitric acid/perchloric acid mixture.

Colour development. Take a 100-ml aliquot of slightly acidic sample solution containing about 0·2 mg of copper. Add 1 ml of 10% hydroxylammonium chloride solution, and complete the determination by one of the following.

1. Add 1 ml of MPH reagent solution, 5 ml of pH 10 buffer solution, and dilute to a specific volume. Mix well and read the absorbance at 426 nm.
2. Add 1 ml of MPH reagent solution, 1 ml of pH 10 buffer solution, transfer quantitatively to a separatory funnel and extract with two 10-ml portions of isopentanol. Combine the extracts in a 25-ml volumetric flask and dilute to the mark with methanol. Mix well and read the absorbance at 426 nm.
3. Add 1 ml of MPTZ reagent solution, 1 ml of pH 6·5 buffer solution, transfer quantitatively to a separatory funnel and extract with 20 ml of isopentanol. Dilute the extract to 25 ml in a volumetric flask. Mix well and read the absorbance at 492 nm.

Calibration curves are constructed from standard solutions treated in the same manner.

RESULTS AND DISCUSSION

Synthesis. The method of Case[5] was modified because it was found that water in the reaction mixture for the preparation of MPH seemed to favour the formation of a secondary product (which was not characterized). For this reason, anhydrous hydrazine was used, anhydrous isopropanol was employed as the solvent and anhydrous magnesium sulphate was added to the reaction mixture. MPH and MPTZ are easier to synthesize than some of the more sensitive reagents which have been proposed.[4]

Colour. The colour of $Cu(MPH)_2^+$ is stable in isopentanol for about 6 hr, after which it begins to fade. The colour of $Cu(MPH)_2^+$ in water is stable for at least 12 hr, after which it begins to fade. The colour of $Cu(MPTZ)_2^+$ in isopentanol is stable for at least 24 hr. The spectral bands are broad. Beer's law is obeyed up to at least 12 ppm with MPH and 10 ppm with MPTZ.

Stoichiometry. Spectrophotometric titration shows that the species $Cu(MPH)_2^+$ and $Cu(MPTZ)_2^+$ are the colour-producing agents in solution. No coloured tris-complex of copper(I) with either reagent was detected at any pH studied.[1] It is possible that the copper is bonded through two nitrogen atoms per ligand to give a complex in which two five-membered rings at right angles to each other are formed.[1,2]

Effects of pH on complex formation. The yellow $Cu(MPH)_2^+$ species is completely formed in aqueous solution and in isopentanol between pH 8 and 11·5. The red-orange $Cu(MPTZ)_2^+$ species is completely formed in isopentanol when extracted from the aqueous phase at pH values between 4 and 10. The formation of both is markedly pH dependent outside these limits.

Suitability as spectrophotometric reagents for copper(I). These reagents are specific, reasonably sensitive and easy to prepare. Of cobalt, iron, nickel, cadmium, molybdenum, calcium, magnesium, chromium, manganese, aluminium, barium, strontium and platinum, only aluminium interferes by forming a precipitate with MPH and only aluminium and chromium interfere by forming a precipitate with MPTZ in a buffered solution. Since $Cu(MPH)_2^+$ and $Cu(MPTZ)_2^+$ can both be extracted, preferably into isopentanol, these interferences can be eliminated. Extraction also reduces the blank value. Ammonium ion, tris(hydroxymethyl)aminomethane, and 2-amino-2-methyl-1-propanol prevent or inhibit the colour development due to $Cu(MPH)_2^+$, probably by formation of non-dissociated complex species with copper(I).

One of the curious properties of MPH and MPTZ is that in contrast to many similar copper reagents, no coloured species are formed with cobalt(II).[1,4,6] Copper may be determined in the presence of 100 times as much iron, even without extraction. No other interferences have been found which cannot be eliminated by extraction. Of the ferroin-type reagents for copper in use at the present time, these two may be said to be among the simplest and least expensive to prepare and use, while giving reasonable sensitivity and maximum selectivity for copper.

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Summary—Two ferroin-type compounds are proposed as spectrophotometric reagents for copper(I): 6-methyl-2-pyridylhydrazidine, which forms a yellow complex with λ_{max} 426 nm and molar absorptivity 700 l.mole^{-1}.mm^{-1}, and 3-(6-methyl-2-pyridyl)-5,6-diphenyl-1,2,4-triazine, which forms a red-orange complex with λ_{max} 492 nm and molar absorptivity of 955 l.mole^{-1}.mm^{-1}. These reagents are specific for copper and the complexes can be extracted into isopentanol for increased sensitivity.

Résumé—On propose deux composés de type ferroïne comme réactifs spectrophotométriques pour le cuivre(I): la 6-méthyl 2-pyridylhydrazidine, qui forme un complexe jaune avec λ_{max} 426 nm et un coefficient d'absorption moléculaire de 700 l.mole^{-1}.mm^{-1}, et la 3-(6-méthyl-2-pyridyl)-5,6-diphényl-1,2,4-triazine, qui forme un complexe rouge-orangé avec λ_{max} 492 mm et un coefficient d'absorption moléculaire de 955 l.mole^{-1}.mm^{-1}. Ces réactifs sont spécifiques du cuivre et les complexes peuvent être extraits en isopentanol pour une sensibilité accrue.

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Amperometric titration of Cd(II), Hg(II) and Zn(II) in molten alkali thiocyanates with electrolytically generated sulphide ions

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FUSED alkali thiocyanates as a solvent have been the subject of a number of investigations in recent years,[1–13] but a paucity of data exists in the literature concerning the precipitation reactions in this value. Ammonium ion, tris(hydroxymethyl)aminomethane, and 2-amino-2-methyl-1-propanol prevent or inhibit the colour development due to $Cu(MPH)_2^+$, probably by formation of non-dissociated complex species with copper(I).

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Amperometric titration of Cd(II), Hg(II) and Zn(II) in molten alkali thiocyanates with electrolytically generated sulphide ions

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FUSED alkali thiocyanates as a solvent have been the subject of a number of investigations in recent years,[1-13] but a paucity of data exists in the literature concerning the precipitation reactions in this solvent.[10] In this work we have investigated the precipitation reactions of some cations [Cd(II), Hg(II), Sn(II), Tl(I) and Zn(II)] by sulphide ions in order to test the feasibility of their titration.

In order to avoid the disadvantages connected with the weighing of titrants, the sulphide ions were produced *in situ* by reduction of thiocyanate at a platinum electrode according to the reaction

$$SCN^- + 2e^- \rightarrow CN^- + S^{2-} \quad (1)$$

the quantitative yield of which has been already checked.[8,9]

The apparatus used was similar to that described elsewhere.[14] In this work a further vessel (anodic compartment) is joined to the main cell (cathodic compartment) by means of a sintered-glass disk.

The quantity of solvent used in the cathodic vessel was about 50 g. The solvent mixture was the sodium thiocyanate–potassium thiocyanate eutectic prepared as described in a previous paper.[13] The solvent in the cell was maintained under vacuum for about 1 hr at a temperature of 443·0 ± 0·2K. The solutes were introduced as pure salts or as pellets of sodium thiocyanate–potassium thiocyanate mixture containing a known weight of metal salts. The concentration of the solutions studied was always in the molality range 3×10^{-4}–2×10^{-3}.

In order to perform electrolysis, platinum electrodes 200 mm^2 in area were used. The current for the production of sulphide ions was supplied by a constant-current electronic generator and measured potentiometrically through the resistance drop across an AEG 100-ohm precision resistor connected in series. The maximum current density was 15 μA/mm^2. Greater current density was not used, in order to prevent sodium ion reduction.[8]

The titration curves were determined amperometrically by recording the diffusion current of the cations by means of a three-electrode Amel model 557/SU polarograph and a Graphispot type GRVAM galvanometric recorder. The potentials were measured *vs.* the glass reference electrode[15,16] standardized as described earlier.[18]

Quantitative results have been obtained for cadmium, mercury and zinc ions, which gave well defined titration curves; typical plots for cadmium and zinc are presented in Fig. 1.

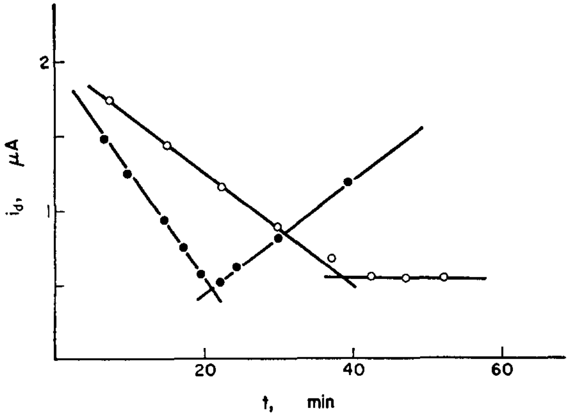

FIG. 1.—Amperometric titration curves of Zn(II) (full points) at −1·0 V and Cd(II) (open circles) at −0·6 V *vs.* Ag/Ag(I) (1*m*).

After the equivalence point the plots of these curves have different slopes, depending on the diffusion potentials of the cations examined. These potentials can lie in the anodic or cathodic branch or in the null current range of the irreversible composite wave which is probably due to the sulphide–polysulphide system. The polysulphide ions, which according to Metzger[9] are probably present, may be formed after the equivalence point from the sulphide ions and sulphur produced by thermal decomposition of the solvent.

The results obtained are summarized in Table I.

TABLE I

Cation	Number of titrations	Concentration range (molality)	S^{2-}-Me(II) mean ratio
Cd(II)	5	5×10^{-4}–2×10^{-3}	1·007
Zn(II)	4	3×10^{-4}–2×10^{-3}	0·982
Hg(II)	3	5×10^{-4}–2×10^{-3}	0·986

In all the titrations the error was always smaller than ±2·5%. Obviously, this result demonstrates that the cyanide ion produced by reaction (1) does not interfere in the precipitation reactions.

On the contrary very large (negative) titration errors have been always obtained for tin(II) and thallium(I) ions.

Acknowledgement—This work was supported by the Italian National Research Council (C.N.R.).

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Summary—The feasibility of the titration of some cations in molten sodium thiocyanate–potassium thiocyanate mixture with electrolytically generated sulphide ions has been tested at 443 K. Quantitative data are given for the titration of cadmium, mercury and zinc ions.

Zusammenfassung—Die Möglichkeit der Titration einiger Kationen in einer Schmelze aus Natrium- und Kaliumthiocyanat mit elektrolytisch erzeugten Sulfidionen wurde bei 443°K geprüft. Quantitative Daten werden für die Titration von Cadmium-Quecksilber- und Zinkionen angegeben.

Résumé—On a essayé la possibilité du titrage à 443°K de quelques cations dans un mélange fondu de thiocyanate de sodium–thiocyanate de potassium avec des ions sulfure engendrés électrolytiquement. On fournit des données quantitatives pour le titrage des ions cadmium, mercure et zinc.

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New chromogens of the ferroin type—VI

Some derivatives of 1- and 3-cyanoisoquinoline and substituted 2-cyanopyridines

(*Received* 26 *January* 1970. *Accepted* 18 *February* 1970)

A VARIETY of new compounds containing the ferroin reacting group (—N=C—C=N—) has recently been synthesized by Case, including some triazines and benzimidazoles from 1- and 3-cyanoisoquinolines,[1] certain new diphenyl and bis(2-pyridyl)-1,2,4-triazines,[2] and some substituted pyridyl tetrazines and pyridazines.[3] As part of a continuing study and search for superior colorimetric

In all the titrations the error was always smaller than ±2·5%. Obviously, this result demonstrates that the cyanide ion produced by reaction (1) does not interfere in the precipitation reactions.

On the contrary very large (negative) titration errors have been always obtained for tin(II) and thallium(I) ions.

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Summary—The feasibility of the titration of some cations in molten sodium thiocyanate–potassium thiocyanate mixture with electrolytically generated sulphide ions has been tested at 443 K. Quantitative data are given for the titration of cadmium, mercury and zinc ions.

Zusammenfassung—Die Möglichkeit der Titration einiger Kationen in einer Schmelze aus Natrium- und Kaliumthiocyanat mit elektrolytisch erzeugten Sulfidionen wurde bei 443°K geprüft. Quantitative Daten werden für die Titration von Cadmium-Quecksilber- und Zinkionen angegeben.

Résumé—On a essayé la possibilité du titrage à 443°K de quelques cations dans un mélange fondu de thiocyanate de sodium–thiocyanate de potassium avec des ions sulfure engendrés électrolytiquement. On fournit des données quantitatives pour le titrage des ions cadmium, mercure et zinc.

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New chromogens of the ferroin type—VI

Some derivatives of 1- and 3-cyanoisoquinoline and substituted 2-cyanopyridines

(*Received* 26 *January* 1970. *Accepted* 18 *February* 1970)

A VARIETY of new compounds containing the ferroin reacting group (—N=C—C=N—) has recently been synthesized by Case, including some triazines and benzimidazoles from 1- and 3-cyanoisoquinolines,[1] certain new diphenyl and bis(2-pyridyl)-1,2,4-triazines,[2] and some substituted pyridyl tetrazines and pyridazines.[3] As part of a continuing study and search for superior colorimetric reagents, the chromogenic reactions of these new compounds with iron(II), copper(I), and cobalt(II) have been examined spectrophotometrically. The results are reported in this brief communication.

Structures of the compounds studied (omitted here for brevity) can be found in the original papers by Case.[1,2,3] For simplicity the compounds (listed below) will be referred to by numeral.

I 6-Methylpicolinimidic acid hydrazide
II 6-Phenylpicolinimidic acid hydrazide
III 3-Isoquinolinecarboximidic acid hydrazide
IV 3-(6-Methyl-2-pyridyl)-5,6-diphenyl-1,2,4-triazine
V 3-(6-Phenyl-2-pyridyl)5,6-diphenyl-1,2,4-triazine
VI 3-(3-Isoquinolyl)-5,6-diphenyl-1,2,4-triazine
VII 3-(6-Methyl-2-pyridyl)-5,6-bis(2-pyridyl)-1,2,4-triazine
VIII 3-(6-Phenyl-2-pyridyl)-5,6-bis(2-pyridyl)-1,2,4-triazine
IX 3-(3-Isoquinolyl)-5,6-bis(2-pyridyl)-1,2,4-triazine
X 3-(3-Isoquinolyl)-1,2,4-triazino[5,6-*f*][4,7]phenanthroline
XI 3-(2-Pyridyl)-5-phenyl-6-(2-pyridyl)-1,2,4-triazine
XII 3-(4-Methyl-2-pyridyl)-5-phenyl-6-(2-pyridyl)-1,2,4-triazine
XIII 3-(4-Phenyl-2-pyridyl)-5-phenyl-6-(2-pyridyl)-1,2,4-triazine
XIV 2-(1-Isoquinolyl) benzimidazole
XV 2-(3-Isoquinolyl) benzimidazole
XVI 2-(1-Isoquinolyl)-3*H*-imidazo[4,5-*h*] quinoline
XVII 2-(3-Isoquinolyl)-3*H*-imidazo[4,5-*h*] quinoline
XVIII 2-(1-Isoquinolyl)-1*H*-imidazo[4,5-*c*] pyridine
XIX 2-(3-Isoquinolyl)-1*H*-imidazo[4,5-*c*] pyridine
XX 2-(1-Isoquinolyl)-5(6)-phenylbenzimidazole
XXI 2-(3-Isoquinolyl)-5(6)-phenylbenzimidazole
XXII 2,4-Diamino-6-(1-isoquinolyl)-1,3,5-triazine
XXIII 2,4-Diamino-6-(3-isoquinolyl)-1,3,5-triazine
XXIV 2-Amino-4,6-bis(1-isoquinolyl)-1,3,5-triazine
XXV 3,6-Bis(4-methyl-2-pyridyl)-dihydro-1,2,4,5-tetrazine
XXVI 3,6-Bis(4-ethyl-2-pyridyl)-dihydro-1,2,4,5-tetrazine
XXVII 3,6-Bis(4-phenyl-2-pyridyl)-dihydro-1,2,4,5-tetrazine
XXVIII 3,6-Bis(4-methyl-2-pyridyl)-1,2,4,5-tetrazine
XXIX 3,6-Bis(4-ethyl-2-pyridyl)-1,2,4,5-tetrazine
XXX 3,6-Bis(4-phenyl-2-pyridyl)-1,2,4,5-tetrazine
XXXI 3,6-Bis(4-methyl-2-pyridyl)-4-phenylpyridazine
XXXII 3,6-Bis(4-phenyl-2-pyridyl)-4-phenylpyridazine

EXPERIMENTAL

Preparative details and elemental analyses of the compounds studied were reported by Case.[1,2,3] The various standard solutions, pH buffers, reagents, and procedures used in this investigation are described in an earlier communication of this series.[4] Mole ratio and conditional formation constants (in ethanol–water mixtures) were determined spectrophotometrically by the method of continuous variations.

RESULTS AND DISCUSSION

All the compounds readily form coloured complexes except the difficultly soluble XXVII and XXX. As expected on the basis of their structures and the steric requirements for chelation, compounds I, II, IV and V do not form coloured complexes with either cobalt(II) or iron(II) but do with copper(I). The pH ranges for colour formation are generally broad. The iron(II) chelates form rapidly between pH 2 and 9, with maximum colour production at pH 5–8. The only exceptions are the iron(II) chelates of X, XXV and XXVI which exhibit maximum colour between pH 3 and 5. Formation of the copper(I) and cobalt(II) chelates occurs rapidly between pH 3 and 11. Maximum colour production results at pH 5–8 for copper and 5–11 for cobalt.

Most of the chelates can be quantitatively extracted in the form of their chloride or acetate salts by a single equilibration with a small portion of isopentanol. The following are only partially extractable: iron(II) chelates of III and IX; copper(I) chelates of X, XXVIII, XXIX and XXX; and cobalt(II) chelates of VII, X, XXVIII and XXXI.

Spectral characteristics are summarized in Table I. The wavelengths given are for maximum absorbance unless otherwise specified, and the molar absorptivity values (ε) correspond to the wavelength cited.

TABLE I.—SPECTRAL CHARACTERISTICS OF THE METAL CHELATES

	Iron(II)		Copper(I)		Cobalt(II)	
Chromogen	λ, *nm*	ε, l.mole^{-1}. mm^{-1}	λ, *nm*	ε, l.mole^{-1}. mm^{-1}	λ, *nm*	ε, l.mole^{-1}.mm^{-1}
I	†	†	425*	550*	†	†
II	†	†	433*	280*	†	†
III	456	$1{\cdot}15 \times 10^{3}$	450*	123*	425*	980*
IV	†	†	492	700	†	†
V	†	†	463	707	†	†
VI	556	$2{\cdot}32 \times 10^{3}$	465	670	512	290
VII	612	$0{\cdot}840 \times 10^{2}$	510	700	463*	210*
VIII	612	950	472	560	463*	250*
IX	569	$1{\cdot}95 \times 10^{3}$	487	550	462*	210*
X	605	$1{\cdot}78 \times 10^{3}$	505*	680*	†	†
XI	558	$2{\cdot}31 \times 10^{3}$	484	550	463*	48*
XII	564	$2{\cdot}33 \times 10^{3}$	496	590	463*	130*
XIII	565	$2{\cdot}44 \times 10^{3}$	490	710	450*	50*
XIV	606	180	437*	96*	412*	$2{\cdot}10 \times 10^{3}$*
XV	447	250	400*	99*	387*	120*
XVI	656	420	450*	137	475*	235*
XVII	425*	89*	437*	55*	412*	52*
XVIII	654	$1{\cdot}19 \times 10^{3}$	400*	84*	400*	300*
XIX	472	490	†	†	†	†
XX	609	810	462*	180*	†	†
XXI	453	350	450*	44*	†	†
XXII	†	†	493	370	†	†
XXIII	†	†	397	490	†	†
XXIV	572	$1{\cdot}45 \times 10^{3}$	412*	120*	515	196
XXV	678	790	453	380	500*	90*
XXVI	542	840	533	700	500*	220*
XXVII	‡	‡	‡	‡	‡	‡
XXVIII	681	780	625*	330*	†	†
XXIX	675	780	612*	160*	†	†
XXX	‡	‡	‡	‡	‡	‡
XXXI	553	$1{\cdot}85 \times 10^{3}$	475	604	500*	240*
XXXII	563	$1{\cdot}87 \times 10^{3}$	455	890	560	170

* Wavelength not a maximum but at shoulder or side of band just before reagent blank absorbance is appreciable.

† Colours and spectra of chelate and chromogen are very similar.

‡ Chromogen not sufficiently soluble for testing.

The most sensitive chromogens of the group for iron are the substituted 1,2,4-triazine derivatives VI, XI, XII and XIII. Yielding iron(II) chelates with high molar absorptivities and extractabilities, these chromogens compare favourably in analytical utility with such outstanding reagents as bathophenanthroline,[5] 2,4,6-tripyridyl-*sym*-triazine[6] and 3-(4-phenyl-2-pyridyl)-5,6-diphenyl-1,2,4-triazine.[7]

Compound XXXII forms the most intensely coloured copper(I) complex of those studied; however, its reactivity with cobalt(II) and iron(II) seriously detracts from its possible analytical use. Less sensitivity but greater selectivity is afforded by the more stereo-selective chromogens IV and V. Popular use of any of these, however, is improbable because of the availability of equally selective but more sensitive copper chromogens—*e.g.*, bathocuproine.[8]

The most sensitive cobalt chromogen of the group is the benzimidazole derivative XIV. Its analytical utility appears promising, although limited by the necessity of making absorbance measurements on the long wavelength side of an absorption band having its maximum in the ultraviolet. Measurement at shorter wavelengths or at the maximum is precluded by the intense absorption by excess of uncomplexed chromogen. Absorbance interferences from copper, iron and nickel constitute another disadvantage.

The metal–ligand ratios and conditional formation constants of certain of the iron(II) chelates are of interest with regard to structural features of the ligands. Pertinent data are given in Table II. An especially interesting finding is that both VII and VIII behave as bidentate rather than terdentate ligands in chelation with iron(II). Both possess multiple ferroin groupings with sufficient versatility to act conceivably either as bi- or terdentate ligands. Since the latter mode should lead to greater

TABLE II.—MOLE RATIOS AND CONDITIONAL FORMATION CONSTANTS OF THE IRON(II) CHELATES

Chromogen	Fe:L	Log K*
VII	1:3	6·3
VIII	1:3	6·3
IX	1:3	13
X	1:3	14
XI	1:3	9·3
XII	1:3	9·3
XIII	1:3	9·5
XIV	1:3	10·4
XV	1:3	9·3
XXIV	1:2	15·2

* Based upon measurements of $5 \times 10^{-5}M$ solutions of the complexes in 65% aqueous ethanol, 0·08*M* in ammonium acetate and 0·02*M* in hydroxylamine hydrochloride.

stability, it is surprising that these ligands co-ordinate preferentially in the bidentate mode. Apparently the terdentate mode is sterically discouraged by the bulky methyl (or phenyl) group adjacent to the nitrogen atom in the substituted pyridyl ring. Steric hindrance of this type was first observed by Stephen[9] in a comparative study of some pyridyl substituted pyrazines. The most reasonable conclusion is that co-ordination of VII or VIII to iron involves the nitrogen atom of the pyridyl ring at position 6 and the nitrogen in position 1 of the triazine ring.

Another surprising observation is that both IX and X prefer a bidentate to a terdentate mode in chelation of iron(II). Similar to VII and VIII, these ligands have multiple ferroin groupings that should permit either bi- or terdentate co-ordination; but, unlike VII and VIII, no significant steric hindrance should be associated with the terdentate mode. The preferred bidentate action of the ligands, therefore, may be presumed to arise from differences in co-ordinating strengths or electron densities of the various nitrogen atoms. Since one of the nitrogen atoms in the triazine ring must be involved, it is more reasonable to conclude that it is the one in positions 1 or 2 rather than 4. If so, then the ligand has no other choice but to assume a bidentate mode, using either the nitrogen in the isoquinolyl or the pyridyl ring to complete the chelation. Which of these two is utilized is suggested by a comparison of the formation constants and spectral characteristics of the iron(II) chelates of VII, VIII, IX and X. Although closely related, the properties of the chelates are grossly dissimilar. This suggests that the nitrogen of the isoquinolyl ring is involved in chelation with IX and X and that of the unsubstituted pyridyl ring in chelation with VII and VIII.

Nothing unexpected is evident for the chelates of XI, XII, XIII, XIV, XV and XXIV. The results in Table II are consistent with the ligand structures.

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Summary—The chromogenic reactions with iron(II), copper(I) and cobalt(II) of 32 recently synthesized pyridazines, triazines, tetrazines and certain other compounds containing the ferroin grouping have been examined spectrophotometrically. Some interesting examples were found of steric and donor-atom selectivities in chelation of iron by ligands containing several ferroin groups. Of the various chromogens studied, the pyridyl and isoquinolyl derivatives of phenyl or pyridyl substituted 1,2,4-triazine show the most promising analytical utility.

Zusammenfassung—Die farbbildenden Reaktionen von 32 neu synthetisierten Pyridazinen, Triazinen, Tetrazinen und anderen die Ferroingruppe enthaltenden Verbindungen mit Eisen(II), Kupfer(I) und Kobalt(II) wurden spektrophotometrisch untersucht. Einige interessante Beispiele sterischer Selektivität und Auswahl des Donoratoms bei der Chelatbildung von Eisen mit mehrere Ferroingruppen enthaltenden Liganden wurden gefunden. Von den verschiedenen untersuchten Farbreagentien versprechen die Pyridyl- und Isochinolylderivate von phenyl- oder pyridylsubstituiertein 1,2,4-Triazin den größten analytischen Nutzen.

Résumé—On a examiné spectrophotométriquement les réactions chromogènes avec les fer(II), cuivre(I), et cobalt(II) de 32 pyridazines, triazines, tétrazines et certains autres composés contenant le groupement ferroïne, récemment synthétisés. On a trouvé quelques exemples intéressants de sélectivités stériques et de donneurs d'atome dans la chélation du fer par des ligands contenant plusieurs groupes ferroïne. Des divers chromogènes étudiés, les dérivés pyridyl et isoquinolyl de la 1,2,4-triazine phényl ou pyridyl substituée montrent l'utilité analytique la plus prometteuse.

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Determination of alumina in sintered aluminium powder by activation with 14-MeV neutrons*

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S.A.P. (sintered aluminium powder) is a sinter of alumina in an aluminium matrix. The alumina content varies from 4 to 14%. The mechanical and physical properties, and the possible applications, depend largely on the dispersion of the alumina in the matrix.

In this work, we describe the determination of the homogeneity and content of the alumina in extruded S.A.P. bars.

The conventional chemical determination of alumina in S.A.P. is not very suitable, as special apparatus is necessary and the operational time is very long. On the other hand, as neutron-activation analysis is very quick for the determination of oxygen in some materials, it is convenient to use it for the indirect evaluation of alumina in S.A.P. by determination of the oxygen content.

The fast neutron reaction $^{16}O(n, p)^{16}N$ is widely used[2-5] because there are easily operated small neutron generators which produce neutrons of 14-MeV energy. The cross-section of this reaction with 14-MeV neutrons is between 35 and 40 mbarn, which is suitable for our purpose. Furthermore there are very few interferences in the reaction and in the subsequent measurement of the induced ^{16}N activity and only a short time is required to reach saturation activity. This reaction also gives the possibility of counting highly energetic beta-particles and gamma-radiation, because the ^{16}N decays with a half-life of 7·14 sec by beta-emission of 10·4 MeV (26%) to the fundamental state of ^{16}O 4·26

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* Work carried out at C.C.R. EURATOM-ISPRA, during tenure of a fellowship of the Consejo Nacional de Investigaciones Científicas y Técnicas de la República Argentina.

Zusammenfassung—Die farbbildenden Reaktionen von 32 neu synthetisierten Pyridazinen, Triazinen, Tetrazinen und anderen die Ferroingruppe enthaltenden Verbindungen mit Eisen(II), Kupfer(I) und Kobalt(II) wurden spektrophotometrisch untersucht. Einige interessante Beispiele sterischer Selektivität und Auswahl des Donoratoms bei der Chelatbildung von Eisen mit mehrere Ferroingruppen enthaltenden Liganden wurden gefunden. Von den verschiedenen untersuchten Farbreagentien versprechen die Pyridyl- und Isochinolylderivate von phenyl- oder pyridylsubstituiertein 1,2,4-Triazin den größten analytischen Nutzen.

Résumé—On a examiné spectrophotométriquement les réactions chromogènes avec les fer(II), cuivre(I), et cobalt(II) de 32 pyridazines, triazines, tétrazines et certains autres composés contenant le groupement ferroïne, récemment synthétisés. On a trouvé quelques exemples intéressants de sélectivités stériques et de donneurs d'atome dans la chélation du fer par des ligands contenant plusieurs groupes ferroïne. Des divers chromogènes étudiés, les dérivés pyridyl et isoquinolyl de la 1,2,4-triazine phényl ou pyridyl substituée montrent l'utilité analytique la plus prometteuse.

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Determination of alumina in sintered aluminium powder by activation with 14-MeV neutrons*

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S.A.P. (sintered aluminium powder) is a sinter of alumina in an aluminium matrix. The alumina content varies from 4 to 14%. The mechanical and physical properties, and the possible applications, depend largely on the dispersion of the alumina in the matrix.

In this work, we describe the determination of the homogeneity and content of the alumina in extruded S.A.P. bars.

The conventional chemical determination of alumina in S.A.P. is not very suitable, as special apparatus is necessary and the operational time is very long. On the other hand, as neutron-activation analysis is very quick for the determination of oxygen in some materials, it is convenient to use it for the indirect evaluation of alumina in S.A.P. by determination of the oxygen content.

The fast neutron reaction $^{16}O(n, p)^{16}N$ is widely used[2-5] because there are easily operated small neutron generators which produce neutrons of 14-MeV energy. The cross-section of this reaction with 14-MeV neutrons is between 35 and 40 mbarn, which is suitable for our purpose. Furthermore there are very few interferences in the reaction and in the subsequent measurement of the induced ^{16}N activity and only a short time is required to reach saturation activity. This reaction also gives the possibility of counting highly energetic beta-particles and gamma-radiation, because the ^{16}N decays with a half-life of 7·14 sec by beta-emission of 10·4 MeV (26%) to the fundamental state of ^{16}O 4·26

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* Work carried out at C.C.R. EURATOM-ISPRA, during tenure of a fellowship of the Consejo Nacional de Investigaciones Científicas y Técnicas de la República Argentina.

MeV (68%) in coincidence with 0·14-MeV gamma-radiation and 3·28 MeV (5%) in coincidence with 7·2-MeV gamma-radiation. Both beta and gamma radiations are able to pass through a common aluminium crystal mount.

This technique of oxygen analysis is specific with most samples but, if interferences are present, it is possible to eliminate them by an absorption screen for beta-radiation[4] and a high discrimination level for gamma-radiation.[5–7] It is also possible to use a multichannel analyser. The principal interfering species to eliminate are fluorine, boron, sulphur, aluminium, magnesium, silver and others which give short-lived nuclides. Fluorine and boron are among the most difficult to eliminate.

EXPERIMENTAL

Equipment and reagents

Fast neutrons of 14-MeV energy were produced by the T(d, n)^{4}He reaction in the IMICAM-CISE 150-kV generator.[8]

Figure 1 shows a block diagram of the neutron generator, pneumatic system and counting equipment.

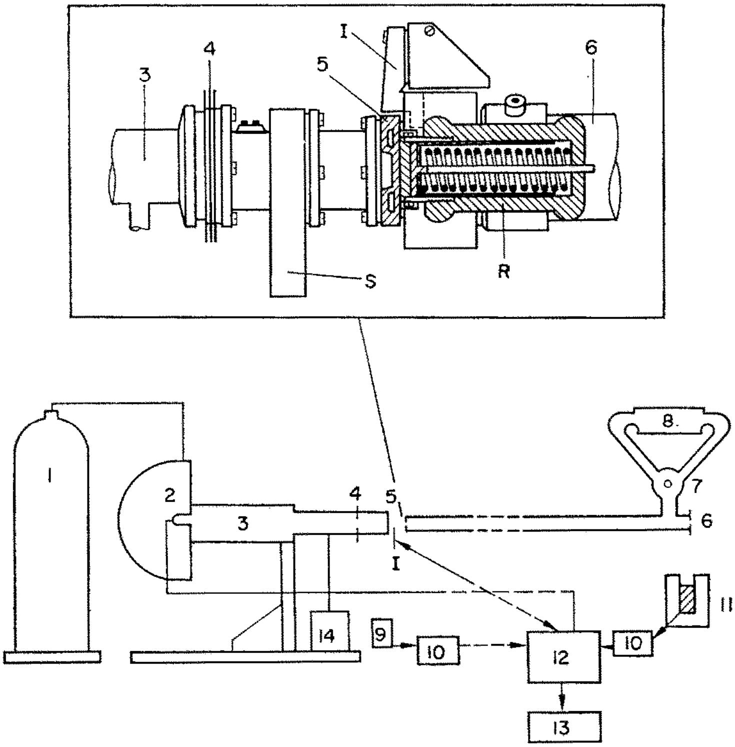

FIG. 1.—Installation scheme.

1—High voltage; *2*—ion source; *3*—accelerator tube; *4*—focussing electrode; *5*—tritium target support; *6*—pneumatic tube; *7*—valve; *8*—compressor; *9*—Hornyak crystal; *10*—amplifiers; *11*—counting unit; *12*—programmer; *13*—neutron counter; *14*—vacuum pumps; *I*—switch; *R*—rabbit. The upper diagram shows a detail of the target zone.

The high voltage source (1) is a Cockroft-Walton system. The ion source (2), of radio frequency type, with an axial magnetic field, is situated in the generator pillow. Between the high voltage pillow and the accelerator tube (3), which is horizontal, there is only one intermediate electrode, used for the electrostatic focussing of the deuteron beam. An additional electrode (4), at the end of the tube, intercepts the external corona of the deuteron beam, and the ionic current collected gives information on how good the focus is.

To prevent unnecessary use of the target, at the end of irradiation a switch (5) sends a signal which causes introduction of a screen *s* in the path of the deuteron beam, and reduces to zero, by a variable transformer, the voltage applied to the ion source.

A titanium–tritium target (0·062 Ci/mm^2) is mounted on a support that has annular refrigeration. It is used to obtain a neutron flux of 10^6 n.mm^{-2}.sec^{-1} by the T(d, n)^{4}He reaction.

The fast-neutron flux was monitored continuously with a Hornyak crystal[9] at a fixed distance from the target, where the reading could be assumed proportional to the neutron production rate.

Transfer of the sample to the flux zone and from there to the counter is *via* a pneumatic tube system (6), because of the short half-life of ^{16}N. This is done by reversing the air-flow by means of a reverse flow valve (7) which inverts the compressor flow (8).

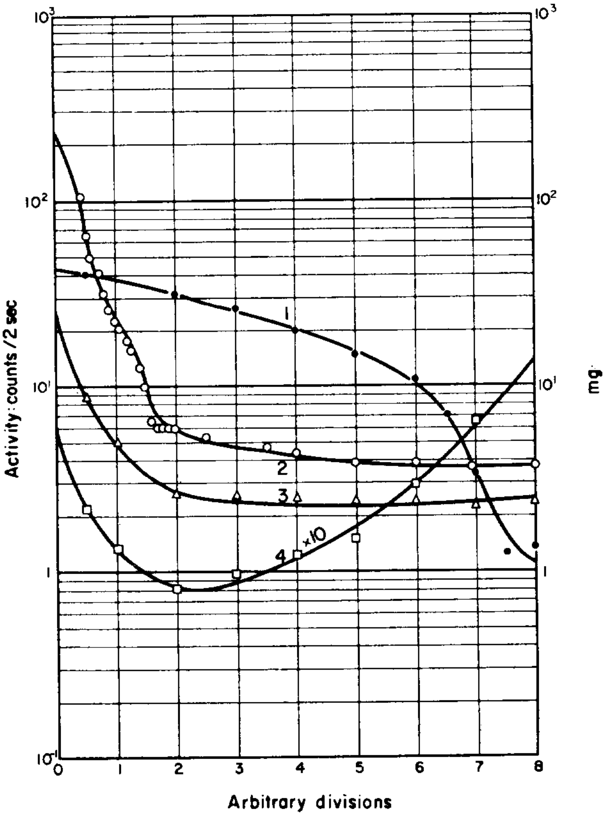

FIG. 2.—Determination of the sensitivity.
1—^{16}N activity which corresponds to 1 mg of oxygen; *2*—background activity (*b*); *3*—minimum number of counts detectable; $n_e = 0{\cdot}26\,[1 + \sqrt{(1 + 14b)}]$; *4*—sensitivity in mg.

A programmer system (12) allows the automatic realization, by means of a switch signal, of the following steps: confirmation of correct sample positions, neutron counting during the irradiation time, and automatic interruption of neutron flux at the end of irradiation. The samples must be introduced in a reproducible way, behind the neutron source; the sample is situated in the centre of the head of a rabbit by means of an adjustable ring.

The rabbit consists of a polyethylene plastic cylinder 0·20 m long with a diameter of 70 mm. Because of the high-gradient neutron flux in the neighbourhood of the source, there is a thin stainless-steel dismountable window in the head of the rabbit. A piston with a polyurethane coat compresses the sample against the window. A full length spring is axially located in the cylinder, in order to absorb the collision impact when the rabbit strikes the source. The rabbit head operates, *via* a switch *I*, a red light to indicate correct positioning of the sample. The counting system consists of a 75 × 75 mm NaI(Tl) crystal and is in optical contact with a "Dumond" multiplier phototube.

Pulses from the phototube are fed to a preamplifier and model AMZ linear amplifier with a discrimination threshold between 0·2 and 4·2 V, and a model CT6 scaler and a unit measuring a prefixed time. All of these were constructed in the Electronic Laboratory of CCR Euratom Ispra. An Olivetti ST2 punch is also used.

Procedure

Irradiation. Individual samples were irradiated for 30 sec and transferred to the NaI(Tl) detector by the pneumatic system in approximately 10 sec. The generator was operated at a deuteron beam current of 200 μA, and accelerating voltage of 125 kV and with a 4-Ci titanium–tritium target.

The determination of the flux was not necessary because a chemically analysed reference S.A.P. standard and a nylon standard were used.

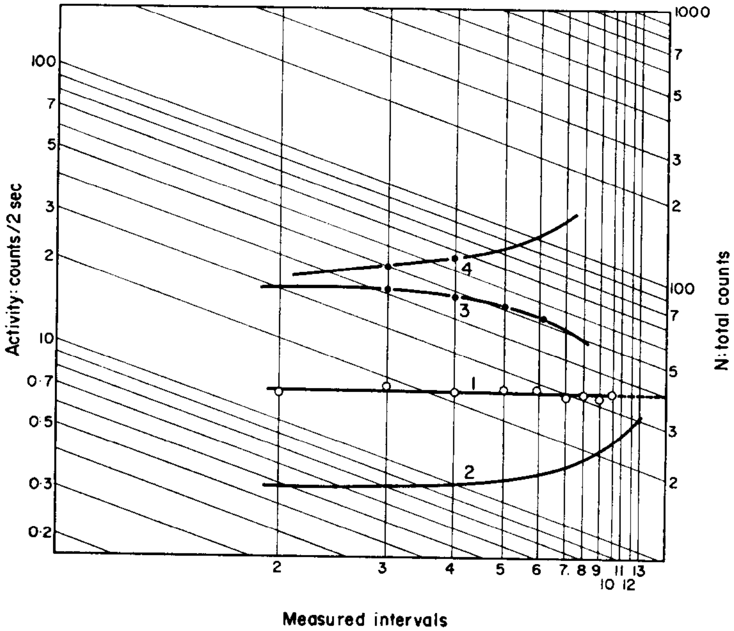

FIG. 3.—Graphic construction for the evaluation of total ^{16}N activity. *1*—Total activity of a pure ^{16}N source (experimental); *2*—total activity of ^{16}N and another activity of $t_{1/2}$ = 20 sec; *3*—total activity of a radioisotope of $t_{1/2}$ = 5 sec; *4*—total activity of a radioisotope of $t_{1/2}$ = 10 sec. Values from reference (6).

The samples and the standard were cylinders 10 mm long and 10 mm in diameter. Both solid samples were placed in the axis of the rabbit head. No containers were used; therefore no problems arose due to oxygen in the containers.

Counting. An irradiation of 2 min and an immediate multichannel counting shows that the fast neutron reactions ^{27}Al(n, p)^{27}Mg, ^{27}Al(n, α)^{24}Na, ^{27}Al(n, γ)^{28}Al with the aluminium of the matrix are the principal interferences. A discrimination of 5·5 arbitrary divisions was used to eliminate them. To avoid the contribution of the oxygen activity from the rabbit materials or of the air in the vessel, the samples are removed from the counter by the operator and inserted by hand in a prefixed place above the crystal with a plastic guide.

Measurement of the ^{16}N was made by counting all the pulses with energy above 3 MeV for 10 intervals of 2 sec in 2π geometry. In these conditions the sensitivity of the method for oxygen determination is 0·2 mg. Figure 2 shows sensitivity *vs.* discrimination level.

The accuracy of the oxygen determination depends on the determination of the ^{16}N activity. Because the source has a short life and quickly arrives at background activity, the optimum counting time is necessarily short for determination of the integral activity of nitrogen-16.

The total sample activity is determined by Girardi and Pauly's graphical integral method. In the nomogram shown in Fig. 3 the accumulated activity value is plotted for each interval p = 2 sec. In this form a line parallel to the x axis is obtained. The extrapolated value gives the total number of counts N produced from the beginning of counting. The plot of our measurements produces a horizontal line, meaning that only ^{16}N is counted. In fact, the curves which belong to radioisotopes of different half-life and which are also plotted do not give a horizontal line and can be easily discarded. Even mixtures with ^{16}N give a line which is not horizontal.

RESULTS

The results were normalized to a 10^4 neutron flux and for a 10-sec count. When a nylon standard was used the effect of the self-absorption of the nitrogen-16 gamma rays of the samples was neglected. This correction was less than the error limits of the method for the range of samples and standards used.

In Tables I and II are shown the results obtained with a known S.A.P. standard and a nylon standard with a content of 106 mg of oxygen.

TABLE I.—Al_2O_3 CONTENT OF S.A.P., MEASURED *vs.* STANDARD S.A.P. (4% Al_2O_3)

Sample	Weight *g*	No. of determinations	Mean Al_2O_3 %	Mean error, % Al_2O_3
FF 23 C	2·154	10	$4{\cdot}2_8$	$0{\cdot}1_3$
FF 24 T	2·132	10	$4{\cdot}7_4$	$0{\cdot}1_4$
FF 24 C	2·131	10	$4{\cdot}3_1$	$0{\cdot}1_8$
FF 20 C	2·177	6	10·9	$0{\cdot}9_0$
FF 20 T	2·192	6	$10{\cdot}1_6$	$0{\cdot}4_8$

Sample FF 23 T is taken as reference standard, containing 4·0% of Al_2O_3; T and C denote the top and bottom of a 2-m extruded bar.

TABLE II.—Al_2O_3 CONTENT OF S.A.P. MEASURED *vs.* NYLON STANDARD (106 mg OF OXYGEN)

Sample	Weight *g*	No. of determinations	Mean Al_2O_3 %	Mean error, % Al_2O_3
FF 23 T	2·030	22	$3{\cdot}6_5$	$0{\cdot}1_0$
FF 23 C	2·154	12	$3{\cdot}7_4$	$0{\cdot}1_2$
FF 24 T	2·132	11	$4{\cdot}0_4$	$0{\cdot}1_2$
FF 24 C	2·131	10	$3{\cdot}7_2$	$0{\cdot}1_6$
FF 20 C	2·177	9	$9{\cdot}1_3$	$0{\cdot}3_5$
FF 20 T	2·192	15	$9{\cdot}5_5$	$0{\cdot}3_2$

The results obtained show that at the higher levels of oxygen content in S.A.P. (2–7%) the relative mean error of the method is approximately 5%. Chemical analysis gives a better precision but nevertheless is very complicated and slow.

The difference between the results obtained with nylon or S.A.P. standards can be explained by their different neutron dispersion.

The high flux gradient present in the irradiation geometry can be a source of error if the position of samples and comparison standard are not exactly reproduced, especially with thick samples. It is possible to overcome this error by the use of internal monitoring of the neutron flux. As an example, we used the aluminium of the matrix as an internal flux monitor. By the reaction ^{27}Al(n, p)^{27}Mg, aluminium is activated to ^{27}Mg of 8·9 min half-life. Gamma-rays of 0·84 and 1·02 MeV are emitted. The specific activity of ^{27}Mg, at zero time, is proportional to the incident neutron flux. Measurements of the ^{27}Mg were made with 5 counts at intervals of 1 min, in the same geometrical conditions, the first of them 2 min after the end of irradiation.

Now with the use of the internal flux monitoring standard we indeed obtain a better precision. For sample FF23C a mean value of 3·83% of Al_2O_3 content was obtained, with a mean relative error of 2% for 12 determinations. In this case the precision is increased but so is the analysis time. For this reason the external standard method was used for the other samples.

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Summary—Fast neutrons of 14 MeV produced in the IMICAM CISE 150-kV generator by the (d, t) reaction in a tritium–titanium target, were used in the indirect determination of Al_2O_3. The samples were irradiated for 30 sec and the total ^{16}N activity was determined, by counting for ten 2-sec periods and graphically integrating. The standards were a known sintered aluminium powder and nylon pieces of identical shape. The method is competitive with the chemical one, because of its quickness, sensitivity and precision.

Zusammenfassung—Schnelle Neutronen von 14 MeV, die im IMICAM CISE 150 kV-Generator durch (d, t)-Reaktion in einem Tritium–Titan-Target erzeugt wurden, fanden Anwendung bei der indirekten Bestimmung von Al_2O_3. Die Proben wurden 30 sec bestrahlt und die gesamte ^{16}N-Aktivität durch Zählen über zehn 2 sec-Abschnitte und graphische Integration bestimmt. Als Standards dienten ein bakanntes gesintertes Aluminium-pulver und Nylonstücke von identischer Form. Das Analysenverfahren kann wegen seiner Geschwindigkeit, Empfindlichkeit und Genauigkeit mit dem chemischen in Konkurrenz treten.

Résumé—On a utilisé les électrons rapides de 14 MeV produits dans le générateur de 150 kV IMICAM CISE par la réaction (d, t) dans une cible tritium–titane dans le dosage indirect de Al_2O_3. Les échantillons ont été irradiés pendant 30 s et l'on a déterminé l'activité totale 16N, en comptant pendant dix périodes de 2 s et en intégrant. Les étalons étaient une poudre d'aluminium fritté connue et des morceaux de nylon de même forme. La méthode est concurrentielle avec la méthode chimique, à cause de ses rapidité, sensibilité et précision.

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TALANTA REVIEW*

RADIOACTIVE KRYPTONATES AND THEIR USES IN CHEMICAL ANALYSIS

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Summary—A review is presented of the uses of radioactive kryptonates in chemical analysis.

A NEW GROUP of radioactive tracers became available to analytical chemists in 1957, as a result of the pioneering work of Chleck and his co-workers[1–5] on the preparation, properties and possible uses of radioactive kryptonates. From this work it would seem that radioactive krypton-85 can be incorporated into such a variety of materials that it can be considered a universal radioactive tracer. Subsequent theoretical and practical studies have shown that kryptonates have applications in several areas of science and technology, but this review is concerned solely with their applications to analysis.[6–12]

DEFINITION AND CLASSIFICATION OF RADIOACTIVE KRYPTONATES

The term "radioactive kryptonates" is used for substances into which atoms or ions of the radioactive nuclide krypton-85 are incorporated, regardless of the structure of the substance. The process of incorporating the krypton into the solid carrier is called *kryptonation*. "Radioactive kryptonate" is the generic term for krypton carriers, regardless of the steric distribution of atoms or ions of the krypton in the kryptonate.

Radioactive kryptonates of solid systems with an ionic, atomic, molecular or metal crystalline lattice, amorphous substances and mixed amorphous–crystalline systems have been prepared. Almost 200 chemical substances have been kryptonated and this number is steadily increasing.[9,10,14–22]

We will use as a symbol for radioactive kryptonates $A[^{85}Kr]$, where A is the carrier substance.

The possibilities of incorporating radioactive krypton atoms into the carrier substance are mainly dependent upon the lattice structure. Solid crystalline substances show many defects in the lattice, and it is the defects of the carrier which are the most advantageous sites for the hetero krypton atom.

Thus, during formation of the radioactive kryptonate, the krypton-85 atoms can be incorporated into the carrier in the positions[13,22,23] of lattice vacancies, where the krypton atoms will have a structural substitutional function; between planes of the structural elements of the lattice, with an interstitial function; of cavities in the crystalline lattice of the carrier's clathrate structure; of other types of dislocation defects in the carrier lattice; of microbubbles in the carrier material.

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PREPARATION OF RADIOACTIVE KRYPTONATES

For the preparation of radioactive kryptonates there are several methods known, which can be divided into two groups: kryptonation of the carrier during formation of the solid phase; kryptonation of the carrier in the solid phase.

The carrier can be kryptonated during formation of the solid phase by crystallization of the carrier substance from a melt or solution in an atmosphere of radioactive krypton or by sublimation of the carrier substance in an atmosphere of radioactive krypton.

Solid phase carriers can be kryptonated by bombardment of the solid carrier substance with accelerated radioactive krypton ions, or by diffusion of radioactive krypton into the solid carrier substance at high pressure and temperature.

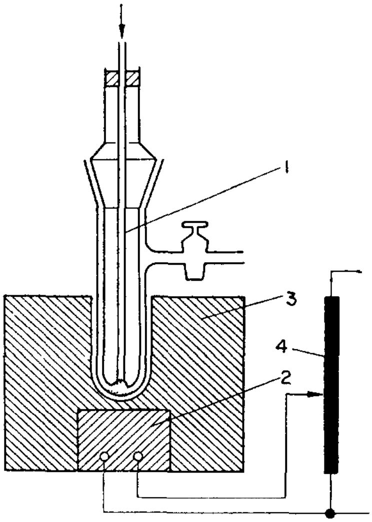

FIG. 1.—Scheme of apparatus for sublimation kryptonation.[25]
1—Sublimation apparatus; *2*—electrical heating; *3*—aluminium block; *4*—transformer.
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The kryptonation technique employed depends mainly upon the character of the carrier and how the radioactive kryptonate is to be used.

Kryptonation during the formation of the carrier's solid phase is of value mainly for the preparation of radioactive kryptonates of the clathrate type. Chleck[1,2] prepared radioactive clathrates of hydroquinone with krypton by slow crystallization of hydroquinone from a melt in an atmosphere of krypton-85 at high pressures. The method of crystallization from a melt is more advantageous than that of crystallization from solution, because it does away with the need for filtration, washing and drying of the kryptonate. It has been modified for the preparation of radioactive hydroquinone kryptonates with high specific activity.[24]

The condensation of the carrier substance during sublimation offers very favourable conditions for incorporation of radioactive krypton atoms into the crystalline lattice of the carrier, mainly in those cases when the subliming carrier forms a clathrate type crystalline lattice,[23,25] and the apparatus is very simple (Fig. 1).

Solid state carrier kryptonation methods represent the most widespread procedure for the preparation of radioactive kryptonates.

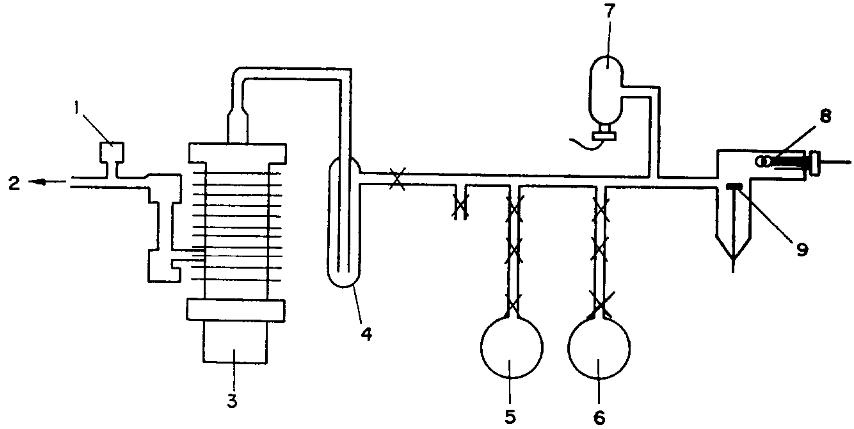

FIG. 2.—Apparatus for ion bombardment.[5]
1—Thermocouple gauge; *2*—forepump; *3*—diffusion pump; *4*—cold trap; *5*—krypton; *6*—^{85}Kr; *7*—ion gauge; *8*—electron gun; *9*—target.
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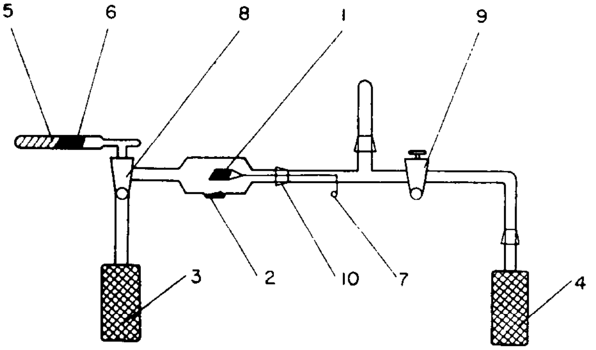

FIG. 3.—Equipment for the preparation of radioactive kryptonates by ion bombardment according to Č. Jech.[27]
1—Anode, *2*—cathode; *3*, *4*—active carbon; *5*—tube with metallic calcium; *6*—glass wool; *7*—platinum eye; *8*, *9*—vacuum valves; *10*—ground joint.
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The technique of kryptonation by bombardment of solid carriers is based on the generation of krypton-85 ions and their acceleration in an electrostatic field to different energies (5–160 keV). The beam of accelerated ions is focused towards the solid carrier target, connected with the negative electrode. Solid carriers with low vapour pressure are regularly kryptonated by this method.

Figure 2 is a diagram of the apparatus for bombardment kryptonation of a target with ^{85}Kr ions at a potential of about 10 kV.[5]

The apparatus may also have an electromagnetic separator,[26] which separates ions according to their specific charge and permits the focusing of krypton-85 ions on the solid target.

Jech[27,28] worked out an instrumentally simple method for kryptonation with accelerated krypton ions. The kryptonated target is inserted between the electrodes of a Tesla transformer. The high-voltage high-frequency discharge ionizes the krypton and accelerates the krypton ions, which are then captured in the crystalline lattice of the target substance. The scheme of the apparatus is shown in Fig. 3. The adsorption

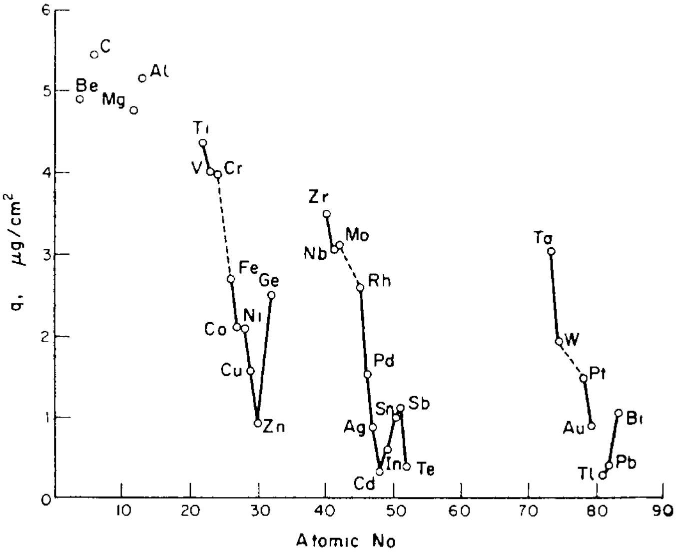

FIG. 4.—Saturation values (q) of Kr in different targets.[26]
0·1 μA . mm^{-2}; 45 keV energy.
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properties of active carbon are utilized for the preparation of the vacuum in the bombardment apparatus and also for binding of the radioactive gas. The adsorption and release of the gas is carried out by changing the temperature of the active carbon.

The sample is placed in the sample chamber. The apparatus is connected by the ground joint *10*, the vacuum stop-cock *9* is opened and the ampoule with active carbon is immersed in liquid nitrogen. Air is adsorbed on the active carbon and the vacuum measured with the Tesla instrument. When a sufficient vacuum has been attained, stop-cock *9* is closed and stop-cock *8* opened, so that krypton-85 fills the anodic space. The anode *1* is formed by an aluminium plate fixed on a platinum wire, which is sealed in the glass vacuum apparatus in such a way that a little eye *7* sticks out. The krypton ions are accelerated by the high-frequency discharge of the Tesla instrument. One pole is attached to the eye forming the anode, the other—fitted with an aluminium plate to give a bigger surface—forms the cathode *2*, and is placed accurately under the sample. Discharge is made in short bursts (a few seconds) to prevent the glass and the sample from preheating. Then the ampoule *3* is immersed in liquid nitrogen and krypton-85 is adsorbed on the active carbon. Stop-cock *8* is closed and stop-cock *9* opened, the pressure rises and the sample is taken out. Ampoule *3*, filled with active carbon carrying the adsorbed krypton, is connected with a little tube filled with metallic calcium, *5*, which serves for the capture of air residues from the gaseous krypton. The ground joint *10* allows the apparatus to be filled with krypton.

When kryptonation is carried out by the method of ionic bombardment a krypton-85 saturation value is reached which is a periodic function of the atomic number of the kryptonated element (Fig. 4).[26]

Solid carriers are often kryptonated by diffusion of the krypton into the solid substance at high pressure and temperature. Pressure bombs are used and a drawback of the method is that after kryptonation the residue of krypton-85 is lost, when the pressure bomb is opened.

Losses of radioactive krypton are markedly lowered by use of microdiffusion techniques,[29,30] which are advantageous for powder samples. This method is very important for the preparation of radioactive kryptonates utilized in analytical applications.

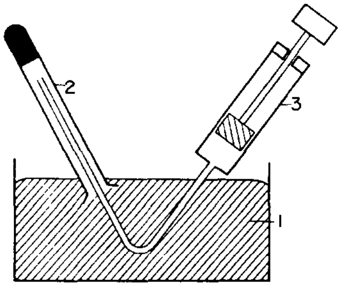

FIG. 5.—Filling of capillaries with radioactive krypton.[29]
1—Vessel with mercury; *2*—sample in capillary; *3*—syringe.
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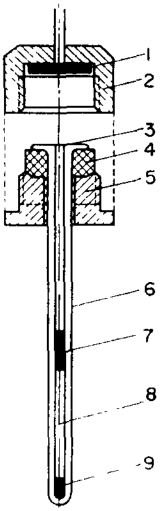

FIG. 6.—Diffusion kryptonation.[29]
1—Matrix sealing; *2*—matrix; *3*—ground part of capillary; *4*—rubber sealing;
5—screw with opening; *6*—glass capillary; *7*—movable mercury plug; *8*—gaseous ^{85}Kr;
9—sample.
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Kryptonation is carried out in thick-walled glass capillaries of 0·24 m length. The mouth of the capillary, with the sample, *2*, is immersed in a beaker containing mercury, *1*. With an injection syringe *3*, air is exhausted and the whole capillary filled with mercury (Fig. 5). The needle is taken out and the needle of another injection syringe, filled with krypton-85 is put in. By injection of krypton, mercury is pushed out from the capillary until only a 4–8 mm length is left at the mouth of the capillary.

The capillary is mounted with a rubber seal and attached to a holder (Fig. 6). Then the capillary is attached to a nitrogen bomb through a copper spiral tube. The pressure is accurately set by an incorporated needle valve, and after the necessary kryptonation time the valve on the bomb is closed and the sealing screw between the bomb and the needle valve is released. Then the needle valve is opened, so that the pressure reaches atmospheric. The capillary is taken out, the mercury removed and the end of the capillary is cut off. The radioactive kryptonate is put into a beaker fitted with a ground joint.

The amount of radioactive krypton incorporated into the carrier by diffusion techniques depends upon the pressure, time and temperature of kryptonation.

PROPERTIES OF RADIOACTIVE KRYPTONATES

The kryptonate can be viewed either as a carrier of krypton-85 or as a chemical labelled with krypton-85 tracer. In chemical analysis the krypton-85 nuclide plays the role of a radioactive tracer.

Krypton-85 has a half-life of 10·27 yr and decays almost entirely by 0·672-MeV β-emission. Krypton-85m has a half-life of 4·36 hr and the decay is associated with 0·305-MeV γ-radiation and 0·830-MeV β-emission. Thus the nuclear characteristics of the isotope make it well suited for the uses described below.

The general properties of the radioactive kryptonates are determined by the properties of the carrier and by the method and conditions of kryptonation. An important requirement in using radioactive kryptonates for chemical analysis is stability with respect to temperature, time and chemical composition of the medium in which the radioactive kryptonate is stored.

The basis of the use of radioactive kryptonates in analytical chemistry is that during the chemical reaction, the crystalline lattice of the kryptonated carrier is destroyed, the carrier consumed and the radioactive krypton released.

If the radioactive kryptonate is to function as an analytical reagent, the amount of krypton-85 released during the reaction must be proportional to the amount of the substance or component to be determined by analysis, *i.e.*, krypton is homogeneously distributed throughout the carrier. If the kryptonate is to function as an titrimetric indicator, krypton-85 must be released at the equivalence point.

Homogeneous distribution of krypton in the carrier substance can be expected in kryptonates prepared by kryptonation of the carrier during formation of the solid phase, *viz.*, during crystallization and sublimation. Kryptonates prepared by these methods are sufficiently stable for analytical use at laboratory temperature. Chemical and kinetic properties of the carrier are only slightly influenced by changes of its lattice characteristics by the presence of the krypton-85 atom in the crystalline lattice.

Radioactive kryptonates with a clathrate crystalline structure also have homogeneous krypton distribution throughout the clathrate cage.[31,32] Hydroquinone seems to be a very advantageous carrier component, because it has an open crystalline structure and cavities of favourable dimensions, and $[C_6H_4(OH)_2]_3[^{85}Kr]$ has been found useful.

The krypton in kryptonates prepared by diffusion technique and by bombardment with ions is distributed inhomogeneously. The krypton atoms are concentrated near to the surface, the depth of their penetration being about 10–10^2 μm. Radioactive kryptonates prepared by diffusion techniques confirm dependences derived from the theory of diffusion phenomena, but according to Chleck[4] the release of krypton—the dekryptonation process—does not occur by a normal diffusion mechanism. For a certain carrier the amount of krypton released from the kryptonate is a function of temperature. During the bombardment of carrier with accelerated krypton ions, the surface layers of the lattice may be disturbed, depending on the energy of the ions.

For analytical purposes the amount of krypton released during the analytical reaction can be determined by standard radiochemical measurement of the activity of the released gas or the residual kryptonate.

Work with radioactive kryptonates needs a minimum of safety precautions, because noble gases do not enter into metabolic systems. Another advantage in working with kryptonates is that krypton-85 is bound to a solid carrier, so work with it is easier and more convenient than with gaseous radioactive krypton.

USES OF RADIOACTIVE KRYPTONATES IN CHEMICAL ANALYSIS

Analytical methods which use radioactive kryptonates are typical examples of "radio-release" methods, *i.e.*, a group of analytical methods based on the release and measurement of radioactive reaction products.[8,11,33–35]

Radio-release methods depend on the selective reaction of the non-radioactive component being determined or the auxiliary reagent (for example the titration solution) with the radioactive agent (in our case with the radioactive kryptonate). During reaction the radioactive component is released, mostly in gaseous form. The determination can be made, (*i*) with a calibration curve, (*ii*) by comparison with a standard, or (*iii*) by titration.

The following are examples of the analytical uses of radioactive kryptonates.

Analysis of gases

Work with radioactive kryptonates has been directed mainly towards the determination of gaseous components and traces of impurities in air. Methods have been developed for the determination of: ozone, oxygen, sulphur dioxide, fluorine, chlorine, chlorine trifluoride, nitrogen dioxide, nitric oxide, amines and hydrogen. Some of these methods are intended for the determination of these components in the atmosphere of other planets (*e.g.*, Mars and Venus). These methods are also of great importance in industrial hygiene for the determination of components in the atmosphere of various hazardous work places.

Oxygen.[3] Krypton-85 is released from radioactive kryptonates during their oxidation, owing to the chemical destruction of the surface layers, the amount being proportional to the degree of oxidation and thus to the concentration of oxygen. The oxidation rate of a substance is generally a function of the temperature and oxygen concentration. Most substances are coated with an oxide film, or in the presence of oxygen an oxide film is quickly formed. This surface film prevents further oxidation. The oxidation rate becomes in practice independent of oxygen concentration and approaches a reaction of zero order. Because of this phenomenon, it was assumed from the start that carbon would be a suitable material for the determination of oxygen. Tests with kryptonated spectroscopically pure graphite rods at various temperatures, pressures and oxygen concentrations proved the applicability of this method.

Figure 7 shows these dependences. It is obvious that as the oxygen concentration changes so the activity of the kryptonate decreases. In large concentrations of oxygen the activity decrease with time is not linear.

The rate of activity decrease of pyrolytic graphite kryptonate as a function of the log of the oxygen concentration was found to be linear at constant temperature for various temperatures. The rate at 1050° is sufficient for the determination of oxygen in the range usually required (0·1 vol. % and total pressure 13–130 mbar, which corresponds to 0·01–0·13 mbar partial pressure of oxygen). The relation $\mathrm{d}(S/S_0)/\mathrm{d}t$, *i.e.*, the rate of loss of kryptonate activity and decrease in oxygen concentration, is given by the equation

$$\frac{\mathrm{d}(S/S_0)}{\mathrm{d}t} = K_1[\mathrm{O}_2]^{1/2}. \tag{1}$$

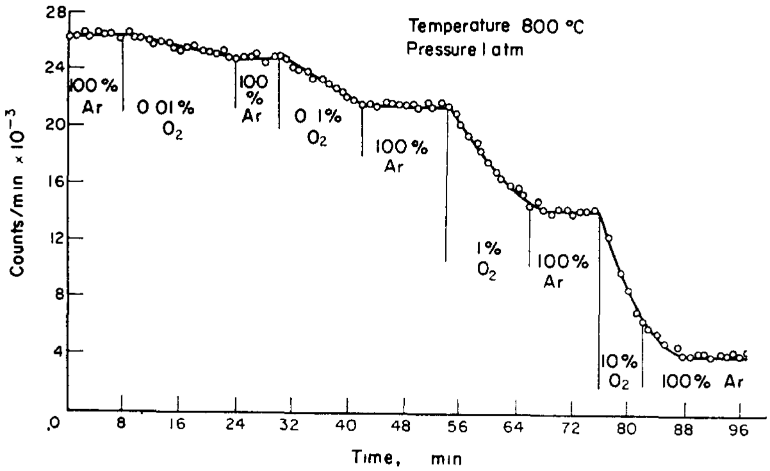

Fig. 7.—Decrease in activity of pyrolytic graphic kryptonate at various O_2 concentrations.[3]
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By use of the radioactive pyrolytic graphite kryptonate it proved possible to determine 2·2 ppm of oxygen in argon.

By the use of radioactive copper kryptonates, at different temperatures, oxygen can be determined in the concentration range 10^{-5}–10^{5} ppm. This kryptonate reacts faster with oxygen than the pyrolytic graphite kryptonate.

The percentage loss of activity of the copper kryptonate is also linearly dependent on the log of the oxygen concentration over the range of 10^{-2}–10^{4} ppm oxygen.[3] The curves [equation (1)] for 250, 300 and 1050° were calculated from the Arrhenius temperature dependence, and, as with the curves for pyrolytic graphite the slope of log % O_2 *vs.* log $\mathrm{d}(S/S_0)/\mathrm{d}t$ is 0·5, indicating that the slow oxidation stage will be the dissociation of oxygen molecules, *i.e.*,

$$O_2 \rightleftharpoons 2O \tag{2}$$

The temperature dependence of the oxidation process is given by

$$\frac{\mathrm{d}(S/S_0)}{\mathrm{d}t} = -K[O_2]^{1/2}\, e^{-24\cdot 2/RT} \tag{3}$$

where the value of the coefficient K is 0·085 %/min.ppm$^{1/2}$, when ln $[O_2] = 0$ (*i.e.*, $O_2 = 1$ ppm) and $T = 773K$. By means of this equation the loss of activity of the copper kryptonate at various oxygen concentrations and source temperatures can be predicted.

The originators of the method, Chleck and co-workers,[3] proposed copper kryptonate for the determination of the oxygen content in the atmosphere of Mars and other planets. Results of experiments showed that other components of the earth's atmosphere (carbon dioxide and nitrogen) which may also occur in the atmosphere of Mars, do not interfere, nor does the density of the Mars atmosphere. The device monitors the activity of a kryptonate by means of a sodium iodide crystal connected to a photomultiplier, power-supply and read-out.

Hydrogen.[6,36–38] Hydrogen as reducing agent reacts with many oxidizing agents. Of the radioactive kryptonates of metal oxides investigated the best hydrogen sensor seems to be platinum(IV) oxide. Chleck and co-workers[37] have found that the kinetics of the process are described by

$$\frac{\mathrm{d}(S/S_0)}{\mathrm{d}t} = -3{\cdot}29\,.\,10^6[\mathrm{H}]\,.\,e^{-7{\cdot}18\times10^3/I} \tag{4}$$

During the investigations the reaction vessel containing the radioactive kryptonate of platinum(IV) oxide was filled with gases of differing hydrogen content, at room temperature as well as at higher temperatures. For work at higher temperatures the kryptonate was preheated in an oven. During preheating the kryptonate becomes thermally stable at the oven temperature and lower temperatures. The activity of the kryptonate will decrease only when reaction takes place. By measurement of activity losses of the kryptonate, the rate of krypton-85 loss was determined. The work was carried out with milligrams of metal oxide kryptonates with specific activities 1–5 μCi/mg.

The log of the rate of activity loss of the kryptonate in %/min is directly proportional to the log of the concentration of hydrogen above the $PtO_2[^{85}Kr]$, when the measurements are made at room temperature in an atmosphere of nitrogen. With air as the diluting gas, no decrease of activity was detected, because the hydrogen was oxidized by oxygen on the surface of the oxide. During this oxidation the surface of the oxide is not disturbed and so no krypton is released. For measurement of the hydrogen concentration in its mixtures with oxygen (*e.g.*, in air), this catalytic oxidation must be avoided. For this purpose various powdered materials are added to platinum(IV) oxide, the best seeming to be aluminium oxide powder. These powdered additives probably function by hydrogen diffusion through them to the surface of the kryptonate $PtO_2[^{85}Kr]$, where the reaction then takes place.[36] The catalytic hydrogen oxidation will be prevented by the inability of oxygen to reach this surface. In this case, to ensure the same sensitivity as with $PtO_2[^{85}Kr]$ alone, the temperature should be increased during the experiments. With a mixture of $PtO_2[^{85}Kr]$ and Al_2O_3 at the maximum working temperature of 435° (given by the thermal stability of PtO_2) 1% hydrogen can be determined within 0·5 sec and 10^{-3}% within 10 min. The higher the specific activity of the kryptonate used, the higher the sensitivity of the determination.

The influence of other gases on the determination of hydrogen was also investigated. Small amounts of hydrogen sulphide, sulphur dioxide, hydrochloric and hydrofluoric acid and water, all present in the laboratory atmosphere, did not measurably interfere with the determination. Water vapour up to saturation, carbon dioxide up to 1% and sulphur dioxide up to 0·5% had no influence on the determination. Hydrogen sulphide did not interfere up to a concentration of 100 ppm; at higher concentrations it does not react with the mixture of kryptonated PtO_2–Al_2O_3, but it prevents the reaction of hydrogen. Methane reacted with the solid carrier only at high concentrations and temperatures.

Chleck designed the prototype of the hydrogen analyser (Fig. 8), the basic part of which consists of an end-window Geiger–Müller counter and a sensor element (a mixture of kryptonated PtO_2–Al_2O_3 on a nichrome wire, fixed on a ceramic ring). The radiation detector is aimed directly at the kryptonate and the reaction of the

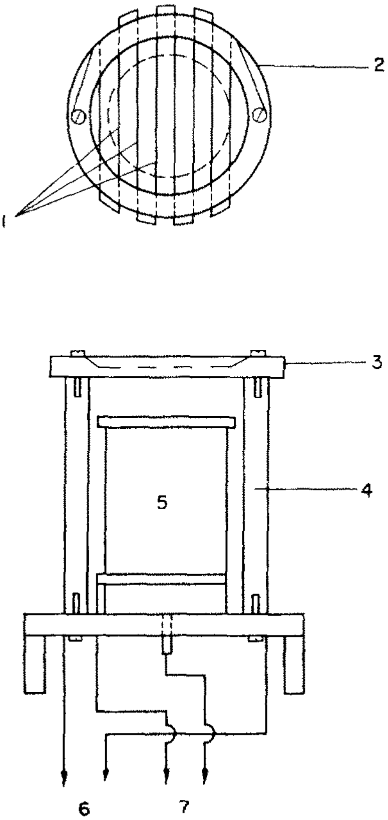

Fig. 8.—Prototype of hydrogen sensor.[36]
1—$PtO_2[^{85}Kr]$ — Al_2O_3 source on nichrome wire; *2*—ceramic insulator; *3*—ceramic insulator; *4*—brass conducting and support rods; *5*—Geiger tube; *6*—source power supply; *7*—ratemeter and recorder.
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hydrogen with the kryptonate is shown by the activity loss. The counter is connected to a ratemeter, which in turn is coupled to a recorder.

Ozone.[3,24,39–42] Determination of ozone is required for monitoring of the atmosphere of workplaces where it is used to bleach fats, oils, waxes, flour, starch, *etc.*, for control of the sterilization of drinking water, and for atmospheric studies.

In ozone determinations with the radioactive hydroquinone kryptonate the following reaction is used

$$[C_6H_4(OH)_2]_3[^{85}Kr] + O_3 \rightarrow 3C_6H_4O_2 + 3H_2O + {}^{85}Kr\uparrow \qquad (5)$$

The log of the activity of the released krypton-85 is linearly proportional to the log of the ozone concentration over a concentration range of 10^{-10}–10^{-6} g of ozone per litre of air. This sensitivity was achieved with a kryptonate the specific activity of which was about 100 mCi/g. Naturally, a higher specific activity proportionally increases the sensitivity value.

The measuring arrangement is that the gas containing the substance to be determined is carried through a dust filter to the reaction cell, where it comes into contact with the radioactive kryptonate. During the reaction with ozone the kryptonate

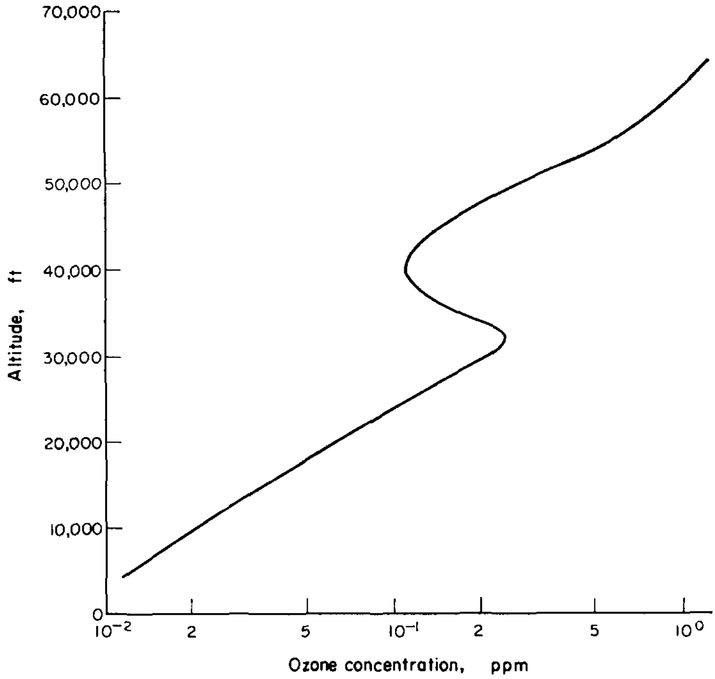

FIG. 9.—Vertical profile of atmospheric ozone.[39]
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releases krypton-85, which is transported by the carrier gas to the measuring cell, where the radioactivity is measured by a Geiger–Müller counter and recorded.

To simulate conditions in the upper layers of the atmosphere, Chleck and Ziegler[41] designed an apparatus in which the ozone was generated by an ultraviolet lamp; by lowering the pressure in the reaction cell it was possible to produce conditions which exist at the maximum height reached by weather balloons.

The general requirements for analysers of air composition in the upper layers of the atmosphere are high sensitivity, low weight, small dimensions and low price. These requirements are met in an ozone analyser which consists of the radioactive kryptonate, a measuring cell with an end-window Geiger–Müller counter, and a little pump.[41] The analyser, in a plastic case, is attached to the upper part of a normal weather radiosonde. The detected activity is recorded directly, and Fig. 9 shows the vertical profile of atmospheric ozone, measured by the analyser.[39]

Chleck and Cucchiara[3] also investigated the possibility of determining ozone by means of radioactive copper kryptonate, since ozone reacts with it at markedly lower temperature than molecular oxygen does. Experiments were made at 200 and 100°, when no reaction with oxygen was found, and it was shown that this kryptonate can be used at temperatures below 100°.

Sulphur dioxide.[40–45] Sulphur dioxide has been determined with the radioactive hydroquinone kryptonate. The determination is based on the mechanism of double release. In the first stage sulphur dioxide releases chlorine dioxide, which is a strong oxidizing agent. The chlorine dioxide oxidizes the radioactive kryptonate and gaseous

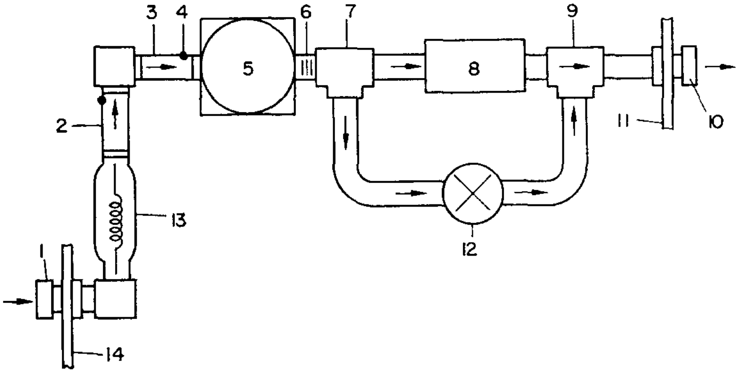

FIG. 10.—The flow diagram for the UDMH monitor.[47]
1—Input; *2*—$NaClO_2$ cell; *3*—clathrate cell; *4*—red dot or arrow; *5*—counting chamber; *6*—flow-meter; *7*—tee; *8*—pump; *9*—tee; *10*—exhaust; *11*—panel; *12*—flow control; *13*—cracking oil; *14*—panel.
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krypton-85 is released. The following reactions are involved:

$$SO_2 + 2NaClO_2 \rightarrow 2ClO_2 + Na_2SO_2 \qquad (6)$$

(this equation is an oversimplification since experimentally it was found that 1 molecule of sulphur dioxide releases between 4 and 8 molecules of chlorine dioxide)

$$ClO_2 + [C_6H_4(OH)_2]_3[^{85}Kr] \rightarrow {}^{85}Kr\uparrow \qquad (7)$$

The activity of the released krypton-85 is linearly dependent on the concentration of sulphur dioxide, which can be determined down to 0·001 ppm.

The only gases that should interfere with the operation of this analyser are those which can oxidize either sodium chlorite or the hydroquinone in the clathrate. The oxides of nitrogen and ozone are the only commonly occurring atmospheric gases that should cause any trouble.

Fluorine.[46] Fluorine can be determined by means of the radioactive hydroquinone kryptonate. In the apparatus described by Hommel and co-workers[46] a radioactive kryptonate with a specific activity of 450 mCi/g was used. The measuring cell contained an amount corresponding to about 50 mCi. One of these measuring cells has a lifetime of many months when traces of fluorine (less than 2 ppm) are measured. However, it is necessary to recalibrate the apparatus from time to time.

Analysers[32,47,48]

Two types of apparatus for determination of atmospheric impurities (F_2, Cl_2, ClF_3, SO_2, NO_2, NO, RNH_2, O_3), of oxidizing or reducing nature, in concentrations of the order of ppm, have been developed in the research institute of Tracerlab. These are the nitrogen dioxide detectors which represents one of the simplest devices and the UDMH (unsymmetrical dimethylhydrazine) unit which is much more complicated. By these instruments gases which can react directly or indirectly (by chemical, catalytic or thermal reaction) with the radioactive kryptonate are measurable.

The flow diagrams for the nitrogen dioxide and UDMH monitors are similar; that of the latter is shown in Fig. 10. The basic system contains a sampling pump, flow adjustment valve, counting chamber and radioactive kryptonate (clathrate). Chemical and catalytic cells are included when necessary (Fig. 10). The sample gas is pulled through the system by the pump. As the gas of interest enters the instrument, it immediately comes into contact with the chemical and catalytic cells, if they are required, and then reacts with the radioactive kryptonate. The krypton-85 released enters a counting chamber of known volume where its concentration per unit volume is determined. This concentration can be related directly to the volume concentration of the gas of interest entering the system.

Experience has shown that a multi-gas system has much poorer operational characteristics than the single-gas units.

With this apparatus the most widely used rocket fuels and oxidizing agents can be analysed. The output from the apparatus is a simple electric signal, which can be used not only for the control of the measuring device and recorder but also for the starting of a control and safety warning device.

A detection limit of 0·5 ppm has been observed regularly on a routine basis, and for special situations 0·1 ppm has been detected. The upper limit depends on the cell-life required and on the saturation characteristics of the Geiger tube.

Analysis of solutions

Radioactive kryptonates can also be used for the analysis of solutions by the direct reaction of the substances determined or reagents used with the radioactive kryptonate. A special position is held by titration methods, which will be treated separately.

With methods described in this part of the review analytical results were gained by the use of calibration curves. Either the activity drop of the radioactive kryptonate or the radioactivity of the krypton-85 released can be measured.

Water in organic solvents.[36–38,49] Determination of water in organic solvents is based on the reaction

$$2H_2O + CaC_2[^{85}Kr] \rightarrow Ca(OH)_2 + C_2H_2 + {}^{85}Kr\uparrow \quad (8)$$

The total activity of the krypton-85 released is measured, and is directly proportional to the amount of water reacting with the radioactive kryptonate of calcium carbide added to the solution investigated. The method is applicable for the determination of 0·25–2·0% H_2O in methanol.[49]

Hydrochloric acid. The determination of acids is based on following their reaction with an appropriate kryptonate by tracing the rate of krypton-85 release. Thus aqueous solutions of 10^{-1}–$10^{-3}M$ hydrochloric acid were analysed by the use of radioactive kryptonates of magnesium.[37,49,50] At constant temperature and under constant reaction conditions rate of release of krypton is directly proportional to acid concentration.

For the determination of the concentration 10^{-1}–$10^{-4}M$ hydrochloric acid, radioactive silver kryptonate has been used with success.[51]

Iron.[34,52] Rotariu, Hoskins and Hattori[52] tried to determine iron(III) in aqueous solution by the use of the radioactive kryptonate of hydroquinone. They assumed that it would be possible to determine iron in ppM concentrations, but at present the range is 2–20 ppm.

In the method proposed, iron(III) was extracted into trifluorotoluene by thenoyltrifluoroacetone (TTA) at pH 2–3 and the organic phase containing iron(III) was transferred to a closed system. For 8 sec gaseous hydrogen chloride was bubbled through the solution and the surplus of gas was removed by nitrogen. One mg of radioactive hydroquinone was added to the solution, which was mixed for 15 min. The reactants were frozen out with a mixture of solid carbon dioxide and acetone and krypton-85 pumped into the ionization cell, where its activity was measured. Although it was possible to determine 2–20 ppm of iron in the trifluorotoluene-TTA solution, the results, after investigation of the distribution coefficient of iron(III) between water and the organic solvent, showed that for quantitative extraction it would be necessary to repeat the extraction three or four times.

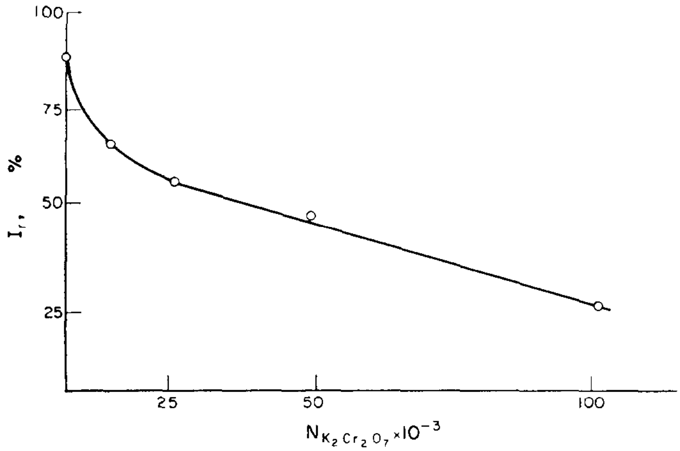

FIG. 11.—Calibration curve from determination of dichromate.[51] (Reprinted by permission of the copyright holder, Elsevier).

Dichromate.[51] For the determination of dichromate ions the reaction with the radioactive silver kryptonate Ag[^{85}Kr] is used.

$$Cr_2O_7^{2-} + 6Ag[^{85}Kr] + 14H^+ \rightarrow 6Ag^+ + 2Cr^{3+} + 7H_2O + {}^{85}Kr\uparrow \qquad (9)$$

Thus, dichromate in the concentration range from 0·0125 to 0·1*N* was determined. Figure 11 shows the calibration curve. It has been shown that iron(III), chloride and nitrate interfere.[53]

Vanadate.[51] Vanadate ions can be determined by a procedure similar to that used for dichromate. The following reaction is carried out in the presence of fluoride:

$$V(OH)_4^+ + 2H^+ + Ag[^{85}Kr] \rightarrow VO^{2+} + Ag^+ + 3H_2O + {}^{85}Kr\uparrow \qquad (10)$$

The sensitivity of Ag[^{85}Kr] to $V(OH)_4^+$ is great. A solution of the order of $10^{-7}N$ is still able to decrease measurably the radioactivity of Ag[^{85}Kr]. At the $10^{-5}N$ level the reproducibility is ±3%.

The comparison of both foregoing determinations shows that the vanadate reacts more sensitively than the dichromate with Ag[^{85}Kr], although the difference in normal potentials is greater for the dichromate. The probable cause of this is the different reaction medium: with dichromate a neutral solution is involved, with vanadate the medium is strongly acid.

Oxygen.[54,55] The determination of small amounts of oxygen dissolved in water or other liquids is one of the most difficult analytical problems, but can be solved by means of the radioactive thallium kryptonate. The determination is based on the reaction

$$4\mathrm{Tl}[^{85}\mathrm{Kr}] + \mathrm{O}_2 + 2\mathrm{H}_2\mathrm{O} \rightarrow 4\mathrm{Tl}^+ + 4\mathrm{OH}^- + {}^{85}\mathrm{Kr}\uparrow \tag{11}$$

The radioactive kryptonate of thallium is added to the solution to be analysed or the solution is passed through the thallium kryptonate. The oxygen present in the liquid reacts with the surface layer of thallium, and krypton-85 is released, the amount of which is proportional to the amount of oxygen dissolved in the liquid.

The fall in radioactivity of the thallium kryptonate, measured in distilled water, is linear with the concentration of oxygen dissolved, down to 0·3 ppm.

The analyser used for determination was calibrated with distilled water saturated with air. The oxygen concentration in pure water at atmospheric pressure and room temperature was determined. The linearity of the calibration curve was such that it was sufficient to calibrate the analyser with one standard solution.

By this method oxygen concentration in potable water, water samples from lakes, rivers, sea-water, *etc.*, can be determined.

Radioactive kryptonates in titrimetric analysis

Titrimetric analysis with radiometric end-point indication (so-called radiometric titration) has assumed greater importance recently, owing to the working out of new methods for separating titration components and to new titration procedures.[56–58] Possibilities of further development are presented by radioactive kryptonates.[36,37,59] This area is being intensively developed in our Institute.[14–22,61–62]

Essence of the method. In the application of radioactive kryptonates to end-point indication, an auxiliary reaction of the radioactive kryptonate with an excess of titrant is used in which radioactive krypton is released. As the reaction product is a gas it is relatively easy to separate it from the other components of the reaction, which are in the solid (kryptonate indicator) and liquid (titrant and titrand) phases.

Radioactive kryptonates can only be used as end-point indicators if the kryptonated solid material does not react with the solution being titrated.

Substances reacting with the kryptonate indicator could interfere with the end-point by releasing krypton-85 prematurely. If this interfering reaction is slow, it will increase the background count but the end-point will be detectable. If the interfering reaction is so fast that it is impossible to determine the exact start of the krypton-85 release during titration, either the interfering ion must be removed, or a different kryptonate must be used.

Amongst the properties of radioactive kryptonates used as indicators dekryptonation of the proper kryptonate in different conditions is of great importance. Therefore, before application of a certain radioactive kryptonate as an indicator, investigation must be made of the radioactivity decrease of the kryptonate in air under laboratory conditions and the influence of the titration medium and of the titrant.

The greater the stability of a given radioactive kryptonate in the air and in the titration medium and the easier the release of incorporated krypton-85, the better it is for titrimetric use. Table I lists radioactive kryptonates which have been used as indicators.

Table I.—Some radioactive kryptonated indicators

Radioactive kryptonate	Relative specific activity	Titrand	Titrant	Titration type	References
Mg[^{85}Kr]*		1·75M NaOH 0·10M NaOH	1·75M HCl 0·10M HCl	neutralization	59
Zn[^{85}Kr]*		0·01M NaOH	0·01M HCl	neutralization	59
Zn[^{85}Kr]*		F^-	0·01M $Th(NO_3)_4$	precipitation	36, 59
$AgIO_3$[^{85}Kr]*	$1·7 \times 10^6$§	Ca^{2+}, Sr^{2+}, Mg^{2+}	$10^{-2}M$ EDTA	complexometric	16, 17
$Y_2(C_2O_4)_3$[^{85}Kr]†	$7·7 \times 10^6$§	Fe^{3+}	$10^{-2}M$ EDTA	complexometric	16, 62
AgI[^{85}Kr]*	$1·9 \times 10^6$§	Ni^{2+}	0·1M KCN	complexometric	18
Glass[^{85}Kr]†	0·3–400‡	Ca^{2+}, Cd^{2+}	0·2M NaF	precipitation	19
Glass[^{85}Kr]†	0·3–400‡	Th^{4+}	0·2M NaF	precipitation	61
Glass[^{85}Kr]†	250‡	H_2SO_4, HCl HNO_3	0·1M, 0·5M NaOH	neutralization	20
Ag[^{85}Kr]†	0·25–300‡	Ba^{2+}	$10^{-3}N$ $K_2Cr_2O_7$	precipitation	15, 51

* Prepared by diffusion technique.

† Prepared by bombardment with accelerated ions.

§ Specific activity in cpm/g.

‡ Specific activity in cpm/mm².

Radiometric titrations using radioactive kryptonates as end-point indicators may be performed discontinuously or continuously.

Discontinuous titration. During discontinuous titrations the radioactivity of the solid indicator or of the krypton released is measured after each addition of the titrant solution. The titration curve is plotted as count rate *vs.* volume of titrant. The radioactivity of the krypton released only can be measured if the radioactive kryptonate has high specific activity. The following methods have been used to date.

1. Solid radioactive kryptonate ($AgIO_3$[^{85}Kr]; $Y_2(C_2O_4)_3$[^{85}Kr]; AgI[^{85}Kr]) is added to the solution in the titration vessel.[14] The kryptonate forms a continuous layer at the bottom of the narrowed part of the titration vessel. Titration is begun 5 min after addition of the radioactive kryptonate. During titration a steady flow of nitrogen is bubbled through the solution, which carries off the released krypton-85. The activity of the radioactive kryptonate is measured regularly 2 min after each addition of titrant. From the measured activity a titration curve is plotted. Activity is expressed relative to the activity measured at the start of the titration.

2. Two types of titration using a radioactive glass kryptonate (kryptonated cover glass) or a silver kryptonate (kryptonated silver plate) have been employed.[15,20,51]

(*a*) The solution investigated and the radioactive silver or glass kryptonate are placed in the titration vessel, fitted with a bubbling tube. During titration, nitrogen is bubbled through, which carries off the released krypton-85. After each addition of titrant the radioactive kryptonate is left in the solution for 3 min and then removed and dried for a fixed time and its radioactivity measured under equal geometric conditions with an end-window counter.

(*b*) The radioactivity of the silver or glass kryptonate is measured directly in the solution, by making use of a cylindrical beta-counter, fitted with a plexiglass ring. The radioactive kryptonate is placed in the ring. Three min after each addition of the titrant solution the kryptonate activity is measured during 2 min, and then the titrant solution is added during 1 min. Continuous titration is also suitable for this method.

Continuous titrations. The titrant solution is added continuously to the test solution and the released krypton-85 is carried off by nitrogen or other suitable carrier gas into a flow-through detector of radioactivity, joined to a ratemeter and recorder.[18]

Figure 12 shows the titration curve for the determination of nickel by continuous titration with 0·1*M* potassium cyanide.

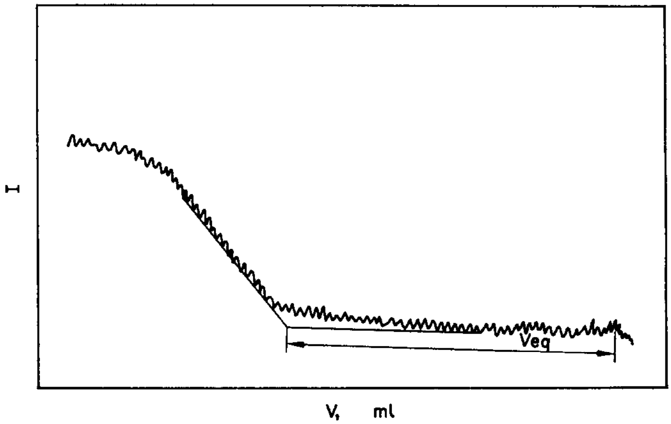

Fig. 12.—Titration curve of nickel determination by continuous titration.[18] (Reprinted by permission of the copyright holder, Akademie Verlag).

Radiocomplexometric titration

Radioactive kryptonates are used with advantage as end-point indicators in complexometric titrations.[16,17] The titration of cation M with complex-forming agent (titrant) C is considered in terms of the reaction

$$\mathrm{M} + \mathrm{C} \rightarrow \mathrm{MC} \qquad (12)$$

The end-point is determined by means of the solid radioactive kryptonate AB[^{85}Kr]. After the termination of reaction (12) the complex-forming titrant reacts with the indicator and forms a soluble compound according to the reaction

$$\mathrm{AB}[^{85}\mathrm{Kr}] + \mathrm{C} \rightarrow \mathrm{AC} + \mathrm{B} + {}^{85}\mathrm{Kr}\uparrow \qquad (13)$$

whereby gaseous radioactive krypton is released. The equilibrium of reaction (12) is characterized by the stability constant of the MC complex and by the solubility product of the solid radioactive kryptonate AB[^{85}Kr].

Titration can be carried out if the following conditions are satisfied.

(*a*) If the formation constant for MC is much greater than that for AC.

(*b*) If the ratio between the stability constant of AC and the solubility product of the kryptonate AB[^{85}Kr] allows the dissolution of the kryptonate by the complex-forming agent according to reaction (13).

During titration to the end-point, reaction (12) takes place. The radioactivity of the kryptonate is constant. After the end-point is passed the excess of the complex-forming agent C reacts with component A and simultaneously dissolves the radioactive kryptonate AB[^{85}Kr] and releases krypton-85. According to this, the radioactivity

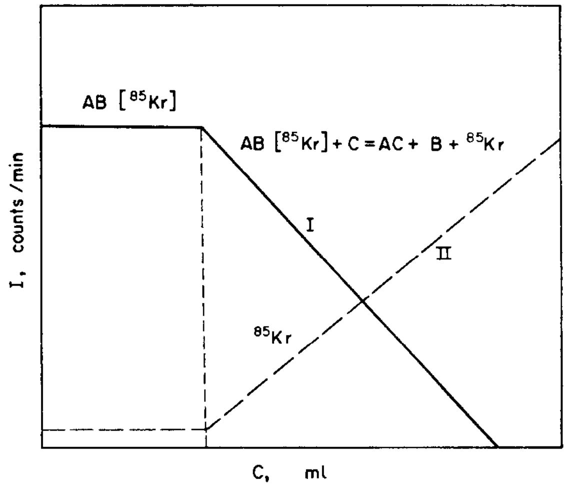

Fig. 13.—Theoretical titration curves of complexometric titration.[60] I—measurement of indicator activity; II—measurement of released ^{85}Kr activity. (Reprinted by permission of the copyright holder, Akadémiai Kiadó).

of the kryptonate proportionally decreases with the amount of the agent C added in excess (curve I, Fig. 13). As already mentioned, during titration the activity of the krypton released can also be measured (curve II, Fig. 13).

On this principle radiocomplexometric titration can be realized by a suitable complex-forming agent, which reacts quantitatively with the ions of the element determined, and a suitable radioactive kryptonate.

The theory of radiocomplexometric titration, the mechanism of indicator action during titration and the choice of suitable radioactive kryptonate as end-point indicator have been studied in detail.[60]

Determination of calcium, strontium, magnesium. In the determination of calcium (and similarly of strontium and magnesium) the pH of the solution is adjusted to 9·0–10·0 with 0·1*M* sodium hydroxide. The radioactive kryptonate $AgIO_3[^{85}Kr]$ is added and discontinuous titration carried out with $10^{-2}M$ EDTA. Up to the end-point the reaction is

$$Ca^{2+} + Y^{4-} \rightleftharpoons CaY^{2-} \qquad (15)$$

After the end-point, the reaction taking place is

$$AgIO_3[^{85}Kr] + Y^{4-} \rightarrow AgY^{3-} + IO_3^- + {}^{85}Kr\uparrow \qquad (16)$$

The reproducibility of the determination is good but there is a negative bias which suggests that krypton is released just before the equivalence point. This agrees with the results of Liebermann and co-workers[63] who determined calcium by titration with a 0·05*M* EDTA solution and the solid indicator $^{110m}AgIO_3$. Probably this is caused by the relatively close values of the stability constants ($\log K_{CaY^{2-}} = 10{\cdot}7$; $\log K_{AgY^{3-}} = 7{\cdot}3$), so that silver begins to react with the EDTA before complete complexation of calcium.

Strontium and magnesium can also be determined by this method. For the determination of calcium and magnesium (*e.g.*, in dolomite, glass, pharmaceutics,

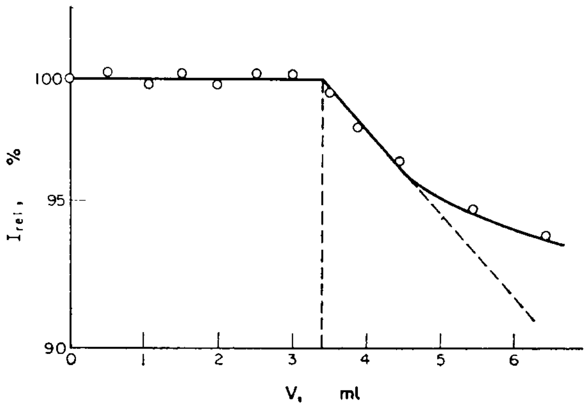

FIG. 14.—Titration curve for titration of nickel with 0·1*M* KCN, radioactive silver iodide kryptonate being used as end-point indicator.[18]
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water) two aliquots are used, one for the sum of calcium and magnesium determined, the other for titration of magnesium in the filtrate after calcium is precipitated as molybdate.

Determination of iron.[62] Iron has been determined by the discontinuous method. The radioactive kryptonate $Y_2(C_2O_4)_3[^{85}Kr]$ is added to the solution tested, which is titrated with $10^{-2}M$ EDTA. Up to the end-point the reaction is

$$Fe^{3+} + EDTA \rightarrow Fe(EDTA) \qquad (17)$$

and after the end-point

$$Y_2(C_2O_4)_3[^{85}Kr] + 2EDTA \rightarrow 2Y(EDTA) + 3C_2O_4^{2-} + {}^{85}Kr\uparrow \qquad (18)$$

As the log of the conditional stability constant of the iron/EDTA chelate, 9·1, and that of the yttrium/EDTA chelate, 17·8–18·1, are appreciably different, the accuracy of titration can be high enough. The system is buffered with sodium acetate (pH 5·0) and tartaric acid is added to keep iron in solution. The method is suitable for the determination of iron in cement.

The determination of iron and aluminium in one solution is possible by radiochelatometric titration. First, iron(III) is titrated at pH 5·0 with EDTA and the indicator $Y_2(C_2O_4)_3[^{85}Kr]$. Then the indicator is filtered off, the pH is adjusted to 9·0 and aluminium is titrated with EDTA and the indicator $AgIO_3[^{85}Kr]$.

Determination of nickel.[18] For the determination of nickel the radioactive kryptonate $Ag[^{85}Kr]$ has been used as indicator and 0·1*M* potassium cyanide as titrant. The titration was carried out in ammoniacal medium by the discontinuous and continuous methods. Up to the end-point the reaction is

$$Ni^{2+} + 4CN^- \rightleftharpoons [Ni(CN)_4]^{2-} \qquad (19)$$

After the end-point the reaction which takes place is

$$AgI[^{85}Kr] + 2CN^- \rightarrow [Ag(CN)_2]^- + I^- + {}^{85}Kr\uparrow \qquad (20)$$

the solid kryptonated indicator dissolves and its activity decreases with increasing volume of titrant added (Fig. 14). This increase is not always linear, especially with kryptonates of low specific activity. According to the diffusion theory there exists a certain concentration gradient in the kryptonated substance. Probably this gradient will cause the non-linear decrease of the activity when the titrant is added, but in practice this is without importance, as it is the relative activity change of the indicator after the end-point that is involved.

Precipitation titration

The sensitivity limit of precipitation titrations is generally of the order of 1 mg depending on the solubility product of the precipitate formed during titration. In spite of this, precipitation reactions are often used in titration. Several types of radioactive kryptonates have been used as indicators in precipitation titrations. Use is made of the dissolution of the surface of a radioactive kryptonate of a metal, or of disturbance of the surface of the radioactive kryptonate of glass, or of redox reactions on the surface of the radioactive kryptonate, caused by the titrant after the end-point.

Use of radioactive kryptonates of metals. At present only one radioactive metal kryptonate has been used in a precipitation titration.

Fluorides have been determined by titration with thorium(IV) with kryptonated zinc foil as the indicator.[36,37,59] After the equivalence point the excess of thorium ion is hydrolysed and the hydrogen ions formed react with Zn[^{85}Kr], releasing krypton-85. Readily evaluated end-points were obtained for concentrations up to $10^{-4}M$ and even 2 μg of fluoride per ml could be determined.

It is known that the end-point in this titration is not stoichiometric. Therefore a calibration curve of moles of fluoride *vs.* ml of standard thorium consumed was used. It was reproducible and gave satisfactory results over the range 0·001–0·1*M* fluoride concentrations.

Use of radioactive kryptonates of glass. The destruction of the glass surface to release krypton is complete and varies according to the action of atmospheric moisture, acids, bases, the composition of the glass *etc.* The loss is initially high but decreases to a stable value, as the surface particles become exhausted to such an extent that decomposition is stopped. The extraction with bases is 200 times as great as that with acids, so radioactive glass kryptonate can be used with advantage as indicator in the titration of acids with bases. Hydrofluoric acid readily attacks glass and this has been exploited in precipitation titrations where the precipitate is a sparingly soluble fluoride.

Cadmium and calcium,[19] and thorium,[61] have been titrated with 0·2*M* sodium fluoride with radioactive fused silica kryptonate as indicator, at pH 6·0, pH 7·0 and in 0·5*M* sulphuric acid respectively. The solubility products of calcium and cadmium fluoride are such that mg amounts can be determined. After the end-point hydrofluoric acid strongly attacks the glass, with the consequent release of krypton-85 and decrease in the radioactivity of the glass. A calibration curve was used to determine the thorium concentration.

Use of redox indicators.[15,51] Some radioactive kryptonates, as for instance Ag[^{85}Kr], may be used as redox indicators. Their surface is decomposed by oxidizing agents after the end-point, with consequent release of krypton-85. For example, barium has been titrated with 0·001*N* potassium dichromate with radioactive silver kryptonate as indicator. Up to the end-point the precipitation reaction is

$$2Ba^{2+} + Cr_2O_7^{2-} + H_2O \rightleftharpoons 2BaCrO_4 + 2H^+ \qquad (21)$$

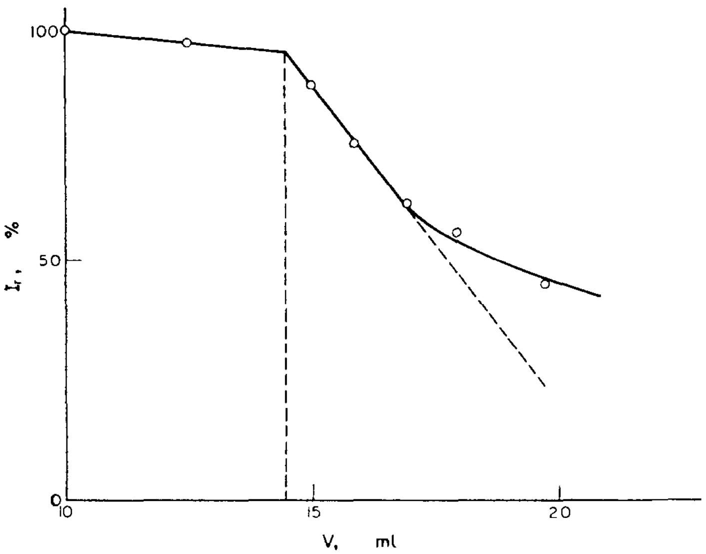

FIG. 15.—Titration curve for titration of Ba^{2+} with 0·001*N* $K_2Cr_2O_7$, using radioactive silver kryptonate as indicator.[15]
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and after the end-point, redox reaction (9) is going on. The activity decrease of the silver kryptonate is measured after each addition of the titrant. The titration curve for such a titration is illustrated on Fig. 15.

Neutralization titration

Radiometric neutralization titrations can now be realized with the advent of radioactive kryptonates.

Use of radioactive kryptonates of metals.[59] Radioactive kryptonates of magnesium and zinc have been used as indicators in the titration of a strong base (1·75, 0·1 and 0·01*M* sodium hydroxide) with a strong acid (hydrochloric acid of the same molarity). The krypton-85 released was determined after each addition of titrant. Figure 16 shows the titration curves obtained during these titrations.

Use of radioactive kryptonates of glass.[20] The radioactive kryptonate of glass is a suitable indicator in the titration of acids with strong bases. Here, after the equivalence point the excess of base decomposes the surface layers of glass, with the consequent release of radioactive krypton and decrease in the radioactivity of the glass. The end-point can be readily determined and coincides with the equivalence point.

CONCLUSION

This review presents a picture of the uses of radioactive kryptonates in chemical analysis. They can be used to determine substances of various character in gaseous and liquid samples by a relative method using calibration curves, by comparison with standards, or by titration methods.

Although one of the most recent areas of nuclear analytical chemistry (belonging to the group of "radio-release" methods) is involved, the analyses already carried out show the wider possibilities which radioactive kryptonates offer in resolving various

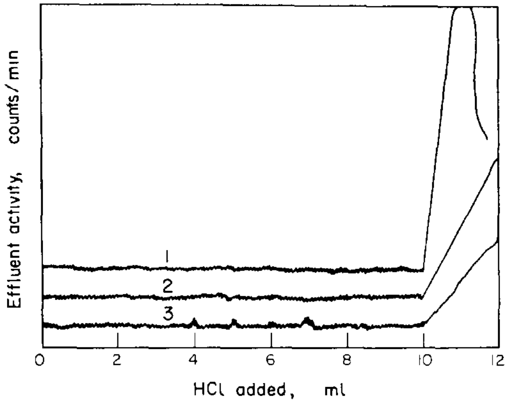

FIG. 16.—Acid–base titration curves.[59]
1—1·75*M* NaOH, Mg-kryptonate; *2*—0·10*M* NaOH, Mg-kryptonate; *3*—0·01*M* NaOH, Zn-kryptonate; for all titrations—10 ml taken.
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problems of chemical analysis. Experimental studies showed that other radio-release methods, using agents labelled with radionuclides, can be advantageously changed to methods using radioactive kryptonates. The importance of analytical methods using radioactive kryptonates is underlined by the fact that leading firms pay great attention to the design and construction of analysers, working on the principles mentioned.

Radioactive kryptonates, besides being of direct analytical application, are also helpful in resolving important problems of physical chemistry, closely related to analytical chemistry (study of kinetics and mechanism of chemical reactions, study of catalysis, adsorption and chemical reactivity, study of structural and surface changes and phase transformations, *etc.*)[9,10] which are, however beyond the scope of this paper. Future work in this field should be of theoretical interest and practical importance.

Zusammenfassung—Es wird eine Übersicht über die Anwendungen von radioaktiven Kryptonaten in der chemischen Analyse gegeben.

Résumé—On présente une revue des emplois des kryptonates radioactifs en analyse chimique.

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VERSATILE INSTRUMENT FOR DIRECT OR DIFFERENTIAL A.C. RESISTANCE OR CONDUCTANCE MEASUREMENTS ON SOLUTIONS

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Summary—A simple but versatile instrument with an electronic (non-servo) measuring circuit is described which is capable of making direct or differential measurements of the resistance or conductance of solutions over an absolute resistance range from 0·1 Ω to 1 MΩ, in six linear ranges. Linearity is better than 2% on all ranges, and reproducibility is better than 1%. Drift is less than 1% over 12 hr. Less than 0·01% change in resistance can be measured in the differential modes, permitting more sensitive measurements than can be made in direct conductance measurements. Applications of the instrument for monitoring ion-exchange separations and conductometric titrations are illustrated.

THERE are many advantages to the automatic, continuous recording of solution conductance or resistance. Kinetic studies become more convenient and applicable over a greater range of conditions than is possible manually, titrations are facilitated, and flowing streams can be continuously monitored. Several types of conductance- or resistance-recording instruments have been reported,[1–9] but all lack certain features of sensitivity, versatility or speed of response. Holm-Jensen[1] has designed an electronic measuring circuit suitable for conductometric titrations, but the circuit requires elaborate adjustments to achieve linearity even over a narrow range of conductances, and the sensitivity is insufficient for most solution chromatographic studies. All of the other instruments that have been reported[2–9] use a servo system in the measuring circuit, whereby any change in conductance in a bridge-type circuit activates a servo-driven potentiometer which restores the balance in the bridge and simultaneously gives recorder read-out. The sensitivity of such bridge circuits is inherently limited by the resistance of the servo slidewire.[2] Additional disadvantages of such servo-balancing systems are "hunting" and/or slow response time, these two characteristics being interdependent and requiring a compromise.[3] The above-mentioned limitations of servo-balanced measuring circuits were confirmed in this laboratory, with circuits similar to those of DeVerdier and Sjöberg[2] and James, Martin and Randall.[4]

The previously reported instruments[1–9] lack versatility in that the available read-out is linear in either resistance or conductance, but not both, and most[1,3,4,6–9] only make direct measurements on a single cell. The designs by DeVerdier and Sjöberg[2] and Wickbold[5] measure the difference in conductivity between two cells, but there is no provision for measuring the absolute conductance of either cell, and servo systems are used in the measuring circuits. This paper describes a simple but versatile instrument with an electronic measuring circuit for making direct or differential measurements of the resistance or conductance of solutions, over a large range of resistances or conductances. Either one or two conductance cells can be used, and a switch selects a read-out which is linear in each of the following functions: (*a*) direct resistance of cell 1 or 2; (*b*) direct conductance of cell 1 or 2; (*c*) differential resistance between the two cells; (*d*) differential conductance between the two cells. The differential functions can be made extremely sensitive by null-balancing the signal from each of the two cells, and amplifying the difference signal by a factor of up to 1000. Applications of the instrument for monitoring ion-exchange effluents and conductometric titrations are illustrated.

EXPERIMENTAL

Apparatus

Conductance resistance instrument. Figure 1 shows a block diagram of the instrument in the differential conductance mode and Fig. 2 shows a complete schematic diagram of the instrument. The voltage source in Fig. 1 is a signal having a constant voltage (E) of about 1·25 V rms and a frequency of either 60 Hz or 2 kHz (selectable by means of switch $S1$ in Fig. 2). The 2-kHz signal is used for solutions of high conductance where electrolysis could be significant, and is provided by the Hartley-type oscillator shown in Fig. 2. The 60-Hz signal is used for solutions of low conductance where capacitive reactance may be important, and is provided by the filament supply winding of power transformer $T3$ (Fig. 2). Potentiometer $R5$ allows the voltage of the 60-Hz and 2-kHz sources to be matched in an initial calibration so that the signal frequency can be switched at any time without significantly disturbing the measurement in process.

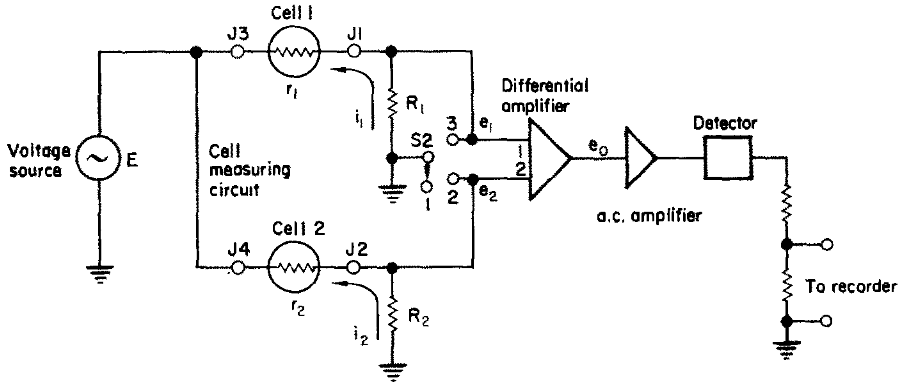

FIG. 1.—Block diagram of the instrument in the differential conductance mode.

The signal voltage is applied to the cell measuring circuit consisting of cells 1 and 2 and a set of range resistors. The range resistors are symbolized in Fig. 1 as R_1 and R_2, and their counterparts in Fig. 2 are the conductance range resistors selectable with switches $S3C$ and $S3D$, respectively. The a.c. voltages e_1 and e_2 generated in the cell measuring circuit are directly proportional to the conductance of cells 1 and 2, respectively, which may be shown as follows. First consider what happens when only the conductance of cell 1 is being measured (function switch $S2$ is in position 2, which amounts to grounding the second input to the difference amplifier at terminal $J2$). It can be seen that

$$i_1 = \frac{E}{R_1 + r_1}. \tag{1}$$

If the range resistor R_1 is chosen to be much smaller than r_1 (in practice R_1 is made one-tenth the full-scale value of r_1), then equation (1) reduces to

$$i_1 \sim \frac{E}{r_1}, \tag{2}$$

and voltage e_1 is given by

$$e_1 = i_1R_1 \cong \frac{ER_1}{r_1}. \tag{3}$$

Since E and R_1 are constants, e_1 is directly proportional to $1/r_1$, the conductance of cell 1. In the same way, when only the conductance of cell 2 is being measured (function switch $S2$ is in position 3),

$$e_2 = i_2R_2 \sim \frac{ER_2}{r_2}, \tag{4}$$

and thus e_2 is directly proportional to $1/r_2$, the conductance of cell 2. When function switch S_2 is in position 1, equations (3) and (4) are simultaneously valid, and if R_1 equals R_2, the differential amplifier generates a voltage (e_0 in Fig. 1) which is directly proportional to the difference in conductivity between cells 1 and 2, namely

$$e_0 = k\left(\frac{1}{r_1} - \frac{1}{r_2}\right), \tag{5}$$

where k is a constant which depends on the gain of the difference amplifier, the source voltage, and the range resistance.

To measure the difference in resistance of cells 1 and 2, function switch $S2$ is turned to position 4, which amounts to interchanging the position of each cell and its range resistor (*i.e.*, interchange r_1 and R_1, as well as r_2 and R_2). Again R_1 is made equal to R_2, but in this case the range resistors are chosen to be much larger than the cell resistances (in practice R_1 and R_2 are made ten times the full-scale value of the cell resistances). Under these conditions equation (1) reduces to

$$i_1 \sim \frac{E}{R_1} = I_1, \tag{6}$$

where I_1 is a constant current. Voltage e_1 is now directly proportional to the resistance of cell 1, as follows:

$$e_1 = I_1 r_1. \tag{7}$$

Similarly, voltage e_2 is now directly proportional to the resistance of cell 2, as follows:

$$e_2 = I_2 r_2. \tag{8}$$

Since R_1 is made equal to R_2, I_1 equals I_2 [equation (6)], and the differential amplifier generates a voltage (e_0) which is directly proportional to the difference in resistance of cells 1 and 2, as follows:

$$e_0 = k'(r_1 - r_2), \tag{9}$$

where k' is a constant which depends on the same factors as k. To measure the resistance of cell 1 only, function switch $S2$ is left in position 4 and a jumper wire is inserted between terminals 2 and 4, thus shorting cell 2 out of the circuit. Similarly, the resistance of cell 1 alone is measured with function switch $S2$ in position 4 and a jumper wire between terminals 1 and 3.

The differential amplifier in Figs. 1 and 2 is a cathode-coupled twin triode fed by a constant-current source to achieve a very high common-mode rejection ratio. The constant-current source is a fixed bias pentode with a dynamic plate resistance of about 1·36 MΩ. The source current is adjusted in an initial calibration with a screwdriver-type potentiometer ($R10$) in order to obtain an optimum rejection ratio, and once adjusted need not be changed. The single-ended output of the differential amplifier is fed into an RC coupled amplifier with a gain of about 10. The gain is adjusted with potentiometer $R14$ each time the instrument is calibrated.

The amplifier circuit was designed to compensate for the non-linearity of the cell-measuring circuit. For example, in the conductance-measuring mode, reference to equations (1) and (2) would indicate that as the solution resistance (r_1) decreases, the non-linearity should increase, causing the current to be up to 10% low at full-scale. However, the operating point of the 12AT7 amplifier tube was chosen to take advantage of the increasing convexity of the 12AT7 characteristic curves as the grid voltage decreases (becomes more positive), thereby compensating almost exactly for the non-linearity of the resistance-divider network.

The a.c. output of the amplifier is rectified with a voltage-doubler type detector having an RC output filter. The resistance portion of the filter is used as a voltage divider to provide full-scale outputs of 10, 1, 0·1 and 0·01 V respectively. Thus, almost any servo-recorder could be used to measure the output voltage. A Heath Model EUW-20A recorder was used in this study.

An added feature of the circuit shown in Fig. 2 is the drop counter, which is used to impose a voltage pulse on the recorder chart each time an increment of solution "shorts" between terminals $J5$ and $J6$. The actual solution contacts consisted of two platinum wires, separated by approximately 3 mm, mounted horizontally and parallel to each other, and positioned immediately below the discharge point of the fraction collector (used in separations), or capillary flow restrictor (used in titrations). Approximately 40-mm lengths of thin platinum wire were used, with electrical connections made to insulated copper wire by twisting and taping, and these copper wires were connected to terminals $J5$ and $J6$. As each increment of solution fell, it momentarily made contact across the two platinum wires, thereby imposing a voltage signal on the detector output. To prevent the retention of any droplets on the platinum wires, a 6-mm tip on each wire was bent downward through 90°. Any liquid adhering to the platinum wires indicated that they were dirty; they were conveniently cleaned by heating in a flame. The size of the pulse could be adjusted with potentiometer $R25$, and the polarity of the pulse could be selected with toggle switch $S5$.

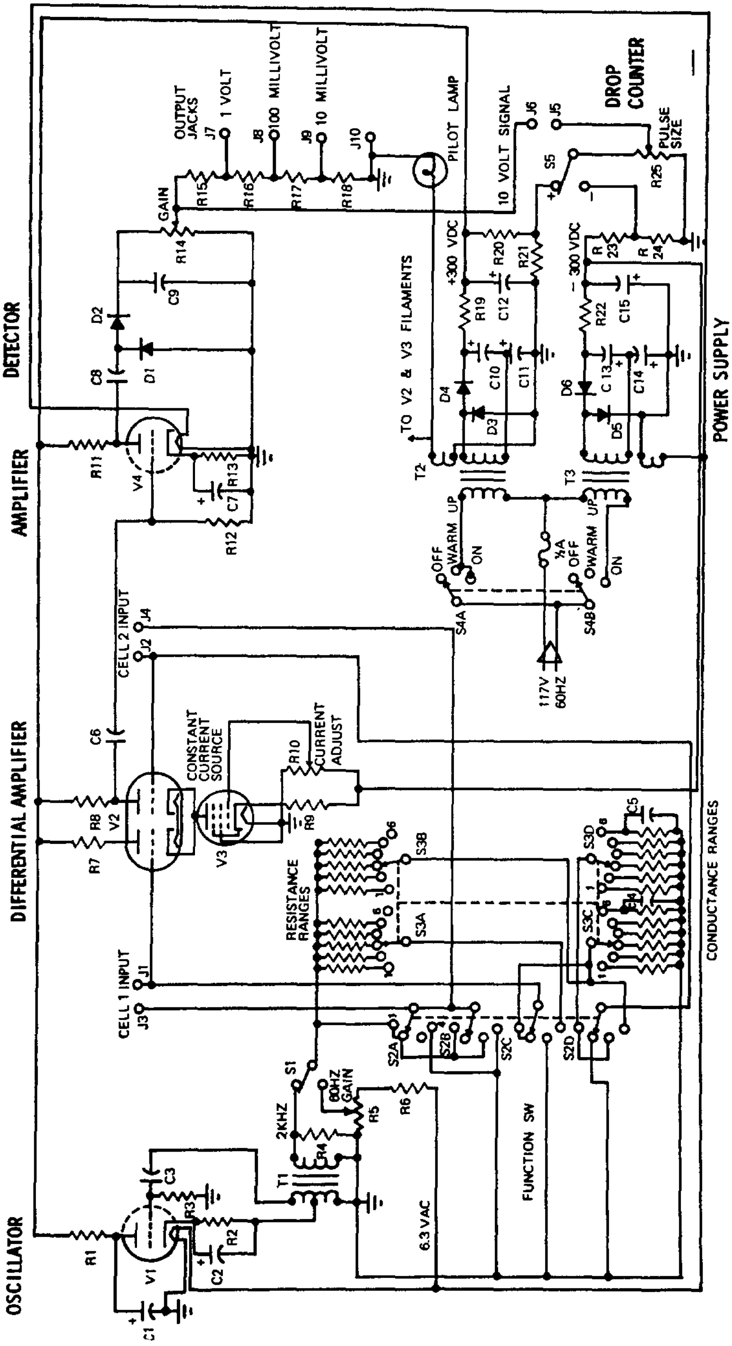

FIG. 2.—Complete schematic of the conductance-resistance instrument.

Legend Key for Figure 2

Tubes, V

1	1/2 12AT7
2	12AU7
3	6BH6
4	1/2 12AT7

Diodes, D

1, 2	1N 34A
3–6	1N438S, 0·1 A, 600 PIV

Resistors, R (all ±10%, 1/2 W unless noted otherwise)

1	22 K
2	470
3, 12	1 M
4	10
5	500 Pot Lin
6	1 K
7–9, 20, 23	100 K ± 5%
10	500 K Pot Lin
11	47 K
13	3·9 K
14	1 M Pot Lin
15	909 K ± 1%
16	90·9 K ± 1%
17	9·09 K ± 1%
18	1 K ± 1%
19, 22	27 K 1 W
21, 24	10 K ± 5%
25	10 K Pot Lin

Pilot Lamp No. 47 filament lamp, 6·3 V, 0·35 A, bayonet fitting

Transformers, T

1	Audio output transformer (Stancor TA-8U)
2, 3	Power transformer, 150 V a.c., 100 mA, and 6·3 V a.c., 1 A

Resistors for Resistance Ranges (All ±1%)

(One set each for switches 3A and 3B)

Switch Position	*Resistor*
1	100
2	1 K
3	10 K
4	100 K
5	1 M

Resistors for Conductance Ranges (All ±1%)

(One set each for switches 3C and 3D)

Switch Position	*Resistor*
1	1
2	10
3	100
4	1 K
5	10 K
6	100 K

Capacitors, C

1, 10–15	50 mF, 450 V d.c.
2, 7	10 mF, 25 V d.c.
3	470 pF, ± 10%, 500 V d.c.
4, 5	220 pF
6	0·1 mF, ± 10%, 400 V d.c.
8, 9	0·22 mF, ± 10%, 200 V d.c.

Switches, S

1, 5	SPDT Toggle, 1/2 A, 125 V a.c.
2	4P4T NS, Rotary
3	4P6T NS, Rotary
4	DP3T, Rotary, 1/2 A, 125 V a.c.

Equipment for ion-exchange separation. The ion-exchange column consisted of a glass tube 0·15 m long by 6 mm inside diameter, closed at the lower end by a coarse sintered-glass disk upon which the resin bed rested, and fitted at the top with a bowl 90 mm in diameter, to hold the eluent. A side-arm funnel, attached to the column and connected to a common outlet through a three-way stop-cock, provided a means of calibration or check on the response of the conductance monitor. A resin (H^+-form) volume of 2·0 ml was used to give a bed height of about 68 mm.

The conductance cells consisted of a flow-cell of fixed cell constant in the effluent stream, and a dip-type cell of variable cell constant dipping into eluent contained in the bowl at the top of the column. The flow-cell was fabricated by sealing two 25-gauge platinum wires about 20 mm in length through the centre of a 2 mm i.d. capillary tube, 25 mm in length, with the second wire 8 mm downstream from the first. After platinizing, the flow cell had a cell constant of 0·61 mm^{-1}, measured by using a solution of known specific conductance. Ball joints were used to attach the flow cell to the column outlet. A pair of dip-type electrodes was fabricated by sealing a 25-gauge platinum wire in the end of each of two 150-mm lengths of glass tubing so that 3 mm protruded. A bead of glass about 3 mm in diameter was then sealed to the protruding wire, nearly covering all of the wire except for a small length of exposed wire between the glass bead and the end of the glass tubing. The exposed wire was barely discernible, but became clearly defined upon platinizing. The pair of electrodes was mounted in a two-holed cork stopper and the cell constant could be varied from about 0·5 to 0·7 mm^{-1} by sliding one or the other of the electrodes up or down (coarse adjustment), or by twisting or rotating one or both electrodes (fine adjustment).

For making differential measurements of solutions of higher resistance, thin sheets of platinum foil were used instead of platinum wires, and connecting wires were shielded. Dip-type cells with variable cell constants were prepared similar to the previously described cell, except that the platinum foil protruding from each piece of glass tubing was bent at right angles to the tubing, so that each foil was horizontal and parallel to the other, allowing the spacing between cell plates to be varied by sliding one or the other of the electrodes up or down.

Equipment for conductometric titrations. The conductance instrument was used in the direct conductance mode (one cell only) for various conductometric titrations. A dip-type conductivity cell (similar to Industrial Instruments Model CEL-BB05) with a cell constant of 0·140 mm^{-1} was used. To automate the addition of titrant increments, a titrant delivery system similar to one described earlier[10] was used, with minor modifications. Instead of addition of titrant in large increments from a siphon pipe,[10] drop-sized increments from a capillary flow-restrictor were used. To mark the addition of each titrant increment on the recorder chart, the drop counter described above was used.

Reagents

The resin was Baker Analyzed Dowex 50W-X8, 100–200 mesh. All other chemicals were reagent grade. The resin was cleaned as described previously.[11]

Procedure

Ion-exchange separation of lithium, sodium and potassium. Two ml of the resin (in the hydrogen-ion form) were washed with 10 ml of 0·100*M* hydrochloric acid. After about 5 ml of 0·100*M* hydrochloric acid had passed, the cell constant of the dip-type cell immersed in the influent solution was precisely "nulled" against the effluent flow-cell of fixed cell constant. This null-balance adjustment was made by first making a direct reading of the absolute conductance of the effluent stream (switch *S*2 in position 2, so that the conductance of only cell 1 was being read) and then, while making a direct reading of the conductance of the influent stream (switch *S*2 in position 3, so that the conductance of only cell 2, was being read), adjusting the cell constant of the dip-type cell in the influent until the influent conductance reading agreed exactly with the effluent reading. To null the cells more precisely, the instrument was switched to the differential conductance mode (switch *S*2 in position 1), and the dip-type cell was fine-tuned to give a minimum differential reading at successively higher gains until a gain of 1000 was achieved. [In practice, the gain was increased in steps of 10, by first moving the positive recorder lead from terminal *J*8 (the 100-mV full-scale output) to terminal *J*7 (the 1-V full-scale output); the next factor of 10 gain was achieved by switching the module range to the next more sensitive range (*e.g.*, from the 10^4-μmho full-scale range to the 10^3-μmho full-scale range); a final factor of 10 gain was achieved by switching the Heath recorder range from 100 mV to 10 mV. After each increment of gain the dip-type cell was renulled more precisely.]

A 0·70-ml sample that was 0·286*M* in lithium nitrate, 0·0286*M* in sodium chloride, and 0·0428*M* in potassium chloride was put on the column at a flow-rate of about 0·5 ml/min, and eluted with 250 ml of 0·100*M* hydrochloric acid at a flow-rate of 1 ml/min. The effluent conductance was monitored continuously with respect to the influent conductance, the difference being amplified by a factor of 1000. To verify the composition of the effluent, 2-ml fractions were occasionally collected and analysed for lithium, sodium and potassium by flame spectrophotometry.

Conductometric titration. Forty ml of 0·025*M* hydrochloric acid were titrated with 0·85*M* sodium hydroxide, with a capillary flow-restrictor giving a flow-rate of 0·5 ml/min and a drop size of 0·040 ml. A nitrogen atmosphere was maintained to minimize carbon dioxide absorption during the course of the titration.

RESULTS AND DISCUSSION

Characteristics of instrument

Table I shows the various resistance and conductance ranges of the instrument. The instrument is capable of making direct measurements of resistances from 0·1 Ω to 1 MΩ in six ranges, with each range linear to within 2% of full-scale. Reproducibility is within 1%. The resistance and conductance ranges listed in Table I cover the entire range of solution conductances normally encountered, from 30% sulphuric acid to high-grade distilled water, for an ordinary cell with a 0·100-mm^{-1} cell constant. Since conductance cells can be purchased or constructed with cell constants ranging from 10^{-4} to 10 mm^{-1}, the range of the instrument could be extended, by proper choice of cells, to cover specific resistances ranging from 10^{-2} Ω.mm to 10 GΩ.mm.

TABLE I.—RESISTANCE AND CONDUCTANCE RANGES

Full-scale resistance, Ω	10	100	1000	10000	—	—
Resistance range, Ω	0–10	0–100	0–1000	0–10000	—	—
Full-scale conductance, *μmho*	—	10000	1000	100	10	1
Conductance range, *μmho*	—	0–10000	0–1000	0–100	0–10	0–1
Resistance corresponding to full-scale conductance, Ω	—	100	1000	10000	100000	10^6

It should be noted from Table I that intermediate ranges of resistance can be measured equally well in terms of either resistance or conductance, whereas low resistance (below 10 Ω) should be measured only on the resistance scale, and high resistances (above 10 kΩ) should be measured only on the conductance scale. For resistances below 10 Ω the conductance mode becomes non-linear because of excessive current drain on the source, whereas for resistances above about 10 kΩ the resistance mode becomes non-linear because currents in the measuring circuit are too low. It was demonstrated that another conductance range of 0–0·1 μmho corresponding to a full-scale resistance of 10 MΩ, could be added with no significant loss of linearity or response, but this was not included in the final design because of the severe shielding requirements that are necessary at such high resistances, and because the availability of cells with small cell-constants makes this range unnecessary.

The sensitivity or detectability of the instrument may be arbitrarily defined as the resistance change necessary to cause a chart deflection of two divisions. Thus, in direct resistance or conductance measurements the sensitivity was about 2% of the full-scale resistance or conductance. In differential resistance or conductance measurements at a gain of 1000, however, it was found that a change of resistance of 0·01% or less caused a deflection of 2 or more divisions from balance. For example, with decade resistance boxes in place of cells 1 and 2 and with about 10 kΩ carefully balanced against each other at a gain of 1000, a 1-Ω change of the decades caused about 2·5 divisions deflection. Similarly, after null-balancing two resistances of about 100 kΩ against each other, a 10-Ω change caused about 3 divisions deflection. In all cases linearity of the differential measurements was within 3% without recalibrating.

The accuracy of the instrument for measuring solution conductances was checked by comparing the conductance of five different concentrations of hydrochloric acid, ranging from 0·050*M* to $1{\cdot}0 \times 10^{-4}M$, using both an Industrial Instrument Model RC-16B2 conductivity bridge, accurate to ±1%, and the instrument described here, with the same conductivity cell. In all cases the conductivities agreed within 3%. After a 30-min warm-up the stability of the instrument was excellent, with a drift of less than 0·5%/hr and less than 1% drift over 12 hr.

Ion-exchange separation

Figure 3 shows an automatically recorded differential conductance curve for the elution of lithium, sodium and potassium ions from Dowex 50W-X8 with 0·10*M* hydrochloric acid as eluent. Shortly after the sample was put on the column the conductivity changed sharply, necessitating a decrease in gain from 1000 to 40. This conductance change is due to the slight difference in anion composition and solute concentration between the sample solution and the 0·10*M* hydrochloric acid eluent which had been used to balance the differential conductance monitor. When the effluent volume had reached about 46 ml, after the sharp lithium peak had emerged,

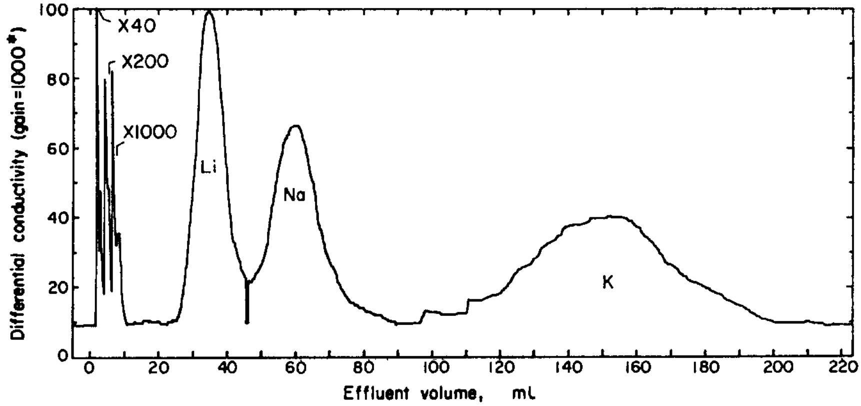

FIG. 3.—Automatically recorded differential conductance elution curve for the separation of lithium, sodium and potassium by ion-exchange.
Chart speed, 2·5 mm/min; flow-rate, 1·0 ml/min.
* Except in initial region, where gain was changed as indicated.

the three-way stop-cock below the column was used to switch the 0·10*M* hydrochloric acid eluent in the side-arm funnel momentarily into the effluent conductance cell, in order to check on response of the instrument, base-line drift, or hold-up in the conductance cell. As can be seen from Fig. 3, the conductance returned immediately to the base-line level, indicating fast response and negligible drift or cell hold-up. The composition of each peak was verified by collecting occasional fractions and analysing with a flame spectrophotometer.

The reproducibility of Fig. 3 was checked by repeating the elution three times, each peak volume being reproducible within ±3 ml, and all peak heights being reproducible to within 6%. No special precautions were taken to maintain constant temperature, except that all solutions were prepared the day before use in order to reach complete temperature equilibrium and the instrument and cells were shielded from draughts. The separation shown in Fig. 3 is not necessarily optimum, as the separation between lithium and sodium could be improved with a slightly longer column or slower flow-rate, but at the expense of a longer total elution time.

The elution curve illustrates the value of differential conductance monitoring, because it would be impossible to locate the peak volumes in this separation with direct measurements of conductance, as the total change in conductance was less than 1% in each peak region. Thus, when this same elution was monitored with direct conductance measurements, a straight line resulted, with no observable changes in conductance in any of the peak regions.

The drop counter provided by the instrument proved very useful when the differential conductance instrument was used to monitor chromatographic effluents while fractions were collected. The drop counter registers a pulse on the conductance chart for each drop, thereby making it a simple matter to correlate precisely the collected fractions and recorded conductance.

Conductometric titrations

Figure 4 illustrates the automatically recorded conductometric titration of 0·025*M* hydrochloric acid with 0·85*M* sodium hydroxide. As each drop was added the drop

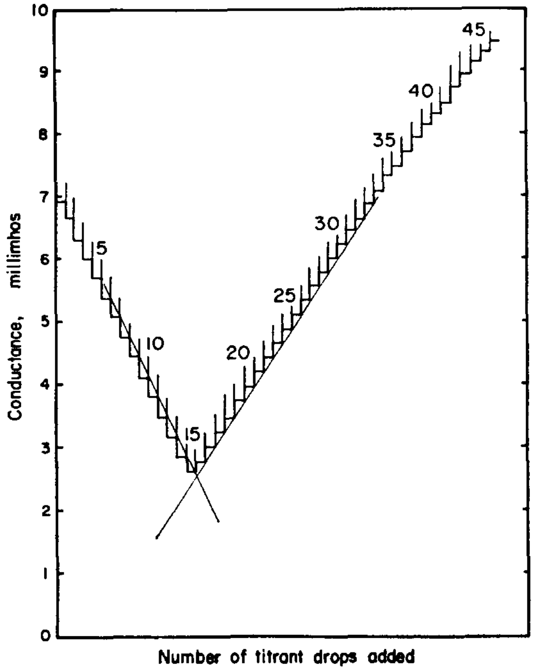

FIG. 4.—Automatically recorded conductometric titration of 40 ml of 0·025M HCl with 0·85M NaOH.
Drop size, 0·080 ml; flow-rate, 0·60 ml/min; recorder speed, 25 mm/min; cell constant, 0·140 mm^{-1}.

counter provided a sharp vertical pulse enabling the number of drops to be easily counted. The end-point was determined by extrapolation of the straight line portions before and after the end-point, with the location of the intersection indicating the drop within which the end-point occurred, and even the precise fraction of the drop needed to reach the end-point.[12] Thus, in Fig. 4, the end-point occurred after the addition of 15·0 drops. The average of seven such titrations had an error of +0·5% with a relative standard deviation of 0·6%. Triplicate titrations of 0·01M potassium hydroxide with 0·10M hydrochloric acid had an error of +0·5% with a relative standard deviation of 0·3%.

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Zusammenfassung—Ein einfaches, aber vielseitiges Instrument mit elektronischem Meßkreis (ohne Servo) wird beschrieben, das direkte oder Differenzmessungen des Widerstandes oder der Leitfähigkeit von Lösungen von 0,1 Ω bis 1 MΩ in sechs linearen Meßbereichen ermöglicht. Die Linearität ist in allen Bereichen besser als 2% und die Reproduzierbarkeit besser als 1%. Die Drift ist in 12 h kleiner als 1%. Im Differenzbetreib konnen kleinere Widerstandsänderungen als 0,01% gemessen werden; das erlaubt empfindlichere Messungen als bei der direkten Leitfähigkeitsmessung. Anwendungen des Instruments bei der Überwachung von Ionenaustauschtrennungen und konduktometrischen Titrationen werden beschrieben.

Résumé—On décrit un instrument simple mais universel avec un circuit électronique de mesure (non-servo) qui est capable de faire des mesures directes ou différentielles de la résistance ou de la conductance dans un domaine de résistance absolu allant de 0,1 Ω à 1 MΩ, en six gammes linéaires. La linéarité est meilleure que 2% dans toutes les gammes et la reproductibilité est meilleure que 1%. Le décalage est inférieur à 1% sur 12 h. On peut mesurer un changement inférieur à 0,01% dans la résistance dans les méthodes différentielles, permettant des mesures plus sensibles que celles pue l'on peut faire dans les mesures de conductance directes. On donne comme exemples des applications de l'instrument aux contrôles de séparations par échange d'ions et de titrages conductimétriques.

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POTENTIOMETRISCHE KIESELSÄUREBESTIMMUNG UNTER VERWENDUNG EINER TITANELEKTRODE—I

DAS VERHALTEN DER TITANELEKTRODE

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Zusammenfassung—Es wird die Empfindlichkeit einer Titanelektrode gegenüber Fluoridionen in Anwesenheit von Fluorosilicationen untersucht. In 3*M* Salzsäure, die etwas Eisen(III) enthält, kann die Elektrode für die Indizierung einer Titration von Kieselsäure mit Fluorid verwendet werden. Da die Reaktionen ziemlich langsam verlaufen, ist die Anwendung eines potentiometrischen Titrators erforderlich.

DIE MEISTEN volumetrischen Bestimmungsmethoden für Kieselsäure beruhen auf der Hydrolyse des Kaliumhexafluorosilicats. Der Umsetzung zwischen löslichen Kieselsäuren und Fluoridionen, d.h. der Bildungsreaktion des Hexafluorosilications, wurde bisher für analytische Untersuchungen wenig Bedeutung beigemessen, da für die Indizierung der Reaktion

$$SiO_3^{2-} + 6F^- + 6H^+ \rightarrow [SiF_6]^{2-} + 3H_2O \qquad (1)$$

in dem zur quantitativen Umsetzung erforderlichen stark sauren Medium kein geeignetes Indikatorsystem bekannt war. Im Rahmen der vorliegenden Arbeit wurde nach einer Elektrode gesucht, die es gestattet, die nach Ablauf der Reaktion (1) auftretenden freien Fluoridionen zu indizieren.

Die Titanelektrode

Bei der Suche nach geeigneten, in sauren Lösungen beständigen Festelektroden wurde im Titan ein geeignetes Elektrodenmaterial gefunden, welches in Verbindung mit der ges.Kalomelelektrode (KE) den gewünschten Forderungen hinsichtlich Empfindlichkeit gegenüber Fluoridionen bei gleichzeitiger Beständigkeit gegenüber Hexafluorosilicondionen entsprach.

Um die zu bestimmenden Kieselsäuremengen in saurem Medium in Lösung zu halten, erwies sich eine 3*M* salzsaure Lösung, gesättigt mit Kaliumhexafluorosilicat und Kaliumchlorid (Grundlösung), als besonders geeignet. Für ihre Verwendung sprechen ferner folgende Argumente.

1. Titan ist in salzsaurer, chloridgesättigter Lösung sehr korrosionsbeständig.[2]
2. Um die Eignung der Titanelektrode für die Umsetzung nach (1) zu prüfen, muß eine Modell-Lösung geschaffen werden, die die Verhältnisse während des gesamten Titrationsverlaufes und am Äquivalenzpunkt eindeutig wiedergibt. Das aber erfordert die Sättigung einer solchen Lösung mit Kaliumhexafluorosilicat.

3. Die Löslichkeit des Kaliumhexafluorosilicats in $3M$ Salzsäure geht nach Sättigung der Lösung mit Kaliumchlorid von $0{,}1M$ auf *ca.* $2.10^{-3}M$ zurück, was die Verschiebung des Gleichgewichts der Reaktion nach (1) fördert. Die Löslichkeit ist in diesem Medium allerdings stark temperaturabhängig. Deshalb ist für eine gute Reproduzierbarkeit eine hohe Temperaturkonstanz erforderlich.

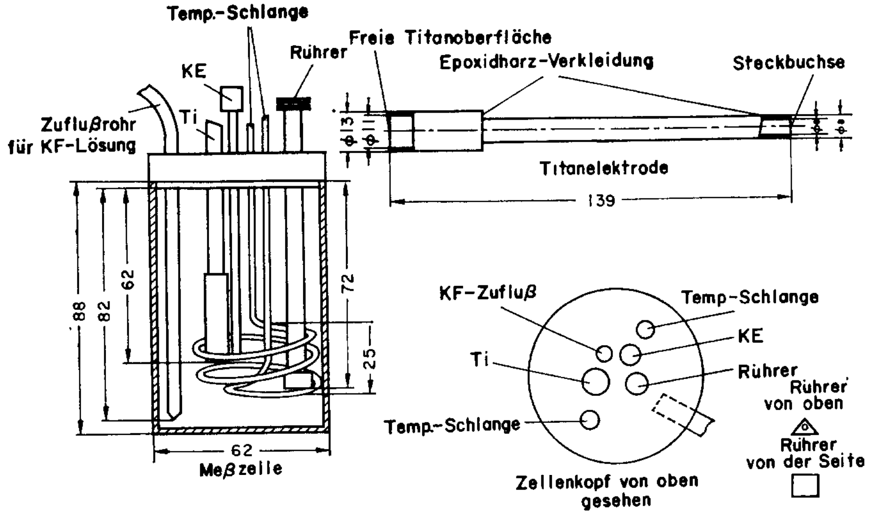

ABB. 1.—Konstruktionszeichnung der Meßzelle und der Titanscheibenelektrode.

In Abb. 1 ist der Aufbau der verwendeten Meßzelle dargestellt, gesondert dazu die in Epoxidharz vergossene Titanscheibenelektrode von 100 mm² Oberfläche, hergestellt aus technischem Titanrundmaterial. Das Epoxidharz wurde so abgedreht, daß nur die 100 mm² große Grundfläche des Titanzylinders mit der Lösung in Berührung kommt. In der Meßzelle ist ferner eine Temperierschlange erkennbar, die in Verbindung mit einem Thermostaten die Lösung konstantauf 20°C hält. Als Maßflüssigkeit fand eine $1M$ Kaliumfluoridlösung Verwendung. Die Titanelektrode wurde vor jeder neuen Messung mechanisch poliert. Hierzu wurde die Oberfläche der Titanscheibe mit einer gummigebundenen Korundpolierscheibe solange bearbeitet, bis sie einen gleichmäßigen matten metallischen Glanz aufwies. Diese Behandlung ist notwendig, um für jede Messung frische und reproduzierbare Oberflächenbedingungen zu schaffen.

Das Elektrodenpotential und seine Stabilisierung

Beim Einsetzen der Meßkette Ti-KE in die Grundlösung stellt sich nach wenigen Sekunden ein Potential von —600 bis —700 mV ein, das auch erhalten wird, wenn eine hexafluorosilicationen-freie Lösung mit einer Fluoridionenkonzentration von $0{,}01M$ verwendet wird. Nach Straumanis[3] entspricht dies dem Auflösungspotential des Titans.

In einer an Hexafluorosilicat- und Fluorid-Ionen freieen $3M$ salzsauren Lösung, ges. mit Kaliumchlorid, steigt das Potential allmählich zu positiveren Werten an, was auf die bekannte besondere Stabilität des Titans in chloridhaltigen Lösungen zurückzuführen ist. Setzt man nach einigen Minuten derartigen Lösungen festes

Kaliumhexafluorosilicat zu, so sinkt das Potential rasch zu stark negativen Werten ab, weil sich das Titan auflöst.

Da die Entstehung und Anwesenheit von Hexafluorosilicationen bei der Durchführung einer Titration nach (1) jedoch unumgänglich ist, muß dafür Sorge getragen werden, daß die Titanoberfläche wohl dem Angriff durch Hexafluorosilicationen widersteht, durch Fluoridionen jedoch meßbare Potentialänderungen hervorgerufen werden. Dies gelingt durch Zusatz geringer Eisen(III)-chlorid-Mengen, deren Konzentration so bemessen sein muß, daß die Empfindlichkeit gegenüber Fluoridionen gewahrt bleibt.

Es wird hierbei die Tatsache ausgenutzt, daß für die Aufrechterhaltung eines passiven Zustandes des Titans ein Oxydationsmittel genügender Stärke und Konzentration zugegen sein muß, wodurch das Korrosionspotential des Titans infolge Bildung schwerlöslicher Deckschichten in den sogenannten oxidpassiven Bereich gehoben wird.[4,5]

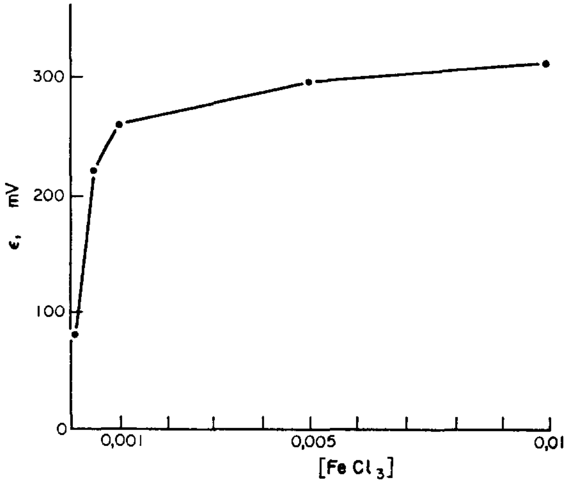

Abb. 2.—Abhängigkeit des Potentials der Titanelektrode in 3*M* Salzsäure, gesättigt mit Kaliumchlorid und Kaliumhexafluorosilicat, von der Eisen(III)-Konzentration, gemessen gegen ges. KE

Abbildung 2 zeigt das Potential der Titanelektrode bei steigender Eisen(III)-chlorid-Konzentration in der Grundlösung. Das Potential strebt einem Grenzwert zu, in gleichem Maße wie die Deckschichtenbildung voranschreitet. Das Potential-Zeit-Verhalten der Titanelektrode in der Grundlösung in Gegenwart von $5.10^{-4}M$ Eisen(III)-chlorid nach Zusatz von $10^{-3}M$ Fluoridionen zeigt die Abb. 3. Der zeitabhängige Potentialanstieg wird beim Auftreten freier Fluoridionen in der Grundlösung solange unterbrochen, bis diese durch Reaktion mit der Titanoberfläche verbraucht sind. Der auf Fluoridzusatz einsetzende geringe Potentialrückgang bildet die Grundlage des entwickelten Verfahrens zur potentiometrischen Kieselsäurebestimmung.

Die Elektroden-Reaktion mit Fluorid

Nach Straumanis und Ballas[6] ist eine Titanoberfläche im oxidpassiven Zustand mit einer Schutzschicht aus Oxiden und Salzen des Titans bedeckt, die in Säure nicht

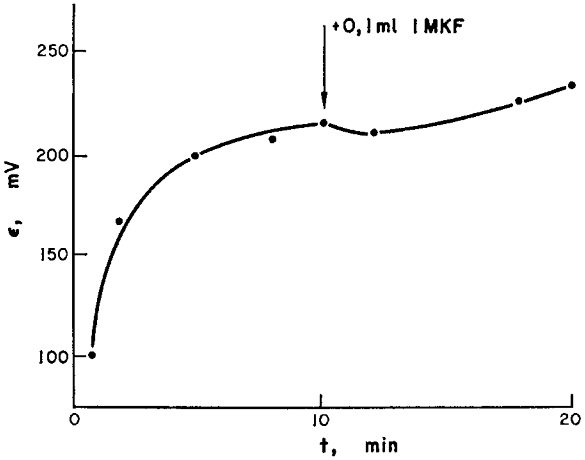

ABB. 3.—Potential-Zeit-Verhalten der Titanelektrode nach Zusatz von Fluoridionen.

oder nur schwer löslich sind. In fluoridhaltigen sauren Medien jedoch lösen sich diese Schutzschichten je nach Konzentration mehr oder weniger rasch unter Bildung von Fluorokomplexen des 3- und 4-wertigen Titans auf. Die dadurch freigelegte Metalloberfläche wird dann sowohl durch die Flußsäure wie auch durch die in der Lösung enthaltene Salzsäure angegriffen. Für den potentialbestimmenden Vorgang kann im vorliegenden Fall angenommen werden:

$$\mathrm{Ti} \rightleftharpoons \mathrm{Ti}^{3+} + 3e^-. \tag{2}$$

Es war nun notwendig zu erfahren, wie die Reaktionsgeschwindigkeit der Umsetzung zwischen Fluoridionen und der Elektrodenoberfläche von der Eisen(III)-Konzentration abhängt. Hierzu wurde als Maß die Potentialänderung pro Zeiteinheit gewählt. Abbildung 4 zeigt diese Geschwindigkeit in Abhängigkeit von der Fluoridkonzentration. Sie nimmt erwartungsgemäß mit steigender Fluoridkonzentration zu und mit steigender Eisenkonzentration ab. Bei einer Eisen(III)-Konzentration von $5.10^{-4}M$ und einer Fluoridkonzentration von $10^{-3}M$ ist aus dem Diagramm eine dem Reaktionsablauf proportionale Spannungsänderung von etwa 0,1 mV/sec entnehmbar.

Der Reaktionsablauf an der Titanoberfläche ist aber auch von der Salzsäurekonzentration abhängig, wie Abb. 5 zeigt. Bei konstanter Eisen(III)-Ionenkonzentration nimmt die Empfindlichkeit mit steigender H^+-Konzentration zu. Orientierende Kieselsäuretitrationen mit $1M$ Kaliumfluoridlösung haben jedoch ergeben, daß in $3M$ salzsäure der potentiometrische Kurvenverlauf am gleichmäßigsten ausgebildet ist.

Daß mit steigender Eisen(III)-Konzentration die Empfindlichkeit der Titanelektrode in $3M$ Salzsäure gegenüber Fluoridionen abnimmt, zeigt die Potential–Zeit-Kurve in Abb. 6. Hier ist bei einer Konzentration von $5.10^{-3}M$ Eisen(III)-chlorid nach Zusatz von 0,1 ml $1M$ Kaliumfluoridlösung auf 100 ml Grundlösung kein Potentialrückgang mehr feststellbar. Die Elektrodenoberfläche ist unter diesen Umständen zu stark passiviert.

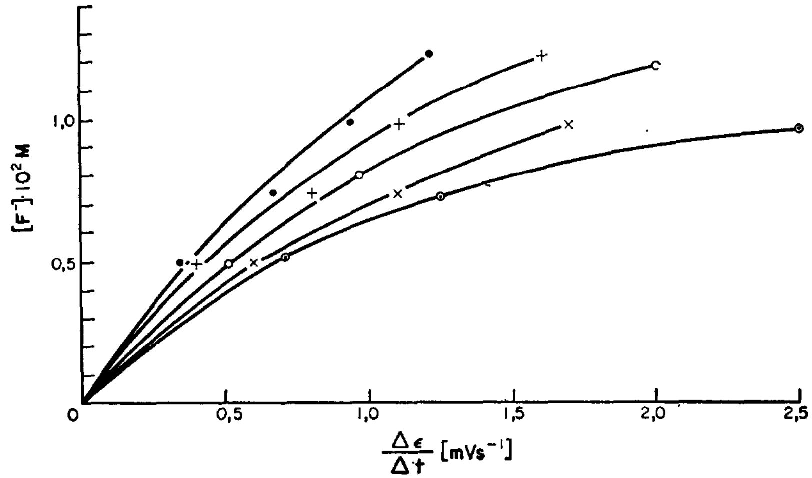

Abb. 4.—Potentialänderungsgeschwindigkeit bei verschiedenen Eisen(III)-Konzentrationen und Fluoridkonzentration. Die Kurven entsprechen nachstehenden Eisen(III)-chlorid-Konzentrationen:

● $10^{-2}M$
\+ $5\cdot 10^{-3}M$
○ $10^{-3}M$
× $5\cdot 10^{-4}M$
⊙ $2{,}5\cdot 10^{-4}M$

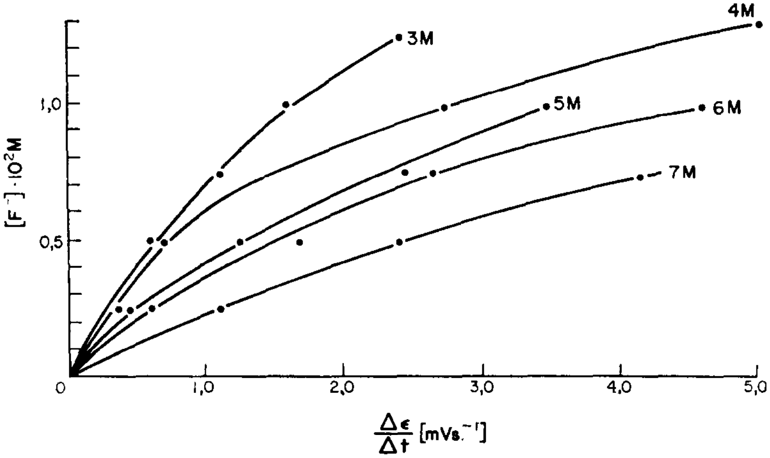

Abb. 5.—Potentialänderungsgeschwindigkeit bei verschiedenen Salzsäurekonzentrationen.

Der Blindwert

Da die Umsetzung zwischen den Fluoridionen und der Titanoberfläche zeitlich gehemmt ist (vgl. Abb. 3) und da zur komplexen Bindung der passivierend wirkenden Eisen(III)-Ionen ebenfalls Fluoridionen benötigt werden, muß angenommen werden, daß kieselsäurefreie Lösungen bei einer Titration ebenfalls Maßlösung verbrauchen, deren Größen in ml im folgenden als Blindwert bezeichnet wird. Aus dem gleichen Grund muß für die Durchführung einer Titration eine automatische Titriereinrichtung eingesetzt werden, die es ermöglicht, den Zufluß an Kaliumfluoridlösung umso langsamer zu gestalten, je mehr sich die Reaktion ihrem Endpunkt nähert. Andernfalls erfolgt eine Übertitration, da man ja im allgemeinen den Endpunkt nicht kennt.

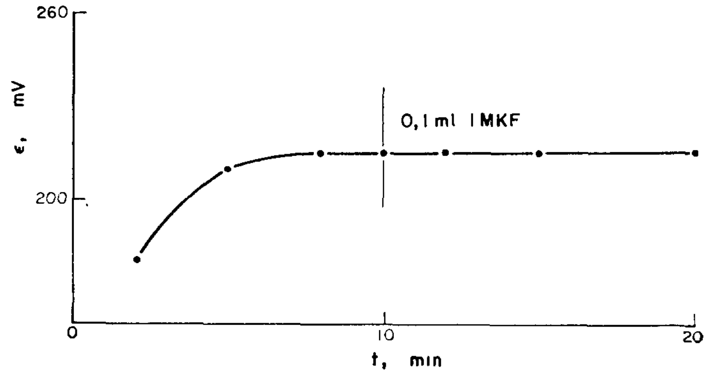

ABB. 6.—Potential-Zeit-Verhalten in der Grundlösung bei einer Eisen(III)-Konzentration von 5 · $10^{-3}M$.

Für den vorliegenden Zweck ist z.B. ein Gerät der Firma Radiometer, Kopenhagen, geeignett, das sich aus der automatischen Bürette ABU 1, dem Potentialmeßgerät PHM 28, dem Steuerglied TTT 11 und dem Schreiber SBR 2 zusammensetzt. Der Schreiber registriert die Potentialänderung pro Zeit als Funktion des Kaliumfluorid-Verbrauches. Der Papiervorschub wurde entsprechend der oben erwähnten Spannungsänderung bei $10^{-3}M$ Kaliumfluorid und $5.10^{-4}M$ Eisen(III)-chlorid auf 0,1 mV/sec eingestellt. Der Zufluß an 1*M* Kaliumfluoridlösung aus der automatischen Bürette wird dann sofort gestoppt, wenn die Potentialänderungsgeschwindigkeit größer als 0,1 mV/sec geworden d.h. wenn der Umschlagspunkt erreicht ist.

Zur Ermittlung des Blindwertes wurden folgende apparative Einstellungen vorgenommen: Schreiber SBR 2 Papiervorschub 1,25 mm/min, Papiereichung —5 mV/mm; Titrator TTT 11 Downscale, Prop. Band 0,1; Autobürette ABU 1, 25 ml; Potentialmeßgerät PHM 28 Skala —200 mV bis +800 mV.

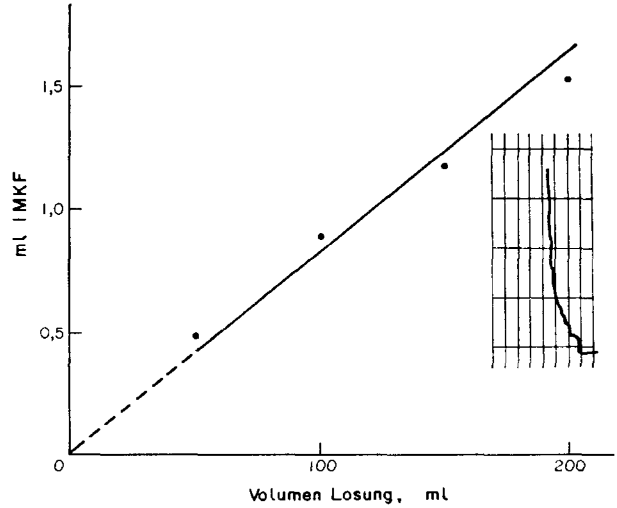

ABB. 7.—Abhängigkeit des Blindwertes vom Gesamtvolumen der Grundlösung.

Als erstes wurde die Abhängigkeit des Blindwertes vom Gesamtvolumen der Grundlösung bei 20°C ermittelt. Bei einer Eisen(III)-Konzentration von $5.10^{-4}M$ in der Grundlösung ergibt sich die in Abb. 7 dargestellte Abhängigkeit. Mit eingezeichnet ist der Kurvenverlauf bei einer Blindwertbestimmung. (Die Kurven des Schreibers SBR 2 werden von rechts nach links aufgezeichnet. Das Potential nimmt von unten nach oben ab. Im vorliegenden Fall lag das Anfangspotential gegen ges. KE bei + 210 mV. Die Titration wurde bei + 25 mV abgebrochen).

Der Blindwert ist erwartungsgemäß auch von der Eisen(III)-Konzentration, der Salzsäurekonzentration und von der Temperatur abhängig. Eine Erhöhung der Eisen(III)-Konzentration von $10^{-3}M$ auf $10^{-1}M$ läßt den Blindwert von *ca.* 1 ml $1M$ Kaliumfluorid auf *ca.* 4 ml ansteigen. Bei Steigerung der Salzsäurekonzentration von $3M$ auf $6M$ sinkt der Blindwert um *ca.* 0,5 ml ab. Ein Kelvin Temperaturerhöhung schließlich bewirkt eine Abnahme des Blindwertes von *ca.* 0,05 ml $1M$ Kaliumfluorid. Für 100 ml Grundlösung entspricht der Blindwert einer Konzentration von *ca.* $0{,}8.10^{-2}M$ an Kaliumfluorid die notwendig ist, um die Eisen(III)-Ionen komplex zu binden und das Potential endgültig aus dem oxidpassiven Bereich herauszulösen.

Die oben erwähnte Mindestkonzentration von $10^{-3}M$ Kaliumfluorid (vgl. Abb. 3) bewirkt zwar eine vorübergehende Unterbrechung des Kaliumfluorid-Zuflusses aus der automatischen Bürette; die passivierende Wirkung des Systems ist aber noch zu groß, um bei dieser Konzentration bereits eine restlose Zerstörung der Passivschicht zu ermöglichen. Somit holt nach einer gewissen Zeit das Kontrollpotentiometer am Schreiber SBR 2 dieses geringfügig in negative Richtung abgewanderte Potential wieder ein, die Titration wird fortgesetzt, wieder gestoppt, fortgesetzt usw. bis der oxidpassive Bereich schließlich durchschritten ist. Nur durch diese Automatik ist es überhaupt möglich, sich an den Endpunkt heranzutasten.

Versuchsauswertung im Hinblick auf die analytische Anwendung

Für die analytische Verwendung des Elektrodensystems Titan—ges.KE zu potentiometrischen Kieselsäurebestimmungen ergeben sich aus den bisherigen Versuchsergebnissen folgende Erkenntnisse.

1. Zur Einstellung eines positiven Potentials gegen die ges.KE in $3M$ Salzsäure, gesättigt mit Kaliumchlorid und Kaliumhexafluorosilicat, ist die Anwesenheit geringer Eisen(III)-Mengen erforderlich, vorteilhaft $5.10^{-4}M$. Bei höherer Konzentration wird die Empfindlichkeit gegen Fluoridionen zu gering; bei geringeren Gehalten ist die Potentialkonstanz nicht mehr gewährleistet und das Potential schwankt unregelmäßig.
2. Für die Einstellung eines relativ konstanten Potentials muß mit dem Titrationsbeginn nach Einsetzen des Elektrodensystems in die Lösung eine gewisse Zeit, am besten 10 min, gewartet werden.
3. Die Elektrodenoberfläche muß vor jeder neuen Messung mechanisch poliert, d.h. erneuert werden, sonst ergeben sich unreproduzierbare Potentialverhältnisse und die Ansprechempfindlichkeit auf Fluoridionen wird gestört.
4. Zweckmäßigerweise wird in salzsaurer, kaliumchloridhaltiger Lösung gearbeitet, da hier das Titan eine besonders hohe Korrosionsbeständigkeit aufweist, und außerdem Störungen durch schwerlösliche Niederschläge kaum zu erwarten sind.
5. Zur Verringerung der Löslichkeit des Kaliumhexafluorosilicats müssen die Lösungen mit Kaliumchlorid gesättigt werden. Einsatz von Kaliumchlorid ist günstiger als das Arbeiten mit organischen Lösungsmitteln, da bei letzteren notwendigerweise eine Verdünnung der zu untersuchenden Silicatlösungen eintritt. Die Kaliumhexafluorosilicat-Konzentration muß aber niedrig gehalten werden, da die Titanelektrode ebenfalls auf Fluorosilicationen anspricht.

6. Es muß für eine gute Temperaturkonstanz gesorgt werden, da eine starke Temperaturabhängigkeit der Löslichkeit des Kaliumhexafluorosilicats in der Grundlösung besteht.
7. Obwohl bei höheren Salzsäurekonzentrationen die Empfindlichkeit gegen Fluoridionen zunimmt, empfiehlt sich ein Arbeiten in 3*M* Salzsäure, denn höhere Salzsäuregehalte bewirken wiederum stärkere Verdünnung der Silicatlösungen, deren Ausgangskonzentration durch den alkalischen Aufschluß begrenzt ist.
8. Da die Titanelektrode nicht augenblicklich auf Fluoridionen anspricht, muß gegen Ende der Titration außerordentlich langsam titriert werden, wozu bei unbekannter Lage des Endpunktes, d.h. bei unbekanntem Kieselsäuregehalt, eine Titrierautomatik notwendig wird.
9. Die Zeitabhängigkeit der Umsetzung zwischen Fluoridionen und der Titanoberfläche bedingt einen Blindverbraüch an Fluoridmaßlösung, der bei Titrationen kieselsäurehaltiger Lösungen zu berücksichtigen ist.

Auf die Anwendung dieser Ergebnisse zur potentiometrischen Kieselsäurebestimmung wird im zweiten Teil der Arbeit eingegangen.

Die Verfasser danken Herrn Prof. Dr. habil. W. Forker, Direktor des Instituts für Chemie an der Technischen Hochschule Karl-Marx-Stadt, für seine nützlichen Ratschläge.

Summary—The response of a titanium electrode to fluoride in the presence of fluosilicate has been investigated. In 3*M* hydrochloric acid containing a small amount of iron(III) the electrode can be used to follow potentiometrically the titration of silicate with fluoride. As the reactions and response are rather slow, an automatic potentiometric titrator must be used.

Résumé—On a étudié la réponse d'une électrode de titane au fluorure en la présence de fluosilicate. En acide chlorhydrique 3*M* contenant une petite quantité de fer(III), on peut utiliser l'électrode pour suivre potentiométriquement le titrage du silicate avec le fluorure. Comme les réactions et la réponse sont assez lentes, il faut utiliser un appareil de titrage potentiométrique automatique.

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POTENTIOMETRISCHE KIESELSÄUREBESTIMMUNG UNTER VERWENDUNG EINER TITANELEKTRODE—II

DAS BESTIMMUNGSVERFAHREN

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Zusammenfassung—Die Bedingungen für die automatische potentiometrische Titration von Kieselsäure mit 1*M* Kaliumfluorid unter Verwendung einer Titanelektrode werden beschrieben. Die Wirkung einer Temperaturänderung und anderer Faktoren wird diskutiert. Die Standardabweichung für die Bestimmung von Proben bis zu 240 mg beträgt 1 mg Aluminium, Eisen, Borat, Nitrat, Sulfat und Phosphat stören dabei.

IM ERSTEN TEIL dieser Arbeit[2] wurde das Verhalten einer Titanelektrode in salzsaurer Lösung gegenüber Fluoridionen bei gleichzeitiger Anwesenheit von Hexafluorosilicat-Ionen im Hinblick auf ihre Verwendung zur Indikation der Umsetzung von Silicat- und Fluoridionen nach

$$SiO_3^{2-} + 6F^+ + 6H^+ \rightleftharpoons [SiF_6]^{2-} + 3H_2O$$

untersucht. Über ihre Eignung bei der potentiometrischen Kieselsäurebestimmung soll nachstehend berichtet werden.

Titrationen von reinen Kieselsäurelösungen

Im Nickeltiegel werden 4 mal 1,000 g auf eine Korngröße von 0,06 mm gepulverter, mit konz. Salzsäure eine Stunde am Rückflußkühler ausgekochter, dann bei 1150° geglühter Quarzsand (SiO_2-Gehalt >99,95%, ermittelt durch Abrauchen mit Flußsäure) mit je 8 g Kaliumhydroxid aufgeschlossen. Hierbei wird zunächst das Kaliumhydroxid allein im Tiegel eingeschmolzen, dann erst die Sandeinwaage auf die erkaltete Schmelze gegeben und erneut aufgeschmolzen. Die vier wiederum erkalteten Schmelzen werden nach Lösen in heißem Wasser gemeinsam in einen 500-ml Meßkolben filtriert und so von ausgeschiedenem Nickelhydroxid befreit. Nach Abkühlen, Auffüllen mit dest. Wasser und Durchmischen entspricht 1 ml dieser Lösung 8,0 mg SiO_2.

Diese Kieselsäurelösung dient als Urtiterlösung. Aliquote Teile dieser Lösung (5 bis 25 ml) werden in den Titrierbecher gegeben, mit dest. Wasser auf 50 ml aufgefüllt und mit soviel ml konz. Salzsäure versetzt, daß die Lösung nach Auffüllen auf 100 ml 3*M* an freier Salzsäure ist (unter Berücksichtigung der für die Neutralisation des Kaliumhydroxids notwendigen Salzsäuremenge je nach aliquotem Teil 24,5 bis 26 ml Salzsäure).

Dann werden aus einer Mikrobürette 0,5 ml 0,1*M* Eisen(III)-chlorid, gelöst in 1*M* Salzsäure, zugesetzt und nach Abkühlen auf Zimmertemperatur auf 100 ml ± 2 ml mit dest. Wasser aufgefüllt (Marke am Titrierbecher). Schließlich werden mit einem Eichmaß *ca.* 25 g Kaliumchlorid und *ca.* 0,5 g Kaliumhexafluorosilicat zugegeben, die Meßkette Titan–ges. Kaliumelektrode (KE) eingesetzt, Rührer und Thermostat eingeschaltet (20°) und nach 10 Minuten mit der automatischen Titration unter Verwendung einer *ca.* 1*M* Kaliumfluoridlösung entsprechend den Ausführungen im ersten Teil dieser Arbeit begonnen.

Die Verwendung einer genau 1*M* Kaliumfluoridlösung, deren Einstellung analytisch sehr aufwendig wird, ist nicht erforderlich, wenn die Lösung gegen bekannte Kieselsäuremengen faktorisiert wird. Wie bei der Titration von kieselsäurefreien Lösungen, d.h. bei der Ermittlung des Blindwertes, tastet sich der Titrator an den

Endpunkt der Reaktion heran und schaltet den Zufluß an Fluoridlösung vorübergehend ab, wenn die Potentialänderungsgeschwindigkeit größer als 0,1 mV/sec wird.

Als Beispiel zeigt die Abb. 1 Titrationskurven von 40 bis 300 mg SiO_2 pro 100 ml Grundlösung. Die Originallänge des Papierstreifens, auf dem die Kurven aufgenommen wurden, beträgt 0,33 m, 10 mm entsprechen eine Potentialänderung von 50 mV. Die Originalbreite des Papierstreifens beträgt 0,25 m, 10 mm entsprechen 1 ml Kaliumfluoridlösung. (1 ml 1*M* Kaliumfluorid entspricht *ca.* 10 mg SiO_2). Die Anfangspotentiale liegen bei 200–250 mV, die Endpotentiale bei 50–100 mV gegen ges. KE. Hier wurde dann der Titrator ausgeschaltet. Trägt man den Verbrauch an 1*M* Kaliumfluoridlösung für verschiedene Kieselsäure-Mengen in ein Koordinatensystem ein, so erhält man eine Gerade die nicht durch den Ursprung geht, sondern die Abszisse bei 0,9 ml schneidet. Dieser Abschnitt ist identisch mit dem früher diskutierten Blindwert.

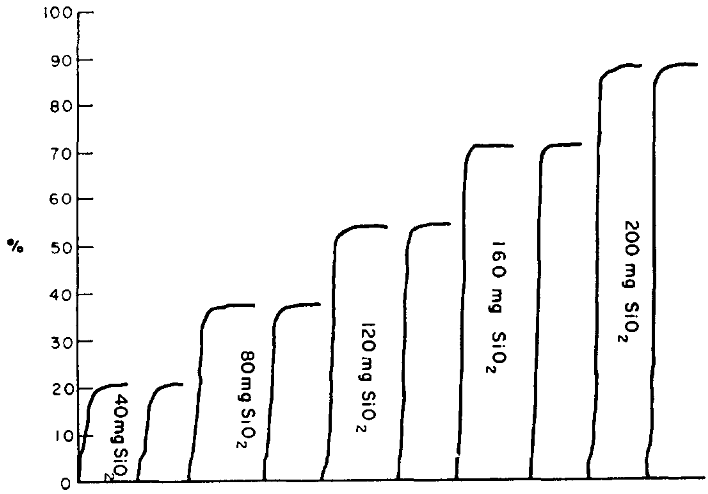

ABB. 1.—Titrationskurven verschiedener SiO_2-Mengen, aufgenommen an aliquoten Teilen homogener Kieselsäurelösungen.

Die sehr guten Ergebnisse automatischer Kieselsäurebestimmungen mit potentiometrischer Indizierung an der Titanelektrode bei Verwendung aliquoter Teile einer homogenen Aufschlußlösung lassen sich jedoch an Lösungen aus individuellen Aufschlüssen nicht bestätigen. Ursache hierfür ist das bekannte Polymerisationsbestreben der Kieselsäure in saurer Lösung, wodurch es selbst unter peinlichster Einhaltung aller experimentellen Bedingungen nicht möglich wird, exakt reproduzierbare Kieselsäuresole zu erhalten. Welche Bedeutung beispielsweise die Standzeit eines sauren Kieselsäuresols auf den Kaliumfluoridverbrauch hat, ergibt sich aus der Tatsache, daß mit zunehmender Wartezeit vor Titrationsbeginn auch der Kaliumfluoridverbrauch zunimmt (Abb. 2). Hierbei wurden jeweils aliquote Teile der oben angeführten homogenen Kieselsäure-Urtiterlösung titriert. Die relativ geringe Löslichkeit der entstehenden Kieselsäuresole begrenzt die Größe der Einwaage bei individuellen Sandproben mit max. 250 mg SiO_2/100 ml Grundlösung.

Zur Bereitung individueller Kieselsäure-Lösungen wurde nachstehender Arbeitsgang eingehalten.

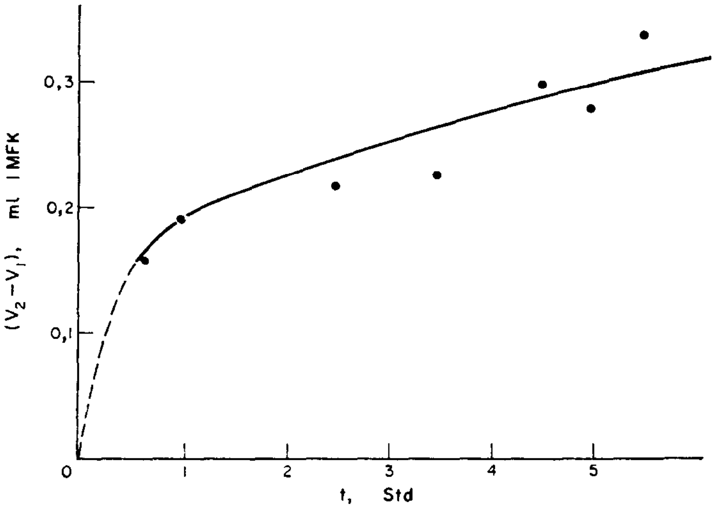

ABB. 2.—Abhängigkeit des Verbrauches an 1*M* Kaliumfluorid vom Alterungszustand des Kieselsäuresols.

V_1 = Verbrauch zur Zeit t_1
V_2 = Verbrauch zur Zeit t_2
$t_2 > t_1$.

Jeweils 0,2100 g Quarzsand (<0,06 mm) werden im Nickeltiegel mit 5 g Kaliumhydroxid—wie oben beschrieben—aufgeschlossen. Die Schmelze wird mit heißem Wasser im Tiegel selbst ausgelaugt, anschließend in den Titrierbecher gespült und mit Wasser auf 50 ml verdünnt. Nach Abkühlen auf Zimmertemperatur wird die alkalische Lösung unmittelbar vor Beginn der Titration mit 30 ml konz. Salzsäure in einem Guß unter kräftigem Rühren versetzt. Man füllt mit Wasser auf 100 ml auf, läßt 15 Minuten bedeckt im siedenden Wasserbad stehen und kühlt dann unter fließendem Wasser auf 20° ab. Schließlich werden aus einer Mikrobürette 0,5 ml 0,1*M* Eisen(III)-chlorid-Lösung, *ca.* 25 g Kaliumchlorid und *ca.* 0,5 g Kaliumhexafluorosilicat zugegeben, wonach die Lösung wie oben beschrieben titriert wird.

Experimentelle Besonderheiten, die den Kurvenverlauf bestimmen

Unter Berücksichtigung der im ersten Teil dieser Arbeit gemachten Ausführungen zum Blindverbrauch an 1*M* Kaliumfluoridlösung für kieselsäurefreie Lösungen, setzt die Präzision der in Abb. 1 gezeigten Kurven die exakte Einhaltung folgender Parameter voraus:

Sättigung der Lösung mit Kaliumhexafluorosilikat und Kaliumchlorid, Temperaturkonstanz von 20 ± 0,5°, Volumenkonstanz, Konstanz und Anpassung der Titriergeschwindigkeit an die Umsetzungsgeschwindigkeit, Konstanz der Geometrie des Zellenaufbaues und damit Konstanz der Diffusionsstromverhältnisse an der Titanoberfläche, sowie hinreichende Reproduzierbarkeit der Titanoberfläche durch mechanische Politur vor Beginn jeder Messung. Welchen Einfluß diese Parameter auf den Kurvenverlauf ausüben, darüber geben die folgenden Abbildungen Auskunft.

In Abb. 3 ist eine Titrationskurve dargestellt, bei der die Grundlösung zu Beginn der Titration wohl mit Kaliumchlorid, nicht aber mit Kaliumhexafluorosilicat gesättigt war. Offensichtlich tritt dadurch unmittelbar nach Beginn der Titration eine vorübergehende Übersättigung der Lösung, d.h. erhöhte Hexafluorosilicat-Ionenkonzentration auf, die einen zeitweiligen Potentialrückgang auslöst und die Titration solange unterbricht, bis sich die Hexafluorosilicat-Konzentration in der Grundlösung wieder stabilisiert hat. Unterbleibt die Sättigung der Lösung mit Kaliumhexafluorosilicat und Kaliumchlorid, so ergeben sich Kurven ohne ausgeprägten Potentialsprung, die nicht verwertbar sind.

Die starke Temperaturabhängigkeit des Verbrauchs an 1*M* Kaliumfluoridlösung von *ca.* 0,05 ml pro Grad Celsius ist in Abb. 4 dargestellt. Mit eingezeichnet sind 2 Kurven für je 165 mg SiO_2, aufgenommen bei verschiedenen Temperaturen. Man erkennt, daß höhere Temperaturen einen stärkeren Potentialrückgang bei gleichzeitig geringerem Kaliumfluoridverbrauch hervorrufen.

Da der Blindwert vom Gesamtvolumen der Grundlösung abhängt,[3] ist der Verbrauch von 1*M* Kaliumfluoridlösung auch bei Kieselsäuretitrationen vom Volumen der zu titrierenden Lösung

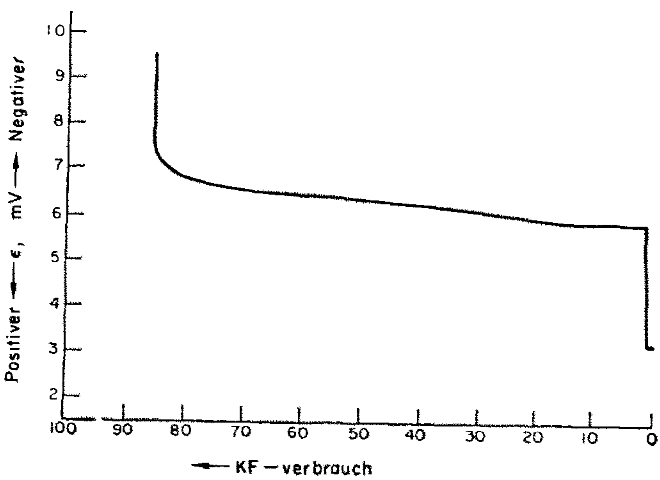

ABB. 3.—Automatisch-potentiometrische Titrationskurve von 200 mg SiO_2 aufgenommen in einer Grundlösung ohne Kaliumhexafluoro silicat.

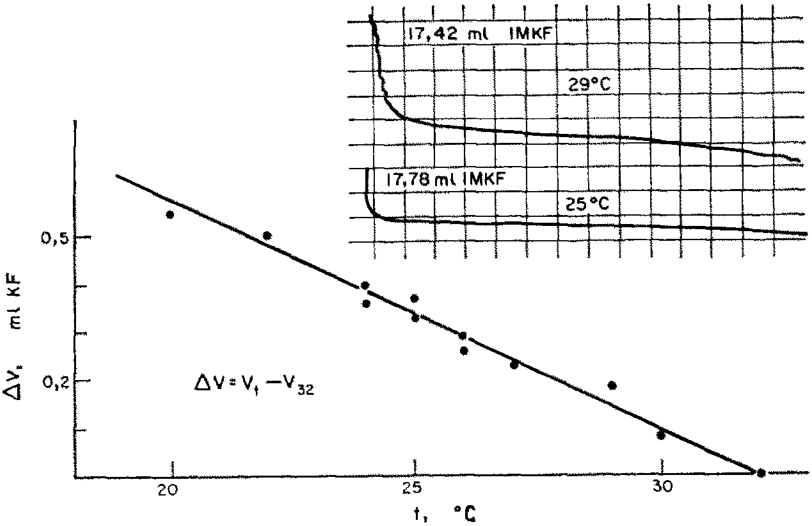

ABB. 4.—Abhängigkeit des Kaliumfluoridverbrauchs von der Temperatur.
V_t = Verbrauch an 1*M* Kaliumfluorid bei der Temperatur *t*
V_{32} = Verbrauch an 1*M* Kaliumfluorid bei 32°C.

abhängig. Eine Volumenvergrößerung von 10 ml bedingt einen Mehrverbrauch von *ca.* 0,1 ml 1*M* Kaliumfluorid.

Besondere Aufmerksamkeit muß der Geometrie des Zellenaufbaues und der Konstanz der Diffusionsstromverhältnisse gewidmet werden. So wird beispielsweise der Einfluß der Rührrichtung in Abb. 5 offensichtlich. Im vorliegenden Falle befinden sich Zulauföffnung und Elektrodenoberfläche in gleicher Höhe in der Mitte der Zelle. Während jedoch bei der oberen Kurve die zufließende Kaliumfluorid-Lösung von der Elektrodenoberfläche weggerührt wurde (Verbrauch 12,63 ml), wurde sie bei der unteren Kurve auf die Oberfläche zugerührt. Dabei wurden nur 12,40 ml für eine vorgegebene Kieselsäure-Konzentration von 110 mg SiO_2 pro 100 ml Grundlösung verbraucht, weil hier die lokale Fluoridionenkonzentration der an die Titanoberfläche anströmenden Lösungspartien zeitweilig größer ist als im ersten Fall. Die Rührgeschwindigkeit selbst ist von untergeordneter Bedeutung, sofern nur der Bodenkörper gründlich aufgewirbelt wird.

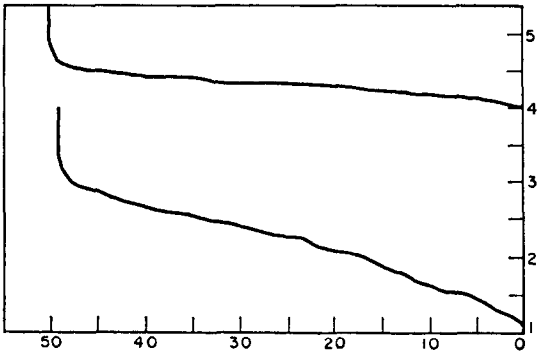

Abb. 5.—Titrationskurvenverlauf und Rührrichtung.

DISKUSSION DES TITRATIONSKURVENVERLAUFES

Neben der maßanalytische verwertbaren Umsetzung nach (1) müssen die nachstehend aufgezeigten Reaktionen für die Deutung des Titrationsverlaufes in Betracht gezogen werden.

$$SiO_3^{2-} + 6F^- + 6H^+ \longrightarrow [SiF_6]^{2-} + 3H_2O \tag{1}$$

$$SiO_3^{2-} \xrightarrow{H^+} (SiO_2 \cdot xH_2O)_y \tag{2}$$

$$Fe^{3+} + xF^- \longrightarrow [FeF_x]^{(3-x)} \tag{3}$$

$$K_2[SiF_6] \longrightarrow 2K^+ + [SiF_6]^{2-} \tag{4}$$

$$Fe^{3+} + Ti^{3+} + H_2O \longrightarrow Fe^{2+} + TiO^{2+} + 2H^+ \tag{5}$$

$$Ti + 4OH^- + 4Fe^{3+} \longrightarrow TiO_2 + 2H_2O + 4Fe^{2+} \tag{6}$$

$$4H^+ + TiO_2 + xF^- \longrightarrow [TiF_x]^{(4-x)} + 2H_2O \tag{7}$$

$$Ti \longrightarrow Ti^{3+} + 3e \tag{8}$$

$$2Ti + 6H^+ \longrightarrow 2Ti^{3+} + 3H_2 \tag{9}$$

Da die Stabilitätskonstanten der Fluorokomplexe in der Grundlösung nicht bekannt sind, müssen die Ergebnisse empirisch erklärt werden. Im einzelnen läßt sich folgendes ableiten.

Reaktionen in der Lösung

Polymerisation der Kieselsäure unter Bildung von Kieselsäuresolen unterschiedlicher Aggregationszustände nach (2) und dadurch Verringerung der Umsetzungsgeschwindigkeit der Ionenreaktion nach (1).

Umsetzung der Fluoridionen mit dem Potentialstabilisator Eisen(III) nach (3) und dadurch Schwächung der Oxydationskraft des Stabilisators.

Temperaturabhängigkeit der Löslichkeit des Kaliumhexafluorosilicats nach (4) und dadurch Veränderung der Konzentration freier Hexafluorosilicat-Ionen bei Temperaturänderung.

Umsetzung in Lösung gegangener Titan(III)-Ionen mit dem Potential-Stabilisator nach (5) und dadurch Verringerung der Stabilisierungswirkung des dreiwertigen Eisens.

Reaktion an der Elektrodenoberfläche

Deckschichtenbildung durch Umsetzung mit Hydroxid-Ionen selbst in stark saurer Lösung[3] nach (6) und dadurch Aufbau und fortschreitende Verstärkung einer Passivschicht.

Auflösung der Schutzschicht durch Fluoridionen nach (7) und dadurch Verringerung der Passivierung.

Auflösung der freigelegten Oberfläche nach (8) als potentialbestimmender Vorgang und schließlich Umsetzung mit Protonen nach (9) und dadurch Auflösung des Titans nach Abtragung der Schutzschicht.

Hierbei verlaufen die Reaktionen nach (2), (6) und (7) nicht augenblicklich, sondern benötigen eine gewisse Zeit.

Unter Berücksichtigung dieser 9 Reaktionen kann nun der Kurvenverlauf bei einer automatisch-potentiometrischen Titration folgendermaßen gedeutet werden:

Der mit Beginn der Titration einsetzende allmähliche Potentialrückgang kommt dadurch zustande, daß wohl die Hauptmenge der Fluoridionen mit der Kieselsäure nach (1) reagiert, ein Teil aber auch nach (7) die Schutzschicht auf der Elektrode abbaut. Da die Reaktionsgeschwindigkeiten zwischen Fluorid- und Silicat-Ionen bzw. Fluoridionen und Titanoberfläche von unterschiedlicher Größenordnung sind, hängt es von den experimentellen Bedingungen, insbesondere von den Diffusionsverhältnissen ab, ob dieser erste Teil der Kurve stark geneigt ist oder flach verläuft, ob ein starker oder mäßiger Potentialrückgang erfolgt.

Maßgebend für die Steigung in diesem Kurventeil sind weiterhin die zeitabhängigen Reaktionen der Kieselsäurepolymerisation sowie der Deckschichtenaufbau durch das Redoxsystem nach (2) und (6).

Als Beweis hierfür kann die Zunahme an Fluoridionenverbrauch bei gealtertem Kieselsäuresol dienen. Die Umsetzungsgeschwindigkeit zwischen den durch Alterung wachsenden Teilchen des Kieselsäuresols und den Fluoridionen wird langsamer, während die Geschwindigkeit nach (7) nicht verändert wird. Als Ergebnis dessen steigt der Kaliumfluoridverbrauch an.

Der immer stärker werdende Potentialrückgang in der Nähe des Endpunkts erklärt sich aus der nunmehr verstärkt einsetzenden Umsetzung zwischen Fluoridionen und Eisen(III) nach (3). Dadurch wird schließlich die Oxydationskraft derart geschwächt, daß das Potential aus dem oxidpassiven Bereich herauswandert und schließlich Auflösung gem. (7), (8) und (9) erfolgt. Die Kurve verläuft dann senkrecht, der Endpunkt ist erreicht.

Mit dieser Deutung des Kurvenverlaufs verknüpft ist die Deutung des schon erwähnten Blindwertes, d.h. des Kaliumfluoridverbrauchs der in kieselsäurefreien Lösungen benötigt wird, um ein eindeutiges Abtreiben des Potentials bis zum Auflösungspotential des Titans von *ca.* −600 mV gegen ges. KE auszulösen. Infolge der zeitabhängigen Reaktion nach (7) steigt der Blindwert mit steigender Titrationsgeschwindigkeit an. Natürlich wird dieser Blindverbrauch nicht allein durch die Titrationsgeschwindigkeit und damit durch die Diffusionsgeschwindigkeit freier Fluoridionen an die Titanoberfläche bestimmt, sondern auch durch Umsetzung dieser Ionen zu Eisenfluorokomplexen nach (3).

In die Deutung des Titrationskurvenverlaufes fügt sich die Abnahme des Kaliumfluoridverbrauchs mit steigender Temperatur gut ein, wenn man annimmt, daß die durch Temperatursteigerung ausgelöste höhere Konzentration an freien Hexafluorosilicat-Ionen ebenfalls zur Auflösung der Schutzschicht beiträgt. Zweifellos spielen hierbei auch die Dissoziationsgleichgewichte der Hexafluorosilicat-Komplexe in saurer Lösung unter Abspaltung von Fluoridionen eine Rolle.

Wird die Schutzschicht jedoch durch Hexafluorosilicat-Ionen angegriffen, dann kann ein äquivalenter Fluoridanteil eingespart werden und der Verbrauch an Kaliumfluorid geht zurück. Dieser durch Temperaturerhöhung ausgelöste Effekt ist infolge der Linearität der Kurve in Abb. 4 ganz sicher nicht auf Vergrößerung der Reaktionsgeschwindigkeit zurückzuführen, da dann ein logarithmischer Kurvenverlauf erwartet werden müßte.

Unter Berücksichtigung des Blindwertes läßt sich zeigen, daß die Umsetzung gem. (1) bei reinen Kieselsäure-Lösungen stöchiometrisch verläuft, d.h. sie entspricht dem atomaren Verhältnis Si:F = 1:6.

KONZENTRATIONSBEREICH UND REPRODUZIERBARKEIT

Der Konzentrationsbereich des entwickelten Verfahrens wird nach oben vor allem durch die Kieselsäuresolkonzentration bestimmt, sowie apparativ durch das Volumen der automatischen Bürette von 25 ml. Ein Nachfüllen der Bürette, d.h. Titrationen mit größeren Verbrauchen als maximal 25 ml, führt apparativ bedingt zu einer Verminderung der Genauigkeit. Bei Verwendung einer 1*M* Kaliumfluoridlösung ergibt sich so eine maximale Konzentration von 240 mg SiO_2/100 ml.

Nach unten ist der Konzentrationsbereich durch die Ansprechempfindlichkeit der Titanelektrode, d.h. durch die Größe des Blindwertes begrenzt, der *ca.* 10 mg SiO_2/100 ml Grundlösung entspricht. Das Verfahren bedarf wie bereits erwähnt prinzipiell einer Eichung mit Lösungen von bekanntem Kieselsäure-Gehalt. Über die Reproduzierbarkeit des Verfahrens bei Untersuchungen aliquoter Teile einer homogenen Kieselsäurelösung und Lösungen aus individuellen Aufschlüssen sowie über die Streubereiche der Einzelmessungen gibt die nachstehende Zusammenstellung Auskunft.

Charakteristische Fehlergrößen

Wiederholstandardabweichung für den geprüften Bereich von 40–200 mg SiO_2 und für 10 aliquote Teile einer homogenen Lösung:

$$S_h = \pm 0{,}19 \text{ mg } SiO_2$$

Vergleichsstreubereich hierfür:

$$\Delta x_h = 0{,}76 \text{ mg } SiO_2$$

Wiederholstandardabweichung für 13 individuelle Aufschlüsse von je 210 mg Sand

$$S_i = \pm 1{,}1 \text{ mg } SiO_2$$

Vergleichsstreubereich hierfür:

$$\Delta x_i = 3{,}3 \text{ mg } SiO_2$$

Störungen

In der nachstehend gegebenen Zusammenstellung sind die überprüften Ionen und ihre Störeinflüsse wiedergegeben.

Unter Berücksichtigung, daß Eisen(III) nicht über das für die Potentialkonstanz notwendige Maß vorhanden sein darf, sind es wie ersichtlich neben den Anionen, Nitrat, Sulfat und Phosphat vor allem die Fluorokomplexbildner wie Aluminium und Bor, die das Verfahren erheblich stören. Sie lassen sich durch Abtrennung des Aluminium bzw. Bor nach bekannten chemischen bzw. physikalisch-chemischen Verfahren nicht beseitigen, da hierbei in jedem Fall der Polymerisationszusatand des Kieselsäuresols verändert wird. Gleichzeitig zeichnen sich damit jedoch für die gegenüber Fluoridionen empfindliche Titanelektrode prinzipielle Einsatzmöglichkeiten zur Indizierung von Fluorokomplexbildungen ab.

TABELLE I. STÖREINFLÜSSE

Kation bzw. Anion	Konzentration, *M*	Zunahme des Verbrauches an 1*M* Kf
Na^{+}	0,01–0,05	keine signifikante Zunahme
Ca^{2+}	0,01–0,05	
$Mg^{2}c$	0,01–0,05	
Ba^{2+}	0,01–0,05	
Zn^{2+}	0,01–0,05	
Pb^{2+}	0,001–0,01	
Ti^{4+}	0,001–0,005	
Al^{3+}	0,005–0,015	*ca.* 2,5 ml
B^{3+}	0,005–0,015	*ca.* 2,5 ml
NO_3^{-}	0,1–0,5	*ca.* 0,5 ml
SO_4^{2-}	0,02–0,25	*ca.* 3,5 ml
PO_4^{3-}	0,02–0,25	*ca.* 10 ml

LITERATUR

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2. G. Ackermann und J. Lange, *Talanta*, 1970, **17**, 701.
3. W. Forker, *Elektrochemische Kinetik*, S. 152–161. Akademie-Verlag, Berlin, 1966.

Summary—The conditions for the automatic potentiometric titration of silica with 1*M* potassium fluoride, using a titanium electrode, are described. The effect of temperature and other factors on the blank value is reported. The standard deviation is 1 mg for samples up to 240 mg of SiO_2. Aluminium, iron, borate, nitrate, sulphate and phosphate interfere.

Résumé—On décrit les conditions pour le titrage potentiométrique automatique de la silice avec le fluorure de potassium 1*M* en utilisant une électrode de titane. On rapporte l'influence de la température et d'autres facteurs sur la valeur du témoin. L'écart type est de 1 mg pour des échantillons allant jusqu'à 240 mg de SiO_2. L'aluminium, le fer, le borate, le nitrate, le sulfate et le phosphate gênent.

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SULPHUR IN FOODSTUFFS—I
DETERMINATION AS SULPHATE

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Summary—Sulphate formed by the oxygen-flask combustion of foodstuffs may be determined colorimetrically with barium chloranilate, titrimetrically with barium perchlorate, or turbidimetrically with barium chloride. The difficulties encountered in each method, including interferences, have been investigated. The turbidimetric procedure is recommended if high precision is not required and due account is taken of interference from phosphate, iron, calcium and magnesium; the other two methods are unsuitable for routine work.

In recent years evidence has been presented that the protein values of most human diets are limited by their sulphur-containing amino-acid content.[1,2] Frequently the sulphur content of foods (often used as an index of the sulphur-containing amino-acids) has been calculated by the application of a factor to the nitrogen content. This is obviously unsatisfactory, especially for mixed diets. In most investigations where sulphur has been determined directly,[2] a simple oxygen-flask combustion[3,4] has been followed by a turbidimetric procedure. The effect of interferences from substances likely to occur in foods has not, however, previously been thoroughly investigated.

Of the methods available for the combustion of foodstuffs before sulphur determinations the oxygen-flask method has undoubted advantages, being simple, inexpensive, quick and, with care, quantitative and reliable. One disadvantage is that the moisture content of the food must be low and many foodstuffs must be dried before combustion.

Most spectrophotometric methods for the determination of sulphate depend on the displacement of a chromogenic molecule from an insoluble complex.[5] The barium chloranilate method is the most widely investigated as it is alleged to be relatively free from interferences from small quantities of many common anions.[6–8] Strict control of pH is essential, however, and several buffers have been suggested to replace the original phthalate buffer, which is frequently incapable of maintaining the desired pH after cation-exchange removal of interfering ions.[9–12] The need to prepare the reagent in a suitable form[13] and of sufficient purity to give a low blank,[14] together with the relative insensitivity of the method when measurements are carried out in the visible region and at pH 4–6, has given rise to several comments and investigations.[14–16] The molar absorptivity of the chloranilate ion is much greater at 280–350 nm than in the visible region.[15]

Titration of sulphate usually involves precipitation with barium or lead.[5] Barium perchlorate is generally preferred to barium chloride as titrant because it gives less co-precipitation error, in accord with the Paneth-Fajans rule.[17,18] Of the many indicators proposed, Thorin has advantages,[19,20] particularly when screened with Methylene Blue.[21,22] The sensitivity has been extended by spectrophotometric detection of the end-point.[23] Many cations interfere by co-precipitation or by forming coloured complexes and must be removed by ion-exchange. It is claimed that addition of excess of potassium bromide eliminates much of this interference.[24] Phosphate is the only common anion that causes serious interference, and standardization of the amount present,[25] or prior removal with zinc oxide,[26] magnesium carbonate,[20,27] magnesium oxide,[23,28] or silver oxide[29] have been suggested.

Sulphate is commonly determined turbidimetrically after the addition of barium chloride to an acidified solution of the sulphate. Several stabilizing agents have been proposed, including gum acacia,[30] gelatin,[31] starch,[32] dextran,[33] peptone, gum-ghatti[34,35] and glycerol.[36] Many other factors influence the precipitation, *e.g.*, pH, temperature, whether the reagent is in solution or solid form, in large or small crystals.[36,37] Garrido[38] has recently suggested the use of "Tween 80" as a stabilizing agent. Several workers claim that their methods are free from interference by more common ions, *e.g.*, ammonium, sodium, potassium, calcium, aluminium, magnesium, chloride, nitrate, silicate and phosphate.[30,39,40]

EXPERIMENTAL

Apparatus

Ion-exchange column. A 15-mm bore tube packed to a depth of 100 mm with Zeo-Carb 225 (H^+-form) 100–200 mesh. The resin was obtained from the Na^+-form by washing 200 g first with four 500-ml portions of 2·5*M* hydrochloric acid and then with distilled water until the washings reached pH 6.

Centrifuge tubes, 50-ml. Graduated by means of a grade A 10-ml burette, and fitted with rubber caps.

Oxygen flask. A 500-ml iodine-flask was fitted with a B24 ground-glass stopper and a 25-mm platinum wire hook (0·6 mm thickness). A detachable platinum spiral made from 90–100 mm of the same wire was fitted with a saucer shaped base made of 0·025-mm thick platinum foil.

Materials

Barium chloranilate. Barium chloride solution (2 l., 5%) was slowly added, with stirring, to chloranilic acid solution (2 l., 0·1%). After one week the aged precipitate was separated (by centrifuge), washed with water until the washings were free from chloride, and then with ethanol (three times) and diethyl ether (once) and finally dried in a desiccator. The commercial salt was unsuitable for analytical work.

Magnesium oxide. Analytical grade reagent was washed with hot water and dried.

Screened Thorin solution. Thorin solution (1 ml, 0·2%) and Methylene Blue solution (1·5 ml, 0·0125%) were added to isopropanol (100 ml). This mixture must be freshly prepared.

Barium chloride–Tween 80 reagent. Tween 80 (20 ml, polyoxyethylene sorbitan mono-oleate, Honeywill Atlas Ltd.) was dissolved in barium chloride solution (80 ml, 10%) with steady stirring, and stored for at least 24 hr before use.

Combustion paper for oxygen flask. Of the papers tested, Whatman No. 541 had the lowest sulphur content (0·004%).

Procedures

Spectrophotometric finish. The method is based on that described by Bertolacini and Barney.[7] An aliquot of sulphate solution was diluted to 10 ml in a test-tube and shaken with about 0·3 g of ion-exchange resin. After 5 min the solution was filtered (sintered-glass Hirsch funnel, porosity 4) and the funnel and resin washed with three 2-ml portions of water. The filtrate and washings were collected in a 50-ml graduated centrifuge tube and diluted to 16 ml; phthalate buffer (4 ml, pH 4·0), absolute ethanol (20 ml) and barium chloranilate (0·1 g) were added and the mixture was stirred for about 3 min. The tube was capped and after at least 15 min, centrifuged (M.S.E Minor Model, setting 8) for at least 15 min. The absorbance was measured against a blank prepared from distilled water, buffer solution and ethanol.

Calibration curves prepared with aliquots of 0·01*N* sulphuric acid were concave (Table I) and differed for different batches of reagent. On variation of the quantity of barium chloranilate from 0·70 to 0·29 g the absorbance for 8·0 ml of 0·01*N* sulphuric acid remained practically constant,

TABLE I.—EFFECT OF SOME ANIONS ON THE CHLORANILATE METHOD

Sulphate, *μequiv*	Anion, *μequiv*	Absorbance (40-mm cell)	Change in absorbance caused by anion, %
0	—	0·009	—
20	—	0·090	—
40	—	0·230	—
60	—	0·395	—
80	—	0·593	—
20	CO_3^{2-} 213	0·085	—
60	106	0·421	+7
80	53	0·629	+6
0	Cl^- 225	0·131	—
20	180	0·233	+160
60	90	0·603	+50
80	45	0·697	+18
0	NO_3^- 129	0·064	—
20	103	0·213	+140
60	52	0·579	+45
80	26	0·639	+7
0	PO_4^{3-} 338	0·043	—
20	270	0·238	+160
40	203	0·417	+80
60	135	0·587	+50
80	68	0·708	+20

confirming that the excess of reagent was adequate. The interference of several anions was investigated by adding measured quantities to standard sulphate solutions and following the procedure. The results (Table I) indicate interference by chloride nitrate and phosphate.

Titrimetric finish. The method was based on that described by Fritz and Yamamura.[20] A distinct end-point was obtained when aliquots of 0·01*N* sulphuric acid were diluted to 10 ml and titrated against 0·004*N* barium perchlorate after addition of isopropanol (30 ml) and screened Thorin solution (10 ml). No systematic error was found in titration of 5–100 μequiv of sulphate, and the relative mean deviation was 0·2% (12 replicates, 100 μequiv). Phosphate was found to interfere seriously (>10% positive error) when present in more than about equivalent ratio.

To remove phosphate, the sample was diluted to 10 ml, boiled gently with 0·3 ± 0·01 g (or with 0·03 ± 0·005 g) of magnesium oxide for 5 min, cooled in ice and kept at 0° for 30 min, then filtered into the ion-exchange column. The filter and column were washed with water (twice with 1 ml, once with 0·5 ml), the column being sucked dry each time. The filtrate and washings were transferred to a 100-ml conical flask with isopropanol (40 ml) and titrated with 0·004*N* barium perchlorate, with 10 ml of screened Thorin solution as indicator. Recoveries were low but could be somewhat improved by adding sodium hydroxide solution before the magnesium oxide (Table II). Tests on solution

TABLE II.—RECOVERY OF SULPHATE IN PERCHLORATE METHOD AFTER TREATMENT FOR REMOVAL OF PHOSPHATE

Sulphate, *μequiv*	NaOH, *μequiv*	Recovery, %	
		0·30 g MgO	0·03 g MgO
20	0	83	93
	100	96	100
	200	97	102
	300	—	99
80	0	83	95
	100	93	99
	200	96	99
	300	—	99
	400	97	—

Blanks for 100–400 μg of NaOH amounted to 0·3–0·4 ml of 0·004*N* $Ba(ClO_4)_2$ for 0·3 g of MgO added, and 0·1–0·2 ml for 0·03 g of MgO.

containing known amounts of phosphate showed that phosphate removal was incomplete, even with sodium hydroxide added, and that sulphate was retained by the residue, especially if ammonia was used instead of sodium hydroxide. These observations were confirmed when solutions labelled with sulphur-35 and phosphorus-32 were treated according to the procedure and the activities of the residues and filtrates were measured.

With certain phosphate:sulphate ratios, the effect of unremoved phosphate fortuitously compensated almost exactly for the loss of sulphate by retention on the magnesium oxide, but the magnesium oxide method was found to be generally unreliable.

Turbidimetric method. An aliquot of sulphate solution (2·5–25 μequiv) plus concentrated hydrochloric acid (1 ml) was diluted to about 40 ml in a 50-ml standard flask. Barium chloride–Tween 80 reagent (5 ml) was added and the mixture diluted to the mark and mixed. After 1 hr the contents were mixed again and the absorbance of the mixture measured against water in a 40-mm cell, a neutral density filter being used. A blank was prepared at the same time. There must be enough hydrochloric acid to dissolve the products of the oxygen-flask combustion, especially iron. The optimum period of standing was determined by transferring the mixture immediately to the 40-mm cell and measuring the absorbance at intervals and by testing samples kept for various times. The results showed that 60–80 min is a suitable development period.

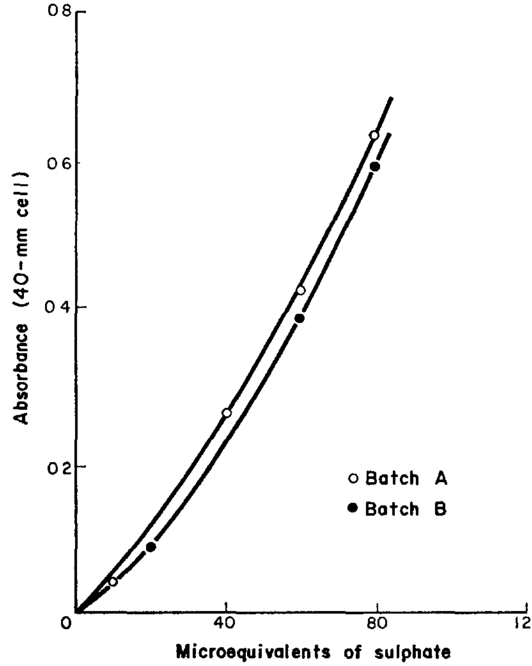

FIG. 1.—Calibration curves for turbidimetric method; different Tween 80 samples.

Calibration curves were steeper if an Ilford 601 filter was used instead of the neutral density (ND) filter, and were linear over most of their length but concave at low sulphate concentrations (Fig. 1). A new calibration curve must be made when a fresh batch of Tween is used (Fig. 1). The relative mean deviation (10 replicates) was 5·6% at the 10-mequiv sulphate level and 1·1% at the 30-mequiv level (ND filter), the values for the 601 filter being 4·6 and 1·8% respectively. Several elements present in foods give rise to ions likely to interfere. Measured quantities of aluminium, calcium, iron, magnesium, phosphate and nitrate were added to test solutions containing 10 μequiv of sulphate and tested: the results are presented in Table III.

Procedure for food analysis

If the food contains a high proportion of moisture (above 15–20%), dry it in a vacuum oven and powder it in a high-speed blender. Fit the platinum spiral to the stopper of the oxygen flask, heat it to redness and allow it to cool. Wrap the weighed sample in a Whatman No. 541 filter paper "flag"[4] and place this in the platinum spiral.

TABLE III.—INTERFERENCE BY COMMON ANIONS AND CATIONS IN THE TURBIDIMETRIC DETERMINATION OF 10 μequiv OF SULPHATE

Ions added, *μequiv*	Recovery of sulphate, %	Ions added, *μequiv*	Recovery of sulphate, %
Al 20	99	Mg 20	103
50	99	Ca 20	
Ca 20	107	Fe(III) 20	100
50	105	Ca 20	
100	93		
		Fe(III) 50	132
		PO_4^{3-} 50	
Fe(III) 10	97		
20	100		
50	103	Mg 20	
100	103	Ca 20	113
		Al 20	
Mg 20	106	Fe 20	
50	97		
		Ca 50	
PO_4^{3-} 10	88	Fe 50	
20	98	Mg 50	110
50	89	NO_3^- 50	
100	99	PO_4^{3-} 50	
NO_3^- 50	108	Ca 50	
100	102	Mg 50	101
		Fe(III) 50	
		PO_4^{3-} 50	

Mix 0·1*N* sodium hydroxide (1 ml), 100-vol hydrogen peroxide (3 drops) and water (4 ml) in the iodine-flask and carry out the combustion as usual.[4] When the flask is shaken to ensure absorption of combustion products the platinum spiral becomes detached, facilitating the dissolution of any residual ash. Leave the flask unopened for at least 15 min after combustion, then add concentrated hydrochloric acid (1 ml) and heat the flask on a boiling water-bath for 15 min with the stopper loosely inserted and 5 ml of water in the wide neck of the flask. Take the flask from the water-bath and remove the stopper so that the water in the neck washes the stopper and neck of the flask. Cool the flask to room temperature and transfer the contents to a 50-ml graduated flask, washing with water to give a volume of about 40 ml. Continue as described under turbidimetric finish. Prepare a blank at the same time and measure sample and blank against water.

RESULTS AND DISCUSSION

The calibration curves obtained for the chloranilate method were in good agreement with earlier results[6,7] and the sensitivity varied with batch of barium chloranilate as previously reported.[9] The interference of chloride and nitrate is greater than that of phosphate or carbonate. This may be a pH effect,[11] however, arising from the use of the ion-exchange resin, and a more effective buffer coupled with the use of an ammonium-form resin may improve results. Sensitivity is the main problem, but measurement at 328 nm may give some improvement.

For pure sulphate solutions, titration with barium perchlorate (screened Thorin as indicator) is satisfactory, but both anions and cations interfere. Magnesium carbonate, suggested for the removal of phosphate,[20] contained impurities that gave rise to serious interference. Magnesium oxide[23,28] could be obtained in a higher state of purity, but removal of phosphate was incomplete and sulphate ions were adsorbed.

The turbidimetric method described lacks precision (in common with other barium sulphate turbidimetric procedures[31,34,38]) and some ions commonly present

Table IV.—Sulphur content of foods (turbidimetric method)

Food	Moisture content, % *w/w*	Sample, *mg*	Net absorbance,	Sulphur content *mg/g*		
				As received	On dry weight (average)	Literature value
Wheat flour	11·8	51·4	0·030	1·0	1·0	1·28
		47·8	0·019	0·7		
Ground rice	13·7	56·0	0·020	0·6	0·6	0·89
		60·0	0·020	0·5		
Whole ground rye	10·9	38·0	0·020	0·9	1·1	—
		45·9	0·030	1·2		
Soya (diastatic)	6·8	50·1	0·174	4·2	4·5	4·56
		53·6	0·183	4·1		
Broad beans (Seville long pod)	9·9	44·6	0·041	1·6	1·8	1·66
		44·6	0·042	1·7		
French beans	11·4	55·3	0·120	2·7	2·9	1·6
		38·4	0·065	2·5		
Pea beans	13·5	43·6	0·055	1·8	2·2	1·87
		56·6	0·085	2·0		
Peas (Kelvedon Wonder)	11·1	68·2	0·122	2·4	2·6	2·32
		54·4	0·080	2·2		
Arachis nuts	5·21	56·0	0·092	2·4	2·1	3·95
		50·2	0·060	2·0		
Coconut (desiccated)	3·02	48·6	0·025	1·0	1·0	0·76
		48·0	0·024	1·0		
Coffee (Brazil)	5·27	50·3	0·028	1·1	1·1	1·15
		40·7	0·023	1·1		
Coffee (Jamaica)	7·29	38·2	0·028	1·4	1·4	1·15
		43·2	0·027	1·2		
Celery (stem)	0	50·2	0·110	2·9	2·9	3·0
		41·9	0·090	2·9		
Horseradish	0	48·3	0·513	7·3	7·7	8·4
		45·9	0·561	8·1		
Mustard seed (white)	7·14	42·7	0·70	12·9	13·6	13·7
		54·4	0·90	12·4		
Onion powder	6·33	37·6	0·118	4·3	4·4	7·04
		43·5	0·142	3·9		
Pepper (green, edible portion)	0	48·9	0·105	2·4	2·3	—
		44·9	0·082	2·2		
Tarragon (leaf)	11·0	44·4	0·095	2·5	2·9	—
		48·2	0·136	2·6		
Milk (National Dried)	2·63	47·8	0·086	2·7	2·7	2·37
		53·0	0·091	2·5		
Milk (skimmed, dried)	4·71	41·0	0·119	3·9	4·1	3·16
		29·4	0·074	3·9		
Egg (dried)	5·9	52·1	0·409	7·2	8·1	6·78
		37·5	0·285	8·0		
Sugar dried egg	5·93	24·8	0·095	5·5	5·7	4·5
		36·8	0·150	5·2		
Beef (cooked, A.F.D.*)	2·37	40·0	0·284	7·4	7·4	—
		53·0	0·409	7·0		
Chicken (cooked, A.F.D.*)	4·3	43·0	0·409	8·6	8·6	7·5
		57·3	0·537	7·9		
Cod (raw, A.F.D.*)	0	42·4	0·60	11·5	11·1	10·1
		46·8	0·61	10·6		
Herring (raw, A.F.D.*)	0	46·0	0·356	7·4	7·5	5·25
		46·8	0·381	7·6		

* A.F.D. = Accelerated freeze-dried.

in foods cause positive interference (Table III). Tween 80 is a suitable stabilizing agent but different batches of reagent may give different results. The neutral density filter gives a lower sensitivity than the 601 filter but a more useful working range.

Although all three methods were found satisfactory for pure organic compounds containing C, H, O and S, in the case of foodstuffs the inorganic ions remaining in solution after the oxygen-flask procedure give rise to interferences. If these interfering ions are to be removed, the chloranilate and perchlorate methods become laborious and unsuitable for routine work. If high precision is not required, however, the interference in the turbidimetric method is not generally serious and this technique may be used for routine analysis.

The agreement of the experimental results on foods with the literature values (Table IV) is satisfactory in view of the uncertain history of certain samples cited in the literature and the inherent lack of precision of the method. Some high results, *e.g.*, for dried egg, skimmed milk and herring may be due to the presence of interfering ions (phosphorus, calcium, iron and magnesium) in these foods, but the results for arachis nuts and onion powder are anomalous.

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Zussammenfassung—Durch Verbrennen von Nahrungsmitteln in Sauerstoff gebildetes Sulfat kann man kolorimetrisch mit Bariumchloranilat, titrimetrisch mit Bariumperchlorat und turbidimetrisch mit Bariumchlorid bestimmen. Die bei jedem Verfahren auftretenden Schwierigkeiten sowie die Strörungen wurden untersucht. Falls keine hohe Genauigkeit notwendig ist und die Störungen durch Phosphat, Eisen, Calcium und Magnesium angemessen berücksichtigt werden, ist das turbidimetrische Verfahren zu empfehlen; die anderen beiden sind für Routinezwecke ungeeignet.

Résumé—Le sulfate formé par la combustion d'aliments en fiole d'oxygène peut être dosé colorimétriquement au chloranilate de baryum, titrimétriquement par le perchlorate de baryum ou turbidimétriquement avec le chlorure de baryum. On a étudié les difficultés rencontrées avec chaque méthode, y compris les interférences. La technique turbidimétrique est recommandée si une haute précision n'est pas nécessaire et l'on tient compte des interférences du phosphate, du fer, du calcium et du magnésium; les deux autres méthodes ne conviennent pas au travail de routine.

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NAPHTHO[2,3-*d*]-2-SELENA-1,3-DIAZOLE AS A REAGENT FOR THE DETERMINATION OF MACRO TO SUBMICRO QUANTITIES OF PALLADIUM

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Summary—Five analytical procedures, gravimetric, spectrophotometric, radiometric, fluorometric and atomic-absorption, have been developed for the determination of macro to submicro amounts of palladium. The methods are based on the reaction of $PdCl_2$ with naphtho[2,3-*d*]-2-selena-1,3-diazole. Analytical conditions such as the reaction time, concentration ranges, effect of pH and of 68 foreign ions, and solvent extraction were studied. Information relating to the structure and formula of palladium–piazselenol reaction products is included.

ONLY a few organic compounds containing selenium have been reported as forming compounds with metals, and these have been reviewed by Livingstone.[1] Recently a number of these selenium donor-type ligands[2,3] and benzo[*d*]-2-selena-1,3-diazole[4] have been investigated, and interest has been generated because of the high selectivity of these reagents for palladium. The piazselenol benzo[*d*]-2-selena-1,3-diazole was first reported as a gravimetric reagent for palladium by Ziegler and Glemser.[5] Recently, Bunting and Meloan[4] employed this reagent for a selective, simple, indirect spectrophotometric determination of palladium. The superiority of 2,3-diaminonaphthalene as a selenium reagent,[6] the high molar absorptivity ($4{\cdot}10 \times 10^3$ l. mole^{-1}. mm^{-1} at 480 nm) and the favourable fluorescence properties[7,8] led to the investigation of naphtho[2,3-*d*]-2-selena-1,3-diazole (DanSe) as a possible reagent for palladium. Furthermore, the kinetics of the reaction and the properties of DanSe have been studied.[9] By use of radioactively labelled DanSe,[8,10] a radiometric method for palladium is possible.

The present paper is a detailed study of the determination of macro and submicro amounts of palladium with DanSe in the presence of foreign ions.

EXPERIMENTAL

Reagents

A standard palladium(II) chloride solution was prepared by dissolving 1·1276 g of the reagent grade chemical in a litre of 0·01*M* hydrochloride acid and standardized by precipitation with nioxime. Other palladium solutions were prepared by dilution of this stock solution with 0·01*M* hydrochloric acid.

A standard selenium solution was prepared by dissolving 8·1680 g of selenous acid in a litre of water and standardized with 2,3-diaminonaphthalene.[6]

The procedure of Lott *et al.*[6] was used to prepare DanSe from 2,3-diaminonaphthalene and selenous acid. Ethanolic solutions of DanSe (about $10^{-3}M$) were prepared by dissolving in volumetric flasks freshly prepared moist precipitates of DanSe with 95% ethanol. More dilute solutions were prepared by dilution with 95% ethanol.

A selenium-75 solution, as selenous acid, was diluted to a specific activity of about $5{\cdot}8 \times 10^7$ cpm/ml and 0·2 ml was added to 2·4 ml of the standard selenium solution and diluted to prepare 100 ml of $1{\cdot}525 \times 10^{-3}M$ radioactive DanSe solution. More dilute solutions were prepared by dilution with 95% ethanol.

For the interference studies, reagent grade chemicals were used to make $0{\cdot}01M$ aqueous solutions except where otherwise specified.

Analytical procedures

Preliminary experiments showed that two different precipitates were formed from the reaction of palladium(II) chloride with DanSe, depending on the molar ratio of palladium to DanSe. With DanSe in excess, a purple precipitate is formed. This reaction takes place in acidic solution and is relatively pH independent over the pH range 1–6 (Fig. 1). The reaction is rapid and highly insensitive to the interference of foreign metal ions. Furthermore, the purple precipitate is stable and insoluble in organic solvents such as ethanol, acetone and diethyl ether. However when palladium is in excess, the purple precipitate that is first formed is gradually converted into a green precipitate.

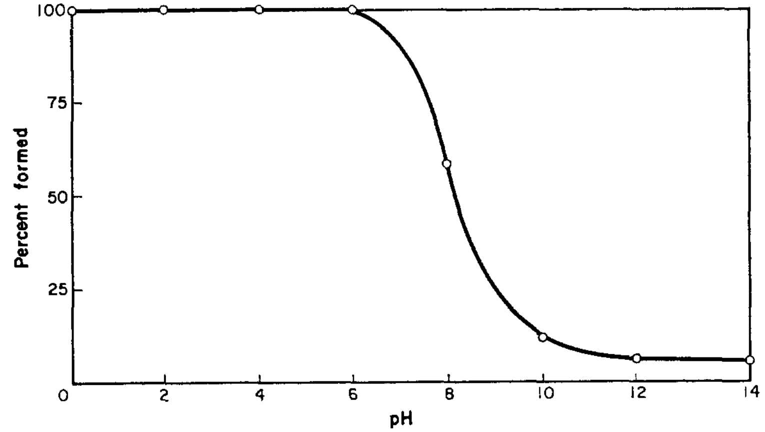


FIG. 1.—Effect of pH on the formation of the purple $Pd(DanSe)_2Cl_2$ complex.

Gravimetric procedure. To 20–80 ml of solution $1M$ in hydrochloric acid and containing from 5 to 20 mg of palladium, 100–400 ml of $2 \times 10^{-3}M$ DanSe are added. After stirring, the reaction mixture is allowed to stand at room temperature for 30 min and then filtered (medium-porosity sintered-glass crucible). The purple precipitate is washed first with 50 ml of acetone, then with 50 ml of water and finally with 30 ml of acetone. The precipitate is dried for 1 hr at 110°. The gravimetric factor for palladium is 0·1653.

Spectrophotometric procedure. A 4-ml aliquot containing up to 5 ppm of palladium and $0{\cdot}1M$ in hydrochloric acid is added to 4 ml of $1{\cdot}525 \times 10^{-4}M$ ethanolic DanSe solution in a 15-ml centrifuge tube. After thorough mixing, the mixture is allowed to stand at room temperature for 30 min. Then the mixture is centrifuged at high speed for 3 min, and the supernatant liquid decanted into a 10-mm quartz cell and the absorbance measured at 380 nm against a reagent blank. The decrease in the absorbance is a measure of the palladium concentration in the sample. To avoid instrumental errors associated with high absorbance measurements, the supernatant liquid can be diluted before the absorbance measurements. Linear calibration curves are obtained over the range up to 5 ppm of palladium.

Radiometric procedure. A radioactive piazselenol solution is added to the palladium sample. The experimental conditions are similar to those for the spectrophotometric procedure, except that stock $1{\cdot}525 \times 10^{-4}M$ radioactive ethanolic DanSe solution is used. After the 3-min centrifugation, 2 ml of the supernatant liquid are accurately transferred into a 5-ml calibrated plastic tube and counted for 3 min. The decrease in the radioactivity, relative to a reagent blank, is a measure of the palladium concentration and a linear calibration curve up to 5 ppm of palladium is obtained.

Atomic-absorption procedure. About 30 ml of sample solution containing approximately 0·2 ppm of palladium and adjusted to pH 2·5 are introduced into a 60-ml separatory funnel. To this solution are added 5 ml of approximately $2 \times 10^{-4}M$ ethanolic DanSe solution (a minimum 5-fold stoichiometric excess). The reaction mixture is briefly shaken, then allowed to stand for 30 min. Exactly 5 ml of n-butyl acetate are added and the palladium–DanSe reaction product is extracted by shaking for 3 min. To remove droplets of water, the organic layer is filtered into the cuvette through a cotton plug in the stem of the separatory funnel. The organic layer is aspirated directly into the burner of the instrument and the absorption measured at 244·8 nm. The calibration curve is linear over the range 0–0·33 ppm of palladium.

Fluorometric procedure. Two procedures were developed, one suitable for 0–5 ppm of palladium and the other for 0–1 ppm. For the former the experimental conditions are similar to the spectrophotometric procedure except that the palladium solution is adjusted to pH 3·5–4·5 before addition of the DanSe solution. After centrifugation, the fluorescence intensity of the supernatant solution is measured. A linear calibration curve is obtained. For the concentration range 0–1 ppm, exactly 4 ml of $1 \cdot 15 \times 10^{-5}M$ ethanolic DanSe are added to a 4-ml palladium sample. After stirring, the mixture is allowed to stand for 20 min before the solution is transferred to the fluorometer cuvette. The fluorescence intensity is measured at an excitation wavelength of 375 nm and a fluorescence wavelength of 520 nm. The decrease in the fluorescence intensity relative to a reagent blank is a measure of the palladium content. A non-linear calibration curve is obtained (Fig. 2) in this range, probably because of dissociation of $Pd(DanSe)_2Cl_2$ at low concentrations.

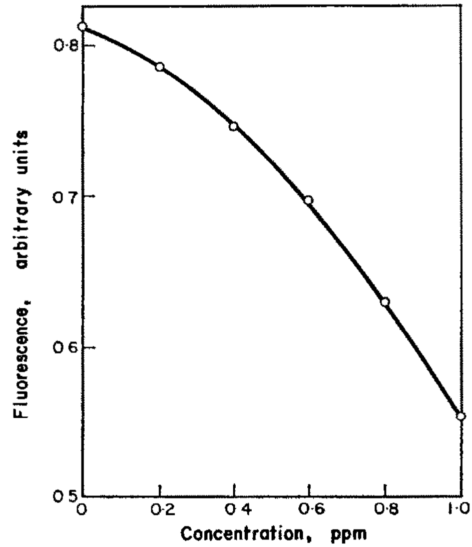


FIG. 2.—A standard curve for the fluorometric determination of Pd(II) with DanSe.

RESULTS

Reaction of DanSe *and palladium*

The reaction of ethanolic DanSe with palladium(II) in acidic solution is greatly influenced by the anion of the palladium salt as well as the palladium(II) concentration. In a strongly acidic hydrochloric acid solution, with excess of DanSe, a stable purple precipitate is formed quantitatively, but on addition of excess of palladium(II) chloride to this reaction mixture, the purple precipitate is gradually converted into a stable green precipitate. Analysis of the purple precipitate confirms the formula $Pd(C_{10}H_6N_2Se)_2Cl_2$: calculated—C 37·33%, H 1·87%, N 8·71% Cl 11·02%, Pd 16·53%; found—C 37·1%, H 1·9%, N 5·4%, Cl 11·5%, Pd 16·5%.

The green complex is also formed quantitatively in acid medium when palladium(II) is in excess. The ratio of Pd(II) to DanSe in the green complex was studied by atomic-absorption spectrophotometry. A Yoe-Jones plot suggested a molar ratio of 1:1 in the green precipitate; elemental analysis, though not giving conclusive results, tended to confirm this.

The anion of the palladium(II) salt enters into formation of the palladium–DanSe precipitate. In a study of nineteen common anions with palladium(II) nitrate and ethanolic DanSe solution at pH 0 and 4, only bromide, chloride, and to a smal extent fluoride, precipitated Pd-DanSe (Table I). These precipitates were purple. yellowish-white precipitate formed with thiosulphate.

TABLE I.—EFFECT OF ANIONS ON THE PRECIPITATION OF PALLADIUM WITH DanSe

Anion	Reaction*	
	pH 0	pH 4
NO_3^-	†	†
$H_2PO_4^-$	†	†
CNS^-	†	†
$S_2O_3^{2-}$	trace white ppte	trace yellow ppte
HPO_4^{2-}	†	†
NO_2^-	†	†
Citrate	†	†
SO_3^{2-}	†	†
$C_2O_4^{2-}$	†	†
Tartrate	†	†
CN^-	†	†
HCO_3^-	†	†
Acetate	†	†
ClO_3^-	†	†
SO_4^{2-}	†	†
F^-	purple ppte	purple ppte
Cl^-	purple ppte	purple ppte
Br^-	purple ppte	purple ppte
I^-	red soln	red soln

* 4·0 ml of $7{\cdot}6 \times 10^{-4}M$ ethanolic DanSe and 2 ml of $0{\cdot}01M$ anion and 0·5 ml of $3{\cdot}09 \times 10^{-3}M$ $Pd(NO_3)_2$ in HNO_3. pH values were adjusted with HNO_3 or NaOH.

† No observable change or a trace amount of black, brown or purple precipitate observed after a day.

Properties of DanSe *and* $Pd(DanSe)_2Cl_2$

Dried DanSe is hard to dissolve in ethanol but DanSe will readily dissolve while still damp immediately after preparation and purification. Concentrated ethanolic DanSe solutions are unstable, because of a tendency toward polymerization;[6,7] however, a $1{\cdot}5 \times 10^{-3}M$ DanSe stock solution could be stored for 2 days at room temperature without effect on the determination of palladium. A $1{\cdot}5 \times 10^{-4}M$ solution was stable for at least one month. Though strong light slowly causes the polymerization or decomposition of ethanolic DanSe solutions, the only precaution taken was to store the stock DanSe solution in darkness. All work was performed in daylight, without deaeration of solutions or purifying of reagents.

Although microgram quantities of palladium could be extracted by butyl acetate and 2-heptanone for the atomic-absorption measurement, no organic solvent was found that would dissolve large quantities of the purple complex. Ziegler and Glemser[4] also observed the insolubility of Pd–piazselenol precipitates in common solvents. From the atomic-absorption measurements, the solubility of both the purple and green precipitates in ethanol-water mixture is estimated to be below $5 \times 10^{-7}M$. Both precipitates are stable to air-drying at 110° and will not decompose below 300°. Both complexes give rise to almost identical infrared spectra (4000–200 cm^{-1}) that are different from the infrared spectrum of DanSe.

Spectral characteristics

Although the absorbance and fluorescence spectra of DanSe have been reported,[6,8] spectra of DanSe in ethanolic solution at various pH values have not. The absorbance spectrum of the ethanol-water solution of DanSe at 380 nm was pH-independent from pH 0 to 12. The fluorescence at 520 nm was, however, sharply quenched by hydrogen ions below pH 3, but remained constant from pH 3 to 12.

Optimum conditions for atomic-absorption spectrophotometry

The optimum acetylene-air ratio and burner position were investigated and it was found that a fuel flow-rate of 3 l./min and air flow-rate of 21 l./min with a burner height setting at 45 mm below the incident beam gave optimum results. Other optimum instrumental settings were a gain of 5, slitwidth 0·3 mm and meter response 2 or 5 (setting numbers refer to the Perkin-Elmer model 303 used for these experiments).

Effect of pH and time

The formation of the purple Pd-DanSe precipitate is pH-dependent (Fig. 1). The effect of pH on the extraction of the palladium complex with *n*-butylacetate is shown in Fig. 3. As indicated, the palladium complex is best extracted between pH 2 and 3.

To study the time required for the completion of the reaction, solutions of DanSe and palladium(II) chloride were mixed in centrifuge tubes and allowed to stand for various times before centrifugation for 3 min. The supernatant liquid was decanted into a quartz cell for measurement at 380 nm. The reaction was found to reach completion in 6 min. However, in all analytical procedures, a 20–30 min reaction time was allowed.

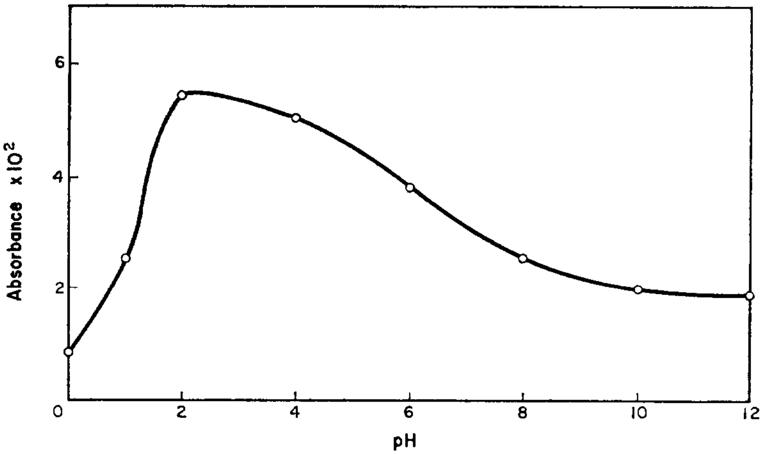


FIG. 3.—Effect of pH on the extraction of palladium with n-butylacetate.

Interference studies

DanSe is highly selective for palladium(II) chloride. Of fifty metal ions studied in 1*M* hydrochloric acid, only palladium complexed with ethanolic DanSe to give a stable purple precipitate. Cerium(IV) gave a white decomposed product; silver gave silver chloride. Bunting and Meloan[5] observed that mercury(II), titanium(IV) and cadmium interfered in the indirect spectrophotometric determination of palladium with benzo[*d*]-2-selena-1,3-diazole; no such interference was observed with DanSe under our reaction conditions. The primary interferences which prevented the precipitation of $Pd(DanSe)_2Cl_2$ were from anions such as iodide, cyanide, thiocyanate and thiosulphate that form stable palladium complexes, and the ions cerium(IV), gold(III) and nitrite which destroy DanSe. The additional interference noted in the spectrophotometric procedure is due to the natural colour of the diverse ions, since they are present at more than a 65-fold molar excess. In the fluorometric procedure, antimony(III), thorium, tin(IV), iron(III), bismuth and beryllium interfered owing to hydrolysis, because of the necessity of using a pH above 3·5. In the presence of arsenic(III) and osmium(VIII), lower results for palladium were observed in the spectrophotometric, fluorometric and radiometric procedures but not in the gravimetric and atomic-absorption procedures. The interference of zirconium in the atomic-absorption procedure was probably due to the formation of an emulsion at the interface of the organic layer. Emulsions did not form with the other ions. The effect of foreign cations and anions is summarized in Table II.

TABLE II.—FOREIGN ION EFFECT

Ion	DanSe*	Pd				
		Gravimetric†	Spectro-photometric§ *Absorbance*	Radio-metric‡ *cpm*	Fluoro-metric¶ *Arbitrary units*	Atomic absorption‖ *% Absorption*
Pd(II)	purple ppte	purple ppte	0·36	982	0·61	29·1
Blank	**	—	0·73	1597	1·13	1·4
Ag(I)	white ppte	white ppte	††	††	††	††
Al(III)	**	‡‡	0·33	828	0·59	30·8
As(III)	**	‡‡	0·61	1477	1·06	27·6
Au(III)	**	§§	0·80	937	0·0	12·6
Ba(II)	**	‡‡	0·33	891	0·57	29·1
Bi(III)	**	‡‡	0·47	980	††	29·0
Be(II)	**	‡‡	0·36	925	††	27·8
Ca(II)	**	‡‡	0·33	861	0·66	27·2
Ce(IV)	white ppte	white ppte	††	††	††	††
Cd(II)	**	‡‡	0·47	891	0·49	27·0
Co(II)	**	‡‡	0·44	891	0·56	29·1
Cr(III)	**	‡‡	0·44	891	0·49	29·1
Cu(II)	**	‡‡	0·44	982	0·53	27·0
Dy(III)	**	‡‡	0·37	1150	0·58	29·1
Eu(III)	**	‡‡				
Fe(III)	**	‡‡	1·90	916	0·0	28·2
Ga(III)	**	‡‡	0·33	982	0·59	29·0
Hg(II)	**	‡‡	0·32	842	0·47	29·1
In(III)	**	‡‡	0·31	927	0·68	27·7
Ir(III)	**	‡‡	0·44	905	0·49	23·2
K(I)	**	‡‡	0·36	980	0·62	29·1
La(III)	**	‡‡	0·36	1016	0·49	23·0
Lu(III)	**	‡‡	0·48	1074	0·49	30·8
Mg(II)	**	‡‡	0·31	861	0·66	27·2
Mn(II)	**	‡‡	0·31	882	0·56	26·2
Mo(VI)	**	‡‡	0·31	882	0·61	26·2
Na(I)	**	‡‡	0·36	982	0·61	29·1
Ni(II)	**	‡‡	0·36	1012	0·56	28·4
Nd(III)	**	‡‡				
Os(VIII)	**	§§	0·47	1513	1·10	29·3
Pt(IV)	**	§§	0·58	1090	0·0	23·8

TABLE II (*Continued*)

Ion	DanSe*	Pd				
		Gravimetric†	Spectro-photometric§ *Absorbance*	Radio-metric‡ *cpm*	Fluoro-metric¶ *Arbitrary units*	Atomic absorption‖ *% Absorption*
Pb(II)	**	‡‡	0·31	904	0·59	31·8
Rh(III)	**	‡‡	0·44	951	0·0	23·2
Ru(III)	**	‡‡	0·72	830	0·40	31·6
Rb(I)	**	‡‡	0·36	982	0·61	29·1
Re(IV)	**	‡‡	0·35	951	0·64	29·1
Sm(III)	**	‡‡				
Sn(IV)	**	‡‡	0·36	904	0·66††	27·0
Sr(II)	**	‡‡	0·35	861	0·66	27·2
Se(IV)	**	‡‡	0·36	828	0·61	29·1
Sb(III)	**	‡‡	0·47††	1227††	††	23·0††
Tb(III)	**	‡‡	0·32	885	0·68	29·0
Ti(IV)	**	‡‡	0·19	861	0·73	22·9
Th(IV)	**	‡‡	0·31	1016	††	28·6
Te(IV)	**	‡‡	0·32	828	0·57	27·7
UO_2(II)	**	‡‡	0·40	1074	0·55	36·2
V(V)	**	‡‡	0·43	894	0·11	36·2
Zr(IV)	**	‡‡	0·31	882	0·68	9·6
Zn(II)	**	‡‡	0·35	891	0·68	27·0
NO_3^-	**	‡‡	0·35	1005	0·71	29·1
$H_2PO_4^-$	**	‡‡	0·35	1005	0·71	29·1
CNS^-	**	no ppte	0·72	1560	1·08	2·3
$S_2O_3^{2-}$	less orange	white ppte	0·73	1562	1·03	6·2
HPO_4^{2-}	**	‡‡	0·37	1005	0·78	29·1
NO_2^-	**	§§	0·51	1375	1·08	22·3
Citrate	**	‡‡	0·37	1005	0·64	29·1
SO_3^{2-}	**	‡‡	0·36	983	0·63	26·2
$C_2O_4^{2-}$	**	‡‡	0·42	1144	0·93	27·2
Tartrate	**	‡‡	0·37	980	0·67	26·2
CN^-	**	no ppte	0·73	1560	1·08	0·0
HCO_3^-	**	‡‡	0·34	980	0·59	26·7
Acetate	**	‡‡	0·34	980	0·63	26·7
ClO_3^-	**	‡‡	0·32	1206	0·60	27·2
SO_4^{2-}	**	‡‡	0·34	980	0·61	27·7
F^-	**	‡‡	0·34	885	0·64	27·5
Cl^-	**	‡‡	0·35	980	0·61	29·0
Br^-	**	‡‡	0·32	845	0·69	27·2
I^-	red soln	red soln	0·73	1580	0·98	7·2

* 2 ml of 2·5 × $10^{-3}M$ ethanolic DanSe + 4 ml of 1*M* HCl + 1 ml of 0·01*M* diverse ion.

† Same as * except 0·2 ml of stock 6·17 × $10^{-3}M$ $PdCl_2$ was added.

§ 4 ml of 1·3 × $10^{-4}M$ ethanolic DanSe + 2 ml of 0·01*M* diverse ion and 4 ml of 8 ppm $PdCl_2$, both in 0·1*M* HCl.

‡ 4 ml of 2·5 × $10^{-4}M$ radioactive ethanolic DanSe + 2 ml of 0·01*M* diverse ion and 4 ml of 10 ppm $PdCl_2$, both in 0·1*M* HCl.

¶ 3 ml of 1·3 × $10^{-4}M$ ethanolic DanSe + 2 ml of 0·01*M* diverse ion and 4 ml of 2 ppm $PdCl_2$, both at pH 4.

‖ 5 ml of 4 × $10^{-4}M$ ethanolic DanSe + 20 ml of 2 ppm $PdCl_2$ in 0·1*M* HCl + 2 ml of 0·01*M* diverse ion; extracted with 5 ml of butyl acetate.

** No observable change.

†† Hydrolysis.

§§ Less purple ppte was formed or slower reaction.

‡‡ Purple ppte of Pd–DanSe.

Analysis of samples

A series of twelve solutions was prepared that contained equal volumes of 0·01*M* solutions of four diverse ions taken as the sulphate, chloride or nitrate salts; foreign anions were added as their potassium or sodium salts. Each solution was adjusted to the appropriate pH with concentrated hydrochloric acid or sodium hydroxide. A known amount of palladium(II) chloride was added, and then the sample was analysed for palladium by all five methods. The results are presented in Table III.

TABLE III.—PALLADIUM DETERMINATION BY DIFFERENT METHODS

	Palladium added				
	6·70 *mg*	2·00 *ppm*	3·00 *ppm*	0·60 *ppm*	0·167 *ppm*
	Palladium found				
Solution number	Gravimetric*	Spectrophotometric†	Radiometric§	Fluorometric‡	Atomic absorption¶
1	6·70 *mg*	1·80 *ppm*	3·02 *ppm*	0·56 *ppm*	0·164 *ppm*
2		2·04	3·27	0·53	0·155
3	6·65	2·02	3·00	0·53	0·165
4		**	3·25	**	0·163
5	6·70	**	3·25	**	0·168
6		2·02	2·75	0·56	0·168
7	6·74	2·01	3·20	0·62	0·169
8		1·80	2·93	0·60	0·162
9	6·61	1·90	2·70	0·53	0·171
10		2·15	2·77	0·53	0·166
11		2·20	2·81	0·55	0·161
12	6·71	2·01	2·83	0·56	0·159

Solution number	Foreign ions			
1	Mn(II)	Ca	Sr	Na
2	K	La	Th	Sn(IV)
3	Sn(II)	UO_2(II)	Cu(II)	Ga
4	Fe(III)	Ni	Al	Lu
5	V(V)	Dy	K	Ba
6	Mg	Co(II)	Hg(II)	Li
7	Cd	Rh(III)	Ir(III)	Cr(III)
8	Mo(VI)	Re(IV)	Ti(IV)	As(III)
9	NO_3^-	HPO_4^{2-}	Citrate	Na
10	Tartrate	HCO_3^-	Acetate	SO_4^{2-}
11	$C_2O_4^{2-}$	ClO_3^-	Br^-	Cl^-
12	Sr	In(III)	Te(IV)	Be

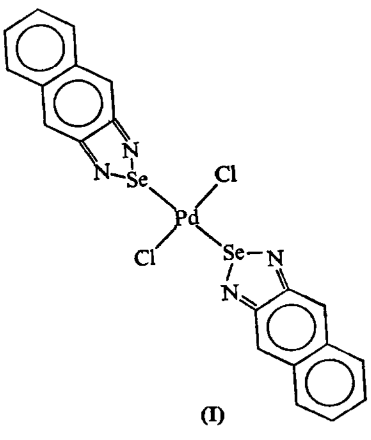
Each solution contains equal volumes of the four foreign ions initially at 0·01*M*.

* 10·00 ml of 6·2920 × $10^{-3}M$ $PdCl_2$ and 5 ml of stock foreign ion solution, both in 1*M* HCl.
† 1 ml of stock foreign ion solution added to a total of 4·00 ml of 2·00 ppm in $PdCl_2$ in 0·1*M* HCl.
§ 1 ml of stock foreign ion solution added to a total of 4·00 ml of 3·00 ppm of $PdCl_2$ in 0·1*M* HCl.
‡ 1 ml of stock foreign ion solution added to a total of 4·00 ml of 0·60 ppm of PdC_{62} at pH 3·5.
¶ 30·00 ml of 0·167 ppm $PdCl_2$ and 1 ml of stock foreign ion solution, both at pH 2·5.
** Interference caused by natural colour of foreign ion, or quenching or hydrolysis.

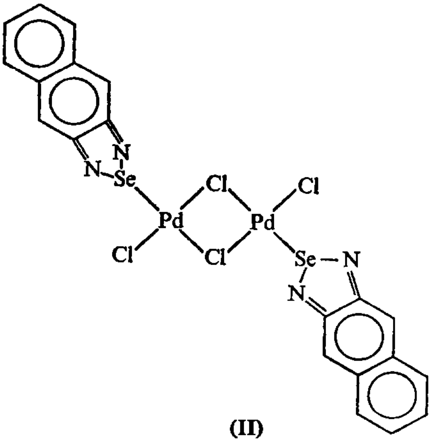
DISCUSSION

Palladium(II) complexes with a d^8 electronic configuration commonly have square planar configurations and Pd–Se metal-to-metal bonding has long been recognized to exist in compounds such as PdSe, $PdSe_2$, Pd_4Se_5 and Pd_4Se.[11] As a general rule, palladium(II) compounds have great affinity for nitrogen (amines and nitro compounds), halogens, cyanide and heavy atoms such as phosphorus, arsenic, sulphur and selenium. Cotton[12] explained that the strong bonding of heavy atoms is due to the formation of π-bonds formed by the overlap of the filled d_{xz}, d_{xy} and d_{yz} orbitals of palladium with empty d_π orbitals in the valence shells of the heavy atoms. Also, the delocalization of the metal electron density by π-bond formation between palladium and selenium atoms was reported by Bark and Brandon[2] as a major factor in determining the stability of their $PdCl_2$-2-(2-pyridyl)benzo[*b*]selenophene chelated complex. Further evidence for this π-bonding and hence the Pd–Se bonding is obtained by considering the inertness of the chlorine atoms in the two complexes towards boiling silver nitrate solution. Delocalization of the electron density cloud around the palladium atom should increase the polarity of the palladium–chlorine bond, and therefore its strength.[2] Regarding the structure of the green complex, palladium(II) chloride is known to react with ligands, *L*, such as amines, phosphines and sulphides to give complexes of the type $[LPdCl_2]_2$ and such complexes have bridging chlorine atoms.[13,14]

Because the *cis*-configuration is generally less symmetrical than the *trans*-configuration, and because both complexes give rise to almost identical infrared spectra, the two complexes are therefore expected to have either both *cis*- or both *trans*-configurations. Ignoring the question of *cis*- and *trans*-configuration, the structure of the two complexes, $Pd(DanSe)_2Cl_2$ (I) and $Pd_2(DanSe)_2Cl_4$ (II), is believed to be:



(I)



(II)

The reagent DanSe had been shown to be extremely selective for palladium in moderately concentrated hydrochloric acid solution. Out of 50 metal ions studied, only palladium appeared to complex with DanSe, as judged by the colour change and precipitate formation. Because of the very high selectivity of DanSe for palladium and the fact that two different coloured precipitates are formed in sequence, DanSe may be a very superior reagent for the spot-test identification of palladium. Since selenium is difficult to determine directly by atomic-absorption spectroscopy[15] and since DanSe contains selenium, an indirect atomic-absorption procedure for the determination of selenium, utilizing the high selectivity of DanSe for palladium, is now being investigated.

Other advantages of DanSe as a palladium reagent are the simplicity of the analytical procedures and the diversity of the methods. Because the reaction is remarkably free from interference and very insensitive to pH changes as long as the solution is acidic, neither masking agents or buffers need be added.

With the exception of the gravimetric, atomic-absorption and to some extent the fluorometric method, the limiting factor in the sensitivity of the palladium determination is not due to the reagent itself, but is the degree of separation of the reagent from the Pd–DanSe precipitate. Very high-speed centrifugation offered only a slight improvement in sensitivity over conventional centrifugation. The Perkin-Elmer sampling boat atomizing system was also tested for the atomic-absorption determination, but a decrease rather than an enhancement in sensitivity was observed.

Precision and accuracy

The recovery of known amounts of palladium was satisfactory. Based on the results in Table III, obtained in the presence of a large excess of foreign ions, the gravimetric procedure shows a relative standard deviation of 0·7%, the spectrophotometric method 6·0%, the radiometric method 7·2%, the fluorometric method 8·7% and the atomic-absorption method 3·2%.

Sensitivity and detection limit

The criterion of Mandel and Stiehler[16] for the evaluation of the sensitivity (γ) of different methods was adopted, *i.e.*,

$$\gamma = \mathrm{d}I/s_\mathrm{I}\,\mathrm{d}C.$$

The main advantage of this criterion is that it takes into account not only the reproducibility of the testing procedure, but also its ability to discern small changes in concentration or amount. In addition, the unit used is amount or concentration, C, and is independent of the scale, I, on which the measurement is expressed. Thus, a direct comparison of the sensitivity of one method with another is made possible. The least-squares method was used to obtain the slope of the linear calibration curve, $\mathrm{d}I/\mathrm{d}C$, and the standard deviation, s_I, of points from the regression line. In the case of the fluorometric calibration curve (range 0–1 ppm Pd), the slope of the non-linear curve was measured at the mid-concentration range and the standard deviation was calculated from data in Table III.

TABLE IV.—SENSITIVITY OF THE DIFFERENT ANALYTICAL METHODS FOR PALLADIUM

Method	Sensitivity, *ppm*$^{-1}$	Detection limit,* *ppm*
Gravimetric	—	—
Spectrophotometric	18·5	0·172
Radiometric	23·2	0·137
Atomic absorption	164·4	0·019
Fluorometric (0–5 *ppm*)	25·2	0·126
(0–1 *ppm*)	33·5	0·095

* Conservative estimate of the detection limit. Values obtained represent a confidence level of 95%.

The reciprocal of the sensitivity is directly indicative of the minimum concentration required to produce a discernible change in the signal intensity. To obtain a conservative and objective evaluation for the detection limit (D.L.), the method of Skogerboe *et al.*[17] was used, *i.e.*,

$$\text{D.L.} = \frac{t(n-1, 1-\alpha)}{\gamma}$$

which takes into account the number of measurements (n) for the calibration curve and the confidence level, $100(1-\alpha)\%$, required. The use of 3·18 for t to obtain the data in Table IV represents a confidence level of 95% for six measurements. The pertinent sensitivity and detection limit data foı the five analytical methods for the determination of palladium are presented in Table IV.

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Zusammenfassung—Fünf analytische Verfahren, je ein gravimetrisches, spektrophotometrisches, radiometrisches, fluorometrisches und ein Atomabsorptionsverfahren wurden für die Bestimmung von Palladium in Makro- bis Submikromengen entwickelt. Sie beruhen auf der Reaktion von $PdCl_2$ mit Naphtho[2,3-*d*]-2-selena-1,3-diazol. Die analytischen Bedingungen wie Reaktionszeit, Konzentrationsbereiche, Einfluß von pH und 68 Fremdionen sowie Extraktion wurden untersucht. Angaben über Struktur und Formel des Reaktions-produktes von Palladium und Piazselenol werden ebenfalls gemacht.

Résumé—On a élaboré cinq techniques analytiques, gravimétrique, spectrophotométrique, radiométrique, fluorimétrique et d'absorption atomique pour la détermination des quantités macro et submicro de palladium. Les méthodes sont basées sur la réaction de $PdCl_2$ avec le naphto (2,3-*d*)2-séléna 1,3-diazole. On a étudié les conditions analytiques telles que le temps de réaction, les domaines de concentration, l'influence du pH et de 68 ions étrangers, et l'extraction par solvant. On présente également des données relatives à la structure et la formule des produits de réaction palladium-piazselenol.

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HYDROCARBURES ET POLLUTION ATMOSPHÉRIQUE

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Résumé—Après avoir envisagé la provenance des hydrocarbures trouvés dans l'atmosphère, nous étudions brièvement leur toxicité, puis nous décrivons les diverses méthodes d'analyse des hydrocarbures aromatiques polycycliques, c'est-à-dire des hydrocarbures cancérigènes.

ON SAIT que la pollution atmosphérique a trois origines principales:

—les foyers domestiques,
—les foyers et les émissions industrielles,
—les gaz d'échappement des automobiles.

NATURE ET PROVENANCE DES HYDROCARBURES TROUVÉS DANS L'ATMOSPHÈRE

Hydrocarbures aliphatiques et aromatiques

L'atmosphère des villes permet de déceler des hydrocarbures aliphatiques et aromatiques légers à des concentrations variant de 0,1 à 1 ppm.

Ces hydrocarbures proviennent de l'évaporation des produits pétroliers au niveau des réservoirs et des carburateurs des automobiles et de leur combustion incomplète pendant le fonctionnement du moteur. On les appelle des "imbrûles".

Hydrocarbures polyaromatiques

Les poussières atmosphériques contiennent des goudrons provenant de la décomposition pyrogénée de la houille, du bitume, des schistes, du pétrole *etc.* Ces goudrons renferment, à côté d'autres substances chimiques des hydrocarbures paraffiniques et surtout des hydrocarbures polyaromatiques, parmi lesquels des hydrocarbures cancérigènes.

Ces hydrocarbures polynucléaires rencontrés dans l'atmosphère proviennent des foyers domestiques et industriels,[1] et également des échappements de moteurs. A l'opposé de ce qui a lieu pour d'autres polluants comme l'anhydride sulfureux, ce sont les conditions de marche et non les produits d'alimentation qui jouent un rôle prépondérant. Par un réglage convenable des facteurs de combustion (en particulier de l'excès d'air), on peut diminuer considérablement l'émission des polynucléaires par un foyer.

Les moteurs en régime normal émettent beaucoup moins de polyaromatiques que lors des démarrages et des ralentis.[2–4]

TOXICITÉ DE CES DIFFÉRENTS HYDROCARBURES

Hydrocarbures aliphatiques et aromatiques

Il ne faut pas oublier le rôle très important des oléfines dans les réactions photochimiques qui conduisent, lorsque les conditions climatiques sont favorables à la formation d'ozone et également à l'apparition de vésicules liquides qui constituent le "smog" oxydant de Californie.[5]

Dans nos régions, il est peu probable qu'on ait à craindre de tels phénomènes; toutefois, la prudence voudrait que l'on surveillât les teneurs en oxydants, en nitrate de peracétyle ou PAN et en hydrocarbures imbrûlés dans les villes où se conjuguent un trafic automobile important, un ensoleillement intense et une inversion de températures qui emprisonne les gaz d'échappement des automobiles dans les couches basses et moyennes de l'atmosphère.

Hydrocarbures aromatiques polynucléaires

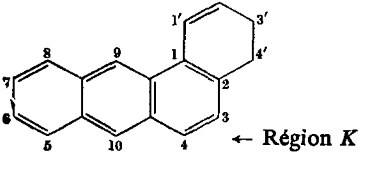
La source principale de toxicité des goudrons provient essentiellement de la présence des hydrocarbures aromatiques polynucléaires en raison de leur activité cancérigène. Rappelons brièvement l'historique de ce problème biologique.

En 1775 Pott constate, chez les ramoneurs, la fréquence anormale du cancer du scrotum. En 1915 Yamagiwa et Ichikawa obtiennent le premier cancer expérimental par application de goudron de houille sur l'oreille d'un lapin. L'école anglaise avec Cook et ses collaborateurs a fait beaucoup progressé la question: ils constatèrent d'abord que les goudrons cancérigènes pouvaient être obtenus à partir de produits contenant uniquement du carbone et de l'hydrogène. Ceci amena à penser que les principes actifs se rattachaient au groupe chimique des hydrocarbures.

Puis on découvrit que les fractions actives présentaient un spectre de fluorescence typique comparable à celui de certains hydrocarbures polycycliques déjà connus. Il s'agissait de trois bandes dans le violet, avec des maximums à 400, 418 et 440 nm environ. Ce test orienta les recherches vers des hydrocarbures aromatiques polycycliques.[6]

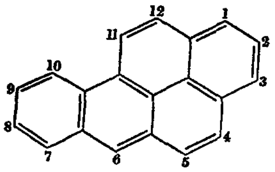
Effectivement en 1930, Kennaway et Hieger démontrent l'activité cancérigène du dibenzo[*ah*]anthracène. En 1933, Cook et ses collaborateurs[7] isolent le benzo[*a*]pyrène du goudron de houille et montrent son action hautement cancérigène. Depuis de nombreux chercheurs ont pu prouver le pouvoir cancérigène sur l'animal d'un grand nombre d'hydrocarbures polycycliques. En 1948, Pullman[8,9] expose sa théorie de l'activité cancérigène: un produit cancérigène doit présenter une affinité pour la cellule vivante. Cette affinité s'explique par l'existence de "régions actives" de la molécule, c'est-à-dire de régions où il se produit une accumulation d'électrons.

Ainsi, le benzanthracène-1,2 n'est pas cancérigène. Par contre, on obtient des dérivés de plus en plus cancérigènes par substitution d'un radical méthyl en 5, en 9 ou en 10. La région active, ou région *K* est celle de la double liaison 3–4 où la concentration électronique augmente d'autant plus que le substituant en est plus rapproché.

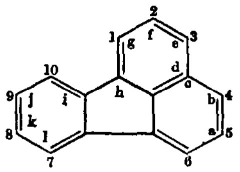


Benzanthracène-1,2

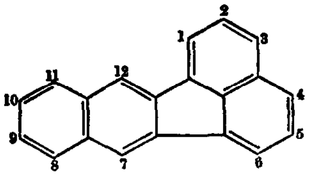
Actuellement, les seuls hydrocarbures cancérigénes couramment rencontrés dans l'atmosphère sont: le benzo[*a*]pyrène, le benzo[*e*]fluoranthène, le benzo[*k*]fluoranthène et le dibenzo[*a,h*]anthracène[10] ainsi que certains dérivés méthylés.



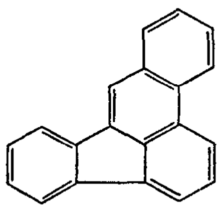
Benzo[*a*]pyrène



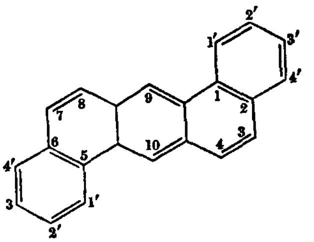
Fluoranthène



Benzo[*k*]fluoranthène



Benzo[*e*]fluoranthène



Dibenzo[*a*,*h*]anthracène

Remarque: nous avons choisi la nomenclature du 'Ring Index'' adoptée par les "Chemical Abstracts''. Il faut signaler que le benzo[*a*]pyrène est souvent appelé benzo-3,4 pyrène dans l'ancienne numérotation.

MÉTHODES D'ANALYSE DES HYDROCARBURES AROMATIQUES POLYCYCLIQUES

Les principales méthodes d'analyse des hydrocarbures aromatiques polycycliques vont être passées en revue. Nous étudierons successivement les méthodes d'extraction, de séparation et de dosage.

Il importe:

—de doser les goudrons dans leur ensemble,

—de doser les hydrocarbures cancérigènes.

Méthodes d'extraction

Nous prendrons ici le terme extraction au sens large et nous parlerons ègalement des techniques de concentration.

Extraction par filtration. Le procédé habituel en pollution atmosphérique consiste à faire passer par pompage un volume déterminé d'air sur un papier-filtre[11–13] ou de la fibre de verre.

Quel que soit le système utilisé, il est important de vérifier:

—que les plus petites particules pouvant contenir des polycycliques sont arrêtées; pour cela, il est bon de placer un deuxième filtre en aval du filtre principal,

—que les polynucléaires adsorbés par le filtre peuvent être remis ensuite quantitativement en solution.

Extraction par les solvants. (*a*) *Avec l'appareil Soxhlet;* on utilise l'appareil Soxhlet avec comme solvant le benzène ou le mélange benzène-méthanol. (*b*) *Extraction liquide-liquide;* l'échantillon à analyser est dissous dans un solvant convenable et on extrait les hydrocarbures polycycliques par un solvant non miscible au premier. (*c*) *Extraction à contre-courant;* l'extraction à contre-courant d'un mélange de polycycliques a été étudiée en se servant de l'ppareil de Craig.[14] Les solvants consistaient en un mélange de cyclohexane méthanol à 90% contenant 0,83% d'acide tétraméthylurique. La séparation est excellente mais la méthode est laborieuse. (*d*) *Sublimation;* des essais d'extraction ont été effectués par sublimation. Les auteurs utilisent un tube chauffé permettant un gradient de température décroissant à partir de 250° et un vide variant de 1,3 à 33 mbar.[15–17] Par cette technique, seul le chrysène, pour l'instant, est récupéré intégralement à partir d'un mélange complexe. (*e*) *Remarques;* Monkman[18] recommande d'éviter l'extraction au Soxhlet pour l'examen des poussières atmosphériques: car il pourrait y avoir destruction par chauffage en présence d'air et de lumière d'une fraction des hydrocarbures polycycliques. Le solvant de choix est le cyclohexane:[19,20] on agite 100 mg de poussière dans 100 ml de cyclohexane pendant trois heures dans un erlenmeyer, puis on filtre sur verre fritté.

La solution provenant de l'extraction des poussières est évaporée à siccité et le résidu est pesé. Il constitue l'extractible, on lui donne le nom de goudron. On reprend par l'éther de pétrole pour pouvoir éliminer les acides, les phénols et les bases lorsque ceux-ci se trouvent en grande quantité.

Méthodes de séparation

Pour séparer les hydrocarbures polyaromatiques entre eux on a recours essentiellement aux méthodes chromatographiques: chromatographie en phase liquide ou chromatographie en phase gazeuse. La chromatographie en phase gazeuse, servant de méthode de séparation mais également de méthode de dosage, sera étudiée en même temps que les procédés quantitatifs. Dans la chromatographie en phase liquide, il faut distinguer la chromatographie d'adsorption sur colonne ou sur couches minces, et la chromatographie de partage sur papier ou sur colonne.

Chromatographie d'adsorption sur colonne. Elle se fait, en général, sur alumine activée ou sur silicagel. On élue par le cyclohexane ou avec des mélanges hexane-diéthyléther.[3,21–23] Le silicagel permet de séparer assez rapidement les hydrocarbures aromatiques des autres hydrocarbures paraffiniques, des cyclanes et des oléfines. Par contre, seule l'alumine permet un fractionnement des aromatiques entre eux.

Chromatographie sur couches minces. Elle permet des séparations du même ordre que celles de la chromatographie sur colonne, mais elles sont beaucoup plus rapides. Le support est constitué par des plaques de verre recouvertes d'un mélange plâtre–silicagel.[24] On utilise également la poudre de cellulose acétylée. Köhler emploie un mélange alumine–acéthylcellulose, il travaille en chromatographie à deux dimensions avec comme solvants: hexane/pentane/toluène et méthanol/éthanol/eau.[25]

Sawicki[26] a comparé l'efficacité de trois méthodes sur couches minces sur un couple particulièrement difficile à séparer: le benzo[*a*]pyrène et le benzo[*k*]fluoranthène. Ces corps sont séparés sur cellulose acétylée avec élution par le mélange: éthanol/toluène/eau (17/4/4). Par contre, ils ne sont pas séparés sur cellulose non acétylée en éluant par le mélange diméthylformamide/eau (1/1), ni sur alumine avec le mélange pentane/éther (19/1).

Chromatographie de partage sur papier. En général on utilise le papier Whatman n° 1 ou Arches 304 et comme solvant le mélange diméthylformamide–éther de pétrole. Malý[27] imprègne le papier avec de l'huile blanche médicinale en le plongeant dans une solution d'huile dans l'éther de pétrole, et en laissant ensuite évaporer l'éther. Il réussit ainsi très bien la séparation du mélange benzo[*a*]pyrène–benzo[*k*]fluoranthène–pérylène des autre hydrocarbures. La phase stationnaire est constituée par de l'huile de vaseline et la phase mobile par du méthanol.

Chromatographie de partage sur colonne. Phases stationnaires: glycols, polyéthylèneglycols *etc.* Phase mobile: iso-octane. L'adjonction de trinitrobenzène sym. améliore beaucoup la séparation des différents constituants par suite de la formation de complexes entre les hydrocarbures et le dérivé nitré.[28]

Déterminations qualitatives et quantitatives

Il faut distinguer:

—les contrôles de routine où le but est d'obtenir des résultats rapides avec des moyens peu onéreux,

—l'analyse approfondie où l'on utilise les techniques les plus précises même si elles sont très longues.

Déterminations qualitatives. On examine directement les chromatogrammes en lumière de Wood ($\lambda = 365$ nm) et l'on mesure le R_f. Il est possible également de mesurer la surface des spots[29] ce qui permet une évaluation très approximative de la teneur. Certains hydrocarbures polycycliques sont fluorescents, d'autres le deviennent à la température de l'azote liquide ou en solution dans l'acide sulfurique ou l'acide trifluoracétique.

Déterminations quantitatives. Les méthodes les plus importantes sont: la spectrophotométrie d'absorption dans l'ultra-violet, la fluorimétrie, la chromatographie en phase gazeuse, et les méthodes biologiques.

(*a*) *Spectrophotométrie dans l'ultra-violet.* Tous les hydrocarbures polyaromatiques absorbent dans l'ultra-violet, et la mesure de l'absorption dans l'ultra-violet reste la méthode quantitative la plus sûre pour doser un polycyclique dont la nature est bien déterminée.

Les maximums d'absorption et les coefficients d'extinction sont donnés dans la littérature.[30,31] Mais il faut se servir de ces données avec circonspection si l'on ne connaît pas les conditions exactes dans lesquelles elles ont été établies.

Quels sont les inconvénients de cette technique? Tout d'abord le rayonnement ultra-violet est actif sur les polycycliques: il modifie leur structure si bien que l'absorption diminue avec le temps. Il est donc nécessaire d'opérer rapidement. Ce changement serait dû à une réaction des hydrocarbures avec l'ozone.[32] De plus, elle manque de sélectivité. Toutefois les travaux d'Haenni[33–37] ont montré que l'on peut établir des limites supérieures d'absorption ultra-violette à des longueurs d'onde convenablement choisies. Si ces limites ne sont pas dépassées, on est assuré qu'aucun hydrocarbure cancérigène ne se trouve dans l'échantillon analysé à une dose supérieure à 0,3 ppm.

On a cherché à appliquer la spectrophotométrie ultra-violette à des solutions contenant plusieurs polynucléaires. Il s'agit, selon un procédé classique en spectrophotométrie, de choisir des longueurs d'onde convenables, de déterminer les coefficients d'extinction respectifs et de résoudre un système de *n* équations à *n* inconnues. Ce procédé si imparfait qu'il soit est très utile pour doser des substances difficiles à séparer par chromatographie.[31,38–41] La principale difficulté vient du fait qu'en pollution atmosphérique, il faut toujours redouter la présence de corps non identifiés susceptibles de fausser le dosage. Korotkov a résolu avec succès le problème du mélange benzo[*a*]pyréne–dibenzanthracène.[39]

D'autre part, il a été montré[42] que le pouvoir cancérigène des poussières atmosphériques est proportionnel à leur teneur en benzo[*a*]pyrène. Et il est admis que le benzo[*a*]pyrène se trouve en proportion assez constante par rapport aux autres polycycliques. Ces deux faits ont amené les auteurs à porter leurs efforts sur la séparation du benzo[*a*]pyrène par chromatographie et son dosage par mesure de l'absorption dans l'ultra-violet.[43–46] Toutefois, il faut signaler que, contrairement à l'opinion de Mme Héros et de M. Amy, le pouvoir cancérigène des diverses poussières atmosphériques est seulement partiellement lié à leur teneur en benzo[*a*]pyrène. C'est ce qui a été démontré par Hueper et ses collaborateurs d'une part[47,48] et par Epstein et ses collaborateurs d'autre part.[49] Dans ces conditions, il est difficile, à partir d'un dosage de benzo[*a*]pyrène, de déduire le pouvoir cancérigène des poussières atmosphériques.

(*b*) *Fluorimétrie.* La fluorimétrie très employée présente un certain nombre d'avantages.

—Tous les hydrocarbures cancérigènes sont fluorescents.

—Elle est extrêmement sensible.

Par contre elle présente quelques difficultés:

—Elle est moins précise que la spectrophotométrie UV.

—Les traces de substances étrangères interviennent intensément par absorption ou inhibition de la fluorescence. Il est donc indispensable qu'un étalonnage préalable soit effectué dans des conditions opératoires strictement identiques.

—La fluorescence dépend de la nature du solvant.

C'est pourquoi, il faut distinguer des méthodes semi-quantitatives et des méthodes précises.

Les procédés semi-quantitatifs concernent surtout le benzo[*a*]pyrène, il est possible d'évaluer grossièrement sa teneur sans séparation préalable, grâce à une méthode par dilution successive et surcharge.[50,51] On effectue les spectres de fluorescence de dilutions successives de solutions de benzo[*a*]pyrène à doser jusqu'à disparition presque totale des bandes ultimes de fluorescence (403 et 427 nm). Ceci a pour but d'éviter les inhibitions éventuelles d'une part et les parties non linéaires de la courbe intensité de fluorescence-concentration. On ajoute alors des quantités connues de benzo[*a*]pyrène ce qui permet une évaluation approximative de la concentration cherchée.

Ce procédé a été perfectionné par Mme Héros[50,51] en l'appliquant après chromatographie.[52] La limite de sensibilité de la méthode est de 10 ng dans une cuve de 1 cm^3. Le benzo[*k*]fluoranthène interfère. Il est possible de résoudre le problème benzo[*a*]-pyrène–benzo[*k*]fluoranthène de la manière suivante:[42]

—dans un premier temps, on détermine la fluorescence du mélange,

—dans un deuxième temps, on élimine la fluorescence du benzo[*a*]pyrène par action du brome et l'on mesure celle du benzo[*k*]fluoranthène qui n'est pas modifiée.

En travaillant à $-190°$, il est possible d'améliorer de beaucoup la sensibilité et le grand nombre des bandes du spectre permet d'identifier le benzo[*a*]pyrène avec une plus grande certitude. On peut déceler, dans ces conditions, 100 ng par mm^3.

Pour les mélanges d'hydrocarbures autres que le benzopyrène, l'excitation par la raie de Wood $\lambda = 365$ nm ou la raie $\lambda = 253{,}7$ nm du mercure provoque l'apparition de la plupart des spectres de fluorescence. Pour n'en exciter qu'un seul, il faut profiter du fait que l'intensité de fluorescence est maximale ou minimale selon que la raie excitatrice se trouve à un maximum ou à un minimum d'absorption.

Pour un corps donné, il faut donc choisir une raie excitatrice à l'aide d'un monochromateur, de manière qu'elle coincide avec un maximum d'absorption de cette substance et un minimum pour tous les autres corps. Il faut également disposer d'une source suffisamment intense pour la détection par les phototubes. C'est ce qui a été réalisé avec les lampes au xénon.

Une autre technique est celle des spectres d'activation. Les spectres d'activation reprèsentent la variation d'intensité d'une bande fluorescente mesurée à longueur d'onde constante, en fonction de la lumière excitatrice supposée d'intensité constante. Pour réaliser un spectre d'activation, il faut un appareillage plus compliqué:

—une source émettant dans un vaste domaine,

—deux monochromateurs indépendants, un pour la lumière excitatrice, l'autre pour l'émission de fluorescence.

Il est possible de combiner les deux méthodes pour analyser un mélange complexe: on enregistre successivement des spectres de fluorescence avec, comme longueurs d'onde excitatrices, celles qui correspondent à un maximum du spectre d'activation pour chaque substance recherchée. Il est possible de faire apparaître chaque spectre de fluorescence séparément presque sans interférences.

Sawicki,[53] van Duuren,[54] Dubois et Monkman[55] ont réussi à doser, par fluorimétrie, des mélanges de polycycliques. Voici le principe pour le mélange benzo[*a*]pyrène–benzo[*k*]fluoranthène:

—à 308 nm il y a excitation de la fluorescence du benzofluoranthène uniquement,

—à 381 nm il y a, à la fois, excitation de la fluorescence des deux composés.

Pour terminer signalons des méthodes qui utilisent la spectrophotométrie dans l'ultra-violet et la spectrofluorimétrie. Ainsi il est possible de doser d'une part un certain nombre d'hydrocarbures par mesure de l'absorption dans l'ultra-violet et d'autre part le benzo[*a*]pyrène et le benzo[*k*]fluoranthène par fluorescence en solution dans l'hexane au moyen de deux longueurs d'onde excitatrices (308 nm et 384 nm).

(*c*) *Chromatographie en phase gazeuse*. Elle est encore peu utilisèe, mais c'est une méthode d'avenir. Elle présente un certain nombre de difficultés:

—multiplicité des produits contenus dans les poussières,

—points d'ébullition élevés des hydrocarbures cancérigènes (benzo[*a*]pyrène: 496°). Si la chambre d'injection du chromatographe est à une température trop élevée pour permettre la volatilisation des substances, on risque une décomposition ou une polymérisation. De plus le choix des phases stationnaires se trouve restreint. Pour remédier à ces inconvénients on effectue un fractionnement préliminaire par extractions successives des solutions de cyclohexane avec le mélange méthanol-eau et ensuite avec le nitrométhane.[56]

Voici les conditions opératoires:

—colonne capillaire en verre de 35 m de longueur et 0,35 mm de diamètre intérieur, chauffée à 200° (les parois internes sont enduites de caoutchouc au silicone),

—température d'injection: 250°.

Les déterminations quantitatives sont faites par la méthode de l'étalon interne avec comme étalon le triphényl-1,3,5 benzène. L'efficacité de la colonne mesurée pour le *n*-hexacosane est de 10^4 plateaux théoriques.

On utilise aussi la chromatographie à température programmée de 150 à 350°,[57] les auteurs se servent d'un dispositif à deux colonnes et deux détecteurs ce qui permet d'annuler la dérive de la ligne de base. La sensibilité est à peu près la même qu'en spectrophotométrie UV, la méthode est assez rapide, elle dure deux heures. Signalons également que, pour obtenir de meilleures séparations on s'est servi à la fois de la chromatographie sur chouches minces et de la chromatographie en phase gazeuse.

(*d*) *Méthodes biologiques.* Dans de nombreux cas, il n'est pas possible de se passer de l'analyse biologique bien qu'elle dure plusieurs mois parfois. On ne peut garantir, par exemple, qu'un échantillon n'est pas cancérigène, même si l'on est sûr qu'il ne renferme ni benzo[*a*]pyrène, ni dibenzanthracène, ni méthyl-cholanthrène. Pour avoir une certitude absolue il est nécessaire de faire un essai sur l'animal.

L'animal de choix est la souris, car le cancer apparaît après deux ou trois mois. Le pourcentage de souris contaminées renseigne sur l'activité cancérigène du produit.

CONCLUSION

Nous avons essayé de donner une idée aussi juste que possible du problème des hydrocarbures cancérigènes en pollution atmosphérique vu sous l'angle analytique.

Les méthodes quantitatives les plus utilisées actuellement sont la spectrophotométrie ultra-violette et la fluorimétrie. Il semble que, dans l'avenir, la chromatographie en phase gazeuse jouera un rôle très important à la fois en tant que méthode de séparation et de dosage.

Summary—A survey is given of the source of hydrocarbons found in the atmosphere, of their toxicity, and of the methods of analysis available for polycyclic aromatic hydrocarbons.

Zusammenfassung—Es handelt sich un eine Übersicht über den Ursprung der in der Atmosphäre gefundenen Kohlenwasserstoffe und ihre Toxizität sowie über die Analysenmethoden für polycyclische aromatische Kohlenwasserstoffe.

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ENTHALPIMETRIC DETERMINATION OF FLUORIDE

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Summary—An injection calorimeter used for analytical and thermochemical purposes is described. Amounts of sodium fluoride between 6 and 8 mg are determined with an error of ±0·04 mg. The calorimeter is also used in determining ΔH for the precipitation of lead chlorofluoride from water solutions with an ionic strength of $1M$. $\Delta H = 36{\cdot}6 \pm 0{\cdot}3$ kJ/mole. Quantitative analysis is made by flow microcalorimeter with amounts of sodium fluoride between 40 and 400 μg and an error of ±4 μg. An ion-exchange system for separation of fluoride from phosphate, sulphate, nitrate and chloride is also described.

CALORIMETRIC methods are of importance not only in thermodynamics but also in the field of analytical chemistry. Enthalpy titration methods have been shown to be of value in both these areas. With this technique a constant flow of reagent is added to the calorimetric vessel, or the reagent is rapidly injected into the vessel containing the sample solution.[1–5]

In this paper results are reported from the enthalpimetric determination of fluoride in water solution. Both complexation and precipitation reactions could be considered.[6] In this work the precipitation reaction

$$\mathrm{Pb^{2+}_{(aq)} + F^{-}_{(aq)} + Cl^{-}_{(aq)} \rightarrow PbFCl_{(s)}} \qquad (1)$$

was used. This reaction is fast and is accompanied by a fairly large heat effect which makes it suitable for the analytical technique used here.

EXPERIMENTAL

Injection Calorimetry

Reagents

The sample solutions were made from sodium fluoride, phosphate, sulphate, chloride and nitrate, all of *pro analysi* quality. The eluent in the anion-exchange was sodium hydroxide solution made from a carbon dioxide-free concentrated solution. The anion-exchange resin was regenerated with sodium hydroxide solution. The cation-exchange resin was regenerated with $3M$ hydrochloric acid. The precipitant was $4{\cdot}9M$ lead(II) perchlorate, prepared from lead(II) oxide and 70% reagent grade perchloric acid. To lower the heat of solution of the reagent, the lead(II) perchlorate solution was diluted with 2% w/v water.

Ion-exchange procedure

If a sample contains other anions it is not possible to measure the fluoride content directly since the presence of these anions influences the enthalpy of reaction. Therefore ion-exchange steps had to be included in the procedure. The ion-exchange arrangement, shown in Fig. 1, consisted of a glass column with 5 g of ion-exchange resin Dowex 1 × 8, 200–400 mesh in OH form and a Teflon column containing 5 g of cation-exchange resin Dowex 50 W × 8, 20–50 mesh. In the analytical experiments with the injection calorimeter, samples containing 6–8 mg of fluoride and usually a 20-fold excess of chloride, nitrate, sulphate or phosphate were put on the anion-exchange column. Flow-rate in the absorption step was 1 ml/min.

If the sample also contained carbonate this ion had to be removed before the ion-exchange step. This was done by blowing carbon dioxide-free nitrogen through the sample solution after its pH had been adjusted to 5·5. After the absorption the resin was washed with distilled water until the effluent was neutral. The fluoride was eluted by $0{\cdot}2M$ sodium hydroxide at a flow-rate of 1·5 ml/min. The

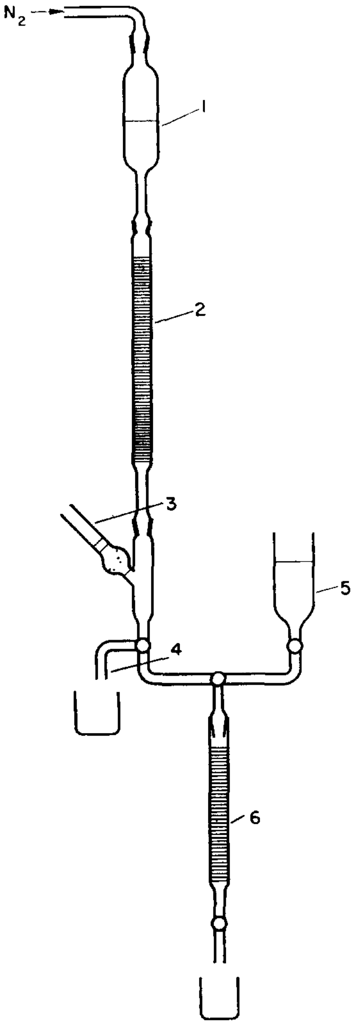

FIG. 1.—Ion-exchange arrangement.
1—Holder for sample solution, water, eluent and regeneration solution. 2—Anion-exchange column with Dowex 1 × 8. 3—Ascarite protection tube. 4—Discharge tube. 5—Holder for water and regeneration solution. 6—Teflon cation-exchange column with Dowex 50 W × 8.

first 60 ml of effluent did not contain any fluoride and were rejected. The following 100 ml contained all the fluoride, but no other anions, as was shown by spot tests[8] performed on the next few drops eluted. The anion-exchange resin was regenerated with 4*M* sodium hydroxide and was washed with distilled water.

The fluoride effluent was alkaline and could not be used directly in the calorimetric experiments. Neutralization with acid would give too high an ionic strength, which would interfere with the calorimetric measurements. The fluoride solution was therefore passed through the cation-exchanger. The hydrofluoric acid coming from the cation-exchanger was absorbed in 5 ml of solution that was 0·117*M* in sodium acetate, 0·033*M* in sodium hydroxide and 0·15*M* in sodium chloride, in a Teflon beaker. After evaporation to 6–7 ml the solution was cooled to room temperature. One ml of 0·915*M* acetic acid was added to the solution to give a pH of 4·4. This solution was diluted to 25 ml and added to the calorimetric cell.

Calorimeter

The reaction cell consisted of a 25-ml Dewar vessel made of Pyrex glass, placed in a polyethylene cover (Fig. 2). The temperature changes were measured with a Veco 32 A 12 2000-Ω thermistor, connected to a Wheatstone bridge. The signal from this was amplified with a Hewlett-Packard Null Voltmeter 491 A, the output signal of which was connected to a Servogor Re 511 recorder. The input signal to the amplifier was usually about 500 μV and was measured on the 1-mV range. The reagent was delivered through a glass spiral which was housed in the sample solution to obtain the same initial temperature for both solutions. The tip of the spiral ended 3 mm above the surface of the solution. The volume of the spiral was 0·83 ml and it was filled directly from a burette. By pressing air into the spiral the reagent was injected into the sample solution. The stirrer was made from Teflon attached to a glass shaft. Temperature was adjusted by means of a 50-Ω manganin heater which also was used for the electrical calibration of the calorimeter.

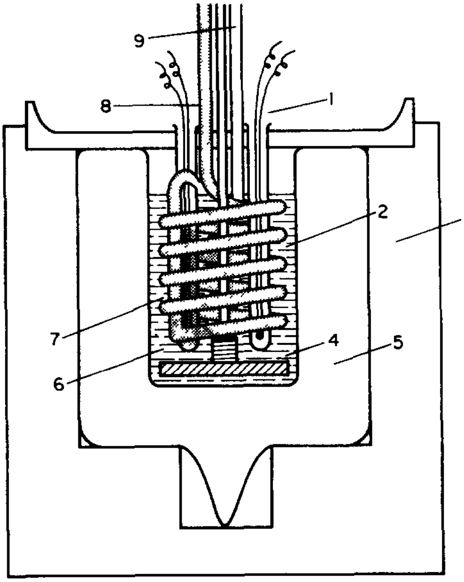

FIG. 2.—Calorimetric cell.
1—Thermistor. 2—Glass spiral. 3—Polyethylene cover. 4—Teflon stirrer. 5—Dewar vessel. 6—Heater. 7—Sample solution. 8—Tube to burette. 9—Tube to air syringe.

Calorimetric procedure

The temperature was adjusted with the heater to 25·0° and the calorimeter was allowed to equilibrate during 5 min, after which a linear voltage–time curve was obtained on the recorder. The reagent was then injected into the sample solution. After 1·5 min a steady state was established and the voltage again changed linearly with time. The distance between the two straight lines on the recorder chart was measured. In the analytical experiments the instrument was calibrated by measurements on known amounts of sodium fluoride, which had been passed through the cation-exchange step.

Flow Microcalorimetry

Reagents

The sample solutions, with a pH of 4·6, were 0·5–4 mM in sodium fluoride, 0·06M in acetic acid–sodium acetate and 0·03M in sodium chloride. The reagent was 0·49M lead perchlorate.

Calorimeter

A commercial instrument, the LKB 10700-1 was used.[7] This calorimeter is a twin heat-leakage calorimeter utilizing semiconducting thermocouple plates for measurements of the heat flow. The mixing cell was made of a gold spiral and had an internal volume of 1 ml. The signal from the thermopiles was amplified with a Keithley 150 B Amplifier, with the input signal measured in the 100-μV range. The amplified signal was recorded in the 50-mV range on the Servogor RE 511 recorder. Two LKB 102000 Perspex pumps were used to pump the reagent and sample solutions through the reaction cell. At steady state the calorimetric signal is proportional to the heat effect from the reaction in the cell. Thus the baseline displacement measured on the recorder is, for a given flow-rate, proportional to the concentration of the flouride in the sample.

Procedure

A blank solution, without fluoride, and the reagent were first pumped into the calorimeter. The flow-rate was 27·8 ml/hr for the sample solution and 15 ml/hr for the reagent. After some minutes a steady potential was obtained and the signal from the amplifier was adjusted to zero. The blank solution was then replaced by the sample solution. After 3–7 min, depending on the amount of fluoride, the potential became stable. The sample was then replaced by the blank solution and the potential returned to zero, Fig. 3.

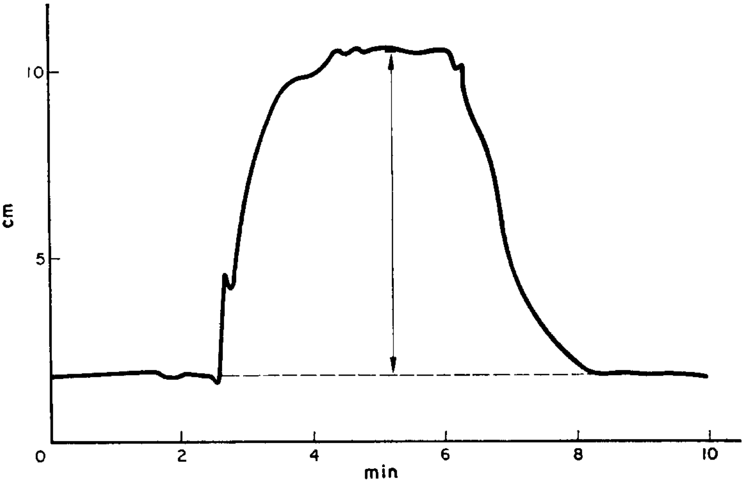

FIG. 3.—Response–time curve for precipitation of lead chlorofluoride in the flow microcalorimeter. The fluoride concentration is ~2·5 m*M*. The arrow shows the deflection read off.

Determination of the Enthalpy Change for the Precipitation Reaction

In a separate series of experiments the enthalpy change of precipitation reaction (1) was determined. These experiments were made with the injection calorimeter. The performance of this calorimeter was tested by measurement of the enthalpy of neutralization of dilute hydrochloric acid by sodium hydroxide solution.

Calorimeter equipment

In order to improve the precision of the recorder reading, 50–80% of the amplified signal was balanced out by a known external voltage signal. To achieve this, the amplifier was switched over to a preset negative off-balance value at the same time as the reagent was injected into the calorimeter. The measurement range of the amplifier was 300 μV and the recorder range was 0·5 V. The calorimeter was calibrated electrically in these experiments. A precision resistance of 10·00 ± 0·005 Ω was connected in series with the heater. Electrical energy evolved in the heater was calculated from measurements of the current through the 10-Ω resistance for the known time of 5·000 ± 0·002 sec.

Reagents

In the test experiments the sample solution was 0·004963*M* hydrochloric acid prepared from a 0·1*M pro analysi* standard in an ampoule, and boiled-out distilled water. The reagent solution consisted of 0·30*M* sodium hydroxide prepared from a carbon dioxide-free 1*M pro analysi* standard in an ampoule, and boiled-out distilled water. Both solutions were stored in bottles fitted with Ascarite protection tubes. In the precipitation reaction the sample solution consisted of 6–8 mg of sodium fluoride in a buffer solution of 0·060*M* acetic acid–sodium acetate and 0·030 *M* sodium chloride. The reagent was 4·9*M* lead(II) perchlorate. The cation-exchange resin was Dowex 50 W × 8, which was kept in a Teflon column.

Calorimetric procedure

In the test experiments 0·83 ml of 0·30*M* sodium hydroxide was reacted with 20–25 ml of the hydrochloric acid. One min after the injection a steady state was reached and the temperature–time curve became linear. After a period of about 3 min the system was calibrated electrically by the addition of 6·368 J.

The enthalpy change for the precipitation is a function of pH because of the partial ionization of the hydrofluoric acid initially present. Therefore a correction must be applied for the enthalpy of dissociation of hydrofluoric acid. In order to avoid systematic errors different amounts of fluoride and different pH values were used in the experiments. Some of the sample solutions were prepared by diluting different amounts of sodium fluoride to 25 ml in an acetate buffer solution and some were prepared by first passing the same amount of fluoride through a cation-exchange resin. The first solutions had a pH of about 4·6 and the others about 4·4.

The enthalpy of dilution of lead(II) perchlorate was measured and was also found to depend on the pH. Therefore, injections of the reagent were made into blank solutions with pH between 4·35 and 4·65 and an acetic acid–sodium acetate concentration of 0·06*M* and sodium chloride concentration of 0·03*M*. As in the test experiments, electrical calibrations were performed immediately after the reaction. In all the calorimetric experiments the injection was made at 25·0°. The temperature rise was about 0·05° both in the test experiments and in the precipitation reaction.

RESULTS AND DISCUSSION

Injection calorimetry

Usually the quantity of fluoride in the sample was adjusted to between 6 and 8 mg of sodium fluoride. Under these conditions the calibration curve was a straight line. With below 5 mg the reaction became slower and the reproducibility was not as good. By regression analysis of the calibration values, it was calculated that the amount of sodium fluoride could be determined within ±0·04 mg for an unknown sample run in duplicate (95% confidence limit). The results in Table I from analysis of solutions which had passed through the ion-exchange process show that the fluoride passes quantitatively through the columns.

TABLE I.

NaF added, *mg*	Other anion 0·5*M*, *ml*	NaF calc. from calibration curve, *mg*	Error, *mg*
6·300	PO_4^{3-} 4	6·296	−0·004
6·800	Cl^- 4	6·763	−0·037
7·000	NO_3^- 6	7·008	+0·008
7·250	Cl^- 6	7·254	+0·004
7·600	Cl^- 6	7·597	−0·003
7·800	Cl^- 4	7·843	+0·043
8·000	SO_4^{2-} 4	8·015	+0·015

Flow calorimetry

A linear relationship between the recorder signal and the fluoride concentration was obtained. By regression analysis it was calculated that for a duplicate sample the fluoride concentration could be determined within ±0·08 m*M* (95% confidence limit). However, the line does not pass through the origin, which indicates that the blank experiments did not completely account for zero effects. In analytical experiments, however, where the instrument can be calibrated with known solutions, such discrepancies are of little importance. The precipitation of lead chlorofluoride is thus shown to be useful for the determination of very low concentrations of fluoride by flow calorimetry. The results from the regression analysis imply that amounts of between 20 and 400 μg of sodium fluoride can be determined within ±4 μg with a duplicate sample. When the fluoride concentration was greater than 4 mM the amount of precipitate became so large that the increasing heat of friction caused irreproducible results. In some cases the flow was stopped by the precipitation. In the injection method the reagent had to be prepared to give a small heat dilution. This is not necessary in the flow calorimeter experiments because the heat of dilution can always be compensated electrically. The constancy of the heat of dilution can also be checked over a long period before the precipitation reaction is started, which is not possible in the injection method.

Determination of ΔH

Test experiments. The recorder signal (equal to the applied negative voltage and plus the value read on the recorder) was taken to be proportional to the heat, $Q_c = 6{\cdot}368$ J, at the calibration and to Q_n in the chemical experiments, respectively. Q_n consists of the heat of dilution and heat of reaction between acid and base. The heat of solution was measured by injecting reagent into a blank solution of boiled-out distilled water. These values were subtracted from Q_n and the remaining value was corrected to infinite dilution.[9,10] By dividing by the number of moles in the sample and changing the sign, the heat of ionization of water was obtained. The value from 13 experiments (95% confidence interval) was 55·79 ± 0·06 kJ/mole. This value is in excellent agreement with values in the literature,[1,9] showing that the calorimetric method is not impaired by any significant systematic errors.

The values obtained were used in regression analysis and showed that when the calorimeter is being used as an analytical instrument it is possible to determine a strong acid to within ±0·4 μmole (95% confidence limits).

Precipitation reaction. The quantity determined Q_p consists of three different heats.

$$Q_p = Q_1 + Q_2 + Q_3 \tag{2}$$

Q_1 = Heat of dilution of lead(II) perchlorate
Q_2 = Heat of dissociation of hydrofluoric acid
Q_3 = Heat of precipitation of lead chlorofluoride

Q_1 was calculated from values obtained when the reagent solution was injected into blank solutions. Q_2 was calculated from the relation:

$$Q_2 = [\mathrm{HF}] \times \Delta H_{\mathrm{diss}} \tag{3}$$

ΔH_{diss} = heat of dissociation of 1 mole of hydrofluoric acid (13·3 kJ/mole).[11] [HF] was calculated from:

$$[\mathrm{HF}] = \frac{[\mathrm{H}^+]\,.\,[\mathrm{F}^-]\,.f_+\,.f_-}{K_{\mathrm{diss}}}\,; \qquad K_{\mathrm{diss}} = 10^{-3{\cdot}17}.^{11}$$

$Q_1 + Q_2$ lies between 0·04 and 0·33 J and depends on the pH. The results are summarized in Table II.

Each value given in Table II is the mean value for 4 determinations performed under identical conditions. The ΔH values derived all refer to the process

$$\mathrm{Pb}^{2+}_{(aq)} + \mathrm{F}^-_{(aq)} + \mathrm{Cl}^-_{(aq)} \rightarrow \mathrm{PbFCl}_{(s)}$$

at an ionic strength of 1M and at 25°. The mean ΔH-value (95% confidence limit) is calculated to be 36·6 ± 0·24 kJ/mole.

TABLE II.

Fluoride, *mole*	pH	Q_3, *J*	ΔH, *kJ/mole*
0·1471	4·61	5·402	36·7
0·1568	4·61	5·772	36·5
0·1680	4·62	6·167	36·3
0·1471	4·41	5·435	36·9
0·1568	4·40	5·830	36·7
0·1680	4·38	6·196	36·5

Acknowledgement—I wish to thank Dr Ingemar Wadsö for his valuable help during this work and the preparation of this report. I also wish to thank Dr K. J. Karrman and Ingvar Pettersson for their helpful advice.

Zusammenfassung—Ein Injektionskalorimeter für analytische und thermochemische Zwecke wird beschrieben. Natriumfluoridmengen zwischen 6 und 8 mg werden mit einem Fehler von ±0,04 mg bestimmt. Das Kalorimeter wird auch bei der Bestimmung von ΔH bei der Fällung von Bleichlorfluorid aus wäßrigen Lösungen der Ionenstärke $1M$ verwendet. $\Delta H = 36{,}6 \pm 0{,}3$ kJ/Mol. Quantitative Analysen werden in einem Mikro- Durchflußkalorimeter mit Natriumfluoridmengen zwischen 40 und 400 μg und einem Fehler von ±4 μg durchgeführt. Es wird auch ein Ionenaustauschsystem beschrieben, mit dem man Fluorid von Phosphat, Sulfat, Nitrat und Chlorid abtrennen kann.

Résumé—On décrit un calorimètre à injection utilisé dans des buts analytiques et thermochimiques. On dose des quantités de fluorure de sodium compris entre 6 et 8 mg avec une erreur de ±0,04 mg. On utilise aussi le calorimètre dans la détermination de ΔH pour la précipitation du chlorofluorure de plomb à partir de solutions aqueuses avec une force ionique de $1M$. $\Delta H = 36{\cdot}6 \pm 0{\cdot}3$ kJ/mole. L'analyse quantitative est effectuée au moyen d'un microcalorimètre à écoulement avec des quantités de fluorure de sodium comprises entre 40 et 400 μg et une erreur de ±4 μg. On décrit aussi un système d'échange d'ions pour la séparation du fluorure des phosphate, sulfate, nitrate et chlorure.

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ETUDE POLAROGRAPHIQUE ET PHYSICOCHIMIQUE DE *N*-OXYDES—II

MÉCANISME DE RÉDUCTION ET PHÉNOMÈNES D'HYDRATATION DES ACÉTYL ET BENZOYL PYRIDINES *N*-OXYDES

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Résumé—Une étude polarographique des acétyl et benzoyl pyridines *N*-oxydes fait apparaître des anomalies identiques à celles déjà signalées dans le cas des dérivés formylés correspondants: lorsque le substituant est en position 2 ou 4, il y a réduction simultanée des fonctions carbonyles et *N*-oxydes; en position 3 la réduction a lieu normalement à tous les pH. Une étude par spectroscopie U.V. a permis de mettre en évidence une hydratation du carbonyle, moins intense toutefois que dans le cas des dérivés formylés.

Nous avons examiné, dans l'article précédent de cette série,[1] le comportement polarographique et spectroscopique des formylpyridines *N*-oxydes. Cette étude nous avait permis de mettre en évidence deux phénomènes. (*a*) Un mécanisme de réduction anormal pour les dérivés 2 et 4, avec réduction simultanée des fonctions carbonyle et *N*-oxyde, le dérivé 3 se comportant normalement. (*b*) Une hydratation importante du carbonyle pour les trois isomères.

Le présent travail, consacré aux acétylpyridines *N*-oxydes et aux benzoylpyridines *N*-oxydes, nous a permis de conclure également à une hydratation du carbonyle, ainsi qu'au même type de réduction anormal pour les dérivés 2 et 4.

ETUDE POLAROGRAPHIQUE

*Acétyl-*3 *et benzoyl-*3 *pyridines* N-*oxydes*

Comme dans le cas du formyl-3 pyridine *N*-oxyde, on observe deux types de vagues (Fig. 1 et 2): une vague *A* à 2F, correspondant à la réduction du carbonyle, et une vague *B* à 2F correspondant à la réduction du groupe *N*-oxyde. La vague *A* se scinde en milieu alcalin en deux vagues à 1F chacune. Dans le cas du dérivé benzoylé, on observe en milieu alcalin une vague B_1 à des potentiels très négatifs; cette vague est peut-être due à la réduction de la fonction *N*-oxyde non protonisée. La réduction conduit donc à l'alcool *N*-oxyde sur la vague *A* et à l'alcool simple sur la vague *B*.

Ce mécanisme a été vérifié par électrolyse à potentiel contrôlé dans le cas du dérivé acétylé. Une électrolyse sur nappe de mercure sur la vague *A* conduit à l'hydroxyéthylpyridine *N*-oxyde. Ce produit ne semble pas avoir été décrit jusqu'ici dans la littérature (voir partie expérimentale).

Part I—*Talanta*, 1969, **16**, 293.

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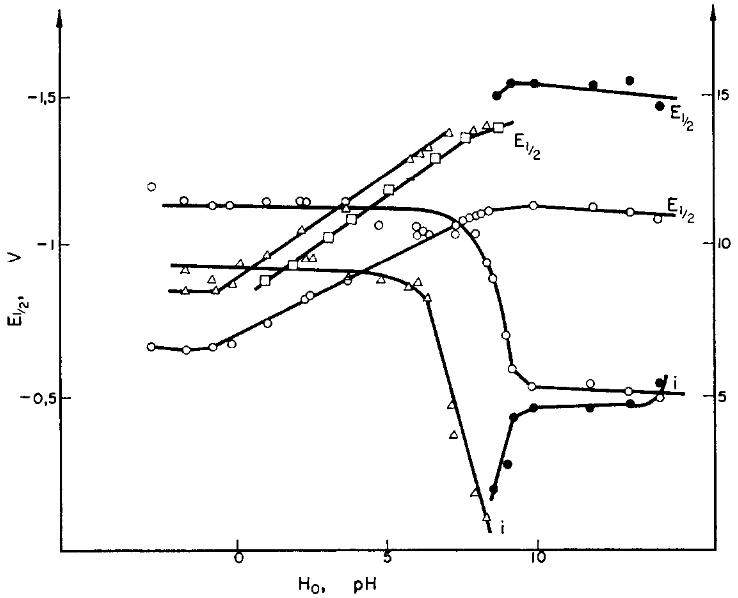

FIG. 1.—Variation de $E_{1/2}$ et du courant limite en fonction du pH pour l'acétyl-3 pyridine *N*-oxyde.
○: vague *A* ou A_1; ●: vague A_2; △: vague *B*; □: (α-hydroxyéthyl)-3 pyridine *N*-oxyde.

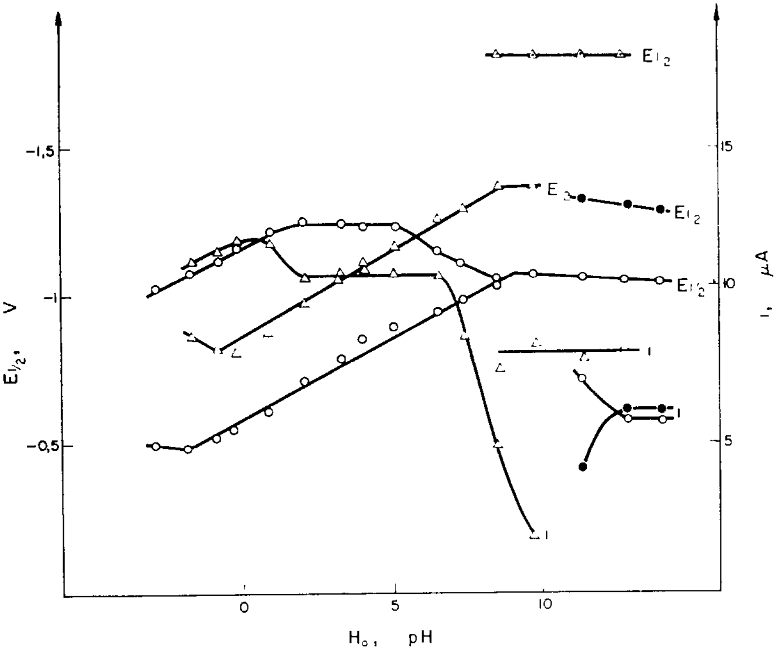

FIG. 2.—Variation de $E_{1/2}$ et du courant limite en fonction du pH pour le benzoyl-3 pyridine *N*-oxyde.
○: vague *A* ou A_1; ●: vague A_2; △: vague *B*; △: vague B_1.

Acétyl-2 et -4 et benzoyl-2 et -4 pyridines N-*oxydes*

Les benzoyl-2 et -4 pyridines *N*-oxydes présentent une vague à 4F dans tout le domaine de pH, avec, pour le dérivé 2, une légère diminution de la hauteur pour des pH supérieurs à 6 (Fig. 3).

L'acétyl-2 pyridine *N*-oxyde présente un comportement assez complexe. La hauteur totale du polarogramme correspond toujours à 4F sauf en milieu très alcalin. En milieu acide et à pH > 6 la vague A se scinde en deux vagues de hauteur égale A_1 et A_2; vers pH 6 la vague A_1 se scinde elle-même (apparition d'une vague A_3), et sa hauteur diminue en forme de courbe de dissociation (Fig. 4 et 5), à la suite sans doute d'un phénomène de recombinaison avec un proton.

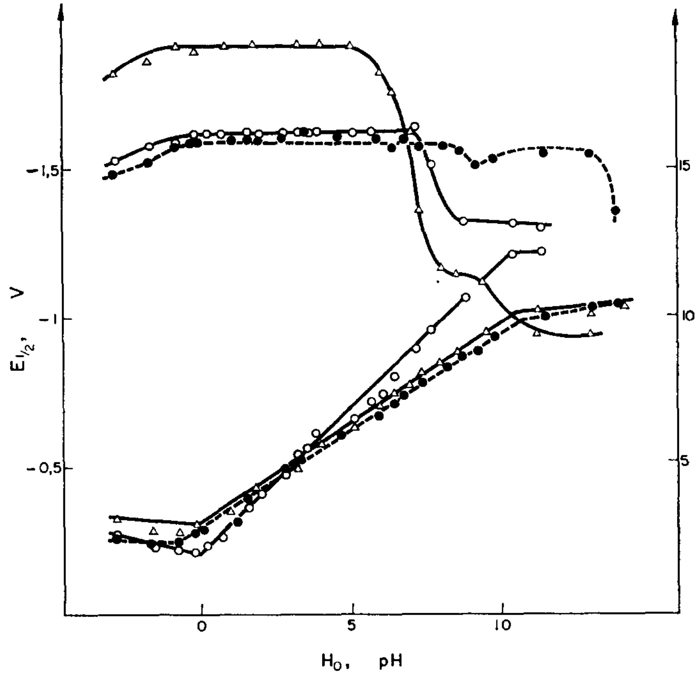

FIG. 3.—Variation de $E_{1/2}$ et du courant limite en fonction du pH pour l'acétyl-4 et les benzoyl-2 et -4 pyridines *N*-oxydes.
○: benzoyl-2 pyridine *N*-oxyde; ●: benzoyl-4 pyridine *N*-oxyde; △: acétyl-4 pyridine *N*-oxyde.

L'acétyl-4 pyridine *N*-oxyde présente une vague à 4F en milieu acide et neutre (la hauteur de vague plus grande que pour les dérivés benzoylés est due à une valeur plus grande du coefficient de diffusion); sa hauteur diminue vers pH 5 et correspond à un processus à 2F en milieu alcalin (Fig. 3).

Ces résultats permettent de conclure que comme dans le cas des formylpyridines *N*-oxydes, il y a réduction simultanée des fonctions carbonyle et *N*-oxyde, du moins en milieu acide et neutre. Le cas de l'acétyl-2 pyridine *N*-oxyde, plus complexe et pour lequel il est peut-être possible de distinguer les deux stades, sera examiné ultérieurement.

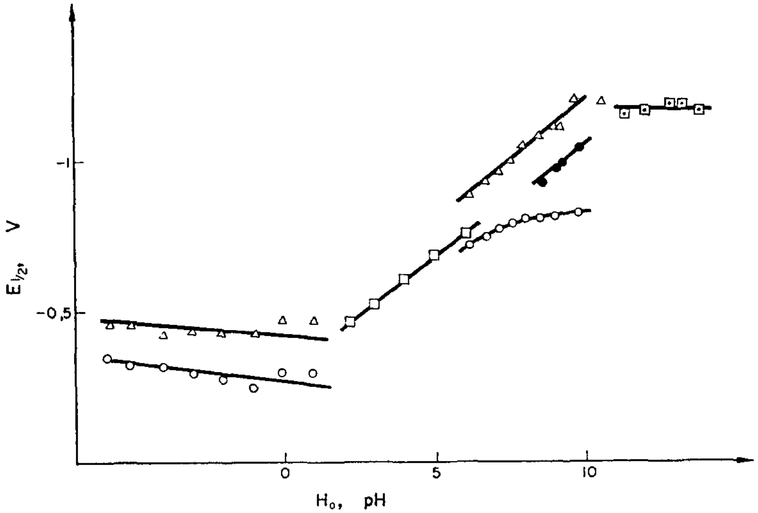

Fig. 4.—Variation de $E_{1/2}$ en fonction du pH pour l'acétyl-2 pyridine *N*-oxyde. ○: vague A_1; △: vague A_2; □: vagues $A_1 + A_2$; ●: vague A_3; ⊡: vagues $A_2 + A_3$.

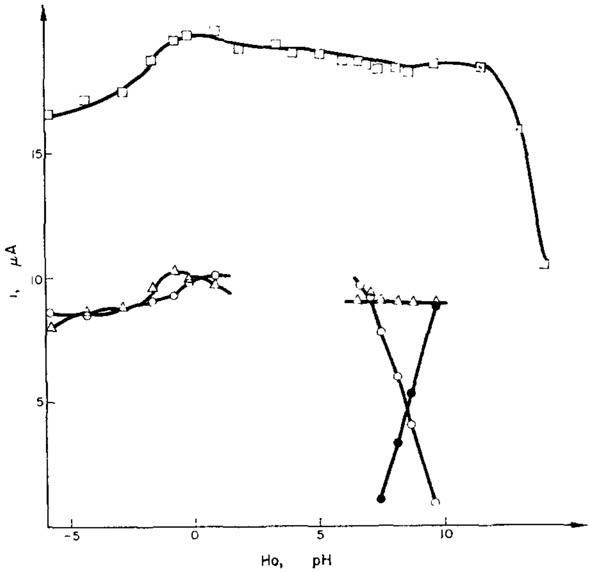

Fig. 5.—Variation du courant limite en fonction du pH pour l'acétyl-2 pyridine *N*-oxyde. Mêmes symboles que pour la Fig. 4.

En milieu alcalin le comportement devient plus compliqué, comme pour les formylpyridines *N*-oxydes. Une électrolyse à potentiel contrôlé de l'acétyl-4 pyridine *N*-oxyde à pH 13, sur le palier de la vague à 2F, a permis d'isoler le di(pyridyl-4′,4″)-2,3 butanediol-2,3 en quantité importante, et une très faible quantité d'hydroxyéthyl-4 pyridine. Dans ces conditions, malgré le processus apparent à 2F de la polarographie, le groupe *N*-oxyde est donc réduit. Les courbes donnant le nombre d'électrons participant à la réaction au cours de l'électrolyse sont d'ailleurs anormales. Au début, la réaction consomme 2F/Mole, puis après un certain temps 4F. Une étude détaillée du phénomène sera reprise ultérieurement.

Comme on peut le remarquer, la hauteur des polarogrammes en milieu neutre est toujours normale, au contraire de ce que l'on observait dans le cas des dérivés formylés correspondants. Ceci montre que l'hydratation dans ce milieu est négligeable.

SPECTROSCOPIE U.V. ET HYDRATATION DU CARBONYLE

Les équilibres entre le diverses formes hydratées ou ionisées ont été donnés dans l'article précédent.[1]

Les spectres U.V. présentent le même type de bandes que pour les formylpyridines simples[2] ou *N*-oxydes[1] (Fig. 6, 7 et 8): une bande *K* à des longueurs d'onde inférieures à 240 nm; une bande *B* d'absorptīon benzénoïde dont le maximum est situé entre 250 et 300 nm suivant le composé et le milieu; la bande *R* d'absorption du carbonyle. La bande *B* est plus intense et plus large pour les dérivés benzoylés que pour les dérivés acétylés ou formylés; ceci est lié à la présence du noyau benzénique (conjugaison, absorption propre du noyau benzénique). La bande *R* n'est visible que dans le cas des acétyl-2 et -3 pyridines *N*-oxydes; pour les autres composés elle est sans doute plus ou moins masquée par la bande *B*.

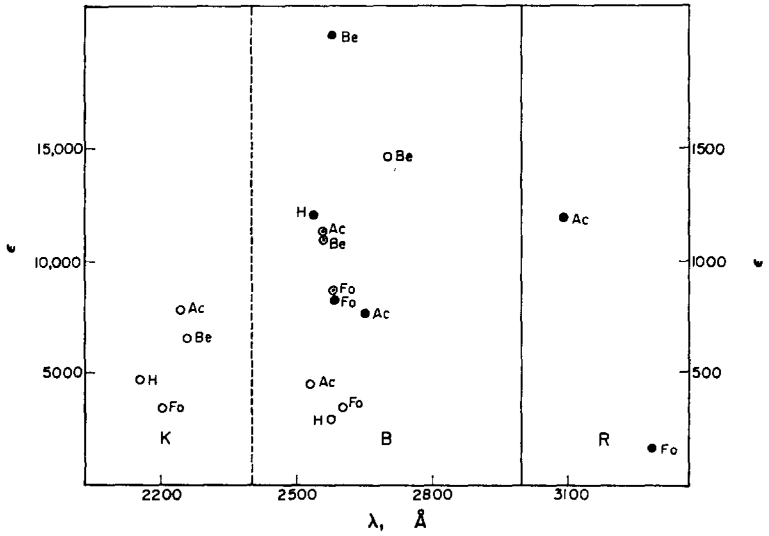

FIG. 6.—Position et intensité du maximum des bandes *K*, *B* et *R* pour les acétyl-2 benzoyl-2 et formyl-2 pyridines *N*-oxydes.
O: milieu acide; ●: milieu neutre; ⊙: milieu alcalin. Ac: acétyl; Be: benzoyl; Fo: formyl; H: pyridine *N*-oxyde non substitué.

Bande B

Milieu neutre. Pour l'acétyl-4 et la benzoyl-4 pyridines *N*-oxydes, on observe une bande *B* unique, dont le maximum se situe vers 290 nm; cette bande correspond donc à la bande B_2 d'absorption du noyau sous l'influence du carbonyle que l'on observait pour la formyl-4 pyridine[2] et le formyl-4 pyridine *N*-oxyde.[1] La bande B_1

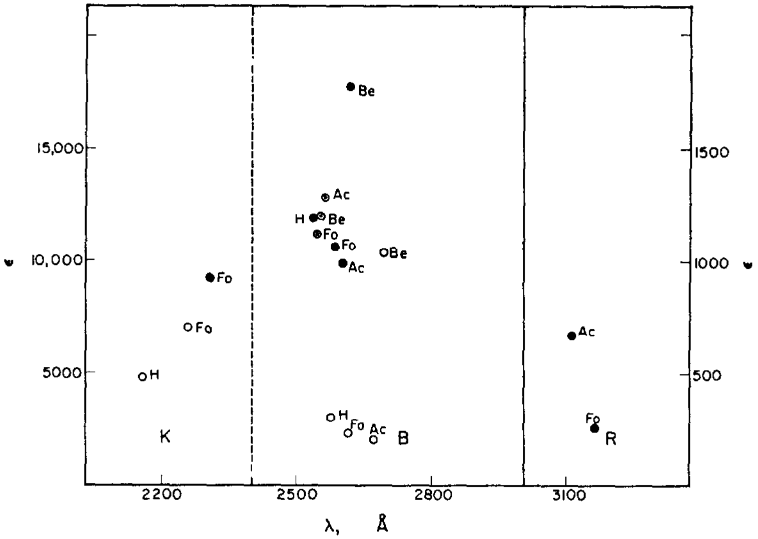

FIG. 7.—Position et intensité du maximum des bandes *K*, *B* et *R* pour les acétyl-3, benzoyl-3 et formyl-3 pyridines *N*-oxydes. Mêmes symboles que pour la Fig. 6.

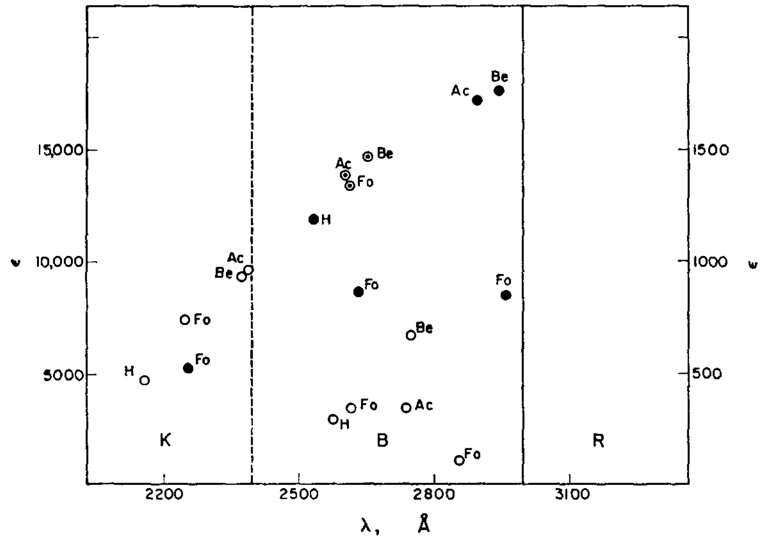

FIG. 8.—Position et intensité du maximum des bandes *K*, *B* et *R* pour les acétyl-4, benzoyl-4 et formyl-4 pyridines *N*-oxydes. Mêmes symboles que pour la Fig. 6.

correspondant[1,2] à l'absorption du noyau sous l'influence du groupement carbonyle hydraté n'existe pas. On en conclut que l'hydratation est pratiquement négligeable en milieu neutre pour les deux composés examinés, ce qui confirme les résultats polarographiques.

Pour les dérivés 2 et 3, la bande a une position normale (cf. dérivés formylés).

Milieu acide. La bande *B* est très diminuée pour tous les composés, conformément à ce que l'on observe normalement pour les *N*-oxydes de la pyridine.[3]

Milieu alcalin. On observe une évolution de la bande *B*. Pour les dérivés 4, la bande B_2 située vers 290 nm disparaît progressivement quand le pH augmente, tandis qu'apparaît une nouvelle bande B_1 vers 260 nm. On observait un comportement analogue pour la formyl-4 pyridine et le formyl-4 pyridine *N*-oxyde.[1] Cette évolution est attribuable à l'ionisation de l'hydrate et au déplacement de l'équilibre d'hydratation[1,4] (voir référence 1 pour les équilibres).

Pour les dérivés 2 et 3 la longueur d'onde du maximum ne varie pratiquement pas, mais on observe une variation de l'intensité, attribuable également à l'ionisation de l'hydrate.

Une étude en fonction du temps nous a permis de constater que les acétyl et les benzoylpyridines *N*-oxydes sont stables en milieu alcalin: par exemple une solution d'acétyl 4 pyridine *N*-oxyde dans la soude 10*M*, abandonnée une heure et ramenée ensuite en milieu acide donne un spectre normal.

Bande R *du carbonyle*

La bande *R* des acétyl-2 et -3 pyridine *N*-oxydes apparaît nettement en milieu neutre. Son intensité, comme dans le cas des dérivés formylés, est très importante pour une bande de carbonyle. L'intensité est d'ailleurs nettement plus forte que celle observée pour les dérivés formylés, ce qui est en accord avec une hydratation négligeable en milieu neutre.

En milieu acide et alcalin, l'intensité de la bande diminue et pour de fortes acidités ou de fortes basicités la bande disparaît. Ceci montre que dans ces milieux il y a une forte hydratation du carbonyle.

Dans le cas de l'acétyl-4 pyridine *N*-oxyde, l'hydratation en milieu acide ne peut être directement mise en évidence, puisque la bande du carbonyle n'apparaît pas. Cependant l'analogie avec les dérivés 2 et 4 permet de conclure à une hydratation extrêmement probable.

Dans le cas des dérivés benzoylés, la bande du C=O n'apparaît pas non plus, et il n'est pas possible d'étudier l'hydratation en milieu acide. Mais étant donné que ces composés présentent en milieu alcalin une hydratation analogue à celle des dérivés acétylés, il est très vraisemblable qu'ils sont également hydratés en milieu acide.

*Etude des p*K

Les valeurs des p*K* apparents, pK_A (milieu acide) et pK_A' (milieu alcalin) figurent au tableau I. (Pour la définition des p*K* apparents, voir réf. 1 et 2.)

Les valeurs de pK_A sont du même ordre de grandeur que pour les formyl pyridines *N*-oxydes.[1] Ces valeurs dépendent[2] de la constante d'ionisation de la forme carbonyle libre et des constantes d'hydratation de la forme neutre et de la forme hydratée.

TABLEAU I.—p*K* DES ACETYL ET DES BENZOYLPYRIDINES *N*-OXYDES

	Position du substituant	pK_A	pK_A'
$COCH_3$	2	−0,1	13,2
	3	+0,2	13,7
	4	−0,6	14,2
COC_6H_5	2	−0,8	13,9
	3	+0,3	14,3
	4	−0,2	14,2

L'ignorance des valeurs des constantes d'hydratation ne permet pas de procéder à une étude quantitative. Cependant on a montré précédemment[2] que le pK_A doit être compris entre le pK de la forme carbonyle libre et celui de la forme hydratée (pK_3 et pK_4, voir réf. 2); comme d'autre part la valeur de ρ de la loi de Hammett appliquée aux pK correspondant à la protonisation du *N*-oxyde n'est pas extrêmement élevée[5] ($\rho \sim 2$), il est normal que les pK_A soient peu différents de ceux des formylpyridines *N*-oxydes.

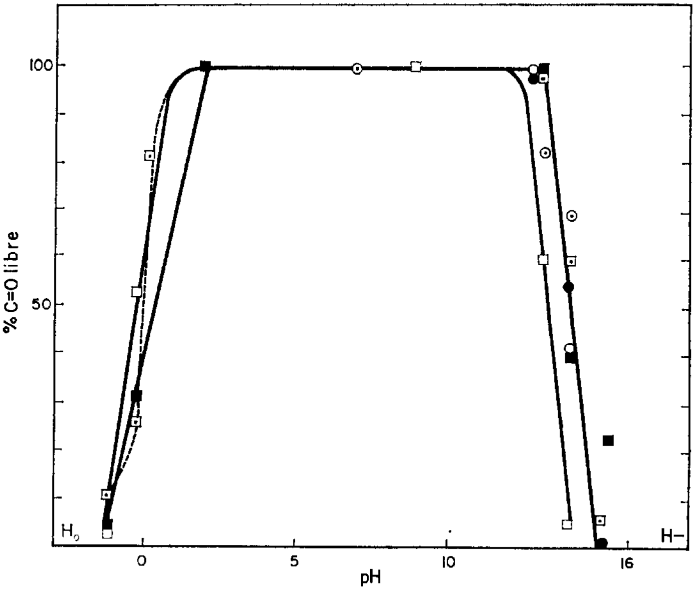

FIG. 9.—Graphique donnant le taux de carbonyle libre en fonction du pH pour les acétyl et benzoylpyridines *N*-oxydes.
□: acétyl-2; ■: acétyl-3; ⊡: acétyl-4; ○: benzoyl-2; ●: benzoyl-3; ○: benzoyl-4.

Les valeurs de pK_A' sont en revanche nettement plus élevées que celles obtenues dans le cas des formylpyridines *N*-oxydes. On peut rendre compte de ce fait de la façon suivante.

Si on suppose que la valeur de K_a (constante d'ionisation de l'hydrate)[1] varie peu d'une série à l'autre, on peut facilement calculer, à partir des données du travail précédent,[1] une formule qui permet de comparer les constantes d'un dérivé acétylé ou benzoylé et celles du dérivé formylé dans la même position:

$$1 + K_{1,x} = (1 + K_{1,f}) \frac{K''_{A,f}}{K''_{A,x}} .$$

Les indices x étant affectés aux constantes relatives aux acétyl et benzoylpyridines *N*-oxydes et les indices f à celles relatives aux dérivés formylés correspondants. L'hydratation étant beaucoup moins forte pour les dérivés acétylés et benzoylés, $K_{1,x}$ est grand ($K_{1,x} \gg K_{1,f}$), d'où la valeur plus faible de $K''_{A,x}$($K''_{A,x} \ll K''_{A,f}$), ce qui justifie le résultat trouvé pour les pK (p$K''_{A,x} >$ p$K''_{A,f}$). Les valeurs des constantes du membre de droite de l'équation précédente étant connues, on peut en tirer une valeur de $K_{1,x}$ qui permet de calculer le taux de carbonyle libre en milieu neutre. Le calcul donne pour tous les composés des valeurs comprises entre 99,5 et 100%. Ces valeurs, bien que très approximatives, étant donné l'hypothèse faite sur les valeurs de K_a, confirment les résultats donnés plus haut en montrant que l'hydratation est très faible en milieu neutre.

Le graphique 9 qui donne le taux approximatif de carbonyle libre, résume les résultats obtenus. Ce taux a été déterminé en prenant 100% pour le milieu neutre, conformément aux résultats obtenus, et en suivant la variation de la bande *R* pour les acétyl-2 et -3 pyridines *N*-oxydes, et de la bande *B* pour les autres dérivés.

PARTIE EXPERIMENTALE

Polarographie, spectroscopie U.V. et potentiel contrôlé

Les conditions expérimentales sont les mêmes que celles utilisées dans le travail précédent.[1] En milieu très alcalin nous avons utilisé lors des mesures spectroscopiques, la fonction d'acidité H_0.[6]

L'acétyl-4 pyridine *N*-oxyde a été électrolysé à pH 13, à −1,1 V (palier de la vague). Un abondant précipité blanc se forme rapidement; il est isolé par filtration et a été identifié par son spectre I.R. comme étant le di(pyridyl-4′,4″)-2,3 butane diol-2,3 (décomposition ~210°). Du filtrat on extrait par le chloroforme de faibles quantités d'hydroxyéthyl-4 pyridine, identifié par son spectre I.R.

L'acétyl-3 pyridine *N*-oxyde a été électrolysé dans l'acide sulfurique 0,1*N* à −1,0 V (vague *A*). Après le fin de l'électrolyse, la solution, neutralisée, est évaporée à sec, puis reprise par de l'alcool. Une deuxième évaporation à sec permet d'isoler un produit semi-solide brun; après séchage à la cloche à vide et recristallisation dans un mélange benzène–hexane, on obtient un solide blanc cristallisé, F = 110°, dont l'analyse correspond à la formule de l'alcool *N*-oxyde correspondant, 1′(α-hydroxyéthyl)-3 pyridine *N*-oxyde.

Analyse:				
	Calculé	C: 60,40%	H: 6,53%	N: 10,07%
	Trouvé	C: 60,6%	H: 6,7%	N: 10,3%

Synthèse des produits étudiés

Ont été préparés d'après les données de la littérature les acétyl-3 et 4 pyridines *N*-oxydes[7] et le benzoyl-2 pyridine *N*-oxyde.[8]

Pour l'acétyl-2 pyridine *N*-oxyde, on a employé la même méthode que pour les isomères 3 et 4, mais après évaporation du chloroforme, on a chassé par distillation sous pression réduite l'acétyl-pyridine qui n'avait par réagi et le résidu a été recristallisé dans le pentane. L'analyse montre que l'acétyl-2 pyridine *N*-oxyde ainsi obtenu cristallise avec une demi-molécule d'eau. F = 32°.

Le benzoyl-3 pyridine *N*-oxyde a été mentionné dans la littérature,[9] mais sa préparation et ses caractéristiques n'on pas été signalées. On a procédé comme pour le benzoyl-2 pyridine *N*-oxyde, mais l'huile obtenue après évaporation du chloroforme a été distillée sous pression réduite. La benzoyl pyridine qui n'a pas réagi passe d'abord; le benzoyl-2 pyridine *N*-oxyde passe ensuite vers 185° sous 0,13 mbar; ce composé fond vers 27° et est plus ou moins hydraté.

Le benzoyl-4 pyridine *N*-oxyde a été préparé comme le benzoyl-2 pyridine *N*-oxyde. F = 128–130°.

Summary—The polarographic behaviour of the acetyl- and benzoyl pyridine *N*-oxides shows the same type of anomalies as those which have previously been mentioned in the case of the corresponding formyl pyridine *N*-oxides: when the substituent lies in the 2 or 4 position, the *N*-oxide group and the carbonyl group are simultaneously reduced, the 3-isomers being normally reduced at all pH values. From the ultraviolet spectra, one concludes that the carbonyl group is hydrated, but not so strongly as in the case of the formyl pyridine *N*-oxides.

Zusammenfassung—Das polarographische Verhalten der Acetyl- und Benzoyl-pyridin-*N*-oxide zeigt dieselbe Art von Anomalien, wie sie früher bei den entsprechenden Formylpyridin-*N*-oxiden erwähnt wurden: bei Substitution in 2- oder 4-Stellung werden *N*-Oxidgruppe und Carbonylgruppe gleichzeitig reduziert, die 3-Isomeren werden bei allen pH-Werten normal reduziert. Aus den Ultraviolettspektren kann man schließen, daß die Carbonylgruppe hydratisiert ist, aber nicht so stark wie bei den Formylpyridin-*N*-oxiden.

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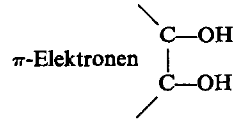
SHORT COMMUNICATIONS

Untersuchungen an Reagenzien für Niob und Tantal—VI Spektrophotometrische Bestimmung von Niob(V) und Tantal(V) mit Dibromgallussäure

(*Eingegangen am* 15 *Dezember* 1969. *Angenommen am* 31 *Januar* 1970)

In einer früheren Mitteilung[1] konnten wir zeigen, daß durch Substitution an einem organischen Grundkörper, welcher die analytisch-funktionelle Gruppe für Niob(V) und Tantal(V) enthält, die analytischen Eigenschaften der Komplexbildungsreaktionen beeinflußt werden können. Als Ergebnis systematischer Untersuchungen wurde die Dibromgallussäure als neues Reagens für die photometrische Bestimmung der Erdsäuren vorgeschlagen.

Von Nachteil ist, daß das System



wenig selektiv reagiert,[2,3] deshalb war zu erwarten, daß auch die Dibromgallussäure mit einer großen Zahl von Elementen farbige Reaktionsprodukte liefert. Im einzelnen wurden in saurer Lösung mit folgenden Ionen Reaktionen beobachtet: Ag(I), As(V), Au(III), Bi(III), Cd(II), Ce(IV), Co(II), Cr(VI), Cu(II), Fe(III), Ga(III), Hg(II), In(III), Ir(IV), Mn(II), Mo(VI), Nb(V), Os(VI), Pd(II), Pt(IV), Ru(IV), Sb(V), Ta(V), Ti(IV), Tl(III), U(VI), V(III), V(IV), V(V), W(VI), Zn(II).

In der analytischen Praxis können jedoch die Störungen bei der Bestimmung der Erdsäuren vielfach durch geeignete Trennungen (Ionenaustausch, Extraktion, Fällung) verringert werden. Die hier beschriebenen Methoden zur Bestimmung von Niob und Tantal sind unter Verwendung von Hilfskomplexbildnern ausgearbeitet, die unerwünschte Nebenreaktionen der Erdsäuren ausschalten und die Selektivität erhöhen. Über die Bildungsreaktionen und die Zusammensetzung der entstehenden Koordinationsverbindungen wurde bereits ausführlich berichtet.[4,5]

Bestimmungsmethoden

Der Einsatz der mitgeteilten Methoden richtet sich nach der jeweiligen analytischen Problematik (geforderte Genauigkeit und Empfindlichkeit, Gegenwart von Fremdelementen). Die angegebenen Bedingungen (Meßwellenlänge, pH-Wert, Reagenzkonzentration und s-Wert*) ergeben eine maximale Empfindlichkeit der Verfahren. Bei der Tantalbestimmung wurde besonders der Störung durch Niob(V) und bei der Niobbestimmung dem Einfluß von Tantal(V) Beachtung geschenkt. Daneben wurde versucht, die Komplexbildung von Dibromgallussäure mit Titan(IV), Wolfram(VI), Vanadin(V) und Molybdän(VI) auszuschalten, da diese Ionen ebenfalls intensiv gefärbte Reaktionsprodukte liefern. Von den üblichen anorganischen Ionen setzen Phosphat bzw. Sulfat in hohen Konzentrationen die Extinktion herab. Neutralsalze wie NaCl, $NaNO_3$ usw. wirken dagegen farbvertiefend. Die Standardabweichungen der einzelnen Verfahren wurden in Abwesenheit von Störelementen nach einer Methode von Dean und Dixon[6] bei $n = 4$ abgeschätzt. Als Störung sind Elementgehalte angegeben, welche die Extinktionen von Niob bzw. Tantal außerhalb der statistischen Schwankung beeinflussen.

Allgemeiner Arbeitsgang

Die Probe wird mit Kaliumdisulfat aufgeschlossen, die Schmelze in einer Hilfskomplexbildnerlösung in der Wärme gelöst und auf ein definiertes Volumen aufgefüllt. Einen aliquoten Teil pipettiert man in einen 50-ml-Meßkolben, erhöht—falls nötig—die Konzentration an Hilfskomplexbildner und bereitet die Lösung nach einer der angegebenen Arbeitsvorschriften vor. Gemessen wird nach dem Auffüllen auf 50 ml in Glas-bzw. Quarzküvetten geeigneter Schichtdicke gegen eine

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* $s = \dfrac{\text{Konzentration an Hilfskomplexbildner}}{\text{Konzentration an Nb bzw. Ta}}$; Konzentration in Mol/l.

Blindprobe. Die Extinktionswerte sind bis zu einer Stunde konstant. Zur Auswertung dient eine Eichgerade, die unter gleichen Bedingungen aufgestellt wird.

Lösungen

Dibromgallussäure,[7] 10%ige wäßrige Lösung.
Ammoniumoxalat, 40 g/l.
Ammoniumtartrat, 15 g/l.
Natriumsulfit, 10%ige Lösung (täglich frisch bereiten)
ÄDTA, 0,1*M*
Salzsäure, 2*M*
Ammoniak, 2*M*

Niob

Methode 1. Die vorbereitete Probelösung mit Tartrat als Hilfskomplexbildner ($s < 100$) wird mit 10 ml Reagens versetzt, sofort 25 ml 2*M* Salzsäure zugegeben und bei 440 nm gemessen. $\varepsilon = 540$ l.Mole^{-1}.mm^{-1}. Das Lambert-Beer'sche Gesetz ist von 0 bis 36 μg Nb/ml erfüllt; Standardabweichung 1,5% (rel.) für 12 μg Nb/ml; Störungen (für 0,6 mg Nb) >1 mg Ta, $>0,1$ mg Ti, $>0,6$ mg W, $>0,5$ mg V, $>0,05$ mg Mo.

Methode 2. Die vorbereitete Probelösung mit Tartrat als Hilfskomplexbildner ($s < 500$) wird mit 5 ml Reagens versetzt, nach 15 Minuten 10 ml Natriumsulfitlösung zugegeben, der pH-Wert auf 4,5 eingestellt und nach 10 Minuten bei 380 nm gemessen. $\varepsilon = 1,08 \times 10^3$ l.Mole^{-1}.mm^{-1}. Das Lambert-Beer'sche Gesetz ist von 0 bis 60 μg Nb/ml erfüllt; Standardabweichung 1,4% (rel.) für 6 μg Nb/ml; Störungen (für 0,3 mg Nb) $>0,3$ mg Ta, $>0,004$ mg Ti, $>0,1$ mg W, $>0,01$ mg V, $>0,1$ mg Mo.

Methode 3. Die vorbereitete Probelösung mit Oxalat als Hilfskomplexbildner ($s < 150$) wird mit 5 ml Reagens sowie 10 ml Natriumsulfitlösung versetzt, der pH-Wert auf 5,3 eingestellt und nach 10 min bei 380 nm gemessen. $\varepsilon = 1,08 \times 10^3$ l.Mole^{-1}.mm^{-1}. Das Lambert-Beer'sche Gesetz ist von 0 bis 60 μg Nb/ml erfüllt; Standardabweichung 0,9% (rel.) für 6 μg Nb/ml; Störungen (für 0,3 mg Nb) $>0,2$ mg Ta, $>0,1$ mg Mo, $>0,1$ mg W, $>0,005$ mg V, $>0,005$ mg Ti.

Methode 4. Die vorbereitete Probelösung mit Tartrat als Hilskomplexbildner ($s < 200$) wird mit 2 ml ÄDTA-Lösung sowie 5 ml Reagens versetzt, der pH-Wert auf 2,4 eingestellt und nach 30 min bei 470 nm gemessen. $\varepsilon = 510$ l.Mole^{-1}.mm^{-1}. Das Lambert-Beer'sche Gesetz ist von 0 bis 36 μg Nb/ml erfüllt; Standardabweichung 1,8% (rel.) für 6 μg Nb/ml; Störungen (für 0,3 mg Nb) >5 mg Ta, $>0,02$ mg Ti, >10 mg W, >3 mg V, $>0,1$ mg Mo.

Tantal

Methode 1. Die vorbereitete Probelösung mit Oxalat als Hilfskomplexbildner ($s < 800$) wird mit 5 ml Reagens sowie 10 ml Natriumsulfitlösung versetzt, der pH-Wert auf 4,6 eingestellt und nach 10 min bei 320 nm gemessen. $\varepsilon = 1,62 \times 10^3$ l.Mole^{-1}.mm^{-1}. Das Lambert-Beer'sche Gesetz ist von 0 bis 100 μg Ta/ml erfüllt; Standardabweichung: 5,8% (rel.) für 10 μg Ta/ml; Störungen (für 0,5 mg Ta) $>0,03$ mg Nb, $>0,01$ mg Ti, $>0,1$ mg W, $>0,01$ mg V, $>0,1$ mg Mo.

Methode 2. Die vorbereitete Probelösung mit Oxalat als Hilfskomplexbildner ($s > 800$) wird mit 5 ml Reagens versetzt, der pH-Wert auf 2,0 eingestellt und bei 400 nm gemessen. $\varepsilon = 420$ l.Mole^{-1}.mm^{-1}. Das Lambert-Beer'sche Gesetz ist von 0 bis 200 μg Ta/ml erfüllt; Standardabweichung 0,3% (rel.) für 20 μg Ta/ml; Störungen (für 1 mg Ta) >30 mg Nb, $>0,05$ mg Ti, >2 mg W, $>0,1$ mg V, $>0,2$ mg Mo.

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Zusammenfassung—Es werden Arbeitsvorschriften zur spektrophotometrischen Bestimmung von Nb(V) und Ta(V) mit Dibromgallussäure in Gegenwart verschiedener Hilfskomplexbildner mitgeteilt. Neben der Empfindlichkeit und Standardabweichung der einzelnen Verfahren wird der Störeinfluß von Nb(V), Ta(V), Ti(IV), Mo(VI), W(VI) und V(V) angegeben.

Summary—Procedures are given for the spectrophotometric determination of Nb(V) and Ta(V) with dibromogallic acid, in the presence of various masking reagents. The sensitivities and standard deviations for the procedures are given, and the interfering elements in each case are listed.

Résumé—On donne des techniques pour le dosage spectrophotométrique de Nb(V) et Ta(V) avec l'acide dibromogallique, en la présence de divers agents de dissimulation. On donne les sensibilités et les écarts types pour les techniques, et l'on énumère dans chaque cas les éléments gênants.

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Separation of rhenium from molybdenum, tungsten, vanadium, platinum metals and other elements by reduction and solvent extraction

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THE SEPARATION of rhenium from molybdenum is often required[1] for its determination in molybdenites, concentrates and flue dusts, and the increasing use of rhenium as a minor constituent in alloys[2] of potential importance in rocketry, defence and atomic energy calls for rapid and simple methods for its determination in the presence of major constituents which are usually transition elements.

From acid solutions, separation from molybdenum is easily achieved by extracting either molybdenum[3–6] or rhenium[7–9] into organic solvents. The latter method has the advantage of separating rhenium from the alkali salts arising in a fusion, and from the bulk of other elements. Sulphuric acid solution is preferable[8] as many elements then accompany rhenium but little into the organic solvent. Isopentanol and isobutyl methyl ketone are two convenient solvents because of their high extractive power for rhenium, ready availability, low cost, quick separation of the phases and easy recovery of rhenium and the solvent. The former is preferable as it permits use of lower acidities. Small amounts of molybdenum, however, always accompany rhenium into the solvent and have to be removed by extraction as the xanthate,[10] the oxinate[11] or the thiocyanate.[8]

Sequestering, or lowering the oxidation state, might be expected to decrease the co-extraction of molybdenum and other elements; the acid concentration for optimum extraction of rhenium is still too high to permit their stable complexation, and decreasing the oxidation state remains the only alternative. However, the usually attainable stable lower oxidation state, Re(IV), is much less extracted[7] than Re(VII) at the same acidity. In sulphuric acid solution, hydrazine sulphate was found useful,[8] reducing Mo(VI) but not Re(VII). Many ions can be removed from solution or prevented from being extracted, by reduction to a very low oxidation state by zinc amalgam. Under these conditions Re(VII) is reduced to Re(−I)[13] which is found to be extractable from sulphuric acid by isopentanol, and this forms the basis of the following simple and rapid method for its separation from other elements.

EXPERIMENTAL

Reagents

Standard stock solutions were prepared by dissolving exact amounts of "Specpure" potassium perrhenate (Johnson Matthey, London) in known volumes of water, and diluting to yield lower concentrations. Solutions of the other elements were prepared from pharmacopoeia or analytical grade chemicals. Zinc amalgam, 2% w/w, was prepared[14] from zinc metal and pure mercury. Isopentanol and other solvents were used without purification.

Synthetic samples, composed as shown in Table II, were made by dissolving a commonly available

Summary—Procedures are given for the spectrophotometric determination of Nb(V) and Ta(V) with dibromogallic acid, in the presence of various masking reagents. The sensitivities and standard deviations for the procedures are given, and the interfering elements in each case are listed.

Résumé—On donne des techniques pour le dosage spectrophotométrique de Nb(V) et Ta(V) avec l'acide dibromogallique, en la présence de divers agents de dissimulation. On donne les sensibilités et les écarts types pour les techniques, et l'on énumère dans chaque cas les éléments gênants.

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Separation of rhenium from molybdenum, tungsten, vanadium, platinum metals and other elements by reduction and solvent extraction

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THE SEPARATION of rhenium from molybdenum is often required[1] for its determination in molybdenites, concentrates and flue dusts, and the increasing use of rhenium as a minor constituent in alloys[2] of potential importance in rocketry, defence and atomic energy calls for rapid and simple methods for its determination in the presence of major constituents which are usually transition elements.

From acid solutions, separation from molybdenum is easily achieved by extracting either molybdenum[3–6] or rhenium[7–9] into organic solvents. The latter method has the advantage of separating rhenium from the alkali salts arising in a fusion, and from the bulk of other elements. Sulphuric acid solution is preferable[8] as many elements then accompany rhenium but little into the organic solvent. Isopentanol and isobutyl methyl ketone are two convenient solvents because of their high extractive power for rhenium, ready availability, low cost, quick separation of the phases and easy recovery of rhenium and the solvent. The former is preferable as it permits use of lower acidities. Small amounts of molybdenum, however, always accompany rhenium into the solvent and have to be removed by extraction as the xanthate,[10] the oxinate[11] or the thiocyanate.[8]

Sequestering, or lowering the oxidation state, might be expected to decrease the co-extraction of molybdenum and other elements; the acid concentration for optimum extraction of rhenium is still too high to permit their stable complexation, and decreasing the oxidation state remains the only alternative. However, the usually attainable stable lower oxidation state, Re(IV), is much less extracted[7] than Re(VII) at the same acidity. In sulphuric acid solution, hydrazine sulphate was found useful,[8] reducing Mo(VI) but not Re(VII). Many ions can be removed from solution or prevented from being extracted, by reduction to a very low oxidation state by zinc amalgam. Under these conditions Re(VII) is reduced to Re(−I)[13] which is found to be extractable from sulphuric acid by isopentanol, and this forms the basis of the following simple and rapid method for its separation from other elements.

EXPERIMENTAL

Reagents

Standard stock solutions were prepared by dissolving exact amounts of "Specpure" potassium perrhenate (Johnson Matthey, London) in known volumes of water, and diluting to yield lower concentrations. Solutions of the other elements were prepared from pharmacopoeia or analytical grade chemicals. Zinc amalgam, 2% w/w, was prepared[14] from zinc metal and pure mercury. Isopentanol and other solvents were used without purification.

Synthetic samples, composed as shown in Table II, were made by dissolving a commonly available compound of the element in 1M sulphuric acid. Tungstic acid precipitated but was not filtered off; it was transferred into the separating funnel along with the solution, and dissolved on reduction to W(III) by the amalgam.

Decomposition of natural samples

Reverberatory flue dust. Fuse about 1 g with sodium peroxide–carbonate mixture (3:2), leach with water and adjust to 1M in sulphuric acid.

Molybdenite. Fuse 0·5 g with sodium peroxide, cool, leach with water and acidify to 1M in sulphuric acid, or dissolve 0·5 g in conc. nitric acid, evaporate to 2 ml, neutralise and adjust to 1M sulphuric acid.

Separation procedure

A cold 1M sulphuric acid solution containing less than 200 μg of Re(VII) per ml and severa hundred mg of other elements was shaken with 15 ml of 2% zinc amalgam in a separating funnel for 3 min, the pressure being gently released at short intervals through the stop-cock. The aqueous layer was quickly covered with an equal volume of isopentanol and the amalgam run off and kept under 1M hydrochloric acid for further use. The aqueous phase was made 3M in sulphuric acid by careful dropwise addition of the concentrated acid, with strong cooling, and then shaken with the solvent for 3 min. The stem of the funnel was filled with solvent and the aqueous phase run off into another separating funnel containing an equal volume of the solvent, with which it was then shaken for 3 min. The end of the stem was immersed in the fresh solvent during the separation. After four such extractions in which contact of the aqueous layer with atmospheric oxygen was avoided as far as possible, the combined extracts were filtered free from any black particles of the elements. The rhenium was stripped by shaking for 2 min each time with two portions of equal volumes of water, after neutralization of the extracted acid with ammonia and oxidation of the reduced states with hydrogen peroxide. The back-extracts were evaporated to a suitable volume (and the peroxide simultaneously decomposed). The small amount of molybdenum, *etc* still accompanying rhenium was completely removed by the thiocyanate–pentyl acetate[8] or the oxine–chloroform[11] method. The aqueous solution was then free from all the elements likely to interfere in the determination of rhenium.

Microgram amounts of rhenium in the extract were determined colorimetrically by the tin(II) chloride–thiocyanate method,[15] the complex being extracted with isopentanol. Standard methods[12,15] were used to test for extraction of other elements.

RESULTS AND DISCUSSION

Mo(VI) is reduced to Mo(III) in sulphuric and hydrochloric acid solutions by zinc amalgam. At 2–8N acidity the extraction of Mo(III) by rhenium-extracting solvents (isopentanol, tributyl phosphate, isobutyl methyl ketone) is less than 1% from sulphuric and 2–10% from hydrochloric acid. Hence sulphuric acid is the preferred medium. The extent to which rhenium is reduced by zinc amalgam depends on its concentration and the acidity.[16] From 1M sulphuric acid and at <250 μg/ml it is reduced to Re($-$I).[13,17] On the basis of the results in Table I, reduction in 1M sulphuric acid and extraction from the 3M acid were chosen. Concentrations of rhenium up to 200 μg/ml give similar results but higher concentrations result in black particles, probably of Re(0). SO_4^{2-}, PO_4^{3-}, Cl^-, F^- (as sodium salts in gram amounts) do not affect (± 1%) the rhenium extraction.

TABLE I.—REDUCTION AND EXTRACTION OF RHENIUM AT DIFFERENT ACID CONCENTRATIONS

[H_2SO_4] for reduction, M	[H_2SO_4] for extraction, M	Extraction of Re, %
1	1	61
1	2	67
1	3	72
2	2	65
3	3	70
5	3	74
5	5	66
6*	3	8

* Black particles, probably of Re(0), appeared.

By shaking with zinc amalgam in 1*M* sulphuric acid[12,18] Pb(II), Hg(II), Tl(III), As(V), Se(VI), Te(VI), Ag(I), Cu(II), Au(III), Pt(IV and VI), Pd(II), Rh(III), Ir(III), Co(II), Ni(II) and perhaps Ru(III) and Os(VIII) are reduced to the elements and partly removed into the amalgam. Ce(IV), Ti(IV), V(V), W(VI), Cr(III and VI), Mn(VII) and Os(VIII) are reduced wholly or partially to Ce(III), Ti(III), V(II), W(III), Cr(II), Mn(II) and Os(?) respectively, which are not extracted by isopentanol from 3*M* sulphuric acid. Mo(VI), U(VI), Fe(III) and Ru(III) are reduced to Mo(III), U(III), Fe(II), Ru(?) and are extracted 0·7, 0·3, 2·0 and 0·04% respectively by isopentanol. Nitrate is reduced if in high concentration. Bi(III) is not extracted.

Except for small amounts of Mo, U, Fe and Ru, all elements of any importance are separated from rhenium by the reduction and subsequent extraction. These remaining elements can be completely separated from rhenium by thiocyanate–pentyl acetate[8] or the oxine–chloroform[11] extraction at a suitable pH. The rhenium in aqueous solution can be determined by any convenient method.

The wide applicability of the method is shown (Table II) by the analysis of molybdenites, flue dusts and synthetic samples containing alloying elements, with satisfactory results. The separation is simple, requiring cheap reagents commonly available in all laboratories, and rapid, taking only 20 min.

TABLE II.—ANALYSIS OF SOME SAMPLES BY THE PROPOSED METHOD

Composition of synthetic sample*				Re found, *µg*
Mo, *mg*	V, *mg*	W, *mg*	Re added, *µg*	
500	—	—	10·0	10·0
100	—	—	50·0	49·0
200	100	50	15·0	15·0
100	50	24	50·0	49·0
Os(15), Ru(15), Pt(14), Pd(15)			18·0	17·5
Os(6), Ru(5), Pt(6), Pd(5)			40·0	38·0
W(50), V(20), Cu(10), Cd(10), Ni(10), Mn(10), Cr(10), Se(10)			24·0	23·0
W(100), V(40), Cu(20), Cd(20), Ni(20), Mn(20), Cr(20), Se(20)			60·0	58·0
Reverberatory flue dust			70·0	69·5
Reverberatory flue dust			25·0	24·5
Molybdenite (Canada)			0·0020%†	0·0018%
Molybdenite (Norway)			0·0036%†	0·0039%

* Figures in brackets are the amount of the element, in mg.
† Reported values.

Under the same conditions, isobutyl methyl ketone extracts 70% Re and can also be used, but tributyl phosphate, isopentyl acetate and ether extract only 22, 16 and 2% Re respectively.

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Summary–Reduction in 1*M* H_2SO_4 with liquid zinc amalgam and extraction with isopentanol from 3*M* H_2SO_4, separates rhenium from almost all the interfering elements of importance in rhenium determination. The small amounts of Mo, U, Fe and Ru still accompanying rhenium are removed by the thiocyanate–pentyl acetate or the oxine–chloroform extraction. The method is simple, rapid and of very wide applicability. It is particularly useful in the determination of rhenium in various alloys and tungsten-containing samples.

Zusammenfassung—Die Reduktion mit flüssigem Zinkamalgam in 1 *M* Schwefelsäure und die Extraktion mit Isopentanol aus 3 *M* Schwefelsäure trennt Rhenium von fast allen wichtigen Störelementen. Die kleinen Mengen Mo, U, Fe und Ru, die das Rhenium noch begleiten, werden durch Thiocyanat-Pentylacetat- oder Oxin-chloroform-Extraktion entfernt. Das Verfahren ist einfach, schnell und sehr vielseitig anwendbar. Besonders nützlich ist es bei der Bestimmung von Rhenium in verschiedenen Legierungen und wolframhaltigen Proben.

Résumé—La réduction en H_2SO_4 1*M* avec l'amalgame de zinc liquide et l'extraction par l'isopentanol de H_2SO_4 3*M* séparent le rhénium de presque tous les éléments gênants qui sont d'importance dans la détermination du rhénium. Les petites quantités de Mo, U, Fe et Ru qui accompagnent encore le rhénium sont éliminées par extraction au thiocyanate-acétate de pentyle ou oxine-chloroforme. La méthode est simple, rapide et de très large possibilité d'application. Elle est particulièrement utile dans la détermination du rhénium dans divers alliages et dans les échantillons contenant du tungstène.

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Application of low-cost operational amplifiers to electrical detection in spark-source mass spectrometry*

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SPARK SOURCE mass spectrometer signals consist of repetitive ion-current pulses. Pulse-width and recurrence rate follow exactly the spark duty-cycle parameters. Figures 1 and 2 show reproductions of oscilloscopic displays of typical signals for a single mass peak in which the time variation of the ion-current is indicated. Heights of the individual pulses vary by approximately one order of magnitude as is shown in Fig. 1, although the average height is dependent upon the intensity of the specific spectral line focussed at the collector slit. Erratic fluctuation within pulses is common as is illustrated

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* Work was performed in the Ames Laboratory of the US Atomic Energy Commission. Contribution No. 2662.

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Résumé—La réduction en H_2SO_4 1*M* avec l'amalgame de zinc liquide et l'extraction par l'isopentanol de H_2SO_4 3*M* séparent le rhénium de presque tous les éléments gênants qui sont d'importance dans la détermination du rhénium. Les petites quantités de Mo, U, Fe et Ru qui accompagnent encore le rhénium sont éliminées par extraction au thiocyanate-acétate de pentyle ou oxine-chloroforme. La méthode est simple, rapide et de très large possibilité d'application. Elle est particulièrement utile dans la détermination du rhénium dans divers alliages et dans les échantillons contenant du tungstène.

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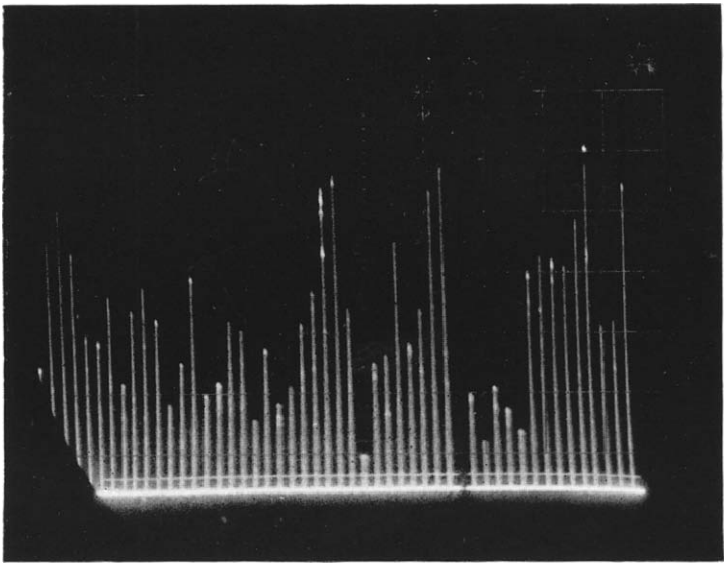

FIG. 1.—Photograph of oscilloscope traces of ion-current pulses. Spark pulse length 3·2 μsec and repetition rate 100 pulses/sec. Oscilloscope sensitivity 2V/cm and sweep rate 50 msec/cm (cm-spacings are the large blocks). The height of the fourth pulse from the right exceeded the maximum amplifier output voltage of 12·5V.

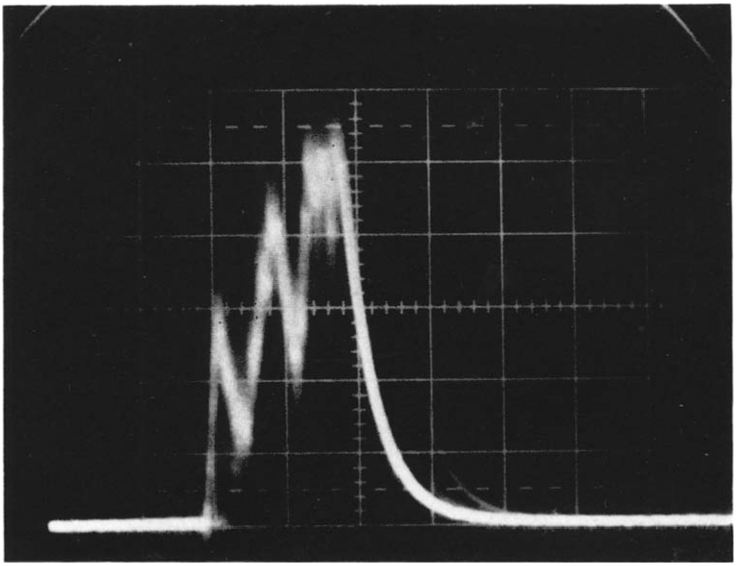

FIG. 2.—Photograph of oscilloscope trace of ion-current pulse. The pulse length was 100 μsec and repetition rate 10 pulses/sec. Oscilloscope sensitivity 10 mV/cm and sweep 50 μsec/cm.

in Fig. 2. A third feature of the signal is that the average ion-current intensity can vary by approximately an order of magnitude.

Owing to these fluctuations, signals detected at the spectrometer slit must be continuously measured as a function of the total ion current. This is accomplished by measuring the ratio of the signal at the main collector slit to the signal obtained from a beam monitor which is normally positioned in the field-free region between the electrostatic analyser and the magnetic analyser. Thus the detection system is required to handle two very erratic d.c. signals. Figure 3 is a schematic drawing of the original equipment used to measure this ratio. When a predetermined charge has accumulated on the monitor capacitor, the spark is shut off and the values of capacitor voltage are read from strip chart recordings of the vibrating reed electrometer (VRE) outputs. Although this system has been used with good accuracy,[2] it is difficult and time-consuming to use on a routine basis.

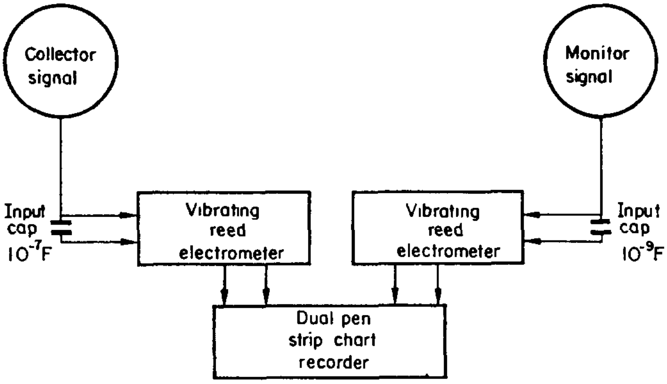

FIG. 3.—Schematic drawing of the original circuit for electrical detection.

An alternative to the capacitor system was assembled in which the input capacitors were replaced by resistors.[3] Input capacitances were adjusted to give time constants of about 0·2 sec. The VRE outputs were converted into frequencies and a ratio measurement was made with a ratio count meter. Again good accuracy was achieved and ease of data accumulation was considerably improved. However closer investigation of the actual operating conditions indicated two principal disadvantages: limited dynamic range and long amplifier time-constant. A long time-constant prevents observation of low-level non-homogeneities in a continuous measuring system since short-term variations will be averaged out. It also means that an error will be incorporated into the measurement, as illustrated in Fig. 4, which shows the voltage at the amplifier input rising very rapidly (*i.e.*, the initial voltage is determined by the size of the input capacitance and the coulombic charge in the initial portion of each pulse). The input voltage will fall according to the input circuit time-constant. As the time-constant for the input circuit becomes much smaller than the amplifier response-time, the area under the amplifier response curve will become less representative of the area under the input voltage curve. This is a source of potentially large systematic error.

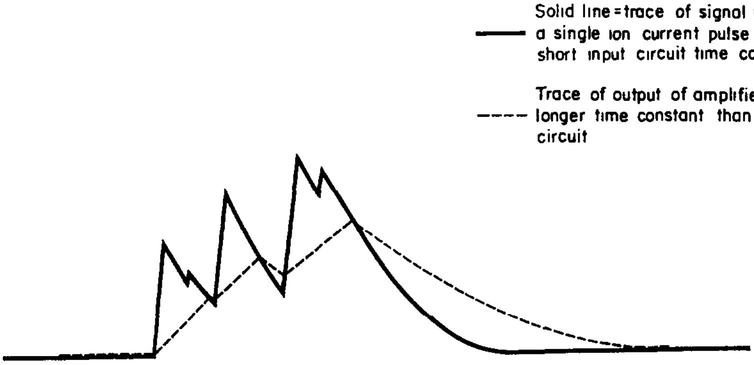

FIG. 4.—Illustration of possible source of systematic error for an amplifier with response time longer than the time-constant of the input signal voltage.

Recently, commercial operational amplifiers have become readily available. They have many desirable features but of principal interest here is their broad frequency response (down to d.c.), high input impedance, low noise and drift, low cost and small dimensions. At the time this work was initiated, Fairchild ADO-26 operational amplifiers were chosen. Since then, Analog Devices Model 147C operational amplifiers have also been tested. Both models have been satisfactory. It is the specific advantage of applying such amplifiers in conjunction with other equipment to the detection of spark-source ion-currents that we wish to stress. A schematic diagram of the circuit is shown in Fig. 5. The circuitry can be constructed to allow a choice of various input-resistances, capacitances or amplifier gain settings with a small space requirement. Optimum parameter settings will be discussed after the input capability of the voltage-to-frequency converters has been considered.

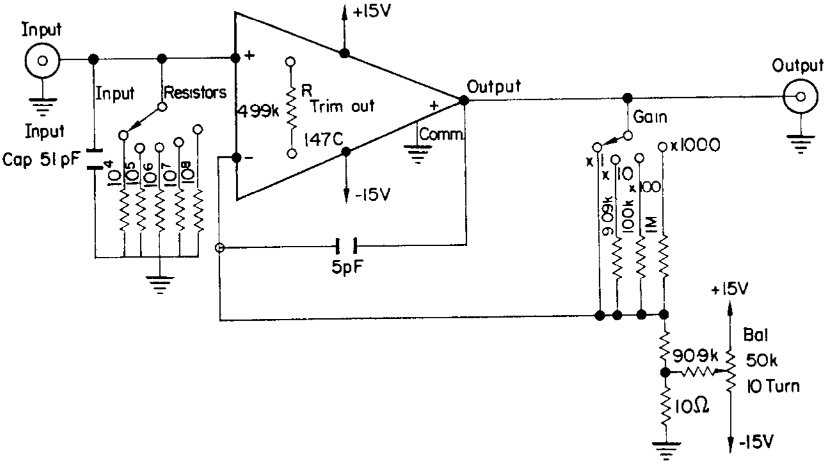

FIG. 5.—Operational amplifier circuit.

Voltage-to-frequency converter input capability

The voltage-to-frequency converters (Hewlett Packard, Model DY-2211/B) were tested for accuracy with pulsed inputs in which the pulse height (0–10 V), width (1–150 μsec), and rate (1–1000 Hz) were controlled. Output accuracy was within ±0·5% throughout all the ranges except for pulse heights greater than 5 V in which case the error rose to several per cent. This accuracy is retained when the maximum average input of 1·2 V-sec is maintained.

EXPERIMENTAL

Choice of operational amplifier operating parameters

Input capacitance and resistance of the amplifiers should be easily altered since optimum conditions will change under different sparking conditions. Maximum useful input resistance is limited by amplifier input resistance, input leakage paths, and amplifier zero stability. It was observed experimentally that the maximum input voltage was determined by the input capacitance. Thus the minimum capacitance must be determined either experimentally or by calculation from signal parameters. Normally an oscilloscope is connected at the amplifier output to display pulse shapes and the maximum amplifier output voltage. Another important condition is maintenance of the RC time-constant of the input circuit at some maximum value which should not exceed approximately $\frac{1}{3}$ of the repetition period. This assures a maximum signal-to-noise ratio while minimizing the possibility of amplifier overload from step-charge accumulation of several large sequential pulses. Typical signal conditions and representative calculations are given below.

$$\frac{\text{Signal (after electron multiplier)}}{\text{Concentration in sample}} = \frac{5 \times 10^{-13}\ \text{VF}}{\text{ppm}} = \text{unit sensitivity}$$

Maximum amplifier output voltage = 5V

Minimum stray capacitance = 20 pF

Maximum repetition rate of signal ~320 pulses/sec

Maximum allowed RC time-constant $= \frac{1}{3} \times \frac{1}{320} \sim 10^{-3}$ sec

Maximum resistance: $= 10^{-3}/2 \times 10^{-11} = 5 \times 10^{7}$ ohm

Maximum concentration measurable, limited by overload considerations (assuming charges arrive simultaneously and with minimum stray capacitance in the input circuit) =

$$\frac{2 \times 10^{-11}\mathrm{F} \times 5\mathrm{V}}{5 \times 10^{-13}\,\mathrm{VF/ppm}} = 200\,\mathrm{ppm}.$$

With a resistance of 10^7 ohm and the same time-constant, the maximum concentration measurable would be 1000 ppm.

The overall circuit may best be considered as one which measures charge on a capacitor as it is discharged rapidly through a resistor. As mentioned earlier, the voltage-to-frequency converter output is directly proportional to the area under this decay curve. This combination of equipment provides some specific advantages. (*a*) The error illustrated in Fig. 4 is now negligible since the amplifier has sufficient speed of response to follow the input voltage pulse. (*b*) The output of the system can now reflect low-level sample inhomogeneities if this is desirable or these real variations can be averaged out by increasing the measuring period. (*c*) A good signal-to-noise ratio over a large dynamic range is obtained. An experimentally determined signal-to-noise ratio of 1000 is obtained between the signal due to an impurity present at 50 ppm and the standard deviation of the noise level with the spark running. An upper concentration limit of 500 ppm has been used without the amplifier overload voltage being exceeded (*cf.* maximum of 1000 ppm calculated above). This range of sensitivity can be achieved with the VRE only if ranging is employed. (*d*) Changing of circuit parameters is convenient and fast though normally not required during a given experiment.

It is generally recognized that capacity measurements can provide good accuracy when ratios of erratic low-level signals are measured. The work described here attempts to take advantage of this fact as well as permitting continuous monitoring of the signal. The system described provided good and variable time resolution for the observation of sample-inhomogeneities, retains the accuracy of capacity measurements, and uses convenient digital handling of data. If ion-counting is to be used at the collector (not feasible at the monitor), then a rapid analogue-to-digital conversion of the monitor signal would allow a more realistic short-term ratio measurement.

Since the advantages of electrical detection in spark-source mass spectrometry are now becoming apparent,[4–6] this work should be of interest to those laboratories considering upgrading photoplate mass spectrographs to allow electrical detection as well as photographic detection. The development of other systems which utilize logarithmic response amplifiers to provide good dynamic range capabilities presents a chance to compare advantages and disadvantages.

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Summary—An electrical detection system for spark-source mass spectrometry has recently been developed. This brief addendum describes an improvement in the signal amplification and its conversion to digital output which has important implications in the future development of electrical detection

Zusammenfassung—Ein elektrisches Nachweissystem für die Massenspektrometrie mit Funkenquelle wurde kürzlich entwickelt. Dieser kurze Zusatz beschreibt eine Verbesserung bei der Signalverstärkung und die Umsetzung des verstärkten Signals in einen digitalen Ausgang; die Verbesserungen haben wichtige Konsequenzen bei der zukünftigen Entwicklung des elektrischen Nachweises.

Résumé—On a élaboré récemment un système de détection électrique pour la spectrométrie de mass à source d'étincelle. Ce bref additif décrit une amélioration dans l'amplification du signal et sa conversion en sortie digitale qui a d'importantes incidences sur le développement futur de la détection électrique.

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Determination of silicone fluid surfactants in polyurethane/polyether blends by atomic-absorption spectroscopy

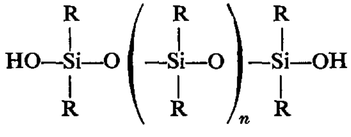
(*Received* 21 *October* 1969. *Revised* 1 *February* 1970. *Accepted* 23 *March* 1970)

SILICONE fluids are widely used as surfactants in foam manufacture, their function being to stabilize the foaming action and the cell size. The concentration of fluid used is critical and for most polyurethane blends is within the range 0·4–1·0 g/100 g of polyurethane polyol. Consequently, for purposes of quality control, costing, *etc*, a quick and accurate method for the determination of the silicone fluid content is desirable. Previous methods for the determination of silicone fluids have involved the decomposition of the silicone to silicate[1,2,3] which could then be estimated by conventional methods. Grantham and Hastings[4] have reported the determination of silicone resin by piperidine extraction but this method is lengthy and not considered suitable for many of the recently developed fluids. A method for the determination of some phenyl-substituted fluids by photoluminescence analysis has recently been described[5] but luminescence yields and hence sensitivities are low.

Atomic-absorption spectroscopy has recently been used for the determination of silicon in steels and similar materials.[6] With a pre-mixed nitrous oxide/acetylene flame, silicon concentrations of less than 1% could be rapidly determined. A fuel-rich flame was employed to suppress oxidation of the silicon to the non-absorbing oxide.

The present work describes the application of atomic-absorption spectroscopy to the determination of the silicone fluid content of some mixtures used in the manufacture of rigid polyurethane foams. By aspirating solutions of these fluids into the flame, attempts were made to measure the absorption of any atomic silicon released from the silicone fluid, the silicon line at 251·6 nm being used. The highly organic nature of the fluid should act to suppress oxidation of the silicon in the flame and so increase the sensitivity.

Two silicone fluids, A and B, have been investigated, together with their respective polyurethane blends, *i.e.*, polyurethane blend (1) was used in conjunction with silicone A and polyurethane blend (2) was used in conjunction with silicone B. Both silicone fluids may be represented by the general formula



$$HO-\underset{R}{\overset{R}{Si}}-O\left(-\underset{R}{\overset{R}{Si}}-O\right)_n-\underset{R}{\overset{R}{Si}}-OH$$

The blends were of the following composition

Polyether/polyurethane blend (1). (*I.C.I. Ltd.*). Polyether/polyurethane resin, water, foam cell modifier, tertiary amine catalyst. Viscosity 0·20 N.sec/m^2 at 25°.

Polyether/polyurethane blend (2). (*I.C.I. Ltd.*). Polyether/polyurethane resin, water, triethanolamine, tertiary amine catalyst. Viscosity 0·06 N.sec/m^2 at 25°.

The optimum experimental and instrumental conditions have been established and calibration graphs both for the pure silicone fluids and for mixtures of the fluids with their respective polyurethane blends have been prepared and compared.

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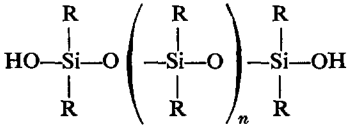

$$HO{-}\underset{R}{\overset{R}{\mathrm{Si}}}{-}O\left({-}\underset{R}{\overset{R}{\mathrm{Si}}}{-}O\right)_n{-}\underset{R}{\overset{R}{\mathrm{Si}}}{-}OH$$

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The optimum experimental and instrumental conditions have been established and calibration graphs both for the pure silicone fluids and for mixtures of the fluids with their respective polyurethane blends have been prepared and compared.

EXPERIMENTAL

Apparatus

Unicam SP 90A Atomic Absorption Spectrophotometer, fitted with a 50-mm path-length nitrous oxide burner, and a high spectral-output hollow-cathode silicon lamp.

Reagents

Analytical grade reagents and distilled, demineralized water were used.

Stock solutions were made of silicones A and B (20 g/l.) in ethanol–water (1:1).

Establishment of optimum conditions

Although the silicone-polyol blends are fluid at room temperature, they must be diluted with a suitable solvent to ensure efficient nebulization into the flame. Therefore 1% w/w mixtures of silicones A and B in polyether blends (1) and (2) respectively, were diluted (5 g/50 ml) with the following solvents: water, 1% aqueous sodium chloride, 1% aqueous ferric alum, ethanol–water (1:1), ethanol and acetone. These solutions were sprayed into the flame under the optimum instrumental conditions described below. The results are given in Table I.

TABLE I.—THE EFFECT OF SOLVENT ON THE ABSORPTION BY SILICONE/POLYETHER BLENDS (1% w/w)

Solvent (blank set to zero)	Absorbance Silicone A/polyether (1) (scale expansion × 2)		Absorbance Silicone B/polyether (2) (scale expansion × 2)	
Water	0·210	0·211	0·200	0·200
1% Sodium chloride	0·240	0·241	0·229	0·231
1% Ferric alum	0·230	0·230	0·220	0·221
Ethanol–water (1:1)	0·200	0·202	0·199	0·198
Ethanol	0·201	0·202	0·200	0·199
Acetone (scale expansion × 1)	0·011	0·006	0·008	0·006

The various instrumental parameters were then investigated, the ethanol–water solution of silicone A/polyether blend (1) being used as sample. The best conditions are shown, together with those recommended by Price and Roos,[6] in Table II.

TABLE II.—OPTIMUM INSTRUMENTAL CONDITIONS FOR THE DETERMINATION OF SILICONE FLUIDS

	Our work	Price and Roos
Wavelength, *mm*	251·6	251·6
Slitwidth, *nm*	1·0	1·0
Observation height, *mm*	10	10
Nitrous oxide flow-rate, *l./min* at 207 kN/m^2 (30 psi)	5·0	5·0
Acetylene flow-rate, *l./min* at 104 kN/m^2 (15 psi)	5·0	4·0–4·5
Scale expansion	×2	—

Calibration graphs were prepared by taking 0–10 ml of stock solution of silicone fluid in 100-ml standard flasks, diluting to the mark with ethanol–water (1:1), mixing, and then measuring the atomic absorption under the conditions given in Table II, and were found to be linear for both fluids A and B. Linear plots were also obtained for the silicone/polyether blends: the standards were prepared by mixing 0–0·2 g of pure silicone with 10 g of polyether blend and diluting 5 g of each prepared standard to 50 ml in a graduated flask, with ethanol–water. Samples for analysis were similarly diluted (5 g to 50 ml).

DISCUSSION

Choice of solvent

In agreement with the findings of Price and Roos,[6] sodium and iron were found to enhance the absorption by silicon in the flame. However, in all the purely aqueous solvents, the silicone B/polyether blend (2) solution was very turbid. Acetone as solvent gave a very high blank reading and an alarming increase in the height of the flame. Furthermore, with both the purely organic solvents, carbon deposited on the burner slit was troublesome and had to be removed at frequent intervals. Ethanol–water proved to be the most convenient solvent and since it gave clear solutions and absorbance values only 10% below the maximum values obtained, it was used for further investigations.

The solution of silicone A containing iron(III) became dark brown on standing for 15 min. Obviously, if the sample to be measured contains appreciable amounts of iron or sodium, then allowances should be made for these in preparing the calibration graphs.

Choice of instrumental conditions

The instrumental conditions used in the present work are similar to those recommended by Price and Roos[6] except for the acetylene flow-rate which in our work is higher. Two advantages are gained here. First, the signal-to-noise ratio was greatest for the flow-rate range 4·8–5·0 l./min (*N.B.*, these flow rates are uncorrected) and secondly, once the flame had been established for about 20 min, carbon build-up on the burner was much less troublesome than at flow-rates between 4 and 4·5 l./min. At the latter flow-rates, a hard, brittle carbon deposit rapidly built up at the burner slit and quickly restricted gas flow; however, at 5·0 l/min, a soft carbon deposit formed which became negligible after 20 min.

Effect of time

For the reasons just given, the burner and lamp should be allowed to warm up for 20 min before any measurements are taken. The effect of time on the signal-to-noise ratio is shown in Fig. 1.

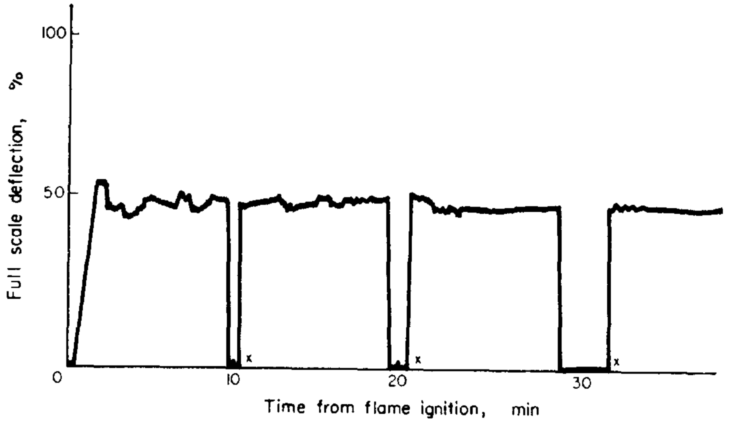

FIG. 1.—Effect of time on the signal-to-noise ratio for a solution containing 0·1 g of silicone A in polyether (1), in ethanol–water (1:1) as solvent (100 ml.). At position 'X', the recorder is on stand-by whilst any carbon deposit is removed.

Examination of the capillary tube, nebulizer chamber and all tubes up to and including the burner head showed no appreciable deposit of the viscose polyol after a long series of experiments, though this was first expected. Carbon build-up was troublesome only during the initial warm-up period and thereafter diminished considerably.

Sensitivity and detection limits

The sensitivity for 1% absorption, *viz.* the concentration of solution having an absorbance of 0·0044,[7] was calculated from each of the calibration graphs. For silicone A both as a solution of the pure fluid and in the presence of the polyurethane blend, it was 20 ppm and for silicone B 23 ppm.

The detection limit, defined as the concentration giving a reading equal to twice the standard deviation of a series of ten determinations at or near blank level, was 40 ppm for silicone A containing 10% of polyether blend (1). A scale expansion of ×4 was used to determine the detection limits.

Accuracy and reproducibility

The accuracy of the method was checked on the basis of the silicon content of fluids A and B, determined gravimetrically[1] and found to be 5·6% for A and 5·3% for B. These values are in agreement with those quoted by the manufacturers. Three random samples of each fluid, mixed with their respective polyether blends, were prepared by one of us and analysed by the other. The results are given in Table III.

TABLE III

Silicone A/Blend (1)		Silicone B/Blend (2)	
Si taken, *g*	Si found, *g*	Si taken, *g*	Si found, *g*
0·25	0·25	0·35	0·35
0·73	0·74	0·85	0·87
1·25	1·27	1·75	1·77

When 20 replicate dilutions of each stock silicone blend were measured under optimum conditions, all absorbance values obtained were within 1·2% of the mean.

The calibration graphs for silicone alone and in the presence of polyether blend had the same slope.

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Summary—A method for the atomic-absorption determination of silicone fluid surfactants present in some polyurethane/polyether blends is described. The silicone fluid in the pure state, or in the presence of polyurethane blend, is diluted with a solvent and sprayed into the nitrous oxide/acetylene flame. The effects of solvent, instrumental conditions, time and presence of the polyurethane blends were investigated. Polyurethane/polyether blends do not interfere with the silicon absorption when the samples are dissolved in aqueous ethanol (1:1) and sprayed into a fuel-rich flame.

Zusammenfassung—Ein Atomabsorptions-Verfahren zur Bestimmung flüssiger oberflächenaktiver Substanzen auf Silikon-basis wird beschrieben, die in einigen Polyurethan-Polyäther-Verschnitten vorkommen. Die Silikonflüssigkeit wird allein oder in Gegenwart des Polyurethanverschnitts mit einem Lösungsmittel verdünnt und in die Lachgas-Acetylen-Flamme gesprüht. Die Einflüsse von Lösungsmittel, Einstellungen am Gerät, Zeit und Gegenwart der Polyurethanverschnitte wurden untersucht. Polyurethan-Polyäther-Verschnitte stören die Silicium-Absorption nicht, wenn die Proben in wäßrigem Äthanol (1:1) gelöst und in eine fette Flamme gesprüht werden.

Résumé—On décrit une méthode pour la détermination par absorption atomique d'agents surfactifs à liquide de silicone présents dans quelques mélanges polyuréthanne–polyéther. Le liquide de silicone à l'état pur ou en la présence de mélange de polyuréthanne est dilué par un solvant et pulvérisé dans la flamme protoxyde d'azote–acétylène. On a étudié les influences du solvant, des conditions instrumentales, du temps et de la présence des mélanges de polyuréthanne. Les mélanges polyuréthanne–polyéther n'interfèrent pas avec l'absorption du silicium lorsque les échantillons sont dissous en éthanol aqueux (1:1) et pulvérisés dans une flamme riche en combustible.

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Stability characteristics of aqueous chloramine-T solutions

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THE PRESENT state of knowledge on the stability of chloramine-T has been critically reviewed by Bishop and Jennings.[1] Both the solid $CH_3C_6H_4SO_2NClNa{\cdot}3H_2O$ and its aqueous solution (pH 7·7 for 0·05*M* solution) are quite stable in absence of other reagents if they are protected from direct sunlight, the titre decreasing by only 0·02% per month.

Most of the earlier work on chloramine-T in analytical chemistry involved its use as an oxidant in sulphuric or hydrochloric acid media, but recently thiourea,[2] thioacetamide[3] and dimethylsulphoxide[4] have been quantitatively oxidized in neutral, alkaline and weakly acidic media respectively by addition of excess of chloramine-T, the excess being determined iodometrically. It therefore became necessary to investigate the stability of aqueous chloramine-T solutions in various media.

EXPERIMENTAL

Chloramine-T of initial purity 98·5% was thrice recrystallized from conductivity water. An approximately 0·05*M* aqueous solution was prepared in triply distilled water and standardized iodometrically. The stability of aqueous chloramine-T solutions under different conditions was tested by comparing the titres before and after conditioning. The reproducibility in the titrations was generally ±0·1%.

RESULTS AND DISCUSSION

Results obtained for the very low pH media are presented in Table I. Solutions of chloramine-T are quite stable for short periods (at least 20 min) in 0·2–2*M* sulphuric acid or perchloric acid. This result is in agreement with the observations made by Nair.[5] In hydrochloric acid up to ~0·3*M*, chloramine-T is as stable as in sulphuric and perchloric acid media, but with higher hydrochloric acid concentrations, it decreases in stability probably because it oxidizes chloride to chlorine (tested for with starch-iodide paper and found to be evolved).

TABLE I.—STABILITY OF AQUEOUS CHLORAMINE-T SOLUTION (~0·05*M*) IN STRONGLY ACIDIC SOLUTIONS AT 25–30°C

		Iodometric titre value,* *ml* of thiosulphate (± 0·02), after	
		5 min	20 min
Perchloric acid	0·3*M*	21·75	21·75
	0·5*M*	21·75	21·75
	2·0*M*	21·75	21·75
Sulphuric acid	0·1*M*	21·75	21·75
	0·5*M*	21·75	21·75
	2·0*M*	21·75	21·75
Hydrochloric acid	0·1*M*	21·75	21·75
	0·3*M*	21·75	21·75
	0·5*M*	21·62	21·50
	1·0*M*	21·60	21·45
	1·8*M*	21·06	20·32

* Standard titre 21·75 ml.

Results for media of pH > 2·65 are presented in Table II. At pH 7·7 and above there was no deterioration in 1 hr in the strength of chloramine-T solution at room temperature. However, a slight but significant decrease in titre occurred at pH values between 2·65 and 5·65. The decrease in titre was rapid at first (during approximately 20 min) and then slowed down appreciably. Hence blank experiments must be made if chloramine-T is to be used in this pH range for indirect (back-titration) procedures. This loss in titre may be correlated mechanistically with Higuchi's recent observation on the rate of formation of dichloramine-T on varying the pH of chloramine-T solutions.

TABLE II.—STABILITY OF AQUEOUS CHLORAMINE-T SOLUTION (~0·05*M*) AT pH 2·65 AT 25–30°C

	Iodometric titre value,† *ml* of thiosulphate (± 0·02), after		
pH*	60 sec	20 min	60 min
2·65	21·75	21·66	21·66
3·14	21·75	21·66	21·66
3·44	21·75	21·66	21·66
3·74	21·75	21·61	21·61
4·00‡	21·71	21·52	21·52
4·15	21·71	21·47	21·47
4·45	21·61	21·23	21·23
4·75	21·61	21·23	21·23
5·00	21·61	21·23	21·23
5·65	21·66	21·48	21·48
7·7§	21·75	21·75	21·75
9·18¶	21·75	21·75	21·75
2*M* NaOH	21·75	21·75	21·75

* Sodium acetate–acetic buffer system used unless otherwise stated.

† Standard titre 21·75 ml.

‡ Potassium acid phthalate buffer.

§ No buffer, pH of aqueous chloramine-T solution.

¶ 0·05*M* Borax buffer.

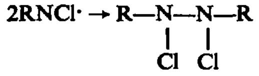
The behaviour of the rate of decrease in titre is similar to that of the rate of disproportionation of monochloramine-T ($CH_3C_6H_4SO_2NHCl$) into *p*-toluenesulphonamide and dichloramine-T[6] ($CH_3C_6H_4SO_2NCl_2$) as a function of pH. This indicates that the kinetics of the side-reaction closely follow those of the disproportionation reaction, and the loss in oxidative titre may be ascribed to minor side-reactions accompanying the major disproportionation reaction. The formation of dichloramine-T is reported[6] to involve the formation and eventual combination of free radicals:

$$R\dot{N}Cl + Cl\cdot \rightarrow RNCl_2$$

where $R = CH_3C_6H_4SO_2$.

The minor side-reactions occurring, namely,

$$2Cl\cdot \rightarrow Cl_2$$



$$2RNCl\cdot \rightarrow \underset{\displaystyle Cl}{R—N}—\underset{\displaystyle Cl}{N}—R$$

would cause a small loss in oxidative titre as the product $R_2N_2Cl_2$ will not oxidize iodide.

The rate of evolution of chlorine was evaluated from the relative intensities of the blue colour developed on starch–iodide paper. From sulphuric and perchloric acid media and media of pH > 7·7, there was no evolution of chlorine within 1 hr. However, in the pH range 2·65–5·65 the rate of evolution increased with increase in pH from 2·65, reaching a maximum at pH 4·7 and then decreasing again. In hydrochloric acid media, there was perceptible evolution of chlorine only when the acid concentration exceeded 0·5*M*. When chloramine-T solution was mixed with 4*M* hydrochloric acid, the starch-iodide paper first turned blue and then was rapidly bleached. This was ascribed to the oxidation of iodine to iodate by the large amount of chlorine evolved under these conditions. Hardy and Robson[7] reported a slow loss of chlorine from alkaline *N*-chloro-*N*-methylbenzamide solutions as a result of unidentified non-reversible reactions.

At higher temperatures (60–80°), chloramine-T solutions are stable only in highly acid (in absence of large concentrations of chloride, *e.g.*, in sulphuric acid) or alkaline conditions. We do not recommend the reagent for quantitative oxidations at higher temperatures in the pH range 2·0–5·65, as the blank values are very high and not reproducible.

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Summary—Aqueous chloramine-T solutions in strongly alkaline medium are quite stable even up to 60°. In 0·2–2M sulphuric or perchloric acid at 25–30°, there is no loss in titre, but in hydrochloric acid solutions $>0{\cdot}5M$, there is a loss in titre which increases with increase in hydrochloric acid concentration. This is ascribed to oxidation of chloride to chlorine. In the pH range 2·65–5·65 there is a small but reproducible loss in oxidative titre which is maximal at pH 4·7. This is ascribed to side-reactions occurring during partial disproportionation of monochloramine-T to dichloramine-T and *p*-toluenesulphonamide.

Zusammenfassung—Wäßrige Chloramin-T-Lösungen sind in stark alkalischem Medium bis 60° stabil. In 0,2–2 M Schwefel- oder Überchlorsäure bei 25–30° erfolgt kein Titerverlust; in salzsauren Lösungen über 0,5 M fällt der Titer mit steigender Salzsäurekonzentration ab. Dies wird einer Oxidation von Chlorid zu Chlor zugeschrieben. Im pH-Bereich 2,65–5,65 fällt der Oxidationstiter schwach, aber reproduzierbar, am meisten bei pH 4,7. Dies wird Nebenreaktionen zugeschrieben, die neben teilweisen Disproportionierung von Monochloramin-T zu Dichloramin-T und *p*-Toluosulfonamid herlaufen.

Résumé—Les solutions aqueuses de chloramine-T en milieu fortement alcalin sont tout à fait stables même jusqu'à 60°. En acide sulfurique ou perchlorique 0,2–2 M à 25–30°, il n'y a pas de perte en titre, mais en solutions d'acide chlorhydrique $>0{,}5$ M, il y a une perte en titre qui croît avec l'augmentation de la concentration en acide chlorhydrique. Ceci est attribué à l'oxydation du chlorure en chlore. Dans le domaine de pH 2,65–5,65, il y a une perte petite mais reproductible dans le titre d'oxydation, qui est maximale à pH 4,7. Ceci est attribué à des réactions secondaires se produisant durant la dismutation partielle de la monochloramine-T en dichloramine-T et *p*-toluènesulfamide.

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Spectrophotometric determination of ruthenium(III) and iridium(IV) with 8-hydroxyquinoline *N*-oxide

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ANALYTICAL applications and metal complexes of 8-hydroxyquinoline *N*-oxide were reported earlier.[1–10] During further investigations we have observed that platinum metal chloro-complexes heated with excess of oxine *N*-oxide at 100° for 30–60 min gave yellow to brown complexes, soluble in 30% v/v ethanol and having molar composition 1:1 and 1:2 (metal:ligand). We have found that oxine *N*-oxide can be used as a spectrophotometric reagent for determination of ruthenium(III) and iridium(IV).

EXPERIMENTAL

Reagents

Oxine *N*-oxide, prepared from oxine,[1] was used as the fresh aqueous solution. Stock solutions of the metals were prepared by dissolving ruthenium trichloride, sodium hexachlororhodate(III), palladium(II) chloride, potassium hexachloro-osmate(IV), sodium hexachloroiridate(IV) and

Summary—Aqueous chloramine-T solutions in strongly alkaline medium are quite stable even up to 60°. In 0·2–2M sulphuric or perchloric acid at 25–30°, there is no loss in titre, but in hydrochloric acid solutions $>0{\cdot}5M$, there is a loss in titre which increases with increase in hydrochloric acid concentration. This is ascribed to oxidation of chloride to chlorine. In the pH range 2·65–5·65 there is a small but reproducible loss in oxidative titre which is maximal at pH 4·7. This is ascribed to side-reactions occurring during partial disproportionation of monochloramine-T to dichloramine-T and *p*-toluenesulphonamide.

Zusammenfassung—Wäßrige Chloramin-T-Lösungen sind in stark alkalischem Medium bis 60° stabil. In 0,2–2 M Schwefel- oder Überchlorsäure bei 25–30° erfolgt kein Titerverlust; in salzsauren Lösungen über 0,5 M fällt der Titer mit steigender Salzsäurekonzentration ab. Dies wird einer Oxidation von Chlorid zu Chlor zugeschrieben. Im pH-Bereich 2,65–5,65 fällt der Oxidationstiter schwach, aber reproduzierbar, am meisten bei pH 4,7. Dies wird Nebenreaktionen zugeschrieben, die neben teilweisen Disproportionierung von Monochloramin-T zu Dichloramin-T und *p*-Toluosulfonamid herlaufen.

Résumé—Les solutions aqueuses de chloramine-T en milieu fortement alcalin sont tout à fait stables même jusqu'à 60°. En acide sulfurique ou perchlorique 0,2–2 M à 25–30°, il n'y a pas de perte en titre, mais en solutions d'acide chlorhydrique $>0{,}5\ M$, il y a une perte en titre qui croît avec l'augmentation de la concentration en acide chlorhydrique. Ceci est attribué à l'oxydation du chlorure en chlore. Dans le domaine de pH 2,65–5,65, il y a une perte petite mais reproductible dans le titre d'oxydation, qui est maximale à pH 4,7. Ceci est attribué à des réactions secondaires se produisant durant la dismutation partielle de la monochloramine-T en dichloramine-T et *p*-toluènesulfamide.

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Spectrophotometric determination of ruthenium(III) and iridium(IV) with 8-hydroxyquinoline *N*-oxide

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ANALYTICAL applications and metal complexes of 8-hydroxyquinoline *N*-oxide were reported earlier.[1–10] During further investigations we have observed that platinum metal chloro-complexes heated with excess of oxine *N*-oxide at 100° for 30–60 min gave yellow to brown complexes, soluble in 30% v/v ethanol and having molar composition 1:1 and 1:2 (metal:ligand). We have found that oxine *N*-oxide can be used as a spectrophotometric reagent for determination of ruthenium(III) and iridium(IV).

EXPERIMENTAL

Reagents

Oxine *N*-oxide, prepared from oxine,[1] was used as the fresh aqueous solution. Stock solutions of the metals were prepared by dissolving ruthenium trichloride, sodium hexachlororhodate(III), palladium(II) chloride, potassium hexachloro-osmate(IV), sodium hexachloroiridate(IV) and chloroplatinic acid in 1*M* hydrochloric acid, and standardized spectrophotometrically[11] and gravimetrically.[12]

A 0·1*M* sodium chloride solution in 30% v/v aqueous ethanol was used as constant ionic strength medium.

RESULTS

Properties

Heating a 10-fold excess of oxine *N*-oxide with 1 ml of 0·004*M* platinum metal chloro-complex solution in a boiling water-bath for about 1 hr resulted in formation of the complex. The absorption spectra of the complexes thus obtained (and diluted to yield 25 ml of solution containing 30% v/v ethanol to make the solution homogeneous, and adjusted to suitable pH) were measured against a reagent blank, and are shown in Figs. 1–6. From the spectra it was concluded that under the conditions used each platinum metal forms two complexes with oxine *N*-oxide.

For complete colour development the initial pH proved important, and should be 1·5–3·0 for ruthenium(III), 4·0–6·0 for rhodium(III), 4·0–7·0 for palladium(II), 4·5–7·0 for osmium(IV), 5·0–7·0 for iridium(IV) and 4·0–6·5 for platinum(IV). The effect of pH on the absorbance of the complexes after formation is also given in Table I.

The complexes were found to be extractable to various extents in a variety of organic solvents (Table II).

The complex formation is slow at room temperature, but at 100° is complete in 30 min. To ensure complete formation the test solutions were all heated for 90 min. Once formed, the complexes were stable for 24 hr at room temperature and for 2 hr at 100°

For complete colour development, at least a 4:1 ligand:metal ratio was necessary. A 10-fold molar excess of reagent was therefore used, and the measurements were made against a reagent blank.

Procedures

Ruthenium(III). To 1 ml of chlororuthenate(III) solution add excess of oxine *N*-oxide solution, adjust the pH to between 1·5 and 3·0, and heat in a boiling water-bath for 60–90 min. Cool, adjust the pH to 3–5, and dilute to give a known volume containing 30% v/v ethanol and 2–20 ppm ruthenium. Measure the absorbance at 400 nm against a reagent blank.

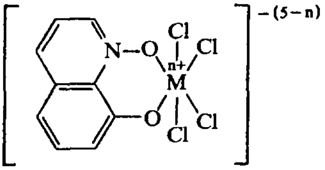
Iridium(IV). Heat the solution containing iridium(IV) and excess of oxine *N*-oxide at pH 4·0–7·0 in a boiling water-bath for 1 hr, cool, adjust the pH to >13, dilute to give a known volume containing 30% v/v ethanol and 1–7 ppm iridium, and measure the absorbance at 400 nm against a reagent blank.

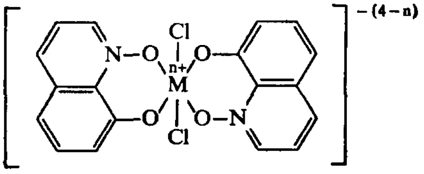
The interferences in the spectrophotometric determination of ruthenium(III) and iridium(IV) are reported in Table III. Chloroaurate(III) does not form a strongly coloured complex with the reagent.

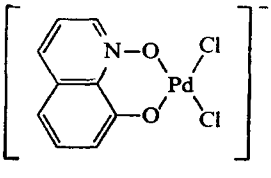
The metal:ligand ratio in the complexes was determined by Vosburgh and Cooper's method,[13] and found to be 1:1 and 1:2 for all the platinum metals.

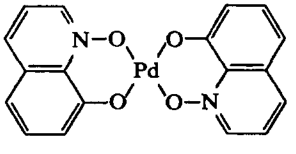
The ruthenium(III) and rhodium(III) complexes were found to be exchanged by IRA 410 anion-exchanger but not by IRC 50 or IRA 120 cation-exchangers. The palladium(II), osmium(IV), iridium(IV) and platinum(IV) complexes were partially exchanged by IRA 410(OH$^-$) and the exchanged complexes were partially eluted with dilute hydrochloric acid (*ca.* 3*M*), but there was no exchange by IRC 50. The species formed are therefore either anionic or neutral complexes.

Tentative structures are shown below.









$M^{n+} = Ru^{3+}, Rh^{3+}, Os^{4+}, Ir^{4+}$ and Pt^{4+}.

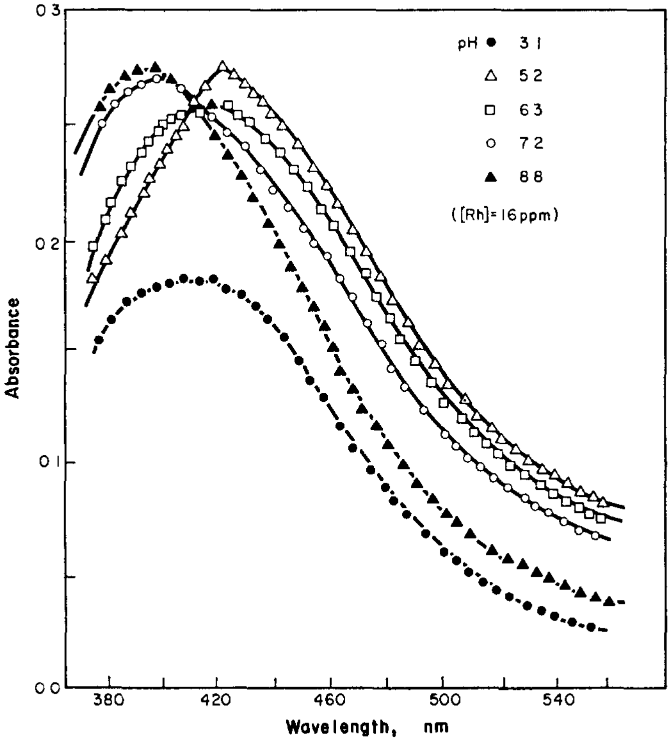


FIG. 1.—Absorption spectra of Rh(III) systems at different pH values.

TABLE I.—SPECTRAL CHARACTERISTICS OF THE PLATINUM METAL COMPLEXES IN 30% v/v AQUEOUS ETHANOL

Ion	Wavelength, *nm*	Molar absorptivity, $l.mole^{-1}.mm^{-1}$	pH range for constant absorbance	Conc. range for Beer's law, *ppm*
Ruthenium(III)	400*	486	3·0–5·0† 7·8–12·5§	1·8–20·0
	620‡	51	5·0–7·8	
Rhodium(III)	422*	183	4·7–5·7	4·0–50·0
	408‡	146	6·1–8·0	
	400*	185	8·2–8·9	
Palladium(II)	390*	253	7·5–8·2	3·5–35·0
	410*	228	9·0–10·0	
Osmium(IV)	420*	280	3·6–5·2	5·0–65·0
	412‡	252	6·0–9·2	
	400*	279	9·6–10·2	
Iridium(IV)	420*	362	2·5–5·0	4·0–48·0
	408‡	312	6·5–12·0	
	398*	1670	>13	1·0–7·0
Platinum(IV)	430*	72	2·3–6·1	20–200
	415‡	70	6·8–8·4	
	408*	75	9·1–10·0	

* Absorption maximum. § For the yellow solution.
† For the green solution. ‡ Isosbestic point.

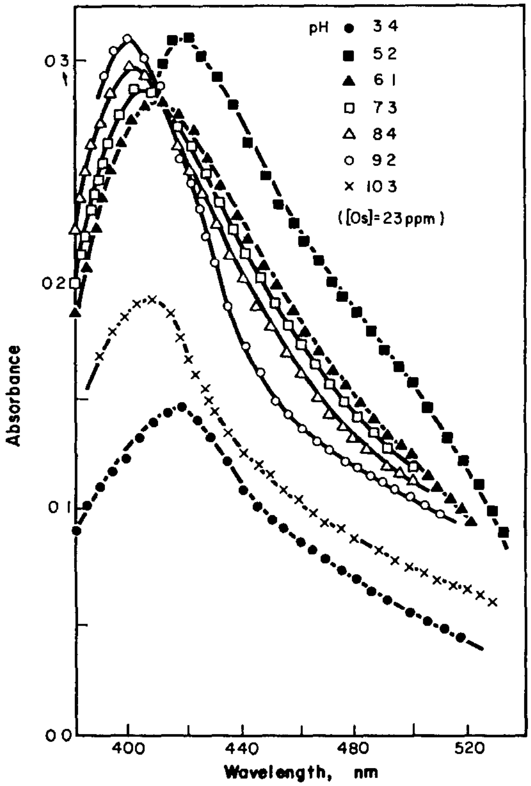


FIG. 2.—Absorption spectra of Os(IV) system at different pH values.

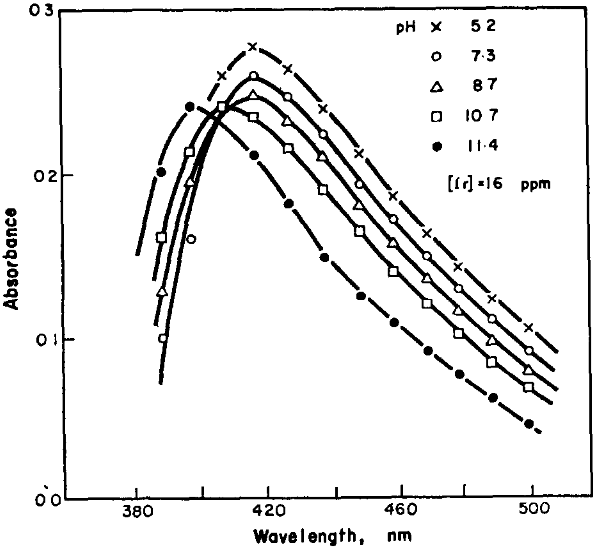


FIG. 3.—Absorption spectra of Ir(IV) system at different pH values.

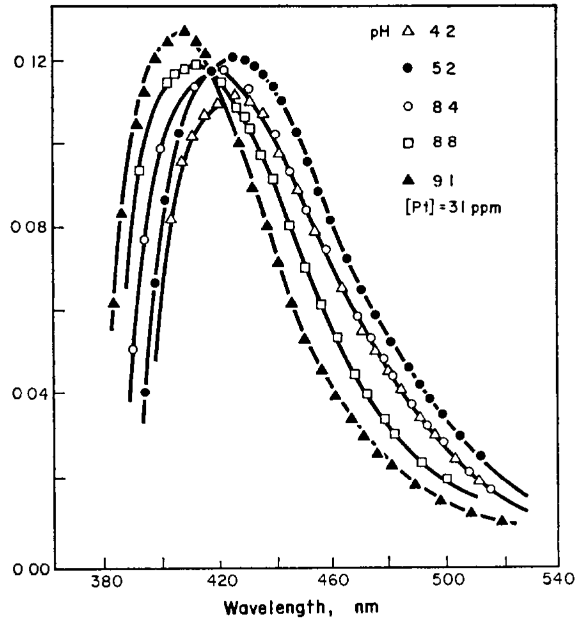


FIG. 4.—Absorption spectra of Pt(IV) system at different pH values.

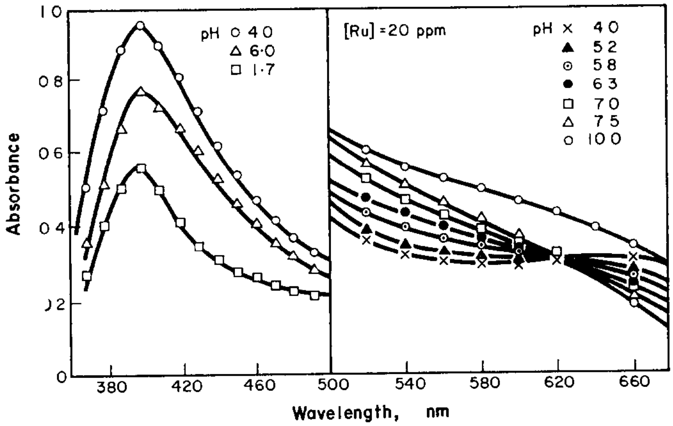


FIG. 5.—Absorption spectra of Ru(III) system at different pH values.

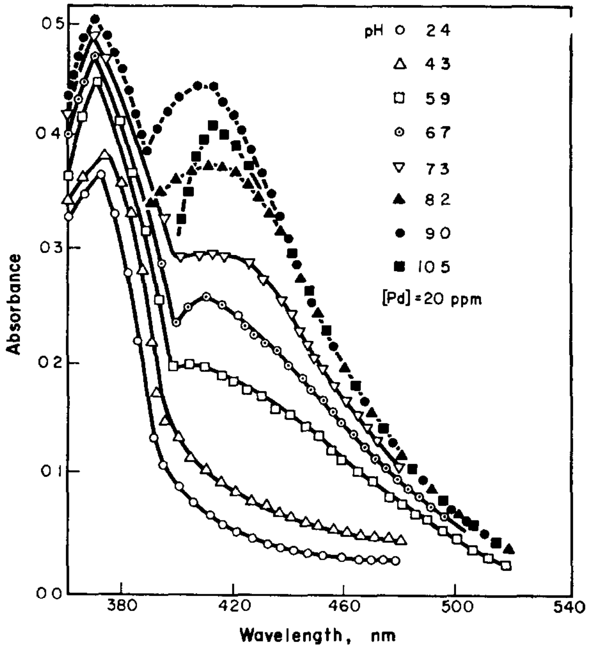


FIG. 6.—Absorption spectra of Pd(II) system at different pH values.

TABLE II.—EXTRACTABILITY OF THE PLATINUM METAL COMPLEXES

Solvent	Ru(III)	Rh(III)	Pd(II)	Os(IV)	Ir(IV)	Pt(IV)
Benzene	0	0	3	2	3	3
Toluene	0	0	3	2	3	3
Xylene	0	0	3	2	3	3
Petroleum ether	0	0	2	1	1	2
Butanol	3	1	3	3	3	3
Isobutanol	2	1	3	3	4	3
Pentanol	2	1	3	3	3	3
Isopentanol	2	1	3	3	3	3
Cyclohexanol	4	2	3	4	4	4
Chloroform	1	1	3	4	3	3
Carbon tetrachloride	0	0	2	1	2	2
o-Dichlorobenzene	2	3	4	2	3	3
Chlorobenzene	1	3	4	2	3	2
Bromobenzene	1	3	4	2	3	3
2-Butanone	4	0	3	2	3	2
Isobutyl methyl ketone	4	2	4	3	4	4
Nitrobenzene	2	2	3	3	3	2
Ethyl acetate	0	0	2	2	3	2
Diethyl ether	0	0	1	2	2	2
Tricresyl phosphate	0	2	3	2	3	2

Key: 0: not extractable; 1: the organic layer is just coloured yellow; 2: the solubility in the organic phase is less than that in the aqueous phase; 3: solubility in the organic phase is more than that in the aqueous phase; 4: extraction of the complex into the organic phase is nearly quantitative.

TABLE III.—INTERFERENCE DUE TO FOREIGN IONS IN THE SPECTROPHOTOMETRIC DETERMINATION OF RUTHENIUM(III) (4 ppm) AND IRIDIUM(IV) (1·2 ppm)

Ion and species	Tolerance *ppm*, for		Ion and species	Tolerance *ppm*, for	
	Ru(III)	Ir(IV)		Ru(III)	Ir(IV)
Ru(III) as $RuCl_6^{3-}$	—	8·0	Cl^- as NaCl	2000	4000
Rh(III) as $RhCl_6^{3-}$	2·8	9·0	NO_3^- as $NaNO_3$	2000	2000
Pd(II) as $PdCl_4^{2-}$	2·0	8·0	SO_4^{2-} as $Na_2SO_4 \cdot 10H_2O$	2000	2000
Os(IV) as $OsCl_6^{2-}$	4·0	15·0	Boric acid	1000	1000
Ir(IV) as $IrCl_6^{2-}$	0·5	—	Citric acid	300	300
Pt(IV) as $PtCl_6^{2-}$	13·0	50·0	Tartaric acid	500	500
Ni(II) as $NiSO_4 \cdot 7H_2O$	24·0	60·0	Oxalic acid, dihydrate	100	1000
Co(II) as $CoSO_4 \cdot 7H_2O$	14·0	16·0	Acetate as CH_3COONa	1000	1000
Fe(III) as $FeCl_3$	4·0	8·0	Au(III) as $AuCl_4^-$	2·0	3·0
Cu(II) as $CuSO_4 \cdot 5H_2O$	1·5	2·0	Ag(I) as $AgNO_3$	12·5	35·0
Cr(III) as $Cr(NO_3)_3 \cdot 9H_2O$	200	200			

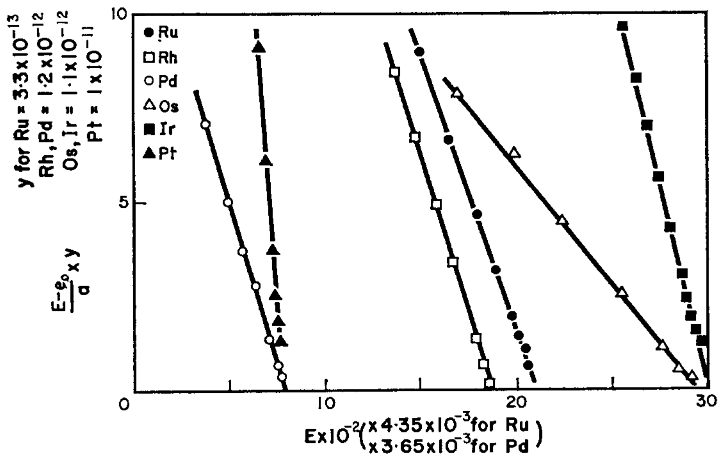


FIG. 7.—Plots of $(E - e_0)/a$ *vs.* E for the 1:1 complexes, at 420 nm.

TABLE IV.—THE STABILITY CONSTANTS OF THE PLATINUM METAL COMPLEXES WITH 8-HYDROXYQUINOLINE *N*-OXIDE

Ion	Wave-length, *nm*	log K_1	log K_2	log β_2	Ion	Wave-length, *nm*	log K_1	log K_2	log β_2
Ru(III)	400	11·48	5·40	16·88	Os(IV)	400	11·11	5·51	16·62
	420	11·34	5·32	16·68		420	11·11	5·56	16·67
	440	11·43	5·42	16·84		430	11·13	5·61	16·74
	460	11·40	5·45	16·85		440	11·12	5·45	16·57
	480	11·48	5·26	16·74		Average	11·12	5·53	16·65
	540	11·40	5·35	16·75					
	600	11·48	5·20	16·88	Ir(IV)	400	12·57	5·28	17·85
	Average	11·46	5·32	16·88		420	12·67	5·35	18·02
						440	12·57	5·28	17·85
Rh(III)	400	10·23	6·08	16·31		460	12·74	5·31	18·05
	420	10·26	5·93	16·49		480	12·58	5·26	17·84
	440	10·17	6·07	16·24		Average	12·62	5·30	17·92
	460	10·23	6·13	16·36					
	Average	10·22	6·05	16·27	Pt(IV)	400	12·85	4·06	16·82
						420	12·78	3·62	16·40
Pd(II)	390	10·40	6·92	17·32		440	12·82	3·88	16·70
	400	10·46	6·96	17·42		460	12·86	4·02	16·88
	410	10·45	6·93	17·38		Average	12·83	3·94	16·77
	420	10·46	6·85	17·31					
	Average	10·44	6·92	17·36					

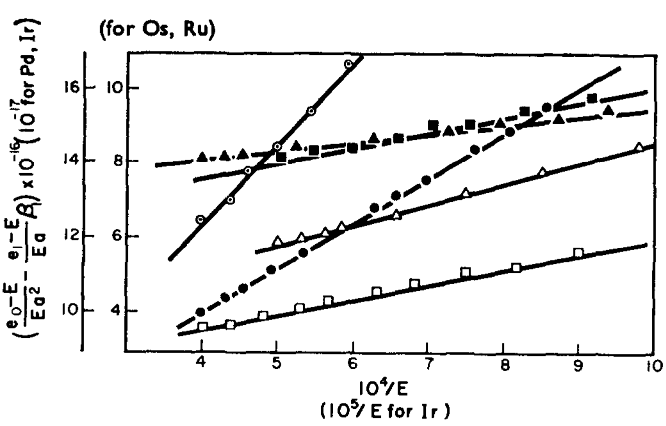


FIG. 8.—Plots of $[(e_0 - E)/a - (e_1 - E)\beta_1]/Ea$ vs. $1/E$ for the mixture of 1:1 and 1:2 complexes, at 420 nm.

Determination of stability constants

In the platinum metal–oxine *N*-oxide systems, besides the free metal ions, two coloured species ML_n ($n = 1$ or 2) are present (the number of chloride ions attached to the metal being ignored, as a constant excess of chloride is present, $0{\cdot}1M$). The stability constants were therefore determined by the following methods.[14]

The molar absorptivity E of a solution containing the complexes ML_n ($n = 0, 1, 2$) at equilibrium is given by

$$\frac{e_0 + e_1\beta_1 a + e_2\beta_2 a^2}{1 + \beta_1 a + \beta_2 a^2} = E, \tag{1}$$

where e_n is the molar absorptivity of the species ML_n, a is the equilibrium concentration of the free ligand, E is measured against a reagent blank, and β_n is the overall formation constant for the nth complex. The values of e_1 and β_1 were calculated by assuming the formation of only a 1:1 complex at low concentrations of free ligand; equation (1) can then be rearranged to

$$\frac{E - e_0}{a} = \beta_1 . e_1 - \beta_1 . E \tag{2}$$

so that plots of $(E - e_0)/a$ against E are straight lines with slope $-\beta_1$ and intercept $\beta_1 . e_1$. Figure 7 shows such plots at 420 nm and the values of β_1 obtained at different wavelengths are given in Table IV.

The values of the second stability constants were then calculated by plotting the left-hand side of equation (3) [which can be readily derived from equation (1)] against $1/E$ for values of a where both

$$\frac{e_0 - E}{Ea^2} + \frac{e_1 - E}{Ea}\beta_1 = \beta_2 - e_2 . \beta_2/E \tag{3}$$

1:1 and 1:2 complexes coexist, *e.g.*, at the isosbestic points, the resulting straight lines having slope $-e_2 . \beta_2$ and intercept β_2. Figure 8 shows such plots at 420 nm and the stability constants determined at different wavelengths are given in Table IV.

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Summary—The spectrophotometric characteristics and the stability constants of the yellow to brown 1:1 and 1:2 complexes of platinum metals with oxine *N*-oxide (existing as chloro mixed-ligand complexes) have been investigated. Oxine *N*-oxide can be used as a spectrophotometric reagent for ruthenium(III) and iridium(IV).

Zusammenfassung—Die spektrophotometrischen Eigenschaften und die Stabilitätskonstanten der gelben bis braunen 1:1-und 1:2-Komplexe von Platinmetallen mit Oxin-*N*-oxid (gemischte Chloro-Ligand-Komplexe) wurden untersucht. Man kann Oxin-*N*-oxid als spektrophotometrisches Reagens für Ruthenium(III) und Iridium(IV) verwenden.

Résumé—On a étudié les caractéristiques spectrophotométriques et les constantes de stabilité des complexes jaune à brun 1:1 et 1:2 des métaux du platine avec le *N*-oxyde d'oxine (existant à l'état de complexes chloro-ligand mixtes). Le *N*-oxyde d'oxine peut être utilisé comme réactif spectrophotométrique pour le ruthénium(III) et l'iridium(IV).

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LETTERS TO THE EDITOR

Use of $LiBO_2$ flux for K–Ar dating

SIR,

Purified vacuum-fused lithium metaborate ($LiBO_2$) has been tested as a flux in the vacuum melting of mineral samples for K–Ar dating and has been found to be completely compatible with typical argon extraction and analysis equipment. It has been tested with gold, molybdenum, and tungsten crucible material. The technique apparently produces no adverse gaseous products to interfere with gettering materials in the argon extraction train or with mass spectrometric measurements.

There are several advantages in using a flux. (1) Melting of even highly refractory samples can be accomplished at a relatively low temperature (~900°) with a greater assurance of complete melting and degassing of the sample. This might be useful in cases such as those reported by Webb and McDougall[1] in which extreme heating was necessary to release all of the radiogenic argon. (2) Power requirements (in this case from a radiofrequency generator) are greatly reduced. In fact, low temperature fusions could easily be produced by resistance heating, eliminating the high costs and safety hazards involved in radiofrequency heating. (3) Previous experiments suggest that lower-temperature fusions result in lower contamination by atmospheric argon, arising from heating of crucibles and fusion chambers. (4) The use of a low-temperature flux might inhibit the volatilization of potassium, allowing potassium determination on the fused residue.

The results of one such experiment with the Pennsylvania State University standard orthoclase Or-1* are shown in the Table. First, the sample was run by standard methods, wherein argon and potassium determinations were made on separate portions of sample. In a second run, 0·5 g of orthoclase was placed in an open thick-walled gold crucible containing 3·5 g of $LiBO_2$. This, in turn, was placed at the bottom of a silica test-tube. After fusion and argon extraction, a potassium determination was made on all the material left in both containers (some of the potassium having been deposited on the walls of the test-tube). Results for both the argon and potassium in this run are comparable to those obtained by the conventional methods. The low value of $14{\cdot}8_2$% K_2O obtained in the experiments reported here may or may not be due to slight potassium loss.

Sample	Experimental conditions	Total atmospheric argon, *mole*	K_2O, %	Radiogenic ^{40}Ar, *mole/g*
Or-1 (as received)	0·1-g sample in molybdenum and alundum crucibles, RF heated to 1400°.	$2{\cdot}6_5 \pm 0{\cdot}0_5 \times 10^{-10}$	$14{\cdot}9_2 \pm 0{\cdot}0_2$	$3{\cdot}5_4 \pm 0{\cdot}1_0 \times 10^{-10}$
Or-1A (sieved to + 325-mesh)	0·5-g sample in gold crucible and 0·15-m silica test-tube, with 3·5 g of vacuum-fused, crushed $LiBO_2$; RF heated to 893°.	$1{\cdot}8_6 \pm 0{\cdot}0_6 \times 10^{-10}$	$14{\cdot}8_2 \pm 0{\cdot}0_2$	$3{\cdot}5_0 \pm 0{\cdot}1_1 \times 10^{-10}$

Although much work remains to be done to prove the method for various types of samples, this experiment indicates that it may be possible to analyse the same portion of a sample for both potassium and argon. This would be most helpful in reducing errors arising from dividing samples, which, in some cases, may be very large.[2]

* Chosen for this experiment because it is known to be a reliable potassium standard. Repetitive analyses have established its homogeneity at the 0·1-g sample level, and it varies by no more than $0{\cdot}0_2$% K_2O. Or-1 was washed through a 325-mesh sieve to prepare Or-1A. Then the original sample, the fines, and the 325-mesh material were compared; they differed by no more than $0{\cdot}0_2$% K_2O. While nothing was known of the argon content of Or-1A, it was hoped that it might be demonstrated to be a useful argon standard as well. The results indicate that, although it has a fairly young apparent age (16×10^6 y), it could, with further work, prove useful as an argon standard.

We are indebted to Dr. Oliver Preston, of the Intracast Division of Macronetics, Inc., of East Palo Alto, California, for assistance in the preparation of the vacuum-fused lithium metaborate used in these experiments.

U.S. Geological Survey
Menlo Park, Calif. 94025, U.S.A.
4 *March* 1970

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Oxidation state of selenium dissolved in pure sulphuric acid

SIR,

Pure sulphuric acid, analytical reagent grade, always contains an ultramicro amount of selenium. The oxidation state of the selenium has not hitherto been established. The oxidation numbers of selenium are—II, 0, IV and VI. The existence of Se(—II) in pure sulphuric acid is highly unlikely, because H_2Se boils at −42° and has a very low oxidation potential.

When 4-nitro-*o*-phenylenediamine is added to pure sulphuric acid, no 5-nitropiaselenol is produced. This indicates that selenium does not exist as Se(IV) in pure sulphuric acid. The oxidation state of selenium in pure sulphuric acid can be determined by comparing the results obtained when the previously described method[1] for determination of selenium [by oxidation of Se(0) to Se(IV) with bromine–bromide buffer and subsequent formation of 5-nitropiaselenol, which is determined by gas chromatography] is used with and without a preliminary reduction step with titanium(III). The results below show that when 0·053 μg of Se(0) is dissolved in carbon disulphide and the solution evaporated to dryness, recovery is quantitative when the 5-nitropiaselenol method[1] is used. Experiment 2 implies that pure sulphuric acid contains selenium only as Se(0). In experiment 3, 0·1 μg of Se(IV) deliberately added was determined quantitatively by the 5-nitropiaselenol method, along with selenium originally present in the sulphuric acid. Experiment 4 reveals that Se(VI) can only be determined if it is first reduced to Se(0). Experiment 5 indicates that the method with a preliminary reduction can be used to determine both Se(IV) and (VI). From these results, only elemental selenium exists in pure sulphuric acid.

Experiment	Se found, μg No reduction	Reduced with Ti(III)
(1) 0·053 μg of Se(0) in CS_2	0·054	
(2) pure H_2SO_4 (1 ml)	0·035	0·036
(3) pure H_2SO_4 (1 ml) + Se(IV) (0·1 μg)	0·133	
(4) pure H_2SO_4 (1 ml) + Se(VI) (0·1 μg)	0·040	0·136
(5) H_2SO_4 (Se-free) (1 ml) + Se(IV) (0·05 μg) + Se(VI) (0·1 μg)	0·080	0·156

For determination of Se(VI) the sample (1 ml of conc. sulphuric acid) is heated at ~90° on a water-bath with 5 ml of 0·03*M* titanium(III) chloride for 10–20 min. Then 3 ml of distilled water and 1·8 ml of 0·1*M* bromine–bromide buffer[1] are added and the solution is heated at 85° for 20 min, and is then processed by the method already described.[1]

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1. Y. Shimoishi and K. Tôei, *Talanta*, 1970, **17**, 165.

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PRACTICAL ANALYSIS OF HIGH-PURITY CHEMICALS—I

PREPARATION AND CHARACTERIZATION OF HIGH-PURITY EDTA

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Summary—Advanced laboratories have requirements for high-purity chemicals with less than 500 ppm total impurities (ultrapure chemicals) and with broad analytical definition of each lot. Some economically feasible approaches to the practical analysis of such chemicals, both inorganic and organic, are delineated. Compounds used in the study of lunar samples and in other advanced programmes are noted. EDTA, as the free acid, has been prepared by dissolution in water with base and precipitation by addition of acid. The product has been broadly characterized. Precision assay is achieved by weight titrimetry, potentiometrically as a triprotic acid and photometrically as a chelating agent. Other tests applied include elemental analysis, ash, loss on drying, particulate matter, and tests for nitrilotriacetate, arsenic, and chloride. Boron, silicon, and trace metals are determined by emission spectrography. Many of the procedures are applicable to other high-purity organic chemicals.

A "PURIFIED" chemical during the first half of the 19th century meant little more than that the product had been either recrystallized or redistilled, with no analytical assessment of quality. For reagent-grade chemicals analytical definition has progressed over the past one hundred years from feeble attempts at semiquantitative expression to the determination of up to 15 or more impurities.[1]

High-purity chemicals with 500 ppm or less of total impurity, often called "ultrapure" chemicals,[2] constitute a present-day challenge. In recent years a number of such chemicals have been offered in laboratory-use quantities. The rule of *caveat emptor* has often prevailed because suppliers have commonly confirmed the quality of a lot, if at all, by a single technique (*e.g.*, emission spectrography for inorganic compounds and gas chromatography for organic ones). High-purity chemicals, both inorganic and organic, with broad analytical definition of each lot, represent the direction of advance. Uses for such products include analytical reagents for exacting trace analysis and characterization of complex materials, such as lunar and geochemical samples, standards for various analytical methods, and reagents for advanced materials research and diverse biochemical studies.

Since knowledge of purification processes is now extensive, the preparation of many high-purity chemicals presents less of a problem than their analysis and storage. In the development of an economically profitable line of broadly defined, high-purity chemicals not only must the preparation and storage be considered from the standpoint of cost, but also the strategies adopted for the analysis. Some analytical approaches to this *practical* analysis of high-purity chemicals are summarized in Table I and most have now been applied to over 50 such products, prepared in 1–200 kg lots.

TABLE I.—SOME METHODS FOR THE PRACTICAL ANALYSIS OF HIGH-PURITY CHEMICALS

Major constituent and assessment of purity	Minor and trace constituents	Physical properties	General tests
Coulometry*	Activation analysis*	Chemical microscopy	Ash
Differential scanning calorimetry	Atomic-absorption photometry	Density	Insoluble matter
Elemental organic analysis	Emission spectrography	Differential thermal analysis	Loss on drying
High-resolution gas chromatography	Extraction-spectrophotometry	Electrical conductivity (low-level)	pH of solution
Phase solubility analysis	Flame emission photometry	Infrared spectra	Residue after evaporation
Precision gravimetry	Fluorometry	Melting point	Trace particulate matter
Precision weight titrimetry (instrumental end-point detection)	Gas chromatography	Refractive index	
	Mass spectrometry*	Specific rotation	
	Nuclear magnetic resonance*	UV-visible spectra	
	Polarography		
	Spot tests		
	Thin-layer chromatography		
	Titrimetry (electrometric or photometric end-point detection)		
	Turbidimetry		
	UV-visible-IR spectrophotometry		

* Not yet applied in our laboratories.

Precision assay by gravimetry or weight titrimetry offers the same success that it has long had for the evaluation of primary standard materials. Weight titrations to a photometric end-point, based on the formation of a metal complex with EDTA have been applied successfully to precision assay (see below). Gas chromatography is applicable to many classes of organic compounds, even high-melting polycyclic hydrocarbons, and can detect as little as 0·01% of an impurity. Subtraction from 100 thereby provides a "GC assay" value to 99·99%.

Differential scanning calorimetry (DSC) is promising for the assessment of chemicals that undergo melting without significant decomposition.[3] Computer processing[4] of the enthalpy-temperature data has been found to reduce labour costs markedly. At mole purities above 99·99% the premelting zone from which the impurity value is derived becomes so small that the purity assigned becomes markedly dependent on the assumptions in the calculations. The practical upper limit of the DSC technique may therefore be about 99·95%, although numerical values as high as 99·99% have been secured for some zone-refined compounds. The DSC technique is "blind" to solid solution formation and therefore should not be used as a sole criterion of purity, especially for chemicals purified by zone refining since this process is less effective when solid solutions form.[5] In our laboratories, for example, for an aromatic hydrocarbon purified by multipass zone refining the DSC technique indicated a mole purity of 99·96%, but gas chromatography gave a single impurity peak corresponding to 1·76%.[6]

Phase solubility analysis[7] is of special value for the assessment of thermally unstable, non-ionic compounds, such as urea.[8] This technique requires little equipment and allows determination of as little as 0·05% (by weight) of impurity.

For trace elements, survey emission spectrography has proved the most valuable single technique. By use of the recently introduced five-level standards with an internal standard,[9] over 40 elements can be evaluated routinely with favourable precision and accuracy. The limits of detection can be improved by preconcentration: organic compounds can be ashed; impurities in inorganic compounds can be collected by the 8-quinolinol–thionalide–tannic acid–indium system, especially if these reagents are used in a high-purity form; liquids such as volatile mineral acids can be evaporated. The limits of detection attained *via* these preconcentration techniques are listed in Table II for 10 key elements. Atomic absorption, especially with preconcentration, is valuable for particular elements.

TABLE II.—DETECTION LIMITS IN D.C.-ARC SPECTROGRAPHY, *ppm*

Element	Ashing*	Collection†	Evaporation‡
Ca	1	0·01	0·0001
Cr	0·1	0·002	0·001
Co	0·1	0·01	0·001
Cu	0·01	0·001	0·0001
Fe	0·02	0·002	0·001
Pb	0·2	0·02	0·001
Mg	0·002	0·0002	0·00005
Ni	0·1	0·02	0·001
Na	2	—	0·001
Zn	2	0·2	0·001

* 50-fold concn.

† 500-fold concn. *via* use of 8-quinolinol-thionalide-tannic acid system with indium.

‡ 10000-fold concn. by evaporation of an acid.[13]

For inorganic compounds of high purity, the determination of anions and nonmetal impurities has often been neglected. So-called "spectrographic grade" chemicals may contain significant anionic impurities. In our experience a costly metal carbonate of alleged 99·99+% purity by emission spectrography was found by acid-base titrimetry to assay only 77·7%; this discrepancy was traced to the presence of over 20% of the metal nitrate.[10] Conventional methods for the determination of anions[1] can be refined by optimizing conditions and by the use of purified reagents to give the detection limits shown in Table III.

Thin-layer chromatography on flexible sheets coated with various adsorbents is valuable in the control of high-purity organic chemicals. A sample can be put on a variety of such sheets and developed rapidly with a number of solvents. Appearance of a spot other than that of the major component immediately indicates that an impurity is present.

For organic liquids, low-level electrical conductivity measurements are valuable. Since literature values for a given compound can range over one or more orders of magnitude, the technique is best used only for the specification of minimum purity.

The general tests summarized in Table III and commonly employed with laboratory-use chemicals[1] can be of value with high-purity chemicals. Evaluation of the residue on evaporation should be considered for any organic liquid purified by preparative gas chromatography to ensure that no substantial bleed of the high-boiling liquid stationary phase has occurred. Some suppliers have overlooked such

TABLE III.—DETECTION LIMITS FOR ANIONS AND FOR SOME GENERAL TESTS

Test	Sample size, *g*	Detection limit, *ppm*
Arsenic (As)*	5	0·05
Bromide (Br) in presence of chloride†	2	1
Halide (as Cl)§	5	1
Phosphate (PO_4)‡	5	1
Sulphur compounds (as SO_4)§	8	0·5
Ash (sulphated)¶	5	20
Loss on drying¶	5	10
Particulate matter‖	10	10

* Evolution and silver diethyldithiocarbamate photometry.

† Hypochlorite oxidation, bromination of *p*-rosaniline, and photometry.

§ Turbidimetry.[1]

‡ Heteropoly blue photometry.

¶ Ref. 1.

‖ Membrane filtration and gravimetry.

contamination by limiting the final control to analytical gas chromatography. Any significant residue can be examined by infrared or other appropriate techniques. Similar remarks apply to materials purified by liquid adsorption chromatography, especially if large volumes of eluent have been used.

High-purity mineral acids, including hydrochloric, hydrofluoric, nitric, perchloric, and sulphuric acids, are used for the dissolution of diverse materials, including lunar samples.[11,12] The introduction of high-purity acids with certificates of actual lot analysis is a significant development. Many trace elements can be determined by emission spectrography after evaporation of the acid under contamination-free conditions (see Table II).[13] The containers for such products (borosilicate glass, or fluorocarbon polymer for hydrofluoric and perchloric acids) are preleached with acid and the filled containers are stored in a cold room at 0° until shipped. In this way purity on delivery corresponds closely to purity on analysis.

Phosphoric acid is a non-volatile acid and so not readily purified. Phosphorus pentoxide, however, can be sublimed to give high purity. The resulting product serves for the preparation of the high-purity phosphoric acid used to dissolve lunar and geochemical samples, especially for isotope abundance studies.[11] Mass spectrometric evaluation of this oxide by a number of laboratories indicates that a lead content of less than 1 ppM (parts per milliard) has been attained. Twelve trace metals have been determined in this oxide, following the technique of Kuzmin and co-workers[14] by neutralization of the derived phosphoric acid and extraction with high-purity 8-quinolinol; the organic extract is evaporated, mineralized, and subjected to d.c.-arc spectrography. In this way all twelve of the metals were found to be present at less than 0·1 ppm and ten of them at less than 20 ppM.[13]

Some high-purity analytical reagents have been prepared; 8-quinolinol has been purified to a total multivalent metal content of less than a few ppm and characterized by over 35 determinations and tests. This chelating agent has proved valuable as an analytical collector (with indium) and as an extractant in trace metal analysis (see above). EDTA, as the free acid, has also been purified (see below).

Standards constitute an important application for high-purity chemicals. Noteworthy has been the large scale production of "ultrapure" calcium carbonate. Remarkably, the strontium content could be reduced to a few ppm. This product is suitable as a primary acid-base and chelometric standard, and has now been certified by the National Bureau of Standards[15] as a clinical standard for calcium.

HIGH-PURITY EDTA

EDTA represents one of the most versatile organic compounds introduced during the past 30 years. As the free acid and simple salts, it finds tonnage application across the entire spectrum of the chemical, food, and pharmaceutical industries.[16,17] In the laboratory, EDTA finds extensive use as a chelating agent[18] and is usually employed in a purified or reagent grade. For the latter grade, specifications and associated procedures have been published by a number of groups.[1,19–21] Additionally a number of analytical studies have made of determination of the nitrilotriacetate (NTA) content of the product[22–26] and of the trace metal content.[27–29]

Interest has developed in an EDTA product of highest purity and close analytical definition. On one hand there is interest in a high-assay product low in nitrilotriacetate content, suitable for use as a chelometric standard, and allowing the simple, direct preparation of an EDTA solution of known concentration. On the other hand need exists for an EDTA product extremely low in multivalent metal content for use as a masking agent in analysis and in the crystallization of ultrapure salts, and as a reagent in enzyme and diverse biochemical studies.

The preparation and analytical definition of high-purity EDTA, as the free acid, has been undertaken in the framework of the extensive programme described in the introduction to this paper.

PREPARATION OF HIGH-PURITY EDTA

The commercial production of EDTA and related compounds has long involved purification based on the solubility of the sodium salts in water and the low solubility of the free acids. The solubility of EDTA as the free acid has been reported[31] to be 0·050 g/l. in water and to increase from 0·6 to 2·5 g/l. in 0·01–1·0*M* hydrochloric acid. The conjoined use of an alcohol in the purification may be of help in reducing the amounts of NTA and intermediates present.[32] Such approaches are utilized in producing EDTA to meet reagent-grade specifications. For the production of high-purity EDTA, as the free acid, the reagent grade disodium salt dihydrate is a feasible starting material. The laboratory procedure given below involves starting with 300 g of this salt, but has been successfully scaled up to the use of 10 kg. All operations must be conducted with meticulous attention to possible contamination and all laboratory ware must either be thoroughly leached with concentrated hydrochloric acid or be treated with a hot, strongly alkaline solution of EDTA. All dilutions should be made with doubly distilled water.

Procedure for preparation of high-purity EDTA

1. Dissolve 300 g of reagent grade disodium (ethylenedinitrilo)tetra-acetate dihydrate ('Baker Analyzed', Commodity No. 8993 or equivalent) in 3·3 l of water by shaking in a polyethylene bottle. Fit a 5-l. borosilicate filter flask with a Millipore filtration assembly and filter the solution through a 0·25-μm solvent-resistant membrane filter (Millipore No. UGWP04700). Transfer the filtrate to a 4-l. polyethylene beaker and add slowly reagent-grade hydrochloric acid (1 + 1, about 250 ml) until the pH is 1·5–2·0 (pH paper). Separate the precipitated EDTA, using a 5-l. borosilicate filter flask with a 126-mm porcelain Buchner funnel and a circle of hardened filter paper (Whatman No. 41H). Wash well with water.

2. Place the product from the previous step in a 4-l. polyethylene beaker, add 3·3 l. of water and then enough reagent-grade 50% sodium hydroxide solution (about 80 ml) from a polyethylene container to dissolve the EDTA and to bring the solution to pH 4·5–5·5 (pH paper). To ensure that the minimum amount of base is used, add it very slowly while stirring vigorously. Again precipitate EDTA with hydrochloric acid (1 + 1) and collect and wash as in step 1.

3. Repeat the operations of step 2 three more times. If the process must be interrupted for an extended period, finally wash the EDTA on the filter with acetone and then twice with ether, then dry in air or vacuum, and store under nitrogen or argon.

4. Dissolve the product from the final precipitation of step 3 with sodium hydroxide as described in step 2. Using a membrane filter as described in step 1, filter the solution and examine it under appropriate illumination to ensure that particulate matter is virtually absent. Precipitate EDTA as described in step 2. Allow the precipitate to settle with the beaker covered.

5. Decant the supernatant liquid, transfer the precipitate to a 2-l. polyethylene beaker, and slurry with 1 litre of water free from particulate matter. Cover the beaker tightly with polyethylene foil and allow to stand overnight at room temperature. Collect the precipitate on a 126-mm porcelain Buchner funnel fitted with a circle of Dacron filter material cut from an E & D Sparkler filter No. 940, (Keeler Co., Wyomissing, Pa.) or equivalent. Wash well with water.

6. As in step 5, again slurry the collected wet precipitate with water, allow to stand for 30 min, collect the precipitate on a Dacron filter, and wash well with water. Repeat this cycle four times. After the final collection, wash the precipitate with water until the washings are chloride-free (silver nitrate test), then twice with reagent-grade acetone, and twice with reagent-grade ether. Air-dry the resulting powder, taking care to protect it from contamination. Store the product in a polyethylene bottle under nitrogen or argon. The yield is 175–180 g.

Remarks. In the production of high-purity chemicals, almost all products, inorganic or organic, are routinely isolated and stored under a protective atmosphere of either nitrogen or argon. Whether this precaution is actually required for high-purity EDTA has not been established. As for all high-purity materials any proposed transfer or subdivision of the final analytically defined product must be considered carefully in order to ensure that the product will not be contaminated.

CHARACTERIZATION OF HIGH-PURITY EDTA

Adequate analytical definition of high-purity EDTA for diverse use involves establishment of the EDTA content through assay or elemental analysis or both, the application of various general and specific methods and tests, and the determination of key trace elements. All of the procedures developed can be described as both practical and economically feasible. Many of the approaches, moreover, are immediately applicable to many other high-purity organic chemicals.

Assay

The evaluation of a standard material by precision titrimetry is often based on a difference approach: in the simplest case, to a weighed amount of the standard a weighed amount of a reagent of unambiguous purity is added, that is either slightly greater or less than that required for complete reaction. This small difference is then measured by a conventional volume-based titration, often with a dilute solution of either the standard or the reagent as titrant. The difference approach has now been applied to EDTA in the free acid form in two ways: its titration as an acid and as a chelating agent.

Assay via *acid–base titrimetry.* A conventional potentiometric acid–base titration of EDTA has been performed by various workers, especially in fundamental studies. From the acidity constants of EDTA (1×10^{-2}; $2{\cdot}1 \times 10^{-3}$; $6{\cdot}9 \times 10^{-7}$; $7{\cdot}4 \times 10^{-11}$)[33] it is apparent that it can be titrated as either a diprotic or a triprotic acid.

A weighed amount of EDTA is taken and brought beyond the third equivalence point by addition of sodium hydroxide solution from a weight-burette. The excess of base is titrated conventionally with dilute hydrochloric acid to a potentiometric end-point. The dilute hydrochloric acid is prepared by dilution of a stock solution standardized by precision silver chloride gravimetry.[34] Additionally this stock solution is used for the standardization of the sodium hydroxide solution *via* weight titrimetry.

Assay via *titration as a chelating agent.* The difference approach can also be applied to precision chelometric titration of high-purity EDTA. A weighed amount of calcium carbonate is reacted with a substoichiometric amount of EDTA. The small excess of calcium in the solution, buffered to pH 9·5, is titrated photometrically with a solution of a weighed amount of the same EDTA dissolved and diluted to known volume. Calmagite (3-hydroxy-4-[(6-hydroxy-*m*-tolyl)azo]-1-naphthalenesulphonic acid)) serves as the indicator.[35] A phototitrator essentially of the design of Flaschka and Sawyer[36] is employed.

Ringbom[37] has shown how mathematical analysis can be applied to the selection of conditions for a chelometric titration to a photometric end-point. Calculation indicates that the photometric titration of calcium with EDTA at about pH 9·5 ($\log K_{\mathrm{CaY}} = 9{\cdot}7$, $\mathrm{pCa_{eq}} \sim 5{\cdot}7$) with Calmagite as the indicator ($\mathrm{pCa_{trans}} = 3{\cdot}2$) should have an adequate "break point". A typical titration curve is shown in Fig. 1.

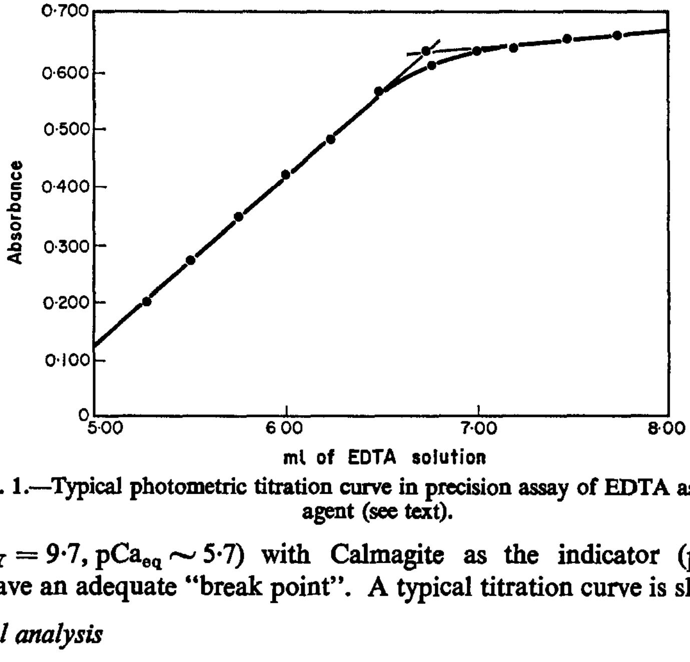

FIG. 1.—Typical photometric titration curve in precision assay of EDTA as chelating agent (see text).

Elemental analysis

As with many organic products, elemental analysis is applied as a preliminary, inexpensive method to ensure that no blunder had occurred during the preparation. Carbon and hydrogen are determined by a conventional micro-combustion technique and nitrogen by a micro-Kjeldahl procedure.

Ash (sulphated)

The conventional determination of the ash (that is, the residue on ignition), often with sulphuric acid added, is a valuable proximate method; however, with materials of low ash content a large sample must be ignited to yield weighable amounts of ash. This limitation becomes most serious with high-purity chemicals because of the preparative cost.

Loss on drying

Experience gained over some years in the examination of reagent-grade EDTA indicates that 105° is a suitable temperature for determination of the loss on drying. Selection of this temperature is supported by differential thermal analysis and thermogravimetric studies by Wendlandt.[38]

Nitrilotriacetate content

For use as a chelometric titrant, EDTA must have a sufficiently low nitrilotriacetate content. The presence of this weaker chelating agent has an adverse effect on the colour change of the metal indicator in some titrations[23] and may influence the titre of an EDTA solution toward different metals.[23,24] Indeed, as little as 1% NTA in EDTA can be determined by titration with different metals at suitable pH values and with appropriate metal indicators.[25] Potentiometric indication allows an NTA content as small as 0·5% to be recognized.[23]

Daniel and LeBlanc[22] have reported that 1% or more NTA in EDTA can be detected both by infrared analysis and by spectrophotometric measurements of the chelates with various metals. However, none of these methods is as sensitive as the polarographic examination of the cadmium–NTA wave, which precedes that for the cadmium–EDTA wave. This method was introduced by Daniel and LeBlanc.[22] who reported that as little as 0·03% w/w of NTA could be determined in EDTA. The method was modified and simplified by Farrow and Hill;[24] by use of a larger sample and a cathode-ray polarograph, NTA down to 0·002% in EDTA was determined by those workers. The polarographic approach has been adopted in the specifications for reagent-grade EDTA.[1,19] The procedure given by *Reagent Chemicals*[1] employs d.c. polarography and in our hands a limit of detection of 0·02% NTA has been established.

Freeman and his associates have summarized in an informal report[26] some experiments on the silylation of EDTA with bis(trimethylsilyl)acetamide and gas chromatographic examination of the reaction products; a peak attributed to nitrilotriacetic acid was resolved at a content of 1%. Such silylation has been briefly restudied by us with the aim of extension to smaller NTA contents. However, the complexity of the reaction mixture and the size of the blank made quantification of the results impossible.

Thin-layer chromatography

It was hoped that thin-layer chromatography might be useful in the detection of trace organic impurities, especially NTA; however, no separations of EDTA and NTA were achieved with a variety of adsorbents and simple solvent systems. Heinerth[39] recently reported the resolution of these compounds on a silica gel plate, with a 5:5:1:1 mixture of dichloromethane–ethanol–aqueous ammonia–water for development, and the copper(II)–PAN complex for visualization. In our laboratories, this separation was confirmed; no impurity spot was found with high-purity EDTA, but NTA could be detected only at a content of 1% or above.

Particulate matter

The particulate matter, that is, the insoluble matter, is evaluated by membrane filtration gravimetry after dissolution of the EDTA in aqueous ammonia.

Arsenic

Arsenic is determined by the silver diethyldithiocarbamate method of Vašak and Šedivec[40] following destruction of organic matter, effected essentially by the general wet ashing procedure recommended by Middleton and Stuckey,[41] employing

96% nitric acid but with the addition of a small amount of sulphuric acid to ensure that arsenic losses are negligible. The procedure is somewhat tedious, but allows the determination of arsenic down to 50 ppM.

The recent findings of Dubois and co-workers[42] have resolved some of the problems initially encountered in the application of this photometric method to extremely low arsenic contents. These workers identified difficulties associated with the presence of silver(I) in excess of that required for the formation of the 1:1 silver diethyldithiocarbamate complex. They also established that when the reagent is recrystallized from pyridine–water, the absorbance maximum is shifted to 525 nm from the longer wavelengths suggested by earlier workers.

Chloride

Since the preparation of high-purity EDTA involves the addition of hydrochloric acid, determination of the trace chloride content of the product is mandatory. A conventional silver chloride procedure with visual comparison of the turbidity with that of standards is applicable; however, it was found that hydrogen peroxide must be added to avoid the otherwise observable reduction of silver.

Trace elements by emission spectrography

Photometric methods have been devised for the determination of copper[27] and iron[27,28] in EDTA. Various trace metals have been determined polarographically, copper, lead, cadmium, and zinc after ashing of the sample, and iron directly.[29] The determination of ten or more trace elements in individual samples not only would be costly in development and working time but might require as much as 2–10 g of the expensive product for each element. Survey emission spectrography after ashing has been applied routinely to the determination of the trace element content of many high purity compounds. Ashing procedures have been reviewed critically by Koch and Koch-Dedic.[43] The procedure employed in the present work involving moistening with sulphuric acid and this pre-ashing treatment appears sound and well founded.

EXPERIMENTAL

For all precision operations use only Class A volumetric ware at or near calibration temperature. All dilutions should be made with doubly distilled water.

Reagents

Hydrochloric acid, 1M. Standardized gravimetrically with high-purity silver as described by Strouts, Wilson and Parry-Jones,[34] exercising all the care and precautions recited by those authors. Store the solution in a heavy-wall polyethylene bottle. Express concentration as mole/kg.

Hydrochloric acid, ~0·5M. Transfer a suitable weight of the 1*M* acid (~50 g) *via* a weight-burette to a 100-volumetric flask and dilute with water to the mark. Express the concentration in terms of g of 1*M* acid per ml.

Sodium hydroxide, 1M. Prepare a 1-litre quantity of approximately 1*M* sodium hydroxide from reagent-grade 50% sodium hydroxide solution and freshly boiled distilled water. Since not all of the solution is used immediately, divide it between several 250-ml screw-cap polyethylene bottles. Screw each cap on fully, invert the bottle, and squeeze to verify that the cap makes an effective seal. Wrap the cap and bottle neck with polyvinyl chloride tape. Standardize the solution against the 1*M* hydrochloric acid by precision weight titrimetry with potentiometric indication, following the recommendations of Strouts and co-workers.[34] Express concentration as mole/kg.

Calcium carbonate. Use calcium carbonate of primary standard quality and take the assay value into account. Preferably establish the assay by acid–base weight titrimetry against the 1*M* hydrochloric acid.

High-purity aqueous ammonia. Bubble high-purity ammonia gas from its cylinder first through an ammoniacal solution of EDTA and then through water and with good cooling absorb in water contained in a polyethylene bottle. Continue the operation, taking care to avoid suck-back, until saturation is approached (sp. gr. 0·900).

Ammoniacal buffer, pH 10. Mix 70 g of reagent grade ammonium chloride and 570 g of high-purity aqueous ammonia and dilute with water to 1000 ml. Store in a polyethylene bottle.

Calmagite indicator powder. Grind 0·20 g of Calmagite with 2·0 g of sucrose to a fine powder, with a mortar and pestle.

High-purity EDTA, 0·05*M*. Weigh 3·77 g of the EDTA under evaluation to the nearest 0·1 mg, dissolve it in about 175 ml of water with addition of high-purity aqueous ammonia, and dilute in a 250-ml volumetric flask with water to the mark.

Inert gases. Use high-purity nitrogen. Alternatively use carbon dioxide-free air scrubbed with sulphuric acid and then passed successively through a soda-lime tower and a smaller tower filled with Ascarite.

Apparatus

Modified titration flask. Take a 500-ml wide-mouth conical flask. At a point 80 mm from the bottom seal in a 6-mm outside diameter right-angled tube. One end of the tube should extend through the flask wall to form a short side-arm and the other end nearly to the bottom of the flask, but well off-centre so that free movement of a magnetic stirring bar is possible and flow from a burette will not fall on the tube. (If a flask fitted with a standard taper ground-glass neck is used, the modified flask can be used to advantage in titrations where carbon dioxide is evolved, by attaching an extension consisting of a full length standard taper inner joint.)

Phototitrator. Use a phototitrator of the design of Flaschka and Sawyer[46] or equivalent.

Procedures

Assay of EDTA by acid–base titration. Put 3·3–3·5 g of the EDTA, weighed approximately, into a 100-mm long vial having a polyethylene "snap" cap, dry with the cap off at 105° for 2 hr, and allow to cool to room temperature in a desiccator. Weigh the sample by difference (to 0·1 mg) into a modified 500-ml titration flask with the side-arm capped with either a closed length of plastic tubing or a rubber policeman. Transfer the sample by holding the vial upright in utility tongs held vertically, inverting the flask over the vial so that the vial mouth reaches to the bottom of the flask, and then up-ending the vial and flask together so that the vial contents fall to the flask bottom without dusting.

Add about 250 ml of water, insert a magnetic stirring bar, and start the flow of either high-purity nitrogen or carbon dioxide-free air. Continue the magnetic stirring and flow of gas for about 15 min. Introduce a thin combination calomel-glass electrode pair connected to an expanded-scale pH-meter. Continue the stirring and passage of gas during the titration. Slowly add the standardized 1*M* sodium hydroxide by means of a 60-ml weight-burette until pH 9·0–9·1 is reached. Since EDTA as the free acid is water-insoluble and dissolves only slowly as base is added, take care that all of the sample dissolves, especially any particles that may creep up the flask walls. Record, to the nearest mg, the weight of the sodium hydroxide delivered. Now back-titrate with the ~0·5*M* hydrochloric acid delivered from a 10-ml burette (0·02-ml divisions) in exactly 1-ml increments. Record the pH value attained after each addition from the start to below pH 7. Calculate the end-point volume by means of second differences in the pH values. Conduct the assay at least in triplicate.

Assay of EDTA by chelometric titration. Weigh approximately 5·86 g of the EDTA into a tall-form weighing vial, dry with the cover off at 105° for 2 hr, and allow to cool in a desiccator. Weigh by difference a sample of the standard calcium carbonate (1·0 g) to 0·01 mg into a 150-ml tall-form beaker containing a magnetic stirring bar. With 10 ml of water wash down the beaker walls and with stirring slurry the carbonate. Cover the beaker with a watch-glass and lift it momentarily to add 10 ml of reagent-grade hydrochloric acid. Complete the dissolution with stirring. Weigh by difference the dried EDTA (5·85 g) to 0·01 mg into the solution and stir briefly. Add dropwise high-purity aqueous ammonia until pH 7·0 is attained. Now add pH 10 ammoniacal buffer with stirring until pH 9·5 is just reached. Transfer the solution quantitatively to the sample cell of the phototitrator and dilute with water to about 100 ml. Position the borosilicate glass stirrer in the cell and adjust the stirring rate so that air bubbles do not occur. Use the 665-nm filter and adjust the galvanometer scale reading to zero for the dark-current and to 100 for the solution. Now add 0·050 g of Calmagite indicator powder and stir until dissolution is complete. Titrate with the 0·05*M* solution of the high-purity EDTA being evaluated, using a 10-ml burette with 0·02-ml divisions.

Record the transmittance readings after each titrant addition. Plot on linear graph paper either absorbance values (taken from a transmittance–absorbance conversion table) or the logarithms of the scale readings against the volume of EDTA solution added. Alternatively plot on semilogarithmic paper the scale readings (log) against the volume of titrant (linear). Since the end-point region used covers only 2 or 3 ml in a total solution volume of over 100 ml, volume corrections are unnecessary.

The end-point corresponds to the intersection of the extrapolations of the inclined and second horizontal portions (see Fig. 1).

Perform the assay at least in triplicate.

Elemental analysis. Determine carbon and hydrogen by conventional microcombustion techniques and nitrogen by a micro-Kjeldahl procedure. Theoretical values for $C_{10}H_{16}N_2O_8$ are 41·01% C, 5·52% H, and 9·59% N.

Ash (sulphated). Use a 5·0-g sample of the EDTA and the procedure given in *Reagent Chemicals*[1] for the determination of the residue after ignition. With this sample weight a sulphated ash content as low as 0·002% can be determined.

Loss on drying. Weigh a 4-g sample of the EDTA to the nearest 0·01 mg, dry for 2 hr at 105°, and reweigh after cooling in a desiccator.

Nitrilotriacetate. Follow the procedure given in *Reagent Chemicals.*[1] The limit of detection by this procedure is 0·02% NTA. The scan need not be confined to the prescribed range, but can be extended over the entire possible range; no spurious wave should occur.

Particulate matter. Slurry a 10·0-g sample of EDTA with 180 ml of water and add sufficient reagent-grade aqueous ammonia (2·3 ml) to effect dissolution; both the water and aqueous ammonia used should be filtered through membrane filters just before use. The pH should be below 7·0. Then use the general gravimetric procedure of the Millipore Corporation,[44] using a 25-mm diameter 0·80-μm membrane filter. Use of a 10-g sample allows the determination of less than 5 ppm by weight of particulate matter.

Arsenic. Weigh a 5·00-g sample of EDTA into a 500-ml iodine flask and add 20 ml of doubly distilled water, 2 ml of reagent-grade sulphuric acid and 10 ml of 70% reagent-grade nitric acid. Place a small short-stem glass funnel in the mouth of the flask. Since the initial reaction can proceed vigorously, warm the flask on a steam-bath until reaction starts, remove promptly, and allow to stand until the reaction terminates.

For the following operations use a hot-plate reliably adjusted to 300°, confirmed, for example, by a surface spot-check thermometer. Evaporate to fumes, partially cool the flask to allow addition of 2 ml of 90% reagent-grade nitric acid, and again evaporate to fumes. Repeat this addition of 2 ml of 90% nitric acid four more times or until there is no darkening of the reaction mixture. Finally, to remove nitric acid, remove the small funnel from the flask mouth and twice add 10 ml of water, evaporating to fumes after each addition.

Cool the solution and transfer it quantitatively with water to the arsine generator flask (conventional design) and determine the arsenic content by the method of Vašák and Šedivec.[40] Read the absorbance at 525 nm, preferably using a 50-mm cell, against the silver diethyldithiocarbamate reagent solution. Run a reagent blank for the entire procedure and correct the absorbance. Read the result from a standard curve, but run a standard with each group of samples to check the validity of the curve. Use of a 5-g sample allows the determination of an arsenic content as low as 50 ppM.

Chloride. Add 5·0 g of the EDTA to 35 ml of water and add sufficient reagent-grade aqueous ammonia (~3 ml) to dissolve the sample. Now add sufficient reagent-grade nitric acid to bring the pH to 3·5, stir, add 0·5 ml of reagent-grade 30% hydrogen peroxide, stir, and add 1 ml of 0·1*M* silver nitrate. After 5 min compare visually the turbidity developed with that of chloride standards prepared to include 3·5 ml of aqueous ammonia and 0·5 ml of 30% hydrogen peroxide and with nitric acid added to pH 3·5. Use of a 5-g sample allows determination of a chloride content as low as 5 ppm.

A refinement of this procedure was also studied in which sufficient nitric acid is added to precipitate EDTA as the free acid, the precipitate is separated by filtration, and washed with a small volume of dilute nitric acid. The combined filtrate and washings are used in the procedure as given. Since identical results were obtained, this refinement seems unnecessary.

Trace elements by emission spectrography. Transfer 2·5 g of the EDTA to a porcelain evaporating dish, moisten with 2 ml of high-purity concentrated sulphuric acid, and pre-ash under contamination-free conditions in a pre-ashing chamber.[45] Then add 25 mg of ultrapure or spectrographic grade lithium carbonate to the residue and ash in a muffle furnace, starting at room temperature, progressively raising the temperature to 450°, and continuing at this temperature overnight. Transfer the cooled residue to a weighed polystyrene vial. Add sufficient lithium carbonate to give a total weight of 50 mg and mix in a vibrator mill for 30 sec. Transfer 10 mg of the mixture to the crater of a preformed high-purity graphite electrode [3/16-in. (5-mm) neck, 3/16-in. (5-mm) deep crater], and use a ¼-in. (6-mm) preformed high-purity graphite counter electrode. Excite with a direct current of 15 A for 120 sec, maintaining a 4-mm gap throughout the burn. Record the 245–460 nm wavelength region on an spectrum analysis plate.

Develop, fix, rinse, and dry the plates in a conventional manner. Read the lines in the 245·0 to 387·5 nm region as well as strontium at 407·8 nm, calcium at 422·7 nm, and barium at 455·4 nm, against commercial standards in lithium carbonate. For key elements found absent, record the basic sensitivity as a "less than" value.

The key elements routinely read are listed for one lot in Table IV. These values were obtained with three-level commercial standards augmented by a fourth standard prepared by dilution of the lowest of those standards. The limits of detection for ten elements, employing 50-fold concentration by ashing as in the procedure above, are presented in Table II. If greater precision is desired, the recently introduced five-level spectrographic standards with indium as an internal standard can be used[9] and line-pair ratios can be measured densitometrically. Internal-line standards of this improved type are being routinely applied to other materials now under study in this laboratory.

TABLE IV.—CERTIFIED VALUES FOR ONE LOT OF HIGH-PURITY EDTA*

Assay ($C_{10}H_{16}N_2O_8$) after drying at 105°C for 2 hr	
Potentiometric acid–base weight titration	$100{\cdot}0_3$%†
Chelometric weight titration with photometric indication§	$100{\cdot}0_4$%‡
Elemental analysis	
Carbon (theory 41·01%)	41·3%; 41·3%
Hydrogen (theory 5·52%)	5·6%; 5·5%
Nitrogen (theory 9·59%)	9·6%; 9·6%
Ash (sulphated)	0·003%
Loss on drying at 105°C for 2 hr	0·07%
Nitrilotriacetate content¶	0·02%
Particulate matter (after dissolution in aqueous ammonia)	0·003%
Non-metallic impurities (*ppm*)	
Arsenic**	<0·05
Boron††	<0·2
Halide (as Cl)	30
Silicon††	0·01
Metallic impurities (*ppm*)††	
Aluminium	0·03
Antimony	<1
Metallic impurities (*ppm*)†† (*Contd.*)	
Barium	<0·04
Beryllium	<0·01
Bismuth	<0·1
Cadmium	<0·2
Calcium	0·1
Chromium	<0·1
Cobalt	<0·1
Copper	0·02
Gallium	<0·1
Germanium	<0·2
Gold	<0·2
Indium	<0·02
Iron	0·1
Lead	<0·2
Magnesium	0·01
Manganese	<0·02
Molybdenum	0·02
Nickel	<0·1
Niobium	<0·2
Silver	0·01
Sodium	25
Strontium	0·1
Tin	<0·1
Titanium	0·02
Vanadium	<0·02
Zinc	<2
Zirconium	<0·1

* Actual lot analysis, Lot UHC 331, ULTREX®, (Ethylenedinitrilo)tetraacetate Acid, J. T. Baker Chem. Co., as packaged under argon in vials. The data support assignment of a 100·0% EDTA value to the product as a chelometric standard.

† Average value for 5 determinations: $100{\cdot}1_0$, $99{\cdot}9_2$, $100{\cdot}0_5$, $100{\cdot}0_3$% and $100{\cdot}0_6$%.

§ Weighed amount of ULTREX® Calcium Carbonate, Lot UMO 450, assay 99·99% $CaCO_3$; reacted with a substoichiometric weighed amount of the EDTA. The small excess of calcium in the solution, ammoniacally buffered to pH 9·5, titrated photometrically with a standard EDTA solution, with Calmagite as indicator.

‡ Average value for 3 determinations: $100{\cdot}0_6$, $100{\cdot}0_4$, and $100{\cdot}0_2$%.

¶ By d.c.-polarographic assessment of the cadmium–NTA wave (−0·94 V *vs.* S.C.E.).

** By evolution and silver diethyldithiocarbamate photometry.

†† By d.c.-arc spectrography.

RESULTS AND DISCUSSION

Values, obtained by the procedures detailed above, for one lot of high-purity EDTA are summarized in Table IV. It will be seen that the agreement for replicates in the two assay procedures is excellent. The loss on drying, 0·07%, for this lot, is for the air-dried material. Obviously this content could be reduced by either vacuum-drying of the product or its heating at 105° for a suitable time; these operations would have to be conducted under contamination-free conditions. For the nitrilotriacetate, the value assigned for the smallest clearly discernible wave-height in the polarogram under the conditions of the procedure is 2 mm, and corresponds to 0·02% NTA. The lot described here showed a wave-height less than this and was conservatively assigned the value of 0·02% NTA. Significant reduction of the halide content (30 ppm) by more persistent washing in the final step of preparation has been unsuccessful. Sodium at 25 ppm is the only metal impurity present significantly above the 1-ppm level. Most of the common metals are present, if at all, at concentrations below the basic sensitivity for them of the spectrographic procedure adopted.

The total amount of EDTA required for the conduct of the various procedures described is about 80 g. Obviously the detection limits of certain of the procedures might be improved by use of larger samples. However, economic considerations speak against this since for a 1-kg lot about 8% is already consumed in the analytical characterization. Some improvement might be secured by using a single portion of the EDTA for more than one determination. However, our experience indicates that if such a portion is carried consecutively through several procedures contaminants accumulate and high blanks result, thereby off-setting any advantages gained.

The question arises as to what else might be attempted in the way of further routine characterization of high-purity EDTA. Gas chromatography after silylation has failed (see *Nitrilotriacetate* in the introduction). According to our results and those of Wendlandt,[38] the temperature of decomposition as measured by thermal analysis appears to have no simple relation to purity.

Mercury is not reported in the spectrographic analysis since this element is probably largely volatilized in the ashing process.[43] For this element highly selective photometric determination based on extraction with dithizone at pH 4–5 with EDTA present to mask any elements might be considered.[46] Silver is the only significant interference reported. In our hands, with various high-purity inorganic salts, the method has given satisfactory results for mercury contents of 1–5 ppm. Conceivably this extraction–photometric method might be adapted for analysis of EDTA.

For the detection and quantification of trace elements spark-source mass spectrometry might also be considered.

One of the problems encountered in this work was how to dissolve the sample of EDTA for analysis. The free acid form of EDTA is relatively insoluble in water and only slightly soluble in many organic solvents, both common and exotic. Usually the free acid is dissolved in water by the addition of sodium or potassium hydroxide, and occasionally with aqueous ammonia. Sodium and potassium hydroxides are as yet not available with sufficiently low multivalent metal content, and reagent-grade aqueous ammonia supplied in glass bottles is high in silica content. Where a solution of the sodium salt is desired, high-purity sodium carbonate can be used. To a water slurry of EDTA an equimolar amount of anhydrous sodium carbonate is added in small portions with precautions to avoid loss by effervescence. To eliminate most of the carbon dioxide the mixture is stirred until reaction ceases and is then warmed briefly and aerated with nitrogen or filtered air for 20 min. The resulting solution has a pH of 4·4–4·5. If dissolution is still incomplete at the required EDTA concentration, additional sodium carbonate or hydroxide is added till pH 5·0 is reached. When a solution of the ammonium salt is to be made, ammonia gas is either bubbled directly into a cooled EDTA slurry or is absorbed (with cooling) in water and the resulting solution used promptly (see under *Reagents*). These two approaches should be of interest for any application of EDTA where low multivalent metal content is mandatory. Indeed these approaches should be considered whenever reagent-grade EDTA, as the free acid, is to be utilized in the laboratory.

For a standard material, the rate of moisture pick-up on exposure to air should be small. For the lot described in Table IV, a portion of the powder was dried at 105° for 2 hr and 3 g of this dried material, weighed to the nearest 0·01 mg, were loosely spread over an area of $1{\cdot}6 \times 10^{-3}$ m^2 on the bottom of a weighing bottle. The open bottle was kept at 50% relative humidity (saturated calcium nitrate solution) and room temperature. After 24 hr the weight had increased by less than 0·01% and then remained essentially constant over a 5-day period.

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Zusammenfassung—Hochentwickelte Laboratorien benötigen Chemikalien hoher Reinheit mit weniger als 500 ppm Gesamt-Verunreinigungen (ultrareine Chemikalien) mit ausführlichen analytischen Angaben für jede Partie. Wirtschaftlich durchführbare Methoden zur praktischen Analyse solcher Chemikalien, sowohl im anorganischen als auch im organischen Bereich, werden skizziert. Bei der Untersuchung von Mondproben und anderen hochentwickelten Untersuchungsprogrammen verwendete Verbindungen werden erwähnt. EDTA wurde durch Lösen in wasser mit Base und Fällen mit Säure als freie Säure hergestellt und ausführlich charakterisiert. Eine Präzisionsgehaltsbestimmung wird durch Wägetitration, potentiometrisch als dreibasige Säure und photometrisch als Chelatbildner erreicht. Andere Prüfungen sind Elementaranalyse, Veraschung, Gewichtsverlust beim Trocknen und Staub sowie Proben auf Nitrilotriacetat, Arsen und Chlorid. Bor, Silicium und Spurenmetalle werden durch Emissionsspektrographie bestimmt. Viele der Verfahren lassen sich auf andere organische Chemikalien hoher Reinneit anwenden.

Résumé—Les laboratoires de niveau supérieur ont des exigences pour des produits chimiques de haute pureté avec moins de 500 *p.p.m.* d'impuretés totales (produits chimiques ultra-purs) et avec une large définition analytique de chaque lot. On délimite quelques progrès réalisables économiquement vers l'analyse pratique de tels produits chimiques, tant inorganiques qu'organiques. Les composés utilisés dans l'étude d'échantillons lunaires et dans d'autres programmes avancés sont notés. L'EDTA, à l'état d'acide libre, a été préparé par dissolution dans l'eau avec une base et précipitation par addition d'acide. Le produit a été grossièrement caractérisé. Le contrôle de précision est réalisé par titrimétrie pondérale, potentiométriquement en tant qu'acide triprotique et photométriquement en tant qu'agent chélatant. D'autres essais appliqués comprennent l'analyse élémentaire, les cendres, la perte au séchage, la matière particulaire, et des recherches de nitrilotriacétate, d'arsenic et de chlorure. Le bore, le silicium et les métaux à l'état de traces sont déterminés par spectrographie d'émission. Un grand nombre des techniques sont applicables à d'autres produits chimiques de haute pureté.

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EXTRACTIONS WITH LONG-CHAIN AMINES—I

EXTRACTION OF SOME METAL-XYLENOL ORANGE COMPLEXES INTO METHYLTRIOCTYLAMMONIUM CHLORIDE (ALIQUAT 336-S)

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Summary—The extraction of traces of metals forming intensely coloured complexes with Xylenol Orange in acidic medium (p H0–3) has been studied. For such extractions in the presence of sulphates, chlorides and nitrates, a solution of methyltrioctylammonium chloride (Aliquat 336-S) in chloroform has been used. It is shown that it is possible to detect small amounts of gallium in indium and *vice versa*, and titanium or zirconium in thorium. These reactions should be capable of adaption to spectrophotometric determinations. The principle of the extraction of metals as their complexes with various metallochromic indicators is briefly discussed.

AMONGST the many new reagents which have been synthesized for complexometric purposes during the last decade, Xylenol Orange (XO)[1,2] and Methylthymol Blue (MTB)[3] have been popular because of their sensitive reactions and very sharp colour change. Both have also been used for the colorimetric determination of at least twenty metals (see Table I), the low selectivity being partly overcome by choice of proper conditions (pH, masking agents). The extraction of highly coloured ion-association, ternary or uncharged complexes has also proved very useful by allowing the development of sensitive and simple colorimetric procedures. We have assumed that similar extraction of intensely coloured complexes of XO, MTB and other compounds of this type would be a welcome contribution to analytical chemistry.

All these complexes are anionic and all attempts to extract them directly with common organic solvents have failed. Recently Moore has found that methyltrioctylammonium chloride (Aliquat 336-S) is able to extract some complexes of such aminopolycarboxylic acids as EDTA, DTPA and HEDTA.[4,5] We can expect that complexes of XO or MTB could also be extracted with a suitable solution of this amine or of other high molecular weight amines which are now on the market (Alamine, Hyamine, Arquad, Zephiramine, *etc*).

Preliminary experiments were very promising. In some cases the extraction of XO–metal complexes proceeded smoothly under proper conditions (pH and presence of suitable anion), in some cases the metal complexes were extracted not at all or only partly. For example, indium is extracted from acidic solution very easily in the presence of sulphate or chloride but gallium is not. Similarly, zirconium and hafnium are extracted, but thorium is not. Also the action of masking agents in some cases differs from that in aqueous solutions. The extracted Ti–XO–H_2O_2 complex does not react with fluoride in chloroform–amine medium. Such selective extractions permit successive separation of trace metals and their colorimetric determination either in the aqueous or the organic phase.

TABLE I.—OPTIMAL CONDITIONS FOR COLORIMETRIC DETERMINATION OF METALS WITH XO

Metal	Acidity	Validity of Beer's law μg/25 ml	Reference
Zr	0·2*N* H_2SO_4	5–63	6
	0·5–1·0*M* $HClO_4$	—	7
Ga	pH 1·2–1·7	0–60	8
	pH 1·5–2·5	5–140	9
	pH 2	—	10
In	pH 3–4	5–80	11
Bi	0·08–0·15*N* H_2SO_4	20–100	12
	0·1–0·2*M* $HClO_4$	0–250	13
	0·1*N* HNO_3 or $HClO_4$ or HCl	10–80	14
Th	pH 2·7–3·3	2–80 per 10 ml	15
Tl	0·25–0·7*M* acetic acid	20–150	16
Ti	pH 3–4·5	—	17
Ti + H_2O_2	0·04–0·06*M* $HClO_4$	7–70	18
Cr	pH 1·9–2·2	0–30	19
	pH 3	—	20
Al	pH 3·4	0–50	21
	pH 3·8	0–60	22
	pH 3·4	5–25	23
Fe	0·04–0·06*M* $HClO_4$, HCl	5–50	24

In this paper we discuss the general conditions for extractive separation of some metal–Xylenol Orange complexes into a chloroform solution of Aliquat 336-S and some examples of qualitative detection of traces of metals. Further applications are also discussed briefly.

EXPERIMENTAL

Reagents

Amine hydrochloride solution. Chloroform solutions (5% w/w) of methyltrioctylammonium chloride (approx. 0·1*M*) were prepared by dissolution of 50 g of Aliquat 336-S in 1 kg of chloroform. Aliquat 336-S (General Mills Inc., Kankakee, Illinois, U.S.A.) is R_3CH_3NCl, where R is an aliphatic amine with 8–10 carbon atoms, with octylamine predominating (90–95%).

Metal ion solutions. Solutions ($5 \times 10^{-3}M$ and $5 \times 10^{-4}M$) of metal salts were prepared by proper dissolution of the nitrates or chlorides (acidified if necessary).

Xylenol Orange, 10^{-3}*M solution.* Prepared daily by dissolution of 70 mg of the reagent (Lachema, Brno) in 100 ml of redistilled water.

Other reagents. These include 0·1*N* hydrochloric, nitric and sulphuric acids either alone or 0·1*M* in potassium chloride, potassium nitrate or sodium sulphate respectively. Buffer solutions of pH 3·0 and 4·6 were prepared from acetic or chloroacetic acid and sodium hydroxide. Solutions at pH 5–5·5 were prepared from acid solutions of metals by adding a 5% solution of hexamine.

RESULTS

Extraction of XO-complexes

Xylenol Orange as a complexometric indicator is used only in acidic solutions from pH 0 up to pH 5–5·5. Above this pH coloured forms of the indicator such as H_2XO^{4-}, HXO^{5-} and XO^{6-} are formed. Complex formation is strongly dependent on the pH of the solution. Generally speaking, the lower the pH, the more selective are the reactions of Xylenol Orange. For this reason we have studied the extraction from relatively acidic solutions (pH below 3), where only a few elements react with XO. Table I includes the values of optimal pH for colorimetric determination of elements with XO. Other elements which react at pH >4 (bivalent metals, rare earths, *etc*) are not included. These are also extracted into a chloroform solution of Aliquat.

A great number of preliminary experiments, where the influence of pH and concentration of anions (nitrate, chloride, sulphate) on complex formation and extraction was studied, led to the adoption of the following procedure.

General procedure

To a test-tube, a solution containing 50 μg of metal was added and acidified with 5 ml of acid ($0{\cdot}1N$ H_2SO_4/$0{\cdot}1N$ Na_2SO_4 or $1M$ HCl/$0{\cdot}1M$ KCl or $0{\cdot}1M$ HNO_3/$0{\cdot}1M$ KNO_3) and diluted to 10 ml with redistilled water. After addition of 1 ml of $0{\cdot}001M$ XO the test-tube was warmed for 5 min in a boiling water-bath. After cooling, the solutions were extracted with 10 ml of the Aliquat solution in chloroform by vigorous shaking for 10 sec. After phase separation, the colour observed eventually gave rise to a precipitate at the interface. The observations were evaluated as follows:

(*a*) Quantitative extraction was indicated by a colourless or slightly yellow water phase and an intensely coloured organic phase. After addition of more XO the water phase became intensely yellow and a second extract was colourless or slightly yellow (free XO).

(*b*) In partial extractions, both phases were coloured (orange, red or violet). By repeated extraction with additional XO, the degree of extraction could be roughly estimated.

(*c*) Where no extraction took place, even of traces, the organic phase was yellow (free XO).

Table II shows the behaviour of some elements in the presence and absence of some masking agents (bromide for Tl and Bi, fluoride for Zr and Th).

TABLE II.—EXTRACTION OF XYLENOL ORANGE COMPLEXES WITH ALIQUAT

Ion	Medium: $0{\cdot}1N$ HCl + $0{\cdot}1M$ KCl	$0{\cdot}1N$ H_2SO_4 + $0{\cdot}1M$ Na_2SO_4	$0{\cdot}1N$ H_2SO_4 + $0{\cdot}1M$ Na_2SO_4		$0{\cdot}1N$ HNO_3 + $0{\cdot}1M$ KNO_3	
			+10% KBr	+10% KBr/ $1M$ NH_4F*	+10% KBr	+10% KBr/ $1M$ NH_4F*
Bi	O	+	O	O	O	O
Ga	—	—	—	—	—	—
Hg(II)	P	+	P	O	—	O
In	+	+	+	+	O	O
Fe(III)	P	P	—	—	—	—
Sc	O	O	O	O	O	O
Fe(II)	O	O	O	O	O	O
Th	O	O	O	O	—	O
Zr	+X	+	PX	O	OX	O
Cu(II)	O	O	O	O	O	O
Al	O	—	—	O	O	O
Pb	O	O	O	O	O	O
Ni	O	W	O	O	O	O
Co(II)	O	O	O	O	O	O
Ti(IV) + H_2O_2	—	+	—	P	P	—
Ti(IV)		+				
Mo(VI)		O				
W(VI)		O				
V(V)		+				

* After extraction in the presence of KBr, the phases were left in contact, NH_4F added, and the phases were shaken again.

+ Extraction into the organic phase.

— No extraction.

X Hydrolysis.

P Partly extracted.

O No reaction with Xylenol Orange.

W Very feebly extracted.

These results are worth studying because quantitative extractions should allow the development of new colorimetric procedures for traces of these elements. With Xylenol Orange we are able to detect less than 1 μg/ml. Because of shortage of Aliquat in our laboratory we have worked out only a few simple qualitative procedures.

Qualitative detection

Detection of gallium in the presence of indium. To a solution containing at least 10 μg of Ga add 5 ml of 0·1 N H_2SO_4/0·1M Na_2SO_4 and dilute to 10 ml with water. Warm the solution in a boiling water-bath, and add 1 ml of 0·001M XO. Allow to cool and shake vigorously for 10 sec with 10 ml of Aliquat solution. An orange-red colour in the water phase indicates the presence of gallium. An intense red colour in the organic phase indicates the presence of indium. This test is reliable up to the ratio In:Ga = 5000 (0·02% Ga).

The extraction can be repeated. Usually the chloroform extract is colourless. If we add to the separated aqueous phase 1 ml of 1M ammonium fluoride and shake again with Aliquat, the Ga–XO complex is extracted (fluoride masks traces of Zr, Hf, Ti and simultaneously raises the pH), and can be stripped by adding 0·5 g of potassium bromide to the aqueous phase and shaking again.

Detection of indium in the presence of gallium. The procedure described above can be used provided that the gallium is not in large excess. To the cold solution containing at least 15 μg of In add acid and water as above, then 1 ml of XO and 10 ml of Aliquat reagent. The red extract indicates the presence of indium, the aqueous phase is an intense orange. Indium can be detected up to ratio Ga:In = 250 (0·4% In).

Detection of gallium in the presence of bismuth. To the solution containing at least 10 μg of Ga add 1 g of potassium bromide and proceed as described above. An orange-red colour in the water phase indicates the presence of gallium. The limit of detection is 0·1% Ga.

In all these tests thallium, thorium and bivalent metals do not interfere. Iron does not interfere if it is first reduced with ascorbic acid.

Detection of zirconium in the presence of thorium. Take a solution of zirconium and thorium sulphates containing at least 10 μg of Zr, adjust the sulphuric acid concentration to 0·5N, add 1 ml of 0·001M XO and warm the solution in a boiling water-bath for 5 min. The solution becomes red-orange during warming. After cooling extract the solution with 5–10 ml of Aliquat reagent. An intensely red or red-violet chloroform phase indicates the presence of zirconium. The detection limit is 0·02% Zr.

In the presence of chloride and nitrate zirconium is hydrolysed during the procedure, but its presence is indicated by the appearance of a red-violet ring at the interface. The sensitivity remains the same.

Detection of titanium in the presence of thorium. To the solution of titanium and thorium in 0·1N sulphuric acid (containing at least 6 μg of Ti) add 1–2 drops of 30% hydrogen peroxide and 1 ml of 0·001M XO. Warm the solution in a boiling water-bath; the solution turns orange or intense red depending on the Ti concentration. Allow it to cool and extract with 5 ml of Aliquat reagent. An intensely red extract indicates the presence of titanium. The aqueous phase remains orange (Th). On addition of 0·5 ml of 1M ammonium fluoride, and shaking again, the orange colour of the aqueous phase disappears, but the colour of the organic phase does not change (Ti–XO–H_2O_2–Aliquat does not react with fluoride). The detection limit is 0·07% Ti.

If the solution contains more than 10 mg of thorium, then after addition of peroxide the thorium is precipitated, the extract becomes very cloudy and colour detection fails.

DISCUSSION

The experiments reported above are the first attempt to extract and successively separate the highly charged complexes of Xylenol Orange. Similar behaviour has been observed with Methylthymol Blue (useful as an indicator at pH 1–11), Glycinethymol Blue (selective for copper), and many others. Such extractions are dependent not only on pH and the chemical composition of the solution to be extracted, but also on the amine used. Extractions proceed differently with different extractants, *e.g.*, Aliquat, simple trioctylamine (Alamine) or tetradecyldimethylbenzylammonium chloride (Zephiramine). In addition, various metals can be suitably extracted as anionic complexes (or as simple anions such as CrO_4^{2-}, MnO_4^-) and determined directly with a specific reagent in the organic phase, with high sensitivity. Quantitative studies are now in progress.

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Zusammenfassung—Die Extraktion von Metallspuren wurde untersucht, die in saurem Medium (pH 0–3) mit Xylenolorange intensiv farbige Komplexe bilden. Für solche Extraktionen wurde in Gegenwart von Sulfaten, Chloriden und Nitraten eine Lösung von Methyltriotylammoniumchlorid (Aliquat 336-S) in Chloroform verwendet. Es wird gezeigt, daß man kleine Mengen Gallium in Indium und umgekehrt sowie Titan oder Zirkonium in Thorium nachweisen kann. Man sollte diese Reaktionen für spektrophotometrische Bestimmungen einrichten können. Das Prinzip der Extraktion von Metallen als Komplexe mit verschiedenen Metallfarbindikatoren wird kurz diskutiert.

Résumé—On a étudié l'extraction de traces de métaux formant des complexes intensément colorés avec l'Orangé Xylénol en milieu acide (pH 0–3). Pour de telles extractions on a utilisé, en la présence de sulfates, chlorures et nitrates, une solution de chlorure de méthyltriocytylammonium (Aliquat 336-S) en chloroforme. On montre qu'il est possible de détecter de petites quantités de gallium dans l'indium et *vice versa*, et le titane ou le zirconium dans le thorium. Ces réactions devraient pouvoir être adaptées aux déterminations spectrophotométriques. On discute brièvement du principe de l'extraction de métaux à l'état de complexes avec divers indicateurs métallochromes.

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INTERACTION OF PALLADIUM WITH SULPHAGUANIDINE

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Summary—The formation constants of palladium with chloride ions have been determined by a new approach to the interpretation of the ultraviolet spectra. The interaction of $PdCl_4^{2-}$ with sulphaguanidine (SG) has been interpreted and evaluated quantitatively. The formation constants of the mixed ligand complex $Pd(SG)_2Cl_2$, were determined spectrophotometrically. The stability constants for the stepwise formation of the palladium chloride complexes are: $\log k_1 = 3·48$; $\log k_2 = 2·79$; $\log k_3 = 2·35$; $\log k_4 = 1·1$, and for the interaction of $PdCl_4^{2-}$ with SG, $\log k_1 = 5·42$; $\log k_2 = 4·38$.

SULPHAGUANIDINE (SG), well known as a drug, was found by the authors to be a reagent with distinct selectivity for palladium. In slightly acidic aqueous media it yields an insoluble crystalline complex of the composition $Pd(SG)_2Cl_2$. SG belongs to a group of compounds having the general formula $RYC(NH)NH_2$ where Y = —CH_2—, —S—, —O— or —NH—, and R = an alkyl, aryl or polymeric matrix, all of which have previously been found to possess some affinity for platinum metals as well as for gold.[1] This suggests the possibility of preparing selective ion-exchange resins by incorporating this type of ligand into a polymeric matrix. The present work will deal with the stability aspects of the palladium–SG complex, in order to yield an understanding of the processes that will take place in the polymeric matrix.

Since a mixed complex is formed, $Pd(SG)_2Cl_2$, separate discussions are needed for its two constituent parts, namely the palladium chloride system and the interaction of that system with SG.

EXPERIMENTAL

Methods

All stability constants were determined spectrophotometrically on samples equilibrated for 2 days and having a pH of 2 and an ionic strength of 1*M* (sodium perchlorate).

Palladium chloride system. A certain quantity, 5 ml, of $1·17 \times 10^{-2}M$ ammonium tetrachloropalladate(II) was measured into a series of 50-ml standard flasks. Enough sodium chloride solution was added to each flask for its final concentration to vary from 10^{-4} to 1·0*M*. After pH and ionic strength adjustments the samples were diluted to 50 ml and equilibrated for 2 days. The spectra of these samples, which are shown in Fig. 1, were taken on a Perkin–Elmer Spectrophotometer No. 350, in the region 200–400 nm, with 10-mm silica cells.

In order to obtain the numerical data for ε_4 (the molar absorptivity of the $[PdCl_4^{2-}]$ species) at 278 nm, the absorbance must be measured at a high free chloride concentration, namely 3*M*. But under these conditions, with the palladium concentration chosen, the absorbance signal saturates the recorder at wavelengths shorter than 223 nm. This measurement was therefore carried out separately and does not appear in Fig. 1.

Sulphaguanidine. Equal quantities, 1·67 mg, of SG were introduced into a series of 100-ml standard flasks. Different quantities of perchloric acid were added to these samples so as to get a variation in pH from 0·2 to 6·70. The spectra of these solutions were recorded in the region 200–400 nm and are shown in Fig. 2.

Palladium chloride–SG system. For determination of k_1, various amounts of SG were placed in a series of 50-ml standard flasks each of which contained $9·4 \times 10^{-4}M$ ammonium tetrachloropalladate(II) and $0·988 \times 10^{-2}M$ hydrochloric acid. The spectra of these solutions in the visible region (350–600 nm) were recorded and are shown in Fig. 3. Absorbance measurements for k_1 were taken at 402 nm.

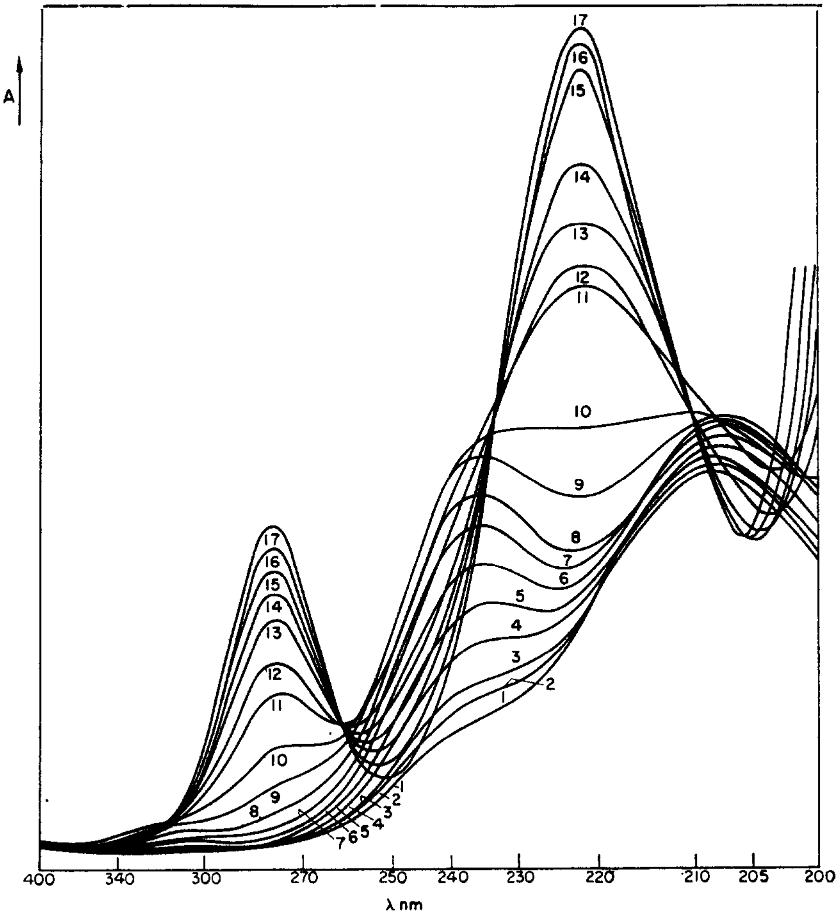

Fig. 1.—Spectral changes during the reaction of palladium with chloride ions. Added chloride concentration: (1) 0; (2) $10^{-4}M$; (3) $2 \times 10^{-4}M$; (4) $5 \times 10^{-4}M$; (5) $9 \times 10^{-4}M$; (6) $1{\cdot}5 \times 10^{-3}M$; (7) $2{\cdot}5 \times 10^{-3}M$; (8) $5 \times 10^{-3}M$; (9) $10^{-2}M$; (10) $2 \times 10^{-2}M$; (11) $4 \times 10^{-2}M$; (12) $6 \times 10^{-2}M$; (13) $0{\cdot}1M$; (14) $0{\cdot}14M$; (15) $0{\cdot}2M$; (16) $0{\cdot}3M$; (17) $1{\cdot}0M$.

For the method of corresponding solutions, in order to determine the free ligand concentration [A], two sets of palladium chloride solutions were prepared: $C_M' = 5{\cdot}63 \times 10^{-4}M$ and $C_M'' = 3{\cdot}75 \times 10^{-4}M$. A series of 50-ml standard flasks was prepared containing solution of concentration C_M' and another series with concentration C_M''. To each of the flasks were added amounts of $1{\cdot}126 \times 10^{-4}M$ SG varying from 1 to 12 ml, and the volumes were made up to 50 ml. Absorbance measurements were taken at 390 nm in 10-mm silica cells.

For the method of continuous variations the ligand-to-metal ratio was determined by measuring absorbances at 390 nm for various mixtures with [metal] + [ligand] = $2{\cdot}21 \times 10^{-3}M$.

RESULTS AND DISCUSSION

Palladium chloride system

Many halide complexes of palladium are known, which have the general formula PdL_2X_2, where L may be dimethylsulphoxide, thiocyanate, trialkylphosphine derivatives, *etc*, and X is a halide.[8] The complex formed between SG and palladium chloride also belongs to this general type. In such complexes two chloride ions of the

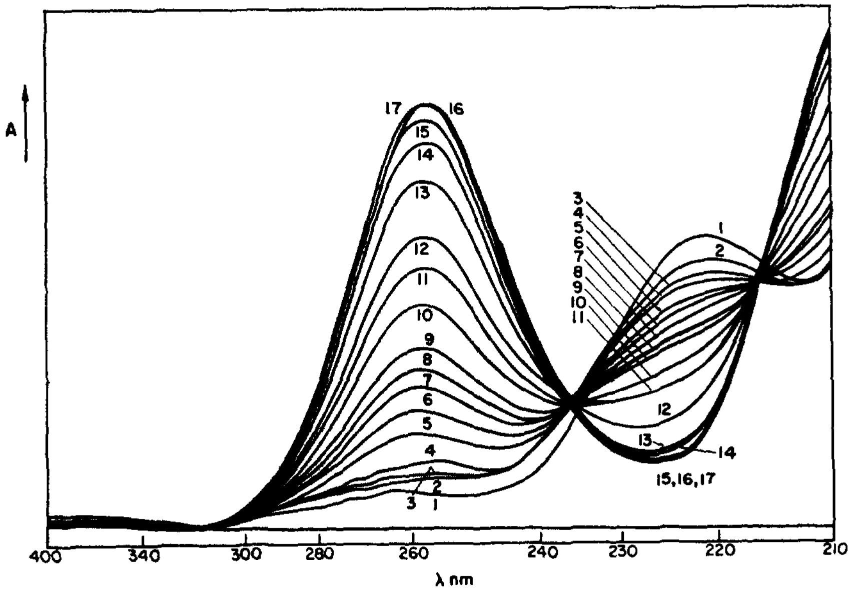

Fig. 2.—Spectral changes of sulphaguanidine with pH.
pH of solutions: (1) 0·2; (2) 1·03; (3) 1·22; (4) 1·40; (5) 1·64; (6) 1·80; (7) 2·01; (8) 2·09; (9) 2·20; (10) 2·35; (11) 2·48; (12) 2·62; (13) 2·95; (14) 3·42; (15) 3·70; (16) 4·77; (17) 6·70.

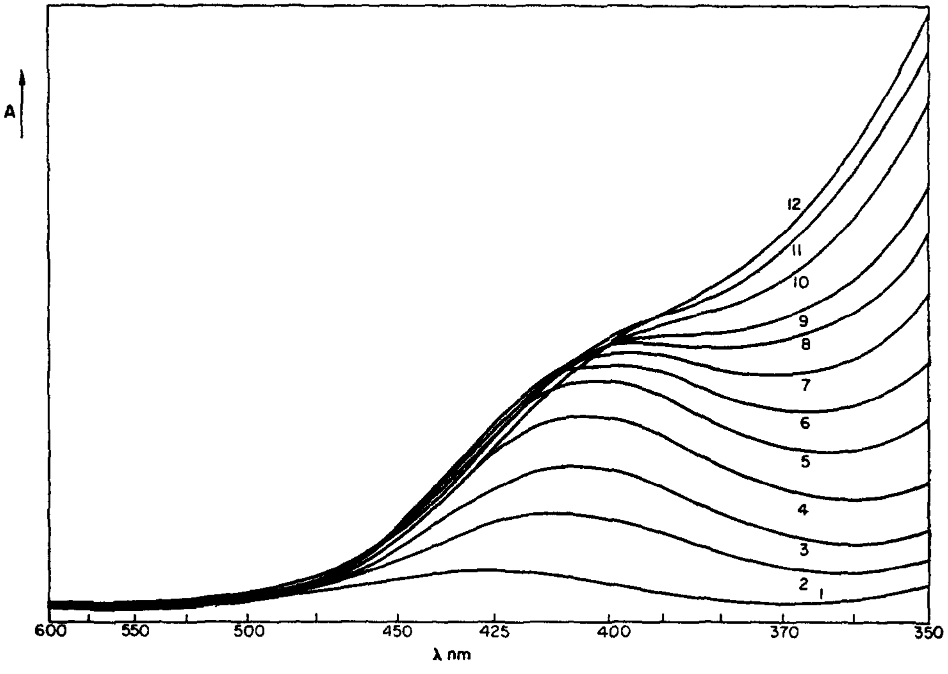

Fig. 3.—Spectral changes during the addition of SG to a palladium chloride solution. Concentration of Pd: $7\cdot5 \times 10^{-4}M$; ratio SG/Pd: (1) 0; (2) 0·25; (3) 0·5; (4) 0·75; (5) 1·0: (6) 1·25; (7) 1·5; (8) 1·75; (9) 2·0; (10) 2·5; (11) 3·0; (12) 3·5.

original $PdCl_4^{2-}$ are apparently bound very strongly, while the other two can be easily substituted by other ligands.

The stepwise formation of the chloro-complexes of palladium in solution has already been studied potentiometrically[3] and spectrophotometrically.[4–9] The numerical results obtained differ considerably, while the values obtained for k_3 and k_4 seem to be too high in most of them. The photometric determinations of the stability constants consisted of measurements taken at the weak *d-d* transition peak (400 nm). Measurements at this wavelength are not very accurate because all the palladium chloride species absorb in this region and there are only slight differences in their peak intensities. The ultraviolet spectra under conditions of stepwise formation of the chloro-complexes offer more detailed and accurate information. Figure 1 illustrates a well resolved spectrum consisting of three different absorption peaks and two isosbestic points.

The peaks appearing in this spectrum can be definitely assigned to three species: $[PdCl_2(H_2O)_2]$ at 208 nm; $[PdCl_3(H_2O)^-]$ at 208 and 236 nm, and a shoulder at 278 nm; $[PdCl_4^{2-}]$ at 223 and 278 nm.

In Fig. 1 the $[PdCl_4^{2-}]$ species is clearly seen to be formed at high chloride concentrations, with its absorption maximum at 278 nm. Curves 1–9 mainly represent the formation of the lower chloro-complexes, the $[PdCl^+]$ and $PdCl_2$ species. Curve 10 is different in shape because at that chloride concentration the quantities of $[PdCl_3^-]$ and $[PdCl_4^{2-}]$ begin to become more appreciable. Curve 11 represents the following concentrations of the various palladium species: $PdCl_4^{2-}$ 31%, $PdCl_3^-$ 62%, $PdCl_2$ 7%. Beyond curve 11 there is a sharp rise in the concentration of $PdCl_4^{2-}$ and a decrease in that of $PdCl_3^-$ and the formation of the well defined absorption peaks at 223 and 278 nm is observed. No changes in the curve were found above $3M$ chloride concentration, which makes the existence of co-ordination numbers higher than 4 very unlikely.[4,6,10,12]

Determination of k_3 and k_4. The formation constant of the fourth chloro-complex,

$$k_4 = \frac{[PdCl_4^{2-}]}{[PdCl_3^-][Cl^-]} \tag{1}$$

can be determined from the data in Fig. 1. For the calculation of k_4 the assumption is made that in the range of chloride concentrations between $4 \times 10^{-2}M$ and $3M$ the system contains only $[PdCl_4^{2-}]$ and $[PdCl_3^-]$. This assumption is supported by the appearance of an isosbestic point at 261 nm, which indicates the existence of an isolated equilibrium between two species. The equation for the system at the 278 nm peak is

$$A = \varepsilon C_M = \varepsilon([PdCl_4^{2-}] + [PdCl_3^-]) = \varepsilon_4[PdCl_4^{2-}] + \varepsilon_3[PdCl_3^-], \tag{2}$$

where A is the absorbance measured at 278 nm, C_M the total concentration of palladium, and ε, ε_3, ε_4 the molar absorptivities of the mixture, $PdCl_3^-$ and $PdCl_4^{2-}$ respectively.

Rearranging equation (2) and multiplying by C_M yields

$$(\varepsilon_4 C_M - \varepsilon C_M)[PdCl_4^{2-}] + (\varepsilon_3 C_M - \varepsilon C_M)[PdCl_3^-] = 0. \tag{3}$$

By substitution of $A_0 = \varepsilon_4 C_M$ (for the absorption measured at the maximal chloride concentration of $3M$ where the only species present is $[PdCl_4^{2-}]$), and $A = \varepsilon C_M$, we arrive at a straight-line correlation between the absorption measured at 278 nm and the free chloride concentration:

$$A = (A_0 - A)[\mathrm{Cl}^-]k_4 + \varepsilon_3 C_M, \tag{4}$$

A plot of A *vs.* $(A_0 - A)[\mathrm{Cl}^-]$ gives a straight line. Similar expressions were developed by Newman and Hume[14,15] in their studies on the formation constants of the bismuth–chloride system. From the slope and the intercept of this line k_4 and ε_3 can be calculated. The experimental results were treated by least-squares methods and gave the following values and standard deviations:

$$k_4 = 12{\cdot}3 \pm 0{\cdot}8$$

$$\varepsilon_3 = \frac{0{\cdot}222 \pm 0{\cdot}042}{C_M \times 10} = 190 \pm 36\ \mathrm{l.mole^{-1}mm^{-1}}.$$

For the calculation of k_3 the same approach as for k_4 was used, and the measurement was also carried out at 278 nm. The chloride concentrations were lower and therefore the existence of the $PdCl_2$ species had to be taken into account. The basic equation has the form of equation (3) with the addition of the absorption of the $PdCl_2$ species:

$$(\varepsilon_4 C_M - A)[\mathrm{PdCl_4}^{2-}] + (\varepsilon_3 C_M - A)[\mathrm{PdCl_3}^-] + (\varepsilon_2 C_M - A)[\mathrm{PdCl_2}] = 0. \tag{5}$$

ε_3 and k_4 are now known and if we substitute:

$$[\mathrm{PdCl_4}^{2-}] = k_3 \,.\, k_4[\mathrm{PdCl_2}][\mathrm{Cl}^-]^2$$

$$[\mathrm{PdCl_3}^-] = k_3[\mathrm{PdCl_2}][\mathrm{Cl}^-]$$

into equation (5) and divide by $[\mathrm{PdCl_2}]$, the following equation is obtained:

$$A = \{(A_0 - A)k_4[\mathrm{Cl}^-]^2 + [\varepsilon_3 C_M - A][\mathrm{Cl}^-]\}k_3 + \varepsilon_2 C_M. \tag{6}$$

The graphical correlation of the measured absorption *vs.* the term in the brackets yields a straight line the slope of which gives the value 224 for k_3, and the intercept the value of ε_2, which is negligibly small.

Determination of k_2 and k_1. The k_1 and k_2 equilibria exist in the regions of lower chloride concentration. In those regions the assumption that the total chloride concentration is equal to the free ligand concentration is not valid. It was therefore decided to use Bjerrum's[16] more general approach, which makes use of the formation function:

$$\bar{n} = N - \frac{\mathrm{d}\log \alpha_n}{\mathrm{d}\log[\mathrm{A}]} = \frac{C_A - [A]}{C_M}, \tag{7}$$

where $\bar{n}$ = the average number of chloride ions bound to palladium, N = maximal co-ordination number, α_n = degree of formation of an individual complex $[\mathrm{PdCl}_n^{2-n}]$, [A] = free chloride ion concentration, C_A = total chloride concentration, C_M = total palladium concentration.

Equation (7) can be used for the graphical construction of the formation function. C_M is known ($1{\cdot}17 \times 10^{-4}M$), and from the spectral data at 278 nm α_n can be calculated, for the special case of $[\mathrm{PdCl_4}^{2-}]$, as a function of chloride concentration, as follows:

$$\alpha_4 = \frac{A/A_0 - \varepsilon_3/\varepsilon_4}{1 - \varepsilon_3/\varepsilon_4}. \tag{8}$$

The formation curve for the Pd–Cl system was constructed, and the following stepwise formation constants were calculated, to a first approximation, at the points $\bar{n} = n - \frac{1}{2}$:

$$k_n = \frac{1}{[\mathrm{A}]_{n-1/2}} \tag{9}$$

$$\log k_1 = 3{\cdot}48$$
$$\log k_2 = 2{\cdot}79$$
$$\log k_3 = 2{\cdot}00$$
$$\log k_4 = 0{\cdot}96$$

These values agree fairly well with those obtained by Burger and Dyrssen,[6] who used different experimental methods; k_3 and k_4, in particular, are in fair agreement with those calculated by the foregoing method and with Jörgensen's low value for k_4.

The ligand sulphaguanidine

The ultraviolet spectra of aqueous sulphaguanidine solutions in the pH range 1–7 were recorded between 210 and 400 nm and are illustrated in Fig. 2. This spectrum demonstrates the existence of two species in equilibrium:

$$\mathrm{SG} + \mathrm{H}^+ \rightleftharpoons \mathrm{SGH}^+. \tag{10}$$

Above pH 3 the basic species SG with an absorption maximum at 258 nm is predominant. At higher acidities a protonated species is formed with a maximal absorption peak at 222 nm. Isosbestic points at 217 and 236 nm support the simple equilibrium shown in equation (10). In solutions more acidic than pH 1 a higher protonated species of the type $\mathrm{SGH_2^{2+}}$ may form, as evidenced by the shift of the isosbestic point.

The dissociation constant of the monoprotonated SG was found potentiometrically by Bell and Roblin[17] to be $\mathrm{p}K_a = 2{\cdot}75$. In the present work, Fig. 2 was used to determine this constant in the same manner as that adopted for the Pd–Cl system. Equation (11) is analogous to equation (4) for the special case of the SG system in different pH media.

$$A = \frac{k_a}{k_w}\{(A_0 - A)[\mathrm{OH}^-]\} + \varepsilon_{\mathrm{HA}} \cdot C_{\mathrm{HA}}, \tag{11}$$

where A = the absorption measured at 258 nm, A_0 = the maximum absorption of SG at 258 nm, $\varepsilon_{\mathrm{HA}}$ = the extinction coefficient of the protonated ligand at 258 nm, k_w is the ionic product for water.

The slope of the straight line obtained gives the value $\mathrm{p}k_a = 2{\cdot}32 \pm 0{\cdot}02$, which seems to be more accurate than the former value.

The reaction between palladium chloride and sulphaguanidine

On addition of sulphaguanidine to a palladium chloride solution the yellow colour of the solution immediately became more intense. With palladium concentrations higher than $10^{-3}M$ a yellow crystalline precipitate slowly formed, with composition $[\mathrm{PdCl_2(SG)_2}]$. The ligand-to-metal ratio was determined experimentally by Job's method, and the palladium-to-chloride ratio by elemental analysis.

Precipitation was carried out in acidic solution (pH 2) in order to avoid hydrolysis of the palladium ions. The acidity of the solution increased slightly during this process, because of displacement of protons from the protonated SG.

The conditions of complex formation between palladium and SG were studied in solution below the limit of precipitation, by measuring the *d-d* transitions of the Pd–Cl system occurring at 400 nm.

Determination of formation constants. The numerical value of the first formation step,

$$K_1 = \frac{[\mathrm{PdCl_2(SG)}]}{[\mathrm{PdCl_2}][\mathrm{SG}]} \tag{12}$$

can be determined by gradually adding small quantities of SG until a palladium:SG molar ratio of 1:1 is reached. The spectra illustrated in Fig. 3 show the complex formation below the limit of precipitation, and indicate that at a wavelength of 402 nm there are no changes in absorption above the 1:1 ligand-to-metal ratio. The species appearing in equation (12) were evaluated by making the following substitutions:

$$\begin{aligned} A_1 &= \varepsilon_0\mathrm{M_0} + \varepsilon_1[\mathrm{PdCl_2(SG)}] = \varepsilon_0[\mathrm{M_t} - \mathrm{PdCl_2(SG)}] + \varepsilon_1[\mathrm{PdCl_2(SG)}] \\ &= \varepsilon_0[\mathrm{M_t} - \mathrm{SG_t}] + \varepsilon_1[\mathrm{SG_t}] \qquad (13)^* \end{aligned}$$

where A_1 = the absorption measured at 402 nm, ε_0 = the molar absorptivity of $[\mathrm{PdCl_4}^{2-}]$ at 402 nm, ε_1 = the molar absorptivity of $[\mathrm{PdCl_2(SG)}]$ at 402 nm, $\mathrm{M_0}$ = concentration of the chloro-complexes of palladium which did not react with the ligand, $\mathrm{M_t}$ = total palladium concentration, $\mathrm{SG_t}$ = total ligand concentration, [SG] = free ligand concentration (*i.e.*, not bound to palladium).

ε_1 can be determined experimentally from equation (13), and the concentration of the species $[\mathrm{PdCl_2(SG)}]$ can now be expressed as a function of measurable quantities:

$$[\mathrm{PdCl_2(SG)}] = \mathrm{M_t} - \mathrm{M_0} = \frac{A_1 - \varepsilon_0\mathrm{M_t}}{\varepsilon_1 - \varepsilon_0} \tag{14}$$

$$\mathrm{M_0} = \frac{\varepsilon_1\mathrm{M_t} - A_1}{\varepsilon_1 - \varepsilon_0}. \tag{15}$$

The free SG concentration can now also be expressed by measurable quantities:

$$[\mathrm{SG}] = \left[\mathrm{SG_t} - \frac{A_1 - \varepsilon_0\mathrm{M_t}}{\varepsilon_1 - \varepsilon_0}\right]\Big/ D \tag{16}$$

where D is a pH correction term for the ligand and is equal to $(1 + [\mathrm{H^+}]/k_a)$

$$[\mathrm{PdCl_2}] = \frac{\mathrm{M_0}}{G} = \frac{\varepsilon_1\mathrm{M_t} - A_1}{(\varepsilon_1 - \varepsilon_0)G} \tag{17}$$

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* Equation (13) is valid under the specific conditions of $\mathrm{SG_t} < \mathrm{M_t}$, when it can be assumed that all the SG is associated with palladium.

where G is a correction term for $[PdCl_2]$ as a function of chloride concentration and is given by

$$G = \frac{1}{k_1k_2[Cl^-]^2} + \frac{1}{k_2[Cl^-]} + 1 + k_3[Cl^-] + k_3k_4[Cl^-]^2. \tag{18}$$

Substitution of equations (14), (16) and (17) into equation (12) yields

$$K_1 = \frac{A_0 - \varepsilon_0 M_t}{(\varepsilon_1 M_t - A_1)} \frac{(\varepsilon_1 - \varepsilon_0)}{(\varepsilon_1 - \varepsilon_0)(SG)_t + (\varepsilon_0 M_t - A_1)} \cdot D \cdot G \tag{19}$$

The experimental plot of equation (19) is a straight line and yields the numerical value $(3{\cdot}13 \pm 0{\cdot}14) \times 10^5$ for the first stability constant K_1, the correction terms at pH 2 and chloride concentration $0{\cdot}988 \times 10^{-2}M$ being $D = 3{\cdot}18$ and $G = 3{\cdot}74$.

Since by spectrophotometric measurements at 402 nm only K_1 could be determined, it was decided to use Bjerrum's general equation since it enables both K_1 and K_2 for the palladium–SG system to be determined.

However, the general Bjerrum equation $\bar{n} = (C_A - [A])/C_M$ can be used only if there is an appreciable difference between the total ligand concentration C_A and the free ligand concentration [A]. The free ligand concentration was determined by the method of corresponding solutions.[11] This method is based on the assumption that if two solutions of different C_M and C_A show the same absorbance, the distributions of all complex species in both solutions are equal. According to Bjerrum the free ligand concentration can then be calculated by the formula

$$[A] = \frac{C_\mu' C_A'' - C_M'' C_A'}{C_M' - C_M''}. \tag{20}$$

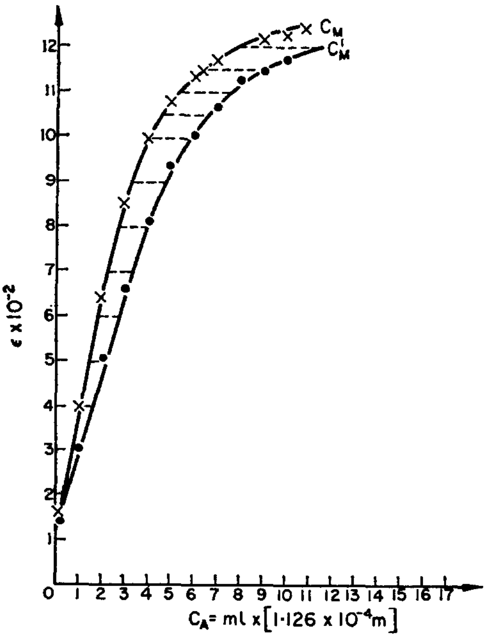

FIG. 4.—Determination of [A] by the method of corresponding solutions.

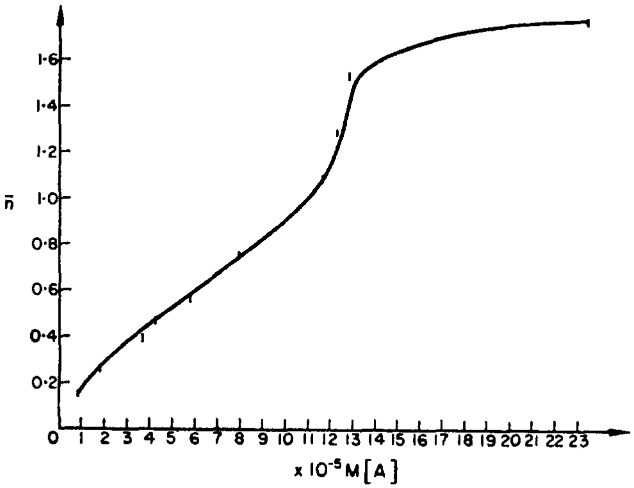

FIG. 5.—Formation curve for the interaction of palladium chloride with SG.

The free ligand concentrations for different C_A and C_M, as determined experimentally, are illustrated in Fig. 4.

Once [A] is known, the formation curve can be constructed (Fig. 5) and the two stability constants calculated.

The numerical values taken from the graph must still be corrected for the terms *D* and *G*. The stability constants obtained after all these corrections have been made are as follows:

$$K_1 = \frac{1}{[\mathrm{A}]_{\bar{n}=0\cdot5}} = \frac{[\mathrm{PdCl_2(SG)}]}{[\mathrm{PdCl_2}][\mathrm{SG}]} = 2\cdot6 \times 10^5$$

$$K_2 = \frac{1}{[\mathrm{A}]_{\bar{n}=1\cdot5}} = \frac{[\mathrm{PdCl_2(SG)_2}]}{[\mathrm{PdCl_2(SG)}][\mathrm{SG}]} = 2\cdot4 \times 10^4.$$

The value of K_1 obtained by the Bjerrum method agrees well with that already obtained, so it was thought justifiable to proceed with the computation of K_2 from Fig. 5.

CONCLUSION

The finding of relatively low stability constants for the palladium chloride–SG complexes leads us to the assumption that SG reacts as a monodentate ligand rather than by forming a chelate, although structurally this reagent could possibly also act as a bidentate ligand. Since two chloride ions are definitely bound to the palladium, chelate formation would require 6-co-ordinated palladium, which is very improbable; most palladium complexes are of the square planar type $PdCl_2X_2$.

Zusammenfassung—Die Bildungskonstanten von Palladium-Chlorokomplexen wurden mit einem neuen Ansatz für die Deutung der Ultraviolettspektren ermittelt. Die Reaktion von $PdCl_4^{2-}$ mit Sulfaguanidin (SG) wurde interpretiert und quantitativ ausgewertet. Die Bildungskonstanten des gemischten Komplexes $Pd(SG)_2Cl_2$ wurden spektrophotometrisch bestimmt. Die Stabilitätskonstanten für die stufenweise Bildung der Palladium-Chlorokomplexe sind $\log k_1 = 3{,}48$; $\log k_2 = 2{,}79$; $\log k_3 = 2{,}35$; $\log k_4 = 1{,}1$ und für die Reaktion von $PdCl_4^{2-}$ mit SG $\log k_1 = 5{,}42$; $\log k_2 = 4{,}38$.

Résumé—On a déterminé les constantes de formation du palladium avec les ions chlorure par une nouvelle approche de l'interprétation des spectres dans l'ultra-violet. On a interprété et évalué quantitativement l'interaction de $PdCl_4^{2-}$ avec la sulfaguanidine (SG). Les constantes de formation du complexe ligand mixte $Pd(SG)_2Cl_2$ ont été déterminées spectrophotométriquement. Les constantes de stabilité pour la formation par degrés des complexes palladium chlorure sont: $\log k_1 = 3{,}48$; $\log k_2 = 2{,}79$; $\log k_3 = 2{,}35$; $\log k_4 = 1{,}1$ et, pour l'interaction de $PdCl_4^{2-}$ avec SG, $\log k_1 = 5{,}42$; $\log k_2 = 4{,}38$.

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COLORIMETRIC DETERMINATION OF TRACES OF SELENIUM, TELLURIUM, MANGANESE AND CERIUM

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Summary—Methods are described for the colorimetric determination of micro- and semi-micro quantities of selenium, tellurium, cerium and manganese. The test solution in 0·35–3*M* condensed phosphoric acid medium is oxidized with an excess of permanganate. The colour intensity of the unreacted permanganate is measured at 530 nm.

THE COLORIMETRIC determination of selenium, tellurium, manganese and cerium has generally been based on the complexation of these metals with suitable organic reagents, though manganese has also been determined by oxidizing it to manganese(III) or (VII), and cerium indirectly through the oxidative action of cerium(IV).[1–3] Although various indirect titration procedures are known, involving oxidation of a lower oxidation state of these elements, followed by back-titration of the excess of oxidant, no-one has hitherto proposed to measure the excess colorimetrically. We have now developed such a method for the rapid and accurate determination of micro to macro amounts of these elements—when they occur individually. Mixtures of them cannot be analysed by this method, of course. The method is made selective for these four elements by using a preliminary treatment which oxidizes other elements to their highest oxidation state. The method is based on oxidizing with permanganate [which is reduced to manganese(III)] in condensed phosphoric acid medium, and measuring the excess of permanganate, at 525 nm.

This method of oxidation was originally developed by Lingane and Karplus[4] for titration of manganese(II).

EXPERIMENTAL

Reagents

Potassium permanganate. A 0·01*M* solution is prepared and diluted to 0·004*M*.

Manganese(II) sulphate. A 0·01*M* solution is prepared and standardized,[4] then diluted to $2{\cdot}50 \times 10^{-4}M$.

Selenium(IV). A 0·01*M* solution is prepared from sodium selenite and standardized,[5] then suitably diluted.

Cerium(III). An approximately 0·05*M* solution is prepared by reducing cerium(IV) sulphate with the required quantity of oxalic acid. The solution is boiled thoroughly, and filtered if necessary. The solution is standardized by the persulphate method,[6] and then suitably diluted.

Tellurium(IV). A 0·01*M* solution is prepared from potassium tellurite and standardized,[7] then suitably diluted.

Condensed phosphoric acid. Orthophosphoric acid (100 ml) is heated in a 250-ml beaker with 3–4 ml of nitric acid (1 + 1) until fumes of nitrogen dioxide are no longer evolved. The acid is stored in a brown bottle.

Preliminary work

It is best to measure the permanganate at ~525 nm. A green filter with maximum transmission at 530 nm can be used.

The rate of oxidation was found to be dependent on the permanganate concentration. When aliquots of standard test solution were treated in 50-ml standard flasks with 1–8 ml of condensed

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phosphoric acid, then diluted to about 30 ml with conductivity water, cooled, treated with different volumes of permanganate and diluted to the mark, the absorbance at 525 nm became constant after 3 min if the permanganate was present in 50% excess or more.

Determination of manganese

Two procedures are proposed for the determination of manganese; in one a calibration curve is used, and in the other it is determined directly. By the second procedure, traces (about 2 μg) of manganese can be determined within 10 min. An exactly known strength of permanganate solution is necessary for the second procedure.

Procedure A. About 2–20 ml of test solution containing from 0·02 to 0·4 mg of manganese are taken in a 50-ml volumetric flask and treated with 2–8 ml of condensed phosphoric acid. The mixture is diluted to approximately 35 ml with water and allowed to cool to room temperature. Exactly 5·00 ml of permanganate solution are then added and the solution is made up to the mark. The reagents must be added in the order given. The absorbance is then measured (green filter or 525 nm) against water or a solution containing the phosphoric acid at the same concentration. A calibration curve is prepared. Since manganese(III) obeys Beer's law at the wavelength used, it does not affect the calibration apart from its effect on the slope.

Procedure B. Three different-sized aliquots of sample solution are taken in 50-ml volumetric flasks, treated with 2–8 ml of condensed phosphoric acid and diluted to about 40 ml with water. An accurately measured volume of permanganate (10 ml of 0·004M will usually do) is added to each flask (the same volume to each). (The normality of the permanganate must be known.) Then the three solutions are made up to the mark and their absorbances measured at 525 nm after 2 min. A graph is drawn of sample volume *vs.* absorbance and is extrapolated to the abscissa. The intercept corresponds to the volume of sample containing manganese(II) equivalent to the permanganate added, in the reduction of manganese(VII) to manganese(III). The concentration of manganese(II) can easily be calculated by simple proportion.

$$N_{\mathrm{Mn(II)}} = \frac{N_{\mathrm{Mn(VII)}} \times V_{\mathrm{Mn(VII)}}}{V_{\mathrm{sample}}},$$

where V stands for volume (ml) and N for normality. The permanganate normality is calculated on the basis of a 5-electron reduction, in order to compensate for 1/5 of the manganese(III) being derived from reduction of the permanganate. The error of the method is ±0·8% by procedure A and ±0·3% by procedure B.

Determination of selenium

Procedure A for the determination of selenium is similar to the one given for manganese.

Procedure B. Take three different volumes of sample in 25-ml volumetric flasks and add an excess of permanganate of known strength as for manganese, and measure the absorbances. In another 25-ml flask add an excess of sample to the amount of permanganate used for the other tests, in order to reduce all the manganese(VII) to manganese(III). Dilute to the mark and measure the absorbance. Plot the absorbance of the first solutions *vs.* volume of sample and read off the volume of sample corresponding to the absorbance of the manganese(III) only. Calculate the result by simple proportion as before except that the permanganate normality is calculated for a 4-electron reduction.

The error is ±0·7% for method A and ±0·4% for method B.

Determination of cerium and tellurium

Procedure A can be applied for the determination of cerium or tellurium; procedure B (for selenium) is applicable to cerium but not to tellurium.

Interferences

Copper(II), cobalt(II), nickel(II), chromium(III), iron(III), vanadium(V), tungsten(VI), uranium(VI), arsenic(V), antimony(V) and molybdenum(VI) do not interfere provided the test solution is used instead of water as a blank. Magnesium, aluminium and calcium also do not interfere.

Applications

To test the reliability of the method under practical conditions, and compare its performance with other methods, a variety of samples was analysed.

In general, a suitable weight of sample was decomposed with an appropriate acid in a 500-ml Pyrex beaker covered with a watch-glass, and after dilution and thorough boiling to remove gaseous reaction products, the resulting solutions were cooled and made up to volume in volumetric flasks. Whenever nitric acid was used to dissolve the samples, 1 g of urea was added before final dilution to volume, to ensure complete absence of oxides of nitrogen. (Separate experiments were made to confirm that permanganate has no action on urea under the experimental conditions.) Aliquots (5, 10, 15 and 20 ml) of these solutions were taken in 50-ml volumetric flasks and diluted to nearly 40 ml with conductivity water. Then 2–8 ml of condensed phosphoric acid were added and the samples were oxidized with a known excessive volume of permanganate of known concentration. The solutions were made up to the mark and the absorbance measured at 530 nm (green filter) against the sample solutions similarly treated but without addition of permanganate. Procedures A and B were applied for the determination of manganese and selenium, but only procedure A for cerium and tellurium. Results are presented in Tables I–III.

Manganese rail steel, chromium–molybdenum steel, chromium–vanadium steel, chromium–nickel steel, nickel–molybdenum–vanadium steel, and copper–nickel–chromium cast iron. Since all these samples contained appreciable amounts of vanadium, an oxidizing attack was used in preparing the solutions to make sure that vanadium would finally be present in the quinquevalent state: 1-g samples were dissolved in 10 ml of nitric acid (1 + 1) and 5 ml of hydrochloric acid. The solutions were then boiled down to a small volume with 20 ml of concentrated nitric acid to reoxidize any vanadium reduced by the hydrochloric acid. The solutions were finally boiled with 5 ml of concentrated sulphuric acid to expel all chloride ion. Before final dilution (to 500 ml), the chloride ion was tested for with silver nitrate.

Cobalt–molybdenum–tungsten steel and molybdenum–tungsten–chromium–vanadium steel. The samples (1 g) were decomposed by boiling with 5 ml of syrupy orthophosphoric acid and 10 ml of sulphuric acid (1 + 1). When the samples were almost completely decomposed, they were boiled with 2 ml of nitric acid and finally diluted to 250 ml.

Copper–manganese, ferrocerium, iron selenide, cerium–uranium–bismuth, uranium–chromium–cerium, tellurium–tin, tellurium–antimony–lead, tellurium–antimony–copper–bismuth alloys and refined selenium powder. Owing to non-availability of samples, synthetic mixtures were prepared by mixing the salts (as oxides and nitrates) in the correct compositions; 1-g samples were decomposed with nitric acid and sulphuric acid. The ions to be determined were added as standard solutions to the solid samples before the decomposition.

Monazite. A 1-g sample was digested in a porcelain evaporating dish with 15 ml of concentrated sulphuric acid on a sand-bath until most of the acid had evaporated. It was then cooled and leached with 1*N* sulphuric acid, filtered and made up to 500 ml.

*Rocks, minerals and ores.** The following general procedure was used for opening out.

A 2-g sample was fused in a silica crucible with 4–5 g of fusion mixture (potassium and sodium carbonates, 1:1). The cooled fused mass was treated with 20 ml of concentrated hydrochloric acid in a platinum dish and the resulting solution boiled down to a small volume on a water-bath. The process was repeated with another 5 ml of concentrated hydrochloric acid, but this time the solution was evaporated almost to dryness. The mass was then leached with 1*M* hydrochloric acid and heated strongly with sulphuric acid until fumes of sulphur trioxide were evolved. (Residual chloride was tested for with silver nitrate.) The solution was diluted to 100 ml.

Selenium dioxide, sodium selenite and sodium tellurite. A 0·5-g sample was dissolved in 1*N* sulphuric acid and diluted to 1 litre.

Rare earth carbonates. A 1–2-g sample was dried at 100° and decomposed with 2*M* sulphuric acid. The solution was boiled down to small volume, cooled, filtered and finally diluted to 500 ml.

Manganese ore. About 1 g of powdered and dried sample was digested in a platinum dish on a sand-bath with 15 ml of hydrochloride acid. Silica was removed by boiling with 5–6 ml of hydrofluoric acid. Then 10 ml of sulphuric acid (1 + 1) and 5 ml of concentrated nitric acid were added and the solution was evaporated until fumes of sulphur trioxide were evolved. The solution was cooled and diluted to 1 litre.

Ferromanganese, manganese bronze and silico-manganese spring steel. A 1-g sample was dissolved in 25 ml of nitric acid (1 + 1) and 20 ml of sulphuric acid (1 + 1). The ferromanganese sample solution was diluted to 1 litre, the other two to 250 ml.

Minerals. "Minerals" were prepared artificially by mixing the salts (sodium silicate, titanium dioxide, potassium alum, ferric alum, magnesium sulphate and calcium carbonate) in the correct composition, with standard manganous sulphate solutions added before starting the decomposition

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* An alternative procedure, for the decomposition of rocks, minerals and ores, was also used to avoid the use of hydrochloric acid: 1 g of sample was dissolved in 10 ml of hydrofluoric acid and 2 ml of sulphuric acid. The hydrofluoric acid treatment was repeated 2 or 3 times. The solution was then boiled down to a small volume with 10 ml of sulphuric acid (1 + 1) and 2 ml of nitric acid to expel all hydrogen fluoride and finally diluted to 100 ml.

TABLE I.—STEELS AND ALLOYS

Sample and composition (%)	Found, %
Manganese rail steel	Mn
Mn 1·38, C 0·617, Si 0·19, P 0·02, S 0·02, Cu 0·12, Ni 0·15, Cr 0·18, V 0·011, Mo 0·005	1·38, 1·39, 1·38
Chromium–vanadium steel	Mn
Mn 0·786, V 0·19, Cr 18·49, V 0·049, Co 0·078, Si 0·283, Sn 0·012, Cu 0·168, Mo 0·038, C 0·069, S 0·012, P 0·017	0·80, 0·79, 0·78
Chromium–nickel steel	Mn
Mn 0·597, Ni 8·99, Cr 18·49, V 0·049, Co 0·078, Cb 0062, Sn 0·012, Cu 0·168, C 0·069, Si 0·483, S 0·025, P 0·017	0·60, 0·61, 0·60
Chromium–molybdenum steel	Mn
Mn 0·458, Cr 5·15, Mo 0·575, Cu 0·076, Ni 0·083, V 0·01, C 0·094, Si 0·383, P 0·017, S 0·01	0·46, 0·46, 0·46
Cobalt–molybdenum–tungsten steel	Mn
Mn 0·22, V 2·03, Cr 4·14, CO 2·26, Ni 0·056, W 1·02, Mo 5·52, S 0·01	0·21, 0·21, 0·22
Molybdenum–tungsten–chromium–vanadium steel*	Mn
Mn 0·155, V 1·68, Cr 3·34, W 2·56, Mo 4·16, Cu 0·132, P 0·076, Ni 0·102, Si 0·098, C 0·062	0·16, 0·16, 0·16
Nickel–molybdenum–vanadium steel	Mn
Mn 0·302, V 1·94, Cr 4·21, Cu 0·023, Ni 1·42, Mo 6·24, C 0·094, P 0·12, Si 0·282, S 0·002	0·30, 0·30, 0·30
Ferromanganese	Mn
Mn 80·07, C 6·83, Si 0·89, P 0·29, S 0·01 Fe 10·56	80·1, 80·1
Copper–nickel–chromium–cast iron	Mn
Mn 1·01, Cu 6·64, Ni 15·89, Cr 2·17, V 0·009, S 0·072 Ti 0·021, Co 0·08, Si 1·60, C 2·42, P 0·113, As 0·007	1·00, 1·04, 1·00
Manganese bronze	Mn
Mn 1·28, Cu 57·40, Zn 37·97, Sn 0·97, Pb 0·27, Fe 0·81, Ni 0·27, Si 0·05	1·28, 1·27
Copper–manganese alloy*	Mn
Mn 4·96, Cu 95·76	4·96, 4·93, 4·96
Cerium–uranium–bismuth alloy*	Ce
Ce 1·92, U 4·68, Bi 2·16	1·93, 1·92, 1·95
Uranium–chromium–cerium alloy*	Ce
Ce 2·63, Cr 12·16, U 1·93	2·64, 2·63, 2·63
Monazite	Ce
Ce 24·14	24·0, 24·1, 24·0
Iron selenide*	Se
Se 58·67, Fe 40·49, Te 0·47	58·9, 59·0, 59·0
Tellurium–antimony–copper–bismuth*	Te
Te 24·18, Sb 22·42, Cu 6·93, Bi 2·18	24·2, 24·2, 24·1
Ferrocerium alloy*	Ce
Ce 24·16	24·2, 24·2
Tellurium–tin alloy*	Te
Te 26·92, Sn 32·16	26·9, 26·9

* Artificial mixtures.

process, and brought into solution by the fusion method described. The compositions were taken from the *Rock-forming Minerals*, Vol. I (W. A. Deer, R. A. Howie and J. Zussman).

For the samples given in Tables I–III, the following general method was adopted for detecting and determining other reducing ions such as iron(II), arsenic(III), antimony(III), vanadium(IV) (other than these, no reducing ion will be present, as can be understood from the compositions and the mode of decomposition).

An aliquot of the sample solution was treated with a known excess of cerium(IV) sulphate solution in 1*N* sulphuric acid containing 1–2 drops of 0·01% osmium tetroxide solution and the unreacted cerium(IV) was back-titrated with standard iron(II) solution, with ferroin as indicator. The amount of cerium(IV) actually required (plus 2–4 drops excess) was added to the sample solutions

TABLE II.—ROCKS, MINERALS AND ORES

Sample and composition (as oxides, %)	Manganese found
Standard rock samples (U.S.A.)	
Granite G-2 Si 69·20, Al 15·42, Fe 2·70, Mg 0·76, Ca 1·98, Na 4·05, K 4·46, Ti 0·47, P 0·13, Mn 0·04, Cl 0·01, F 0·13, S 0·01	0·041, 0·041
Granodiorite GSP-1 Si 67·22, Al 15·35, Fe 4·20, Mg 0·99, Ca 2·07, Na 2·79, K 5·50, Ti 0·66, P 0·28, Mn 0·05, Cl 0·03, F 0·39, S 0·03	0·050, 0·050
Andesite AGV-1 Si 59·00, Al 17·10, Fe 7·45, Mg 1·50, Ca 4·89, Na 4·23 K 2·87, Ti 10·05, P 0·49, Mn 0·10, Cl 0·02, F 0·04	0·10, 0·10
Periodotite PCC-1 Si 40·55, Al 0·31, Fe 8·11, Mg 43·35, Ca 0·40, Na 0·00, K 0·01, Ti 0·01, Mn 0·12, Cr 0·42, Ni 0·30, Ba 0·01	0·12, 0·12
Dunite DTS-1 Si 40·55, Al 0·31, Fe 8·60, Mg 49·85, Ca 0·03, Na 0·05, K 0·01, Mn 0·12, Cr 0·65, Ni 0·30, Ba 0·02	0·12, 0·12
Basalt BCR-1 Si 54·10, Al 13·70, Fe 13·21, Mg 3·47, Ca 6·91, Na 3·26, K 1·69, Ti 2·25, P 0·35, Mn 0·19, Cl 0·01, F 0·05, S 0·04	0·19, 0·19
Minerals (prepared artificially)	
Almandine garnet Si 37·39, Ti 0·16, Al 20·72, Fe 37·23, Mn 0·86, Mg 3·85, Ca 0·41	0·86, 0·86
Red garnet Si 36·59, Ti 1·68, Al 22·42, Fe 32·20, Mn 1·42, Mg 5·41, Ca 0·54	1·42, 1·42
Garnet Si 36·96, Al 20·65, Fe 35·15, Mn 2·45, Mg 3·17, Ca 1·85	2·44, 2·43
Pink almandine garnet Si 37·23, Al 20·66, Fe 39·16, Mn 7·30, Mg 2·00, Ca 1·31	7·33, 7·31
Almandine-spessartine garnet Si 36·38, Ti 0·27, Al 19·42, Fe 23·62, Mn 18·42, Mg 0·82, Ca 0·56	18·4, 18·4
Ores	
Manganese ore Mn 54·86, Fe 15·93	54·8, 54·8

TABLE III.—OTHER PRODUCTS

Sample and composition (%)	Found by the present method, %
Selenium dioxide, Se 76·86	Se 76·9, 76·9
Sodium selenite, Se 46·65	Se 46·5
Potassium tellurite, Te 43·68	Te 43·7
Laboratory cerium(IV) sulphate solution, Ce(III) 10·14, Ce(IV) 89·73	Ce(III) 10·2, 10·2, 10·2
Cerium(IV) sulphate solution (Commercial) Ce(III) 1·16, Ce(IV) 98·84	Ce(III) 1·17, 1·17, 1·17
Rare earth carbonates Ce(III), 24·35, Ce(IV) 3·73	Ce(III) 24·34
Selenium powder* Se 99·65, Te 0·26, SiO_2, CuO 0·0014, PbO 0·012 Fe_2O_3 0·021, HgO 0·005, Sb_2O_5 0·0033	Se 99·8 99·9, 99·9.

* Artificial mixture.

before the addition of phosphoric acid and permanganate. Since the resulting cerium(III) concentration was known, a correction for it could be applied. When vanadium was present, the unreacted cerium(IV) was titrated with arsenic(III), which has no action on vanadium(V).

Acknowledgement—One of us (Dr. P. P. Naidu) desires to express his grateful thanks to the Council of Scientific and Industrial Research for the award of a Junior Research Fellowship, and also to the University Grants Commission for awarding a Senior Research Fellowship. Thanks are also due to Dr. Francis J. Flanagan, U.S. Geological Survey, for kindly supplying the set of six new standard silicate rocks.

Zusammenfassung—Verfahren zur kolorimetrischen Bestimmung von Mikro- und Halbmikromengen Selen, Tellur, Cer und Mangan werden beschrieben. Die Probelösung in 0.35–3*M* kondensierter Phosphorsäure wird mit einem Überschuß Permanganat oxidiert. Die Farbintensität des nicht verbrauchten Permanganats wird bei 530 nm gemessen.

Résumé—On a décrit des méthodes pour le dosage colorimétrique de micro- et semi- micro-quantités de sélénium, tellurium, cérium et manganése. La solution essai en milieu acide phosphorique condensé 0,35–3*M* est oxydée avec un excés de permanganate. On mesure l'intensité de coloration du permanganate non réagi à 530 nm.

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SULPHOXIDES AS SOLVATING REAGENTS FOR THE SEPARATION OF METAL IONS*

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Summary—The solvent extraction properties of the following sulphoxides have been evaluated: di-n-octyl sulphoxide (DOSO), bis(n-octylsulphinyl)methane (BOSM), bis(n-octylsulphinyl)ethane (BOSE) and *p*-tolyl sulphoxide (PTSO). By use of reversed-phase paper chromatography as a qualitative surveying technique, the interactions of these sulphoxides with some fifty metal ions were investigated in several acid–ligand systems. All sulphoxides were studied in 1–10M hydrochloric and nitric acids; DOSO and BOSM were also studied in perchloric acid and ammonium thiocyanate–perchloric acid mixtures. Observations are made concerning sulphoxide–metal interactions and the existence of several useful analytical separation systems is pointed out. The synthesis and characterization of BOSM and BOSE are described.

ORGANIC sulphoxides contain the semi-polar sulphur-oxygen grouping $>S \rightarrow O$, which is very effective in solvating metal ions and metal–ligand complexes. This ability is amply demonstrated by the simplest sulphoxide, dimethyl sulphoxide, which forms a large number of metal complexes. The higher molecular-weight sulphoxides, unlike the analogous organophosphorus compounds, have received scant attention as reagents for separations. The small amount of work that has been reported, however, has verified that such sulphoxides are excellent reagents for solvent extraction of metal ions in solution. The extraction of uranium from nitric and hydrochloric acids has been studied.[1–3] Other investigations have been concerned with the extraction of thorium,[4,5] gold,[6] zirconium,[7] mineral acids[8,9] and with fundamental studies on the nature of sulphoxide–metal interactions.[3,8] Symmetrical alkyl sulphoxides have mainly been used, but there has been mention of methyl alkyl sulphoxides.[10,11]

The purpose of the present work is to survey the analytical possibilities of separations with higher molecular-weight sulphoxides, by using paper chromatography. Paper is impregnated with an appropriate sulphoxide, and approximately 50 different metal ions are studied, aqueous solutions of different acids at varying concentrations being used as eluents. Complexation by the sulphoxide (or solvation of a metal–ligand complex by the sulphoxide) is indicated when the R_f value is significantly lower than that on unimpregnated paper. For conditions where complexation is indicated, it is expected that a metal ion will be extracted from aqueous solution into an organic solvent containing a dissolved sulphoxide. Obviously, chromatographic experiments on paper impregnated with a solid sulphoxide do not exactly duplicate the situation existing in solvent extraction, where the sulphoxide is dissolved in an organic solvent. At high acid concentrations, for example, some solid complexes might exhibit some

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solubility in the eluent, and this could be mistaken for decreased complex stability. Nevertheless, for all systems where solvent extraction was investigated extraction of metal ions does occur in approximately the same concentration range of acid ligand that gives low R_f values in paper chromatography. Paper chromatography has the advantage of permitting far more rapid survey of variables such as metal ion, acidic ligand, and acid ligand concentration, than would be feasible with solvent extraction.

EXPERIMENTAL

Apparatus

Pyrex jars, 0·3 m high, and 0·4-m diameter plate-glass covers were used for chromatographic tanks. Rectangular frames 0·23 m wide and 0·28 m high, constructed of 6-mm glass rod, were used to support the chromatographic paper.

Reagents

Di-n-octyl sulphoxide (*DOSO*). Prepared by oxidizing di-n-octyl sulphide at room temperature with hydrogen peroxide added slowly as a dilute solution in glacial acetic acid. After the 2-hr reaction period, a large amount of water was added and the solid sulphoxide was filtered off, washed with water, air-dried, and recrystallized from 95% ethanol. The m.p. (71·5–72·5°) and the infrared spectra (ν_{S-O} = 1049 cm^{-1}) correspond to those reported in the literature.[7]

p-*Tolyl sulphoxide* (*PTSO*). Commercial material used without further purification; m.p. 93–95°.

Bis(n-octylsulphinyl)methane (*BOSM*). The corresponding sulphide was first prepared by refluxing octyl mercaptan with an excess of di-iodomethane in the presence of ethanolic potassium hydroxide. The product was purified by extracting several times first with aqueous ethanol and then with water. After drying over anhydrous sodium sulphate, the sulphide, in glacial acetic acid, was oxidized with a slight excess of a dilute solution of hydrogen peroxide in glacial acetic acid, added slowly; the mixture was allowed to react at room temperature overnight. A large amount of water was added to precipitate the sulphoxide, which was then filtered off, washed with water, and air-dried. The crude BOSM was recrystallized several times from ethanol until the sulphone peaks in the infrared spectrum of the compound were reduced to a low, constant level.

The final product, a soft, waxy solid, melted in the range 112–114°. The mass spectra revealed a prominent peak at $m/e = 336$ which corresponds to the molecular weight of the parent ion of the bis-sulphoxide. A peak at $m/e = 338$, 10% of the intensity of the $m/e = 336$ peak, is indicative of the presence of two sulphur atoms in the parent ion. A peak was observed at $m/e = 352$ with 4% of the intensity of the parent ion. This ion, which also appears to contain two sulphur atoms, corresponds to a species containing one sulphoxide group and one sulphone group. A peak was also observed at $m/e = 378$ with an intensity of less than 1% of that of the parent ion. The position of this peak corresponds to the molecular weight of the bis-sulphone.

The infrared spectrum of BOSM in chloroform shows a very intense, broad band centred at 1033 cm^{-1}, indicative of the sulphoxide group. The existence of a small amount of sulphone impurity was indicated by the presence of two weak peaks at 1136 and 1321 cm^{-1}.

The NMR spectrum of BOSM in deuterochloroform displayed a distorted triplet at δ 0·88 and an intense singlet at δ 1·31 which are characteristic of the n-octyl methylene and methyl protons. A triplet observed at δ 2·95 is attributable to the n-octyl methylene protons adjacent to the sulphoxide group. The isolated methylene protons were manifested as a singlet at δ 3·94 and a doublet centered at 3·93 (J = 20 Hz). The singlet is believed to correspond to the *dl* configuration of the bis-sulphoxide whereas the doublet is believed to arise from the non-equivalent methylene protons of the *meso* configuration. The proton integration gives a ratio of 6·0:23·0:3·8:1·9 for $(CH_3)_2$:$[(CH_2)_6]_2$:$(CH_2SO)_2$:$SOCH_2SO$. The ratio of *meso* to *dl* appears to be approximately unity.

Analysis of the compound gave 10·0% oxygen and 17·3% sulphur (theoretical values 9·56% oxygen and 19·17% sulphur). The oxygen:sulphur ratio indicates that the sulphone impurity is considerably higher than that indicated by the mass spectrometry.

Bis(n-octylsulphinyl)ethane (*BOSE*). The corresponding sulphide was first prepared by refluxing n-octyl bromide with a 10% excess of 1,2-dimercaptoethane in the presence of ethanolic potassium hydroxide. The product was purified by extracting several times with aqueous sodium hydroxide solution followed by extractions with water. The sulphide was dried over anhydrous sodium sulphate and then oxidized with hydrogen peroxide by the procedure described for BOSM. A large amount of water was added to the acetic acid solution and the solid product which formed was filtered off, washed with water and air-dried. The crude bis-sulphoxide was purified by two fractional crystallizations from ethanol. The final product, a white solid in the form of light, platelike crystals, melted in the range 132·5–133·5°.

The mass spectra revealed only a small peak at $m/e = 350$ corresponding to the molecular weight of the parent ion of the bis-sulphoxide. In the fragmentation pattern, however, several strong peaks were observed at m/e values corresponding to logical fragmentation ions of the bis-sulphoxide.

The infrared spectrum of BOSE in chloroform displayed a strong absorption peak centred at 1021 cm^{-1} indicative of the presence of the sulphoxide group. Two weak absorption peaks were observed at 1132 and 1318 cm^{-1} suggesting the presence of a small amount of sulphone impurity.

The NMR spectrum of BOSE in deuterochloroform showed essentially the same pattern for the n-octyl methylene and methyl protons as that described for BOSM. A distorted triplet, centred at δ 2·79 was interpreted as arising from the n-octyl methylene proton adjacent to the sulphoxide group. A complex pattern centred at δ 3·11 was attributed to the isolated methylene groups. This is compatible with the complicated splitting expected from the AA′BB′ system present in the expected mixture of diastereoisomers. The proton integration gives a ratio of 3·0:12·6:2·0:1·9 for CH_3: $(CH_2)_6$:CH_2SO:—CH_2.

Analysis of BOSE gave 18·3% sulphur and 9·9% oxygen (theoretical values of 18·40% sulphur and 9·18% oxygen), indicating some sulphone impurity.

Di-n-octyl sulphone. Di-n-octyl sulphoxide was oxidized with a large excess of hydrogen peroxide in glacial acetic acid. The product was precipitated by adding water and was filtered off, washed, and air-dried. The infrared spectrum of the compound in chloroform revealed intense sulphone absorption peaks at 1130 and 1318 cm^{-1}. No sulphoxide absorption could be observed. The m.p., 76–77°, corresponds to that reported in the literature.[1]

Several metals were chromatographed on paper impregnated with di-n-octyl sulphone to determine whether, as assumed, sulphones posses little co-ordinating ability. The metals studied were chosen on the basis of being the ones most likely to be extracted by a neutral donor from the particular acids used as eluents. Impregnation of the paper with di-n-octyl sulphone had very little effect on the R_f values, indicating that the presence of small amounts of sulphone impurities (such as in BOSE) should not effect the solvent extraction behaviour of sulphoxides other than to act as inert diluents.

Chromatography

For chromatographic work 0·05M solutions of the sulphoxides in isopropanol or 80% isopropanol–20% chloroform were used. Metal ions were used as 0·01–0·05M solutions of the perchlorates, where possible, or as the nitrates or chlorides. For studies involving thiocyanate, the eluting solution consisted of ammonium thiocyanate in 1M perchloric acid.

Whatman No. 1 chromatographic paper (0·23 × 0·285 m sheets) was used for all chromatographic work.

Procedure. The chromatographic paper was fastened to the glass frames with either rubber cement or with Teflon clamps. The frames were then dipped in the 0·05M solutions of sulphoxide to impregnate the paper with the compound under investigation. The excess of solution was allowed to drain off and the frames were suspended in a fume-chamber to permit all solvent to evaporate. Metals were then applied to the impregnated paper with 2-mm disposable wooden applicator sticks. For most metals, comparison chromatograms were also run on untreated paper.

After elution of the papers with the appropriate acid, they were sprayed with one of two colour-forming reagents to determine the location of the metal ions. Metals of the hydrogen sulphide group were detected by spraying with a 50% solution of ammonium polysulphide in methanol. The remaining metals were detected by spraying with a 0·1% solution of Arsenazo I in 90% methanol–water, followed by exposure to ammonia gas.

R_f values were calculated for the geometrical centre of the spot as the point of reference.

RESULTS

Hydrochloric acid systems

Papers impregnated with various sulphoxides were used to chromatograph 46 different metal ions at hydrochloric acid concentrations ranging from 1 to 10M. Results are summarized in Figs. 1–4. A low R_f indicates that the metal ion or its chloride complex is complexed by the sulphoxide, which is held stationary by the paper. (A probable exception is barium, which has a low R_f because of the low solubility of barium chloride in concentrated hydrochloric acid).

Comparison of Figs. 1 and 2 shows generally lower R_f values for DOSO than for PTSO, indicating stronger complexation by DOSO. Apparently the electron-withdrawing tendencies of the aromatic rings weaken the polarity of the S—O group, through which co-ordination to the metal atom occurs.

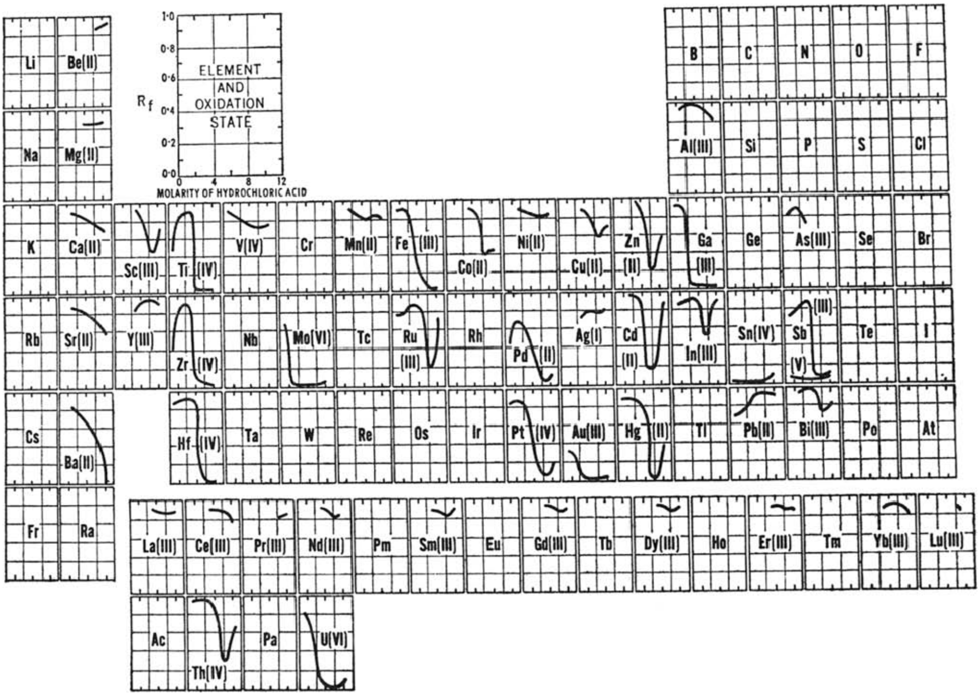

FIG. 1.—The chromatographic behaviour of metal ions on paper impregnated with di-n-octyl sulphoxide, eluted with hydrochloric acid.

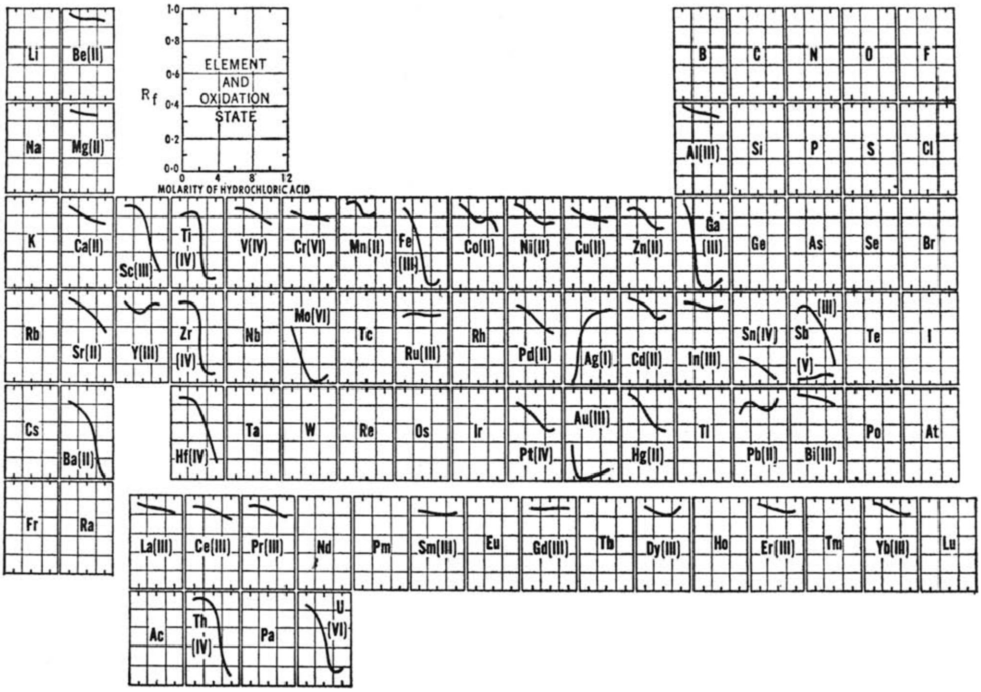

FIG. 2.—The chromatographic behaviour of metal ions on paper impregnated with *p*-tolyl sulphide, eluted with hydrochloric acid.

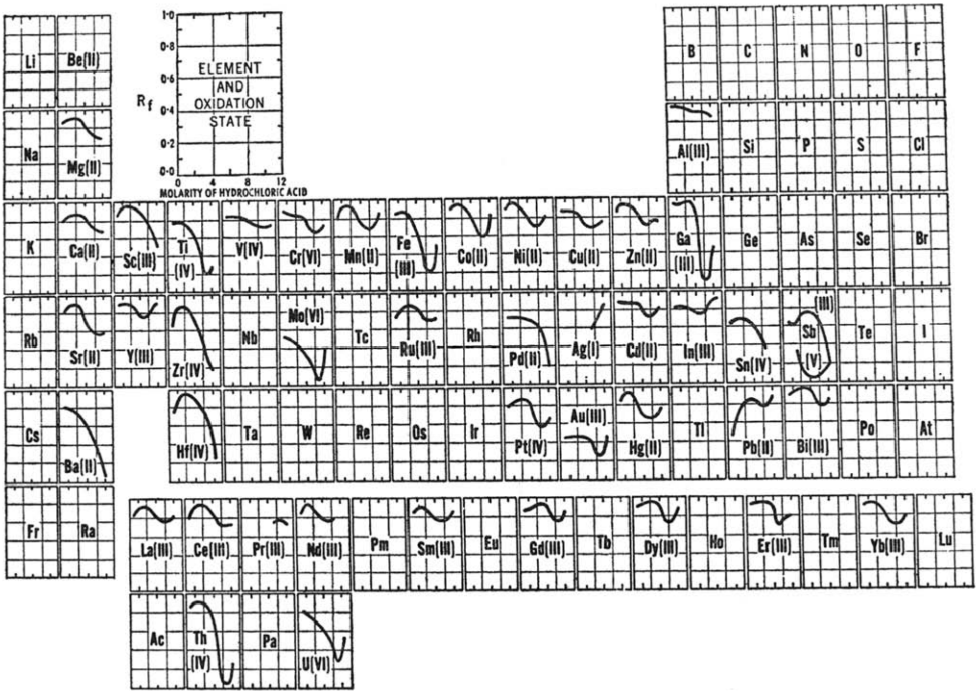

FIG. 3.—The chromatographic behaviour of metal ions on paper impregnated with bis(n-octylsulphinyl)methane, eluted with hydrochloric acid.

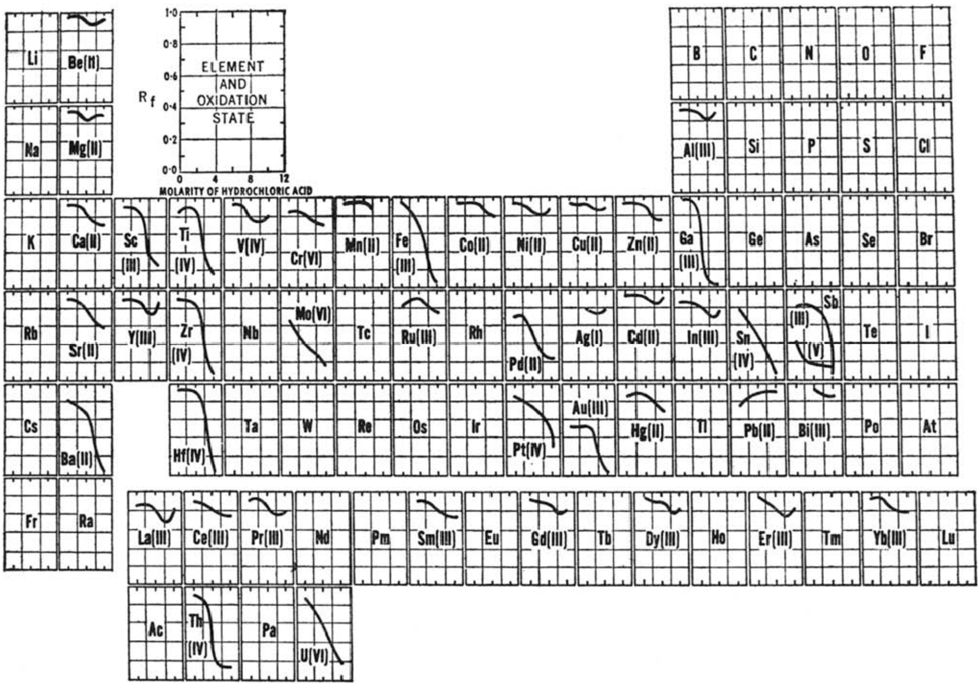

FIG. 4.—The chromatographic behaviour of metal ions on paper impregnated with bis(n-octylsulphinyl)ethane, eluted with hydrochloric acid.

It was thought that both S—O groups in BOSM might co-ordinate with the metal ion, forming a 6-membered ring that would be a stronger complex than would be possible with DOSO. However, the R_f values for both BOSM and BOSE are in general higher than for DOSO at comparable acidities, indicating that chelation probably does not occur. It is possible that steric effects make it impossible for a metal to co-ordinate several chloride ions and at the same time co-ordinate both S—O groups.

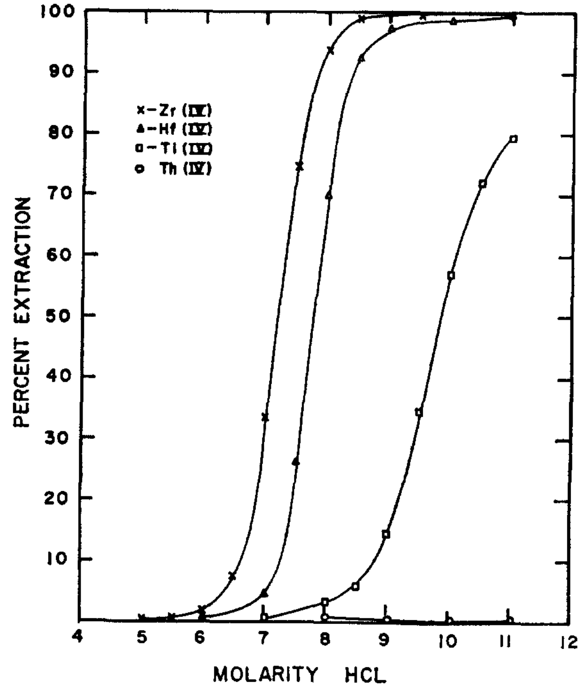

Fig. 5.—The degree of extraction of titanium(IV), zirconium, hafnium, and thorium into 0·1*M* DOSO in chloroform as a function of hydrochloric acid concentration.

Figures 1–4 and especially Fig. 1 suggest many separation possibilities. For example, the low R_f values for titanium(IV), zirconium and hafnium with 6–11*M* hydrochloric acid indicate that these elements might be extracted by solutions of DOSO in an organic solvent. Actual curves for extraction of these elements and of thorium by 0·1*M* DOSO in chloroform confirm this (Fig. 5). The data in this figure indicate that in 8–11*M* hydrochloric acid zirconium and hafnium can easily be separated from thorium by batch extraction. The intermediate extraction of titanium(IV) will prevent its separation from the other metals by batch extraction. However, it was found that the addition of a drop of 30% hydrogen peroxide to the aqueous phase completely suppresses the extraction of titanium(IV), apparently owing to the formation of a peroxy complex. The extraction of zirconium and hafnium is not affected by the hydrogen peroxide.

Before attempting actual separations it was first determined that zirconium and hafnium could be quantitatively back-extracted by 5*M* hydrochloric acid. Binary mixtures of 0·01M metal ions in 10·5M hydrochloric acid were separated by extraction with 0·1M DOSO in chloroform. Hydrogen peroxide was added to prevent extraction of titanium(IV). After back-extraction with 5M hydrochloric acid, the metal ions in the original and back-extracted aqueous phases were determined by titration with 0·01M EDTA. Table I summarizes the results of these separations.

TABLE I.—LIQUID–LIQUID BATCH EXTRACTION SEPARATIONS

Experiment	Metal	Amount added, *mmole*	Amount found, *mmole*	Recovery, %
1	Zr(IV)	0·136	0·136	100·0
	Th(IV)	0·140	0·139	99·4
2	Hf(IV)	0·125	0·123	98·7
	Th(IV)	0·140	0·140	100·0
3	Zr(IV)	0·136	0·137	100·7
	Ti(IV)	0·173	0·165	95·4
4*	Zr(IV)	0·136	0·134	98·6
	Ti(IV)	0·173	0·173	100·0

* Separation performed in 9·5M hydrochloric acid.

Figure 1 indicates that in approximately 1M hydrochloric acid only tin(IV) and antimony(V) have low R_f values on DOSO-impregnated paper. In ~3M hydrochloric acid molybdenum(VI) also has a low R_f. Thus it may be possible to separate these elements from all other elements studied. Still another possibility suggested by Fig. 1 is the separation of gallium from aluminum, indium, iron(III) and other metal ions in 4–5M hydrochloric acid.

Nitric acid systems

Paper impregnated with various sulphoxides was used to chromatograph metal ions in nitric acid solutions ranging from 1 to 11M. Results are given in Figs. 6–9. Fewer metal ions have low R_f values than in hydrochloric acid, but complex formation by DOSO is indicated for some metal ions including Ti(IV), Zr, Hf, Pd(II), Au(III), Sb(V), Bi, Th and U(VI).

For most metal ions the R_f values indicate weaker complexation for PTSO, BOSM and BOSE than for DOSO. An interesting exception is the behavior of Fe(III) and Ru(III) which are complexed by PTSO, but not by DOSO. This phenomenon has been confirmed by solvent extraction and is being studied further. The rare earths are another exception. Little complexation is indicated for DOSO; there is some complexation for BOSM and rather strong complexation for BOSE in 6–8M nitric acid. Yttrium and scandium are also complexed by BOSE.

When the rare earths were chromatographed on papers containing various loadings of BOSE, a plot of log $1/R_f$ *vs.* log of relative BOSE loading gave a straight line of slope = 1, indicating a 1:1 combining ratio of BOSE:rare earth. The plot in Fig. 10 shows that retention of rare earths by BOSE on paper reaches a maximum near the middle of the rare earth series. The decrease in retention in the latter half of the series is surprising because the formation constants of the rare earth–nitrate complexes, which are assumed to be extracted, increase regularly from lanthanum

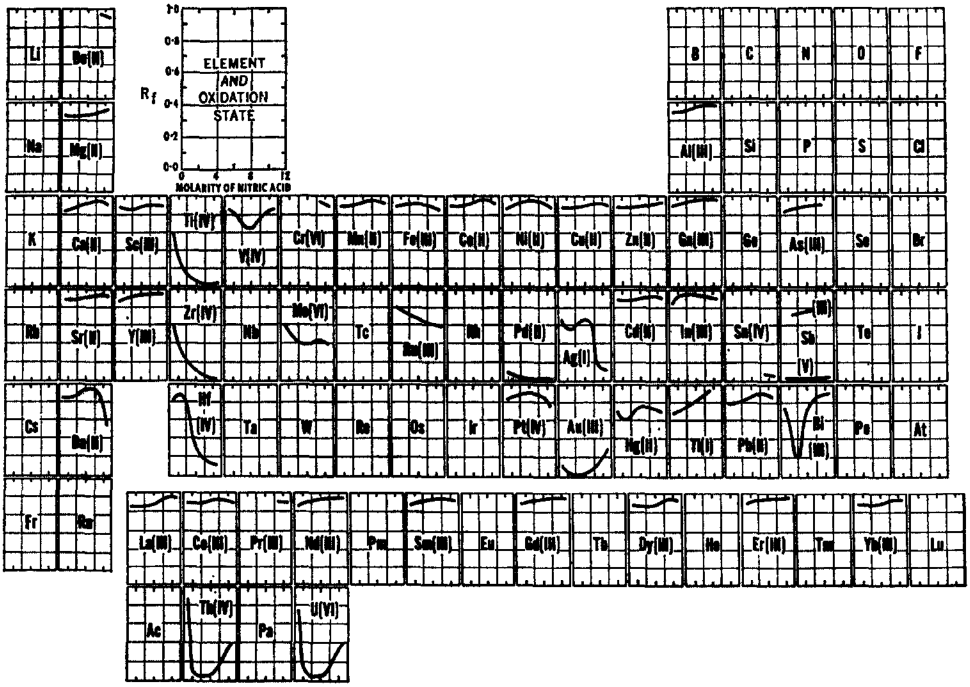

FIG. 6.—The chromatographic behaviour of metal ions on paper impregnated with di-n-octyl sulphoxide, eluted with nitric acid.

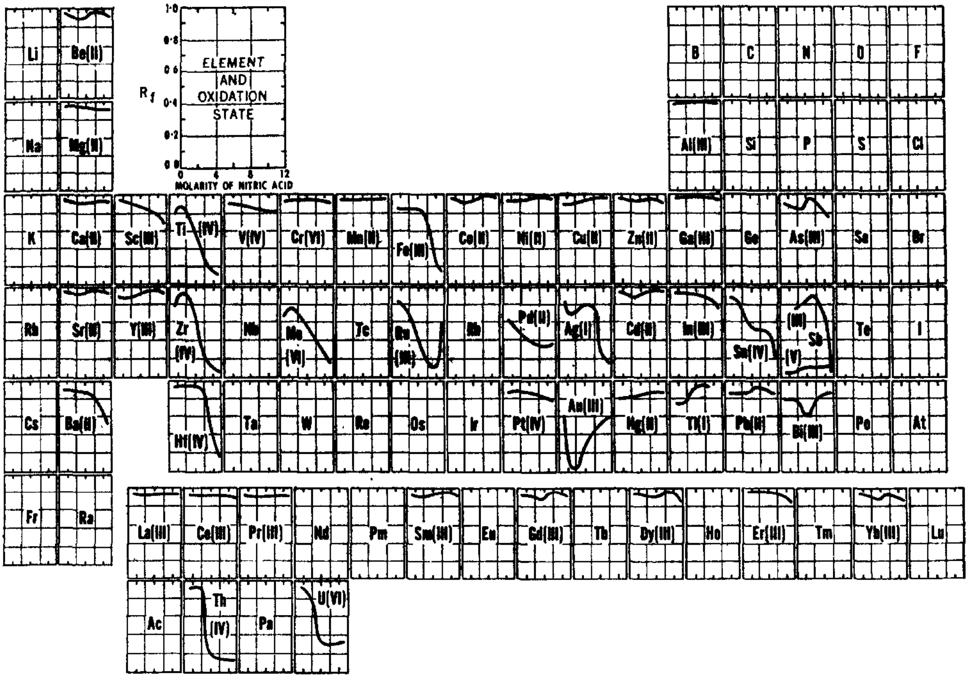

FIG. 7.—The chromatographic behaviour of metal ions on paper impregnated with *p*-tolyl sulphoxide, eluted with nitric acid.

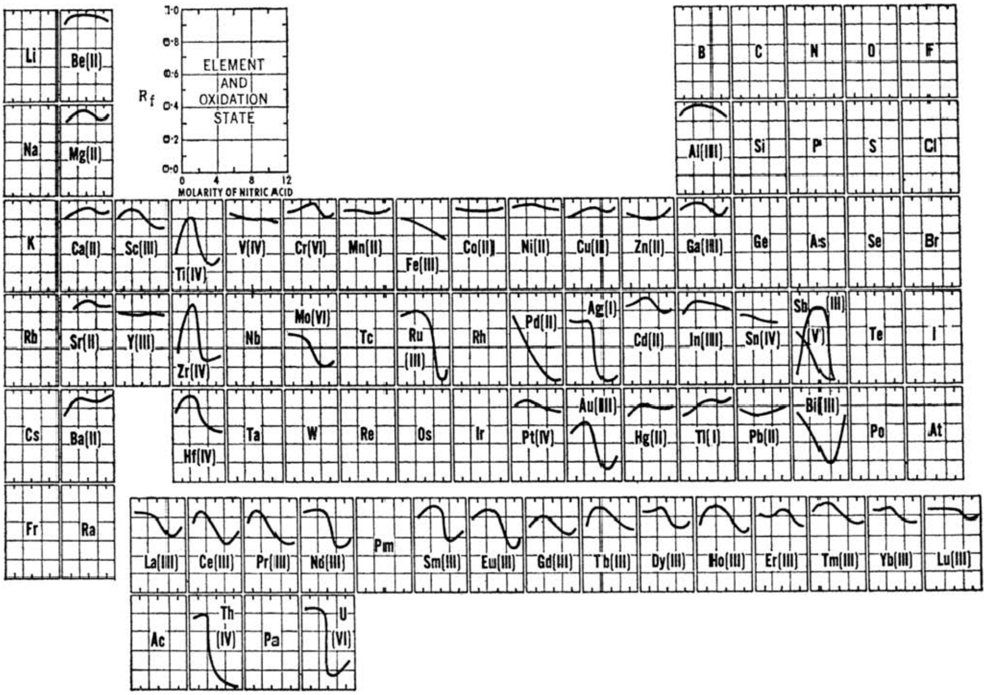

FIG. 8.—The chromatographic behaviour of metal ions on paper impregnated with bis(n-octylsulphinyl)methane, eluted with nitric acid.

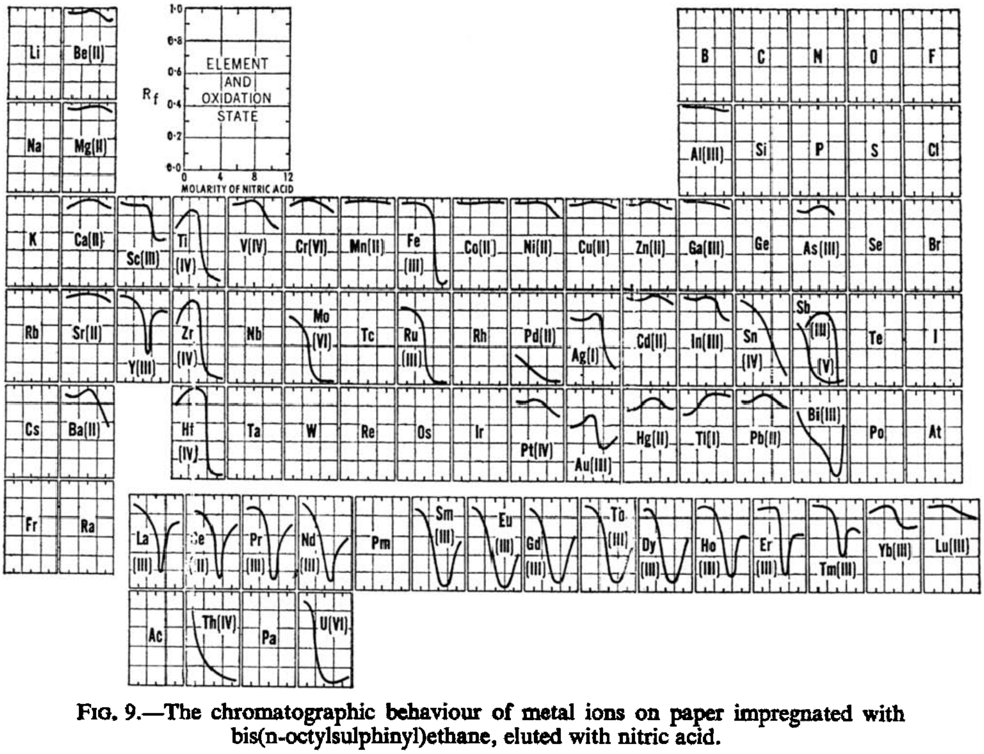

FIG. 9.—The chromatographic behaviour of metal ions on paper impregnated with bis(n-octylsulphinyl)ethane, eluted with nitric acid.

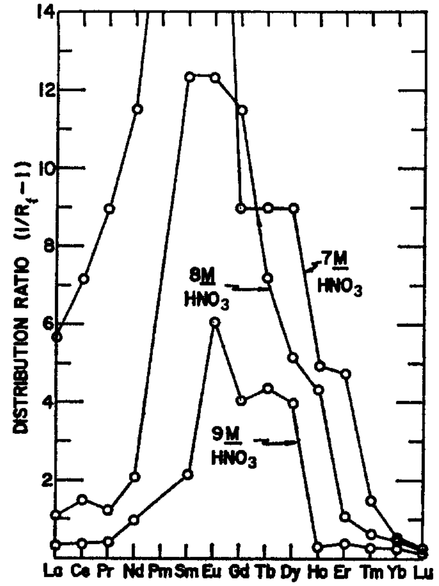

FIG. 10.—The chromatographic behaviour of the lanthanides on paper impregnated with bis(n-octylsulphinyl)ethane, eluted with nitric acid.

to lutetium. Apparently, the steadily decreasing ionic radii of the lanthanides, coupled with the aforementioned steric effects, weaken the co-ordinating ability of the bis-sulphoxides towards the higher rare earths.

Thiocyanate systems

Behaviour of metal ions on paper impregnated with DOSO and BOSM, with aqueous perchloric acid–ammonium thiocyanate solutions, is summarized in Figs. 11 and 12. Again DOSO retains most metal ions more strongly than BOSM. The following metal ions are strongly retained by DOSO on paper over the entire range of thiocyanate concentrations studied: Ti(IV), Zr, Hf, Mo(VI), Sn(IV), Th and U(VI). The behaviour of zinc and cadmium is unusual. The possibility of separating them was confirmed by solvent extraction studies using 0·5*M* DOSO in 1,2-dichloroethane. From 1*M* perchloric acid–0·5*M* ammonium thiocyanate, zinc was 98·5% extracted while cadmium was only 2·2% extracted.

Perchloric acid systems

Finally, the chromatographic behaviour of metal ions on DOSO-impregnated paper was studied as a function of aqueous perchloric acid concentration (Fig. 13). Very few metal ions show evidence of any co-ordination. The outstanding exception is uranium(VI) which shows quite low R_f values over a broad range of perchloric acid concentrations. More detailed studies on the extraction of uranium will be the subject of a forthcoming paper.

Low R_f values are also observed for Pd(II) and Au(III). For Au(III) this behaviour is probably due to the chloride used to prepare the aqueous solution. In the case of

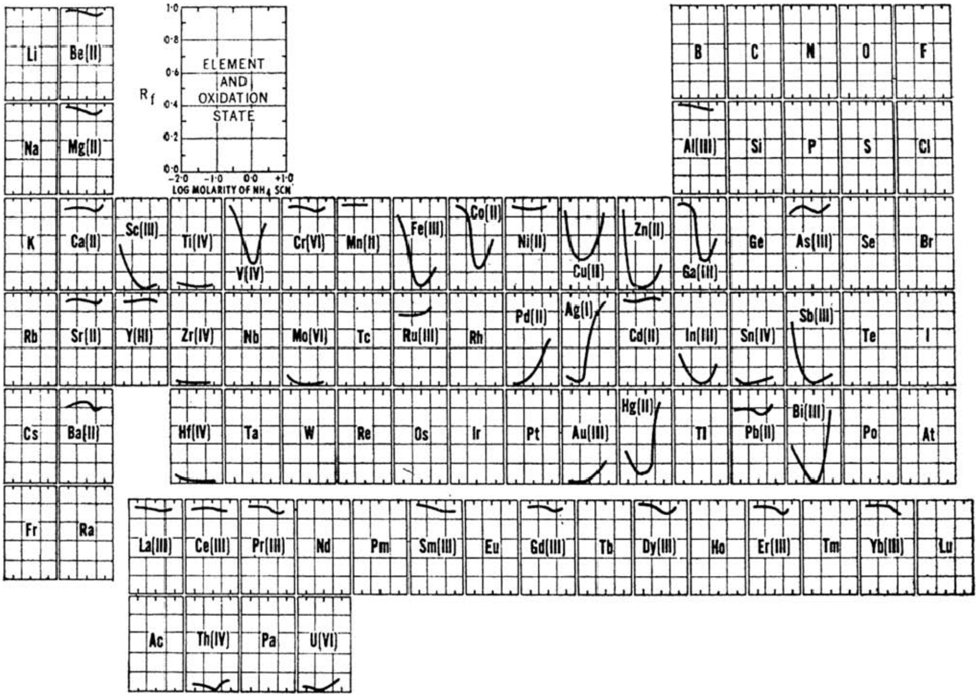

FIG. 11.—The chromatographic behaviour of metal ions on paper impregnated with di-n-octylsulphoxide, eluted with 1*M* $HClO_4$–NH_4SCN.

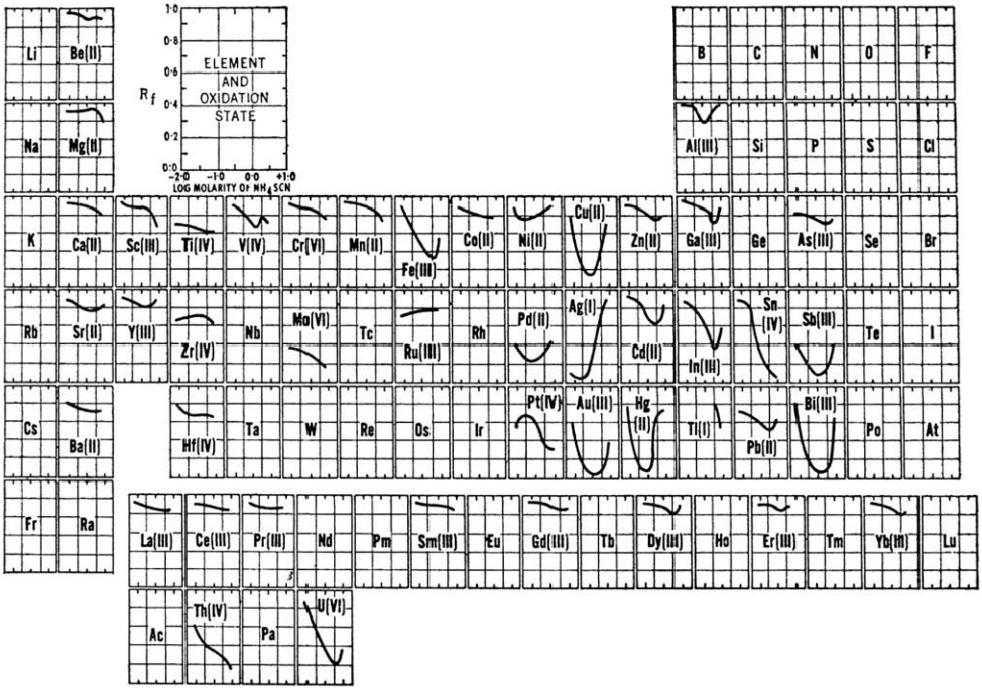

FIG. 12.—The chromatographic behaviour of metal ions on paper impregnated with bis(n-octylsulphinyl)methane, eluted with 1*M* $HClO_4$–NH_4SCN.

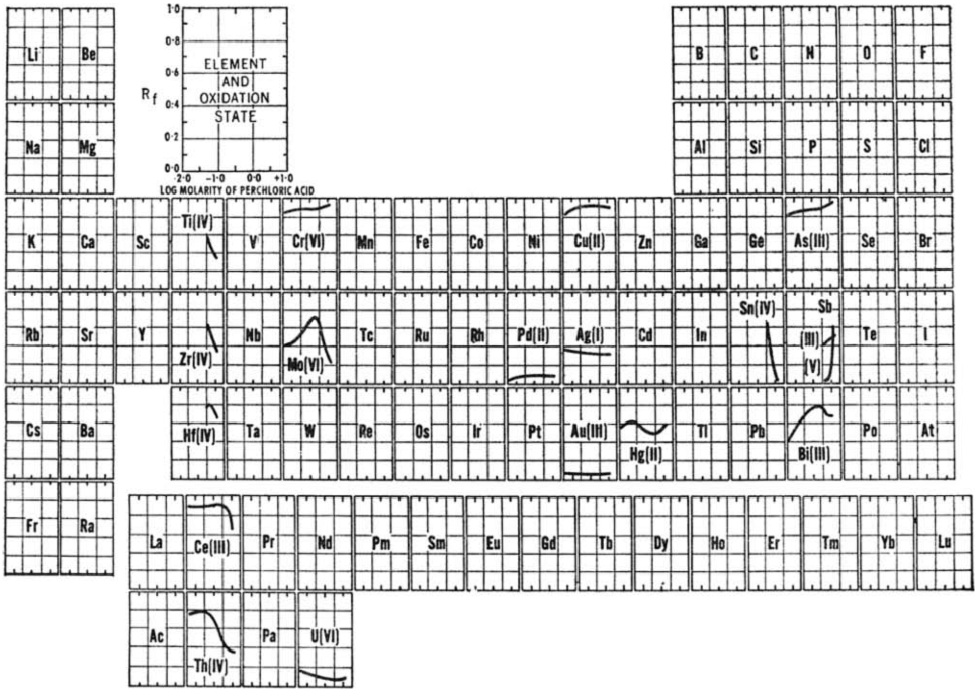

FIG. 13.—The chromatographic behaviour of metals ions on paper impregnated with di-n-octyl sulphoxide, eluted with perchloric acid.

Pd(II), there is a possibility that the low R_f value may be due to Pd ← S co-ordination with DOSO. This type of interaction is well documented for the analogous DMSO complex; $PdCl_2 \cdot 2DMSO$.[12]

Acknowledgement—The assistance of Dr. Roy King in interpreting the NMR data is gratefully acknowledged.

Zusammenfassung—Die Extraktionseigenschaften folgender Sulfoxide wurden ermittelt: Di-n-oktylsulfoxid (DOSO), Bis(n-oktyl-sulfinyl)-methan (BOSM), Bis(n-oktylsulfinyl)äthan (BOSE) und p-Tolylsulfoxid (PTSO). Mit Hilfe der Papierchromatographie mit umgekehrten Phasen zur qualitativen Übersicht wurden die Wechselwirkungen dieser Sulfoxide mit etwa 50 Metallionen in mehreren Säure-Ligand-Systemen untersucht. Alle Sulfoxide wurden in 1–10*M* Salzsäure und Salpetersäure untersucht; DOSO und BOSM auch in Überchlorsäure und Mischungen aus Ammoniumthiocyanat und Überchlorsäure. Es werden Beobachtungen über Wechselwirkungen zwischen Sulfoxid und Metall mitgeteilt und auf verschiedene nützliche Trennsysteme hingewiesen. Synthese und Charakterisierung von BOSM und BOSE werden angegeben.

Résumé—On a évalué les propriétés de solvant d'extraction des sulfoxydes suivants: di-n-octyl sulfoxyde (DOSO), bis(n-octylsulfinyl) méthane (BOSM), bis(n-octylsulfinyl)éthane (BOSE) et *p*-tolyl sulfoxyde (PTSO). Par l'emploi de la chromatographie sur papier à phases inversées comme technique qualitative d'étude, on a étudié les interactions de ces sulfoxydes avec quelques cinquante ions métalliques dans plusieurs systèmes acide-ligand. Tous les sulfoxydes ont été étudiés en acides chlorhydrique et nitrique 1–10*M*; DOSO et BOSM ont aussi été étudiés en acide perchlorique et dans des mélanges thiocyanate d'ammonium acide perchlorique. On effectue des observations concernant les interactions sulfoxyde métal et l'on fait ressortir l'existence de plusieurs systèmes de séparation analytique utiles On décrit la synthèse et la caractérisation de BOSM et BOSE.

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EXTRACTION CHROMATOGRAPHY OF URANIUM WITH DIOCTYL SULPHOXIDE*

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Summary—Uranium(VI) is quantitatively extracted from aqueous perchlorate media into dioctyl sulphoxide in 1,2-dichloroethane. The extracted species contains four sulphoxides for each uranium. Most other metal ions are not appreciably extracted. On columns containing a solid support impregnated with dioctyl sulphoxide in 1,2-dichloroethane, uranium(VI) may be separated quantitatively from metal ions such as thorium(IV), zirconium(IV) and rare earths(III).

IN A RECENT report[1] the evaluation of sulphoxides as solvent extraction reagents was described; reversed-phase paper chromatography was used as a qualitative technique to investigate the interaction of several sulphoxides with a large number of metals in several acid systems. It was observed that uranium(VI) was strongly retained on paper impregnated with di-n-octyl sulphoxide (DOSO) and eluted with perchloric acid. The weak extraction of the 50 other metals studied [except of gold(III) and palladium(II)] indicated that a nearly specific analytical separation of uranium(VI) might be possible in this system. It was decided, therefore, to study the extraction of uranium(VI) and other metals from perchloric acid solutions into DOSO dissolved in an organic diluent. From the results of this study, it was hoped that an extraction system could be developed which would permit the analytical separation of uranium from most other metals.

EXPERIMENTAL

Reagents

Dioctyl sulphoxide (DOSO) was prepared as described earlier.[1]

Chromatographic column

The support used was XAD-2, a macroreticular polystyrene resin obtained from Rohm and Haas. It was ground and sieved to 60–80 mesh. Conventional glass chromatographic columns were filled with XAD-2 slurry in methanol. When the methanol level had dropped just to the top of the resin bed, 0·5*M* DOSO in 1,2-dichloroethane was passed slowly through the column and sorbed by the XAD-2 support. The interstitial DOSO solution was then displaced by aqueous 0·9*M* lithium perchlorate–0·1*M* perchloric acid.

Column separations

Samples added to the column contained approximately the same concentrations of perchlorate as the eluents. Eluents were pre-equilibrated with the organic phase. Flow-rates varied from 1 to 3 ml/min.

Analytical methods

Metal ions were determined by standard analytical procedures, mostly involving titration with EDTA. Uranium was determined spectrophotometrically with Arsenazo I.[2]

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FUNDAMENTAL STUDIES

First a number of organic solvents were evaluated as diluents for DOSO; 0·01*M* solutions of uranium(VI) in 1*M* perchloric acid were extracted with 0·1*M* DOSO in various diluents. The results of these extractions are summarized in Table I.

TABLE I.—EXTRACTION OF U(VI) FROM 1*M* $HClO_4$ INTO 0·2*M* DOSO (IN ORGANIC SOLVENT)

2-Phase Systems		3-Phase Systems	
Diluent	Extraction, %	Diluent	Extraction, %
Chlorobenzene	50	Butyl acetate	70
Chloroform	50	Diethyl ether	88
n-Octanol	50	Benzene	95
n-Butanol	55	Toluene	95
IBMK	65	Carbon tetrachloride	97
n-Butyronitrile	70	Xylene	99
2-Octanone	75	Cyclohexane	99·5
1,2-Dichloroethane	75	Methyl laurate	99·8
Tributyl phosphate	89		
Nitrobenzene	95		

The diluents in Table I are divided into two categories; two-phase systems and three-phase systems. In the three-phase systems, a viscous yellow liquid or flaky yellow solid (which apparently contained all the uranium) was formed between the aqueous phase and the diluent phase. Although the three-phase systems are characterized by generally high extraction, they were considered to be unsuitable analytically. Of the two-phase systems, n-butyronitrile and 1,2-dichloroethane behaved well, and the latter was selected as the most satisfactory. Tributyl phosphate was not studied further because of its limited ability to dissolve DOSO.

The effect of the concentration of DOSO on the extraction of uranium(VI) was the subject of the next experiment; 0·01*M* solutions of uranium(VI) in 1*M* perchloric acid were extracted with 0·1–0·5*M* DOSO in 1,2-dichloroethane. The results of this study gave a linear log–log plot of distribution coefficient *vs*. DOSO concentration, with a slope of 3·97, confirming that the combining ratio of DOSO with uranium(VI) in perchlorate media is 4:1, indicating the formation of the species $UO_2(DOSO)_4{}^{2+}$ in which DOSO ligands have completely filled the inner co-ordination sphere of the uranyl ion. A practical consequence of the composition of the complex is that the distribution coefficient is a function of the fourth power of the DOSO concentration. Thus if the latter is changed from 0·1 to 0·5*M*, the distribution ratio increases nearly 500-fold. The concentration of DOSO was fixed at 0·5*M* for further extraction studies.

A few brief experiments were performed to determine how the uranium(VI), once extracted, could best be recovered from the organic phase. Back-extraction with dilute sulphuric acid was found to be best. It was found that uranium(VI) which had been extracted into 0·5*M* DOSO in 1,2-dichloroethane could be quantitatively recovered by back-extracting three times with 0·1*M* sulphuric acid or twice with 1*M* acid.

The effect of perchlorate concentration on the extraction of uranium(VI) was next studied. The perchloric acid solutions used ranged in concentration from 0·05 to 6·0*M*. The lithium perchlorate solutions used were 0·025*M* in perchloric acid and varied in perchlorate concentration from 0·05 to 4·22*M*, the concentration of a

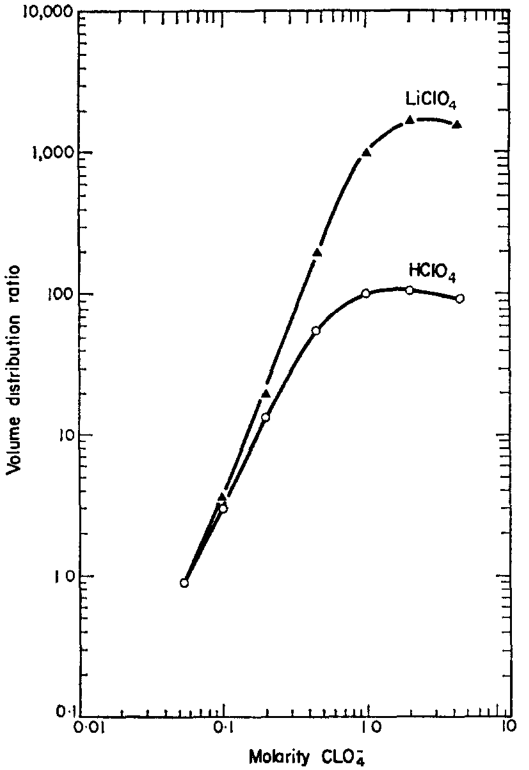

FIG. 1.—The distribution ratio of uranium(VI) extracted into 0·5*M* DOSO in 1,2-dichloroethane as a function of the concentration of perchloric acid or lithium perchlorate in the aqueous phase.

saturated solution of lithium perchlorate at 27°. The results of this study are presented in Fig. 1.

The distribution ratios for the perchloric acid solutions, after an initially linear increase reach a limiting value of 100 for 1–2*M* acid and then decrease slightly. This behaviour at high perchloric acid concentrations is probably due to competitive extraction of the acid by DOSO. The linear portion of the curve has a slope of 2·0, confirming that the formula of the extractable complex is $\{[UO_2(DOSO)_4^{2+}][ClO_4^-]_2\}$.

The curve for the extraction of uranium(VI) from lithium perchlorate at constant hydrogen ion concentration has a longer linear portion than the perchloric acid curve and also a higher slope, 2·6. This curve also deviates from linearity and decreases at higher concentrations of perchlorate, possibly owing to partitioning of lithium perchlorate. At all concentrations above 1*M* lithium perchlorate, however, the distribution ratio is greater than 1000, the magnitude necessary for quantitative (99·9%) extraction of uranium(VI).

A series of extractions was next performed to determine the effect of hydrogen ion concentration on the extraction of uranium(VI) from 1*M* perchlorate solutions. The solutions [0·01*M* in uranium(VI)] contained lithium perchlorate and perchloric acid. The pH of each was measured before extraction. A plot of distribution ratio as a function of pH is presented in Fig. 2.

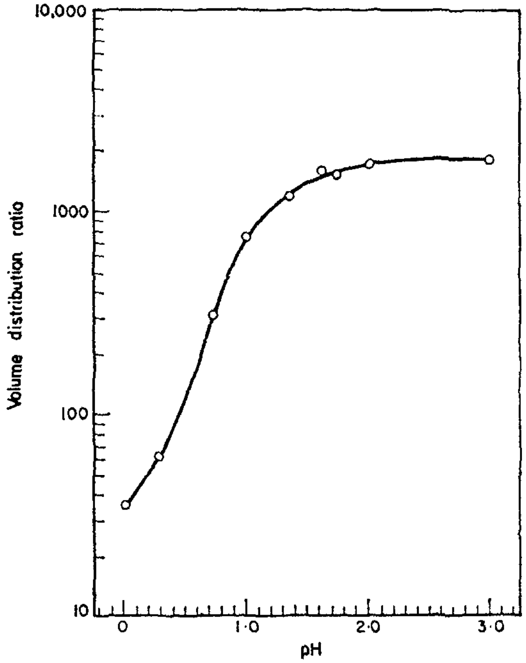

Fig. 2.—The distribution ratio of uranium(VI) extracted into 0·5*M* DOSO in 1,2-dichloroethane from 1·0*M* aqueous perchlorate mixtures, as a function of the pH of the aqueous phase.

The distribution ratios for the extraction of uranium(VI) from 1*M* perchlorate approach a limiting value of about 1900 with decreasing hydrogen ion concentration. The decrease in extraction at low pH is again apparently the result of competitive extraction of perchloric acid. These data show that a quantitative extraction of uranium(VI) is possible from 1*M* perchlorate solutions at pH 1 or higher. On this basis, it was decided to limit further extraction studies to a 1*M* lithium perchlorate medium that was 0·025*M* in perchloric acid (pH 1·65).

A study was next made of the extraction of other metals (0·01*M* solutions) under the conditions established for quantitative extraction of uranium(VI). The metal perchlorates were used when possible. Nitrates or chlorides were used only when it was known that the metals would not form complexes with these anions. For other metals, such as iron(III), palladium(II), gallium(III), where strong complexation by the chloride ion was expected, the chlorides were fumed to near dryness with concentrated perchloric acid and taken up in a solution of 1*M* lithium perchlorate. An exception to this procedure was tin(IV); a considerable amount of hydrochloric acid was required to keep it in solution.

The metal solutions were extracted for 5 min with 0·5*M* DOSO in 1,2-dichloroethane and the extent of extraction was quantitatively determined. Table II lists the metals studied, in order of decreasing extraction. An examination of the data in Table II reveals very few metals, in addition to uranium(VI), which are strongly extracted. Palladium(II) and gold(III) are two notable exceptions. These two metals are also strongly extracted by DOSO on paper.[1] The behaviour of palladium(II) and gold(III) is an indication of strong sulphur-metal interaction in their complexes.

TABLE II.—THE EXTRACTION OF METALS FROM 1·0*M* LITHIUM PERCHLORATE–0·025*M* PERCHLORIC ACID INTO 0·5*M* DOSO IN 1,2-DICHLOROETHANE

Metal	Extraction, %	Volume distribution ratio	Metal	Extraction, %	Volume distribution ratio
Pd(II)*	~100·0	$>5 \times 10^5$	Ti(IV)	2·9	0·030
U(VI)	99·9	$1·63 \times 10^3$	Lu(III)	2·0	0·020
Au(III)	98·7	75·9	Al(III)	0·61	0·006
Hg(II)	94·4	16·9	Cd(II)	0·55	0·0056
Ce(IV)†	72·5	2·63	Hf(IV)	0·39	0·0039
Sc(III)	42·7	0·744	Cs(I)	0·28	0·0028
Sn(IV)§	31·7	0·464	As(III)	0·24	0·0024
Ag(I)	28·9	0·406	Cr(III)	0·19	0·0019
V(IV)	15·6	0·185	Zn(II)	0·13	0·0013
Fe(III)‡	12·7	0·145	Ce(III)	0·12	0·0012
Pb(II)	9·9	0·110	Zr(IV), Ba(II)	<0·10	<0·0010
Mo(VI)	9·3	0·103	Co(II), Sr(II)		
Th(IV)	8·0	0·087	Cu(II), Ni(II)		
In(III)	5·7	0·060	Mn(II), Gd(III)		
Ga(III)	5·7	0·059	Y(III), Pt(IV)		
Bi(III)	5·5	0·058	Ru(III)		

* In the presence of 0·1*M* HCl kinetics are slow and $D_v = 530$.

† Reduced slowly to Ce(III).

§ Hydrochloric acid required to keep Sn(IV) in solution.

‡ In the presence of 0·1*M* HCl extraction = 35·6%.

The decrease in the rate and magnitude of extraction of palladium(II) in the presence of dilute hydrochloric acid (footnote 1) shows that DOSO must compete with chloride ions for co-ordination sites to form the extractable complex. This indicates that the composition of this complex is probably similar to that of uranium(VI), *i.e.*, $[Pd(DOSO)_4^{2+}][ClO_4^-]_2$.

It should be pointed out that the strong extraction of uranium(VI) from perchlorate solution is not a phenomenon unique to this system. The important step is the formation of the cation $UO_2(DOSO)_4^{2+}$. Once this is accomplished, an anion is needed merely to give charge equivalence and yield an ion-pair that is readily solvated in the organic phase. The perchlorate ion is a fairly good counter-ion, but other anions could serve the purpose equally well or better. It might be expected that an organic anion, such as an aromatic sulphonate, would be a better counter-ion than perchlorate. This was demonstrated for the case of 2-naphthalene sulphonic acid. Qualitative experiments showed that the extraction by DOSO of uranium(VI) in the presence of this anion was nearly quantitative. Gillette[3] studied the extraction of a number of aromatic sulphonic acids by an analogous organic cation, tricaprylammonium chloride.

Separations

Examination of the data in Table II reveals the potential for separating uranium(VI) from a large number of other metal ions. Simple solvent extraction should separate uranium(VI) quantitatively from the last dozen or so metal ions listed in Table II. However, if a column packed with a solid support impregnated with DOSO in 1,2-dichloroethane is used, uranium(VI) should be retained quantitatively from an aqueous perchlorate solution while all other metals listed [except palladium(II), gold(III) and probably mercury(II)] should pass through the column.

The sorption (and subsequent elution) of uranium on a 90 × 20 mm column containing 0·5*M* DOSO (in 1,2-dichloroethane) on 60–80 mesh XAD-2 was first studied. When 0·05 mmole of uranium(VI) was sorbed on the column, no metal could be detected in the effluent during elution with 250 ml of 1*M* perchloric acid. Elution with 100 ml of 1*M* sulphuric acid gave 99·8 % recovery of the added uranium. Similarly, 1·87 μmole (0·445 mg) of uranium(VI) sorbed on a 100 × 6 mm column were not eluted with 60 ml of 1*M* perchloric acid, but elution with 10 ml of 1*M* sulphuric acid gave 100·5 % recovery of the added uranium. The uranium may also be desorbed by elution with 10 ml of methanol.

TABLE III.—SEPARATION OF URANIUM(VI) FROM THORIUM(IV) AND ZIRCONIUM(IV)

Metal	Added, *mmole*	Found, *mmole*	Recovery, %
U(VI)	0·0510	0·0508	99·5
Th(IV)	0·234	0·233	99·8
U(VI)	0·0510	0·0510	100·8
Zr(IV)	0·266	0·265	99·6

Two experiments were performed in which moderate amounts of uranium(VI) were separated from thorium and zirconium. Mixtures containing 0·05 mmole of uranium(VI) and 0·25 mmole of the other metal in 1*M* perchloric acid were sorbed on the large column. Zirconium and thorium were both eluted with 30 ml of 1*M* perchloric acid, and uranium(VI) was eluted as previously described. Table III gives the results of these analyses.

The separation and recovery of small amounts of uranium(VI) from large amounts of other metal ions was next attempted. Samples of rare earth oxides weighing from 3 to 5 g were dissolved in perchloric acid. The acid concentration was adjusted to 1*M* and the solution passed through a 90 × 20 mm column containing 0·5*M* DOSO (in 1,2-dichloroethane) on XAD-2. Known quantities of uranium(VI) were added to some samples. The uranium(VI) was then eluted from the column with 100 ml of 1*M* sulphuric acid and determined spectrophotometrically with Arsenazo. The results are reasonably good (see Table IV). The "uranium" found in the blanks appears to stem at least partly from Arsenazo absorbance resulting from metal impurities in the sulphuric acid eluent.

TABLE IV.—DETERMINATION OF TRACES OF URANIUM IN SALTS

Salt	U added, *ppm*	U found, *ppm*
3·5 g Sm_2O_3	0	37
3·5 g Sm_2O_3	686	646
3·5 g Eu_2O_3	0	6
3·5 g Eu_2O_3	137	134
5·0 g $ThCl_4$	0	4·2
5·0 g $ThCl_4$	0	4·0

Separation of possible traces of uranium from specially purified thorium chloride was next attempted. A 1*M* perchlorate solution containing a total of 5 g of thorium chloride was passed through a smaller (100 × 6 mm) column of 0·5*M* DOSO (in 1,2-dichloroethane) on XAD-2, and the uranium was eluted from the column with methanol. Analysis of this effluent by the Arsenazo spectrophotometric method gave an average uranium content of 4·1 ppm in the solid thorium chloride sample, after subtraction of a column blank (no $ThCl_4$ present) of 1·2 ppm. That the substance measured in the thorium sample was actually uranium was proved by extracting a thorium sample 5 times with fresh DOSO in 1,2-dichloroethane, evaporating the solvent and analysing the solid DOSO by neutron activation. Uranium was definitely identified from the gamma-ray energies of the fission products, and the uranium content of the thorium chloride was found to be 3·6 ± 1·8 ppm, which is in good agreement with the values reported in Table IV.

Zusammenfassung—Uran(VI) wird aus wäßrigen Perchloratmedien quantitativ in Dioktylsulfoxid in 1,2-Dichloräthan extrahiert; die extrahierte Spezies enthält 4 Sulfoxidmoleküle pro Uran. Die meisten anderen Metallionen werden nicht in merklichem Umfang mit extrahiert. Auf Säulen, die einen mit Dioktylsulfoxid in 1,2-Dichloräthan imprägnierten festen Träger enthalten, kann man Uran(IV) quantitativ von Metallionen wie Thorium(IV), Zirkonium(IV) und dreiwertigen seltenen Erden trennen.

Résumé—On extrait quantitativement l'uranium(VI) de milieux perchlorate aqueux en dioctyl sulfoxyde dans le 1,2 dichloréthane. L'espèce extraite contient quatre sulfoxydes par uranium. La plupart des autres métaux ne sont pas extraits de manière appréciable. Sur des colonnes contenant un support solide imprégné de dioctyl sulfoxyde en 1,2 dichloréthane, on peut séparer quantitativement l'uranium(VI) d'ions métalliques tels que thorium(IV), zirconium(IV) et terres rares(III).

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DETERMINATION OF SILVER, GOLD AND PALLADIUM BY A COMBINED FIRE-ASSAY ATOMIC-ABSORPTION PROCEDURE

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Summary—A method is described which combines the best features of the fire-assay procedure with an atomic-absorption technique. The precious-metal bead resulting from the fire-assay concentration step is dissolved in acids, the solution evaporated to dryness and the residue dissolved in a measured quantity of cyanide solution. The atomic-absorption measurement of this solution allows the determination of as little as 0·017 ppm of silver, 0·08 ppm of gold, and/or 0·08 ppm of palladium in various precious-metal-bearing materials with a precision of ±1%.

THE CLASSICAL fire-assay method provides an excellent way to extract and concentrate traces of precious metals from large samples of inhomogeneous materials. Its chief limitations are related to transferring quantitatively small amounts of precious metal (often <0·05 mg) to an analytical balance and to separating the various components by chemical methods.

A number of workers have reported methods for determining silver and gold in specific ores by a direct chemical attack followed by atomic-absorption measurements.[1–7] Such procedures may be suitable for routine analyses of relatively rich ores taken from particular mines, but both the sensitivity and accuracy of these direct methods suffer from the use of relatively small samples and from potentially incomplete extraction of silver and gold. Nonetheless, the sensitivities of the atomic-absorption technique for gold, silver, and palladium are sufficiently great to suggest that atomic absorption may be ideally suited to the analysis of the final bead of precious metals resulting from the fire-assay procedure.

A typical fire-assay bead results from a complete decomposition of an assay ton (29·1666 g), or a fraction thereof, of sample and consists only of the silver, gold, and platinum metals. As will be shown below, such a bead can be decomposed in acids and concentrated into 5 ml of solution for atomic-absorption measurements. It was found that 0·1 ppm of silver, 0·3 ppm of gold or 0·3 ppm of palladium can be measured by atomic absorption with a precision of ±1%. Thus, 0·5 μg of silver, from a 30-g sample (0·017 ppm or 0·0005 oz/ton) can be determined with good precision by combining atomic-absorption with fire assay. To achieve such remarkable sensitive and precise results, it is necessary to establish suitable means for dissolving the beads and for maintaining the noble metals in stable solution for atomic-absorption measurement.

Various media have been recommended for the atomic-absorption measurement of gold, silver and palladium. These include 25% hydrochloric acid,[3–7] dilute nitric acid,[8] potassium cyanide solution[1] and organic extracts.[7] Concentrated hydrochloric acid is unsatisfactory because of its significant attack on the steel aspirator.

Preliminary experimentation revealed that hydrochloric acid solutions must be avoided when analysing samples containing significant quantities of gold, because of possible reduction of the gold in the steel capillary of the aspirator, resulting in clogging of the capillary and loss of a significant fraction of the gold. In addition, the solubility of silver chloride in moderately concentrated hydrochloric acid is quite limited. Nitric acid solutions are deemed inadvisable, because of the probability of losing traces of silver by chloride contamination. Potassium or sodium cyanide solutions, in contrast, form extremely stable complex ions with all the metals of interest and, in addition, provide a high concentration of readily ionized alkali metal atoms in the flame to minimize ionization of gold, silver, and palladium atoms. Five ml of 2% potassium cyanide solution will hold over 50 mg of silver or palladium and even larger amounts of gold as stable complexes. Thus relatively large quantities of silver, gold, or palladium can be concentrated into a small volume, permitting the determination of traces of the other individual precious metals.

EXPERIMENTAL

Decomposition of the sample

Gold, silver, and/or palladium in ores and concentrates. A fire-assay fusion and, if necessary, a scorification are carried out, producing a lead button which should contain a minimum of 0·5 μg of silver, 1·5 μg of gold or 1·5 μg of palladium. In the case of concentrates, the final bead resulting from the cupellation step will usually contain more than 2 mg and sometimes in excess of 100 mg of combined silver and gold. Silver is usually the preponderant element.

If the sample charge contains less than 1 mg of combined silver and gold, a few mg of silver are added to the fusion flux for the quantitative collection of gold and/or palladium. Similarly, for the determination of silver, a few mg of gold are added to the flux, when the expected combined weight of silver plus gold is less than 1 mg.

The bead is weighed, if one of the elements is determined "by difference", transferred to a 50-ml beaker, and treated with 15 ml of hot 4*M* nitric acid. When there is no further reaction 5 ml of concentrated hydrochloric acid are added and the solution is heated until decomposition is complete. (If gold was added to collect the silver, the bead is attacked with 20 ml of hot *aqua regia.*) After dissolution, the cover is washed and removed and the solution evaporated to dryness at low temperature, preferably on a steam-bath.

Gold and/or silver in copper. The sample is decomposed by heating strongly with concentrated sulphuric acid, with a mercury salt as catalyst. When decomposition is complete, the cold solution is diluted with water. A few drops of dilute hydrochloric acid or sodium chloride solution are added to precipitate the silver. After standing overnight, the solution is filtered and the residue is washed with cold water and ignited in a scorifier. Following scorification and cupellation, the bead is treated with nitric, then hydrochloric acid, as described above.

Gold and silver in drill cores and other survey samples. Since such material is usually low in silver and gold, it is advisable to add silver to a portion of the sample for the collection of the gold, and gold to another portion for the collection of the silver. In the case of extremely low-grade material, the purity of the gold or silver collector should be examined by running portions of it through the entire fusion, scorification, cupellation and atomic-absorption steps.

Gold, silver and/or palladium in jeweller's sweeps. The material may be nickel, chromium or copper-base containing varying amounts of gold, silver, palladium, and/or platinum. Decomposition can be achieved by assay fusion, scorification and acid decomposition or by a combination of these. The final bead, depending on its composition, is first attacked with nitric acid, followed by hydrochloric acid (if silver is the preponderant element), or by *aqua regia* (if gold, palladium and platinum are the preponderant elements). In the case of samples with a silver to gold ratio of less than 3:1, it may be necessary to decant the solution, saturated with silver chloride, and attack the remaining metal by heating with fresh hydrochloric acid, with intermittent addition of nitric acid.

If the silver content exceeds 25 mg, the silver chloride, after evaporation of the excess of acid and dilution, may be filtered off and weighed. If the silver chloride is discoloured by co-precipitated gold, palladium or platinum, it should be reprecipitated. This, it was found, can be done most expeditiously by treating the silver chloride in 1–5% v/v sulphuric acid with zinc metal,[9] followed by filtration and dissolution of the silver sponge in nitric acid and precipitation of silver chloride with hydrochloric acid.

The filtrate from the silver chloride, or the solution containing silver, gold, and palladium, is evaporated to dryness.

Gold, palladium, and silver in electronic scrap. Some samples can be dissolved directly in acids. However, the sample frequently is not homogeneous and may contain a large quantity of base metals which would complicate a direct determination of small amounts of precious metals. It is therefore advantageous to use preliminary fire-assay procedures until a bead is obtained which contains the three metals under discussion and possibly also platinum. In cases of extreme inhomogenity, it may be desirable to melt all of the material either directly or by matting, in order to obtain a satisfactory analytical sample.

The final bead resulting from the cupellation step is dissolved by heating with concentrated hydrochloric acid, with occasional addition of concentrated nitric acid. As the attack slows down, more nitric acid is added from time to time. If dissolution of the bead is incomplete, additional hydrochloric acid is added. In extreme cases, the solution is decanted off and the undissolved sample is treated with fresh acids. All solutions are finally combined.

Silver alloys for palladium, and palladium sweeps with silver added as collector. The bead is dissolved in nitric acid, without addition of hydrochloric acid, thus avoiding the handling of large quantities of silver chloride. The solution may contain undissolved gold, which can be disregarded.

Atomic-absorption measurements of the solutions

The solution resulting from one of the decomposition steps is evaporated to dryness in a 50-ml beaker on a steam-bath. An exactly measured volume of 2% w/v potassium cyanide solution is added to the cold dry salts and stirred until a clear solution is obtained. If dilution to more than 25 ml is contemplated, about 30 ml of cyanide solution are used to dissolve the salts, with a little heat if needed, and then the solution is washed into an appropriate volumetric flask with additional cyanide solution.

Using the three-slot Boling burner with the Perkin–Elmer 303 Atomic Absorption Spectrophotometer, we find the wavelengths and concentration ranges indicated in the following table to be suitable.

Element	Concentration range, *μg/ml*	Wavelength, *nm*
Au	0·3–50	242·8
	10–100	267·6
Ag	0·1–10	328·1
	2–20	338·3
Pd	0·3–30	247·6
	5–60	340·4

In some cases, a single volume can be chosen to place the concentrations of all three elements in their optimum ranges for measurement. In other cases, it will be necessary to prepare a more concentrated solution for determining the minor constituents, followed by dilution of aliquots with cyanide solution for determining the major constituents.

Standard solutions are prepared by dissolving weighed quantities of silver, gold or palladium in nitric and/or hydrochloric acids, evaporating to dryness, dissolving in 2% w/v potassium cyanide solution and diluting to definite volumes with cyanide solution. Between 10 and 12 standard solutions are required to cover the useful concentration range of each element. These solutions have been found to be stable for periods of up to 6 months, when stored in polyethylene bottles.

Each absorbance measurement of a sample is immediately followed by measurement of the closest standard. By running samples in duplicate and reading each portion twice, results are precise to within about 1% of the amount present. A recording attachment has proven to be extremely useful for evaluation of the measurements. A digital read-out accessory lessens the opportunities for human error and minimizes the time required to calculate results.

DISCUSSION

To avoid mechanical losses during fire-assay steps, it is necessary that for the determination of gold the sample charge contain at least five times as much silver as gold. Similarly, for the determination of trace amounts of silver, it is necessary that the sample charge contain an excess of gold to avoid silver losses during fire-assaying. When required, the addition of 10 mg of silver or gold respectively is recommended

Table I.—Effect of collector in fire assay procedure

Test No.	Element determined	Taken, μg	Found, μg	Collector
1	Ag	10	none	—
2	Ag	—	1·8	10 mg Au
3	Ag	10	10·6	10 mg Au
4	Ag	100	85	—
5	Ag	100	104	10 mg Au
6	Ag	200	182	—
7	Ag	200	203	10 mg Au
8	Ag	500	482	—
9	Ag	500	504	10 mg Au
10	Ag	1000	953	—
11	Ag	1000	1009	10 mg Au
12	Ag	5000	4670	—
13	Ag	5000	4985	50 mg Au
14	Au	10	none	—
15	Au	—	0·5	10 mg Ag
16	Au	10	10·5	10 mg Ag
17	Au	100	93	—
18	Au	100	101	10 mg Ag
19	Au	500	481	—
20	Au	500	496	10 mg Ag
21	Au	1000	990	—
22	Au	1000	1007	10 mg Ag
23	Au	3000	2985	20 mg Ag
24	Au	5000	5060	50 mg Ag
25	Pd	10	none	—
26	Pd	—	0·3	10 mg Ag
27	Pd	10	10·4	10 mg Ag
28	Pd	100	98	10 mg Ag
29	Pd	200	205	10 mg Ag
30	Pd	500	493	10 mg Au
31	Pd	1000	1009	10 mg Ag
32	Pd	3000	2965	10 mg Au
33	Pd	5000	5021	10 mg Ag

for quantitative collection. Silver and gold serve equally well as collector for palladium. The necessity of adding a collector is demonstrated in Table I. The absence of a collector yields distinctly low silver values (Tests 1, 4, 6, 8, 10, 12), gold values (Tests 14, 17, 19, 21) and palladium values (Test 25). The presence of 10 mg of collector ensures the quantitative recovery of silver (Tests 3, 5, 7, 9, 11, 13), gold (Tests 16, 18, 20, 22, 23, 24), and palladium (Tests 27 to 33). In these tests, the desired element was added in the form of a standard solution to the assay crucible containing an appropriate flux. The collector (silver or gold) was added to the assay crucible as metal. The final beads were dissolved in an appropriate acid, as described in the procedure, prior to atomic-absorption measurements in a cyanide medium. The standard solutions were examined by atomic absorption in the same cyanide medium, and the results indicated that the precision of the measurements were ±1 %. Although only high-purity reagents were used which gave no positive silver tests by pure fire-assay methods, the high silver results in Tests 2 and 3 indicate that the flux contains parts per milliard amounts of silver which are collected by the gold.

Table II indicates that atomic-absorption measurements of gold, silver or palladium are not dependent on the relative proportions of the metals, nor are they significantly affected by the presence of other platinum metals.

TABLE II.—DETERMINATION OF GOLD, SILVER, AND PALLADIUM IN THE PRESENCE OF EACH OTHER AND OF OTHER PLATINUM METALS

Element determined	Amount taken, *μg*	Amount found, *μg*	Other elements present					
			Au, *mg*	Ag, *mg*	Pd, *mg*	Pt, *mg*	Ru, *mg*	Rh, *mg*
Au	3	2·5	—	10	5	2	1	1
Au	5	4·5	—	10	5	2	—	—
Au	10	10·6	—	10	5	—	—	—
Au	50	49	—	10	5	2	1	1
Au	100	101	—	10	5	5	5	5
Au	300	303	—	5	10	5	5	5
Au	600	604	—	50	2	2	—	—
Au	600	599	—	—	30	1	1	1
Ag	2	2·5	10	—	3	2	1	1
Ag	10	11·5	10	—	5	2	1	1
Ag	20	21	50	—	5	5	1	1
Ag	100	99	15	—	3	3	1	1
Ag	300	302	10	—	2	2	2	2
Ag	300	303	30	—	1	1	1	1
Ag	500	502	50	—	2	2	—	—
Ag	500	497	—	—	30	—	—	—
Pd	3	3·5	—	5	—	1	1	1
Pd	10	10·6	5	5	—	1	1	1
Pd	20	18	5	5	—	1	1	1
Pd	50	52	10	10	—	2	2	2
Pd	100	103	10	10	—	1	1	1
Pd	300	298	5	5	—	1	1	1
Pd	500	496	10	10	—	—	—	—

Table III gives some comparison of gold results obtained in our laboratory by (*a*) fire assay, followed by parting and weighing of gold bead and (*b*) fire assay, followed by acid dissolution and atomic absorption.

TABLE III.—DETERMINATION OF GOLD: COMPARISON OF CONVENTIONAL FIRE-ASSAY/PARTING AND WEIGHING PROCEDURE WITH FIRE-ASSAY/ATOMIC-ABSORPTION PROCEDURE

Material	Weight of sample, *assay ton* (29·16 *g*)	Au found by weighing, *mg*	Au found by atomic absorption, *mg*
Copper Conc. 1	0·5	trace	0·011
2	0·5	trace	0·005
3	0·5	0·27	0·285
4	0·5	0·14	0·147
5	0·5	0·34	0·352
6	0·5	0·84	0·83
7	0·5	1·04	1·048
Blister Copper 1	1	0·15	0·152
2	1	1·23	1·21
Zinc Conc. 1	0·5	0·06	0·073
2	1	0·22	0·233
Lead Conc. 1	1	0·10	0·098
2	1	0·82	0·83
Silicate 1	1	0·09	0·092
2	1	0·94	0·93

Zusammenfassung—Ein Verfahren wird beschrieben, das die besten Eigenschaften der Schmelzanreicherung mit einer Atomabsorptionsmessung verbindet. Die Edelmetall-Perle aus dem Schmelzanreicherungs-Schritt wird in Säuren gelöst, die Lösung zur Trockne eingedampft und der Rückstand in einer gemessenen Menge von Cyanidlösung aufgenommen. Die Atomabsorptionsmessung dieser Lösung erlaubt die Bestimmung von immerhin 0,017 ppm Silber, 0,08 ppm Gold und/oder 0,08 ppm Palladium in verschiedenen edelmetallführenden Materialien mit einer Genauigkeit von ±1 %.

Résumé—On décrit une méthode qui combine les meilleurs caractères de la technique par voie sèche avec une technique d'absorption atomique. La bille de métal précieux résultant du stade de concentration par voie sèche est dissoute dans des acides, la solution évaporée à sec et le résidu dissous dans une quantité mesurée de solution de cyanure. La mesure d'absorption atomique de cette solution permet la détermination de quantités aussi faibles que 0,017 p.p.m. d'argent, 0,08 p.p.m. d'or, et/ou 0,08 p.p.m. de palladium dans divers produits contenant des métaux précieux, avec une précision de ±1 %.

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ABSORPTIOMETRIC DETERMINATION OF SULPHIDE ION

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Summary—An absorptiometric method is described for sulphide ion, based on the green colour which is formed when sulphide ions are treated in ammoniacal solution with iron(III) and an excess of nitrilotriacetic acid. The recommended procedure can be applied from 1200 down to 8 ppm of sulphide and is interfered with seriously only by selenite from amongst seventeen other anions examined. The colour system is stabilized by an excess of sulphite. Suggestions are made about the nature of the colour body and its mechanism of production.

ALTHOUGH the inorganic reactions of sulphide ions are probably better known than those of most ions, there are few methods available for the determination of small amounts of sulphide. The best known is probably the colorimetric method based on the reaction product formed between sulphide ions and *p*-amino-*N*,*N*-dimethylaniline in the presence of iron(III) chloride.[1] According to Mecklenburg and Rosenkränzer[2] as much as 3 hr development time is required for the complete formation of the blue colour with sulphide concentrations as low as 0·02 ppm. The temperature must also be controlled within 2° for precise results to be obtained. Generally this method has been applied to gas analysis. Several other anions, *e.g.*, sulphite and hyposulphite, interfere. Numerous empirical recipes for this colour reaction have been described, but need not be detailed here.

Measurement of the absorbance of suspensions or sols of insoluble sulphides of various metals, *e.g.*, of lead,[3] has been used from time to time, but generally such methods have not found favour because of the unstable nature of the systems. In other instances the sulphide has been converted into thiocyanate which is then determined with iron(III). More recently a fluorimetric method has been described in which the sulphide ion is caused to react with the non-fluorescent palladium complex of 8-hydroxyquinoline-5-sulphonic acid at pH 9·2, thus liberating the free ligand which fluoresces quite strongly at this pH.[4] In this way, as little as 0·2 ppm has been detected, but several ions interfere.

In this contribution we describe a colour reaction between sulphide ion, iron(III) and various complexing agents such as nitrilotriacetic acid and apply it to the determination of small amounts of sulphide in aqueous solution.

In the course of investigations several years ago,[5] of the masking action of derivatives of iminodiacetic acid on various colour formation and precipitation reactions of inorganic ions it was found that very intense green colours were formed upon mixing solutions of iron(III) with iminodiacetic acid, methyliminodiacetic acid or nitrilotriacetic acid, *etc*, and sulphide ions in the presence of ammonia. Other reagents of the same group, such as EDTA, *trans*-1,2-diaminocyclopentane-*N*,*N*,*N'N'*-tetra-acetic acid and *trans*-1,2-diaminocyclohexane-*N*,*N*,*N'N'*-tetra-acetic acid yielded transient

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cherry red colours which rapidly faded to a light grey shade and subsequently developed a dark green colour.

It is possible to differentiate the aminopolycarboxylic acids into two groups, *viz.* those which form relatively weak iron(III) complexes and give green colours, and those which form relatively strong iron(III) complexes and give transient cherry red colours which eventually fade to green. It is also possible to devise a colorimetric method for the determination of iron(III).[5] Since absorptiometric methods for iron(III) abound, however, and since the sensitivity of the sulphide reaction for iron is not particularly high, we have not investigated this possibility further. We did, however, establish that an absorptiometric method could be devised for the determination of moderate concentrations of sulphide ion, based on this colour formation.[5] The colour was not very stable at low sulphide concentrations, however, and lacked sufficient intensity to make it worthwhile as a practical procedure, so the method was not then investigated further. This paper describes a re-examination of the problem.

Evolution of analytical procedure

Preliminary absorption spectra obtained by mixing iron(III) ammonium sulphate solution with an excess of nitrilotriacetic acid (NTA), sulphide ion and ammonia and measuring quickly against a water blank showed that pronounced maxima were formed at 435 nm and 640 nm with a very slight maximum at 550 nm. In the absence of sulphide, some absorption was shown at 435 nm, but very little at 640 nm. The sensitivity of detection was considerably greater at 640 nm than at 435 nm. Attempts were then made to find the optimal time for development of maximum absorbance. These experiments revealed that colour formation was instantaneous and that the colour of solutions not containing an excess of sulphide faded rapidly, whilst those containing an excess maintained a steady absorbance for at least 30 min. These observations provided valuable guidance subsequently, but further experiments were limited to those in which an excess of iron(III), NTA and ammonia was added with respect to sulphide.

It was found that it was best to maintain the NTA in considerable excess over the ferric iron to obtain the maximum yield of colour. A composite solution containing iron(III) and a 5-fold molar ratio of NTA was therefore added as a single reagent. The order of addition of reagents was also found to be important in that most colour was generated when the test (sulphide) solution was treated first of all with ammonia and then with the composite solution. Maximum colour formation occurred when the mixture of all the reagents was diluted immediately to the mark and measured, rather than allowed to stand for a few minutes before dilution. This evidence and the obvious stability of the colour suggested that aerial oxidation of the coloured compound was responsible for the fading. The incorporation of hydroxyammonium chloride or ascorbic acid in the mixture to prevent such oxidation had a deleterious effect, however, owing to the reduction of iron(III) to iron(II). At this point, the causes of colour instability were also thought to be due to coagulation of the green colour body, and it appeared that the system was behaving as a sol rather than as a true solution. Various surface-active agents and protective colloids were, therefore, incorporated in the colour system to try to stabilize it, *e.g.*, Cetavlon, Triton X 100, Lissapol NX, polyethylene glycol, glycerine and gelatin. Only gelatin showed any sensitization and stabilization effect, and that was only slight. The addition of various inorganic electrolytes was finally examined in an effort to provide some stabilization, *viz.* potassium chloride, potassium aluminium sulphate, disodium hydrogen orthophosphate, sodium selenite, sodium selenate and sodium sulphate. With the exception of potassium chloride which was without any effect, and of sodium selenite which inhibited the colour formation if added first to the sulphide solution, all showed some degree of sensitization, but it was most marked with sodium sulphate and sodium selenate. It was found that when the sodium sulphate (or selenate) was added to the ammoniacal sulphide solution before the iron(III)–NTA solution there was a gradual increase in colour for 1 min followed by a stable period of 3–4 min and a slow decrease in absorption on further standing.

The slight enhancement and stabilization effect of sulphate was attributed to a protective action on the (suspected) colloidal colour body, and the subsequent fading to gradual oxidation of the green reaction product. It is known that sulphite does not readily reduce iron(III) to iron(II) except in the presence of catalysts such as thiocyanate,[6] yet it may be used to reduce dissolved oxygen in aqueous solutions (*e.g.*, in polarography). Consequently, further experiments were performed with sodium sulphite in place of sodium sulphate. This had the desired effect of giving considerable sensitization of the colour reaction, stabilization and prevention of short-term fading of the green colour. Stable colours could now be maintained for up to 10 min and the maximal colour formation occurred within 2 min of mixing the solutions. This effect is shown in Table I for the determination of 600 µg of sulphide in a final volume of 50 ml. Because of the protective action of sulphite all dilute standard sulphide test solutions were subsequently prepared in the presence of an excess of sodium sulphite (10%).

TABLE I.—MAXIMAL COLOUR FORMATION IN THE Fe(III)/NTA/S^{2-} SYSTEM (600 µg OF S^{2-} + 1 ml OF NH_3 SOLUTION + 20 ml OF 20% Na_2SO_3 SOLUTION + 0·5 ml OF Fe(III)/NTA DILUTED TO 50 ml)

Standing time, *min*	0	1	2	5	10	12	15
Absorbance (5-mm cell)	0·70	0·715	0·725	0·725	0·725	0·725	0·715

Figure 1 shows the absorption spectra obtained. The sulphide solutions used in (2) and (3) did not contain sodium sulphite. These curves were measured in 10-mm cells against distilled water between 2 and 12 min after preparation of the solutions. They show that the maximum absorption for sulphide now occurs at 635 nm in the presence of sulphite and that the blank absorption of the reagents is almost negligible at this wavelength. The difference between curves (3) and (2) shows the benefit of the presence of excess of sulphate ions whilst that between curves (3) and (4) shows the superior sensitization by excess of sulphite.

The best conditions for devising a method for the absorptiometric determination of sulphide ion having thus been established, a test was made of adherence to the Lambert–Beer law. It was found that in the presence of excess of sulphite ion, by the method recommended, Beer's law was obeyed in the range 200–1200 µg of sulphide in a final volume of 50 ml. The extrapolation of the calibration curve showed a slight positive intercept on the concentration axis. The molar absorptivity at 635 nm for the sulphide ion corresponds to 540 $l.mole^{-1}.mm^{-1}$. When the standard sulphide

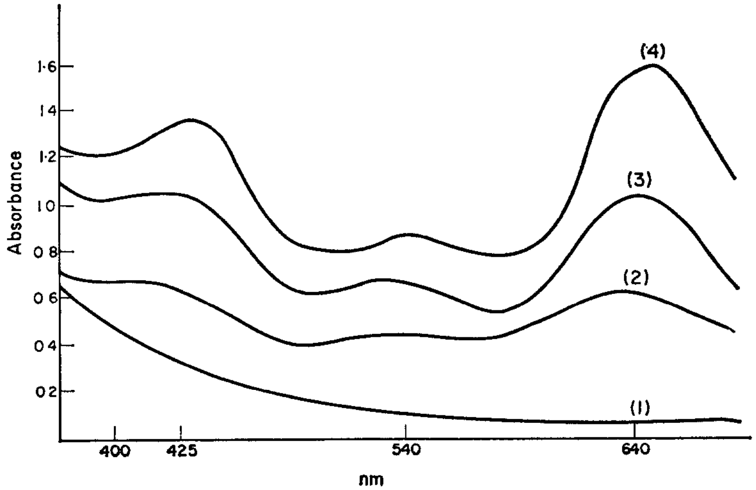

FIG. 1.—Absorption spectra of FeIII/NTA/S^{2-} system.
(1) Blank reaction: Na_2SO_3 + 1 ml of NH_3 solution + 0·5 ml of Fe(III)/NTA solution, diluted to 50 ml; 10-mm cuvette; reference distilled water. (2) As (1) plus 600 μg of S^{2-} and without Na_2SO_3. (3) As (2) plus 20 ml of 20% Na_2SO_4 solution. (4) As (3) but with 600 μg of S^{2-} prepared in 10% Na_2SO_3 solution and with 20 ml of 20% Na_2SO_3 solution in place of Na_2SO_4. All spectra were measured on a scanning spectrometer within 5 minutes of preparation.

test solution was prepared in the absence of sodium sulphite, but 20% sodium sulphite solution was still added in the procedure, the molar absorptivity fell to 420 $l.mole^{-1}.mm^{-1}$. This difference is attributed to loss of sulphide ion by attack from dissolved oxygen when the test solution is not protected in this way. In the absence of excess of sulphite either in the standard solution or in the procedure [Curve (2)], the molar absorptivity was 210 $l.mole^{-1}.mm^{-1}$.

Effect of other ions on the analytical method

The effect of cations was not examined in detail since it is known that many are not compatible in solution with sulphide ion.

Of 17 anions examined, however, the following did not interfere in 100-fold molar excess relative to sulphide: SO_3^{2-}, SO_4^{2-}, SeO_4^{2-}, NO_3^-, CO_3^{2-}, ClO_3^-, Cl^-, Br^-, I^-, CH_3COO^-, PO_4^{3-} and OH^-. The following ions, which interfered at 100-fold excess, could be tolerated at <10-fold excess: oxalate, citrate, tartrate and chromate (negative error). Selenite completely inhibited the colour formation.

The precision of the method was tested by replicate analyses of 0·4 ml of a $3 \times 10^{-2}M$ sulphide solution by the recommended procedure. This yielded a mean absorbance of 0·97, standard deviation 0·027.

EXPERIMENTAL

Reagents

Standard sulphide solution, 1000 ppm. Dissolve and dilute to 100 ml 0·7490 g of analytical-reagent grade $Na_2S.9H_2O$ with freshly prepared 10% w/v sodium sulphite solution. This solution should be prepared fresh daily.

$$1 \text{ ml} \equiv 1000\ \mu g\ S^{2-}.$$

Sodium sulphite solution, 20% *w/v*.

Iron(III)/NTA composite solution. Dissolve 1·91 g of nitrilotriacetic acid in 25 ml of 1*M* sodium hydroxide with warming. Dissolve 1·92 g of iron(III) ammonium sulphate in water containing 1 drop of 1*M* sulphuric acid. Mix the two solutions and dilute to 100 ml in a volumetric flask.

Calibration curve and procedure

Transfer 0·2–1·2-ml aliquots of the 1000-ppm sulphide test solution (*i.e.*, 200–1200 μg) to 50-ml standard flasks. Add 20 ml of 20% sodium sulphite solution, 1 ml of concentrated ammonia solution and 0·5 ml of the iron(III)/NTA reagent solution. Immediately dilute the contents of the flasks to 50 ml and measure the absorbance of each solution 2–12 min from the time of preparation in 5-mm cuvettes at 635 nm against a water blank.

Use this procedure in the same way for unknown solutions containing 8–1000 ppm of sulphide, using sample volumes containing, 200–1000 μg of sulphide.

DISCUSSION

The proposed method for sulphide can be applied down to 8 ppm if 25 ml of sample are available and up to 1000 ppm in a 1-ml test sample. The sensitivity is not very high, but the selectivity is good.

We have been able to reach no definite conclusions as to the exact nature of the green absorbing species. Application of the usual Job, mole-ratio and slope-ratio plots led to meaningless numerical results. It is also known[7] that the complexones never act as direct chromogenic reagents. The action of protective colloids and, more particularly, electrolytes such as sodium sulphate, and sulphite, taken in conjunction with the non-stoichiometric reaction relationships and the obvious tendency for coagulation to occur, lead us to believe that we are dealing with a colloidal basic form of iron(III) sulphide. The action of the NTA appears to be to form a protective complex of iron(III) which hydrolyses progressively as shown in Fig. 2(*a*). An alternative mechanism is shown in Fig. 2(*b*).

The former postulate seems the more probable since the progressive hydrolysis of polyaminocarboxylate complexes of iron(III) in alkaline solution is known, whereas there appears normally to be little preferential affinity for sulphide ion relative to

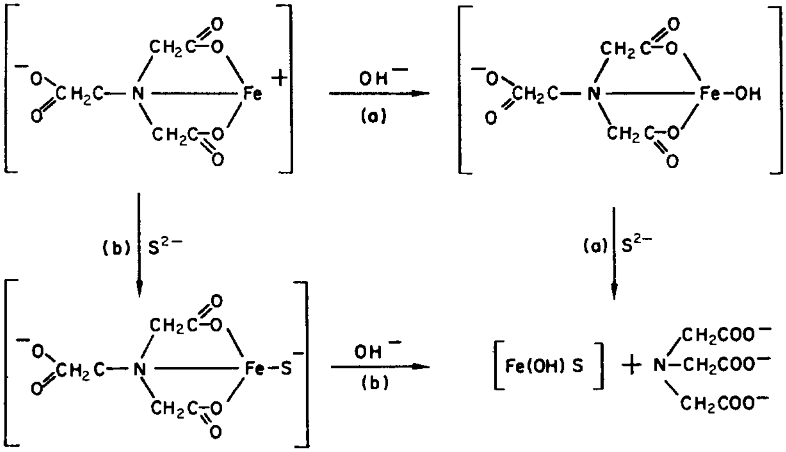

FIG. 2.—Probable mechanisms for colour production in the Fe(III)/NTA/S^{2-} system. (*a*) S^{2-} replacement of NTA in the partially hydrolysed Fe(III)/NTA complex. (*b*) OH$^-$ replacement of NTA in a ternary Fe(III)/NTA/S^{2-} complex.

hydroxyl ion in the absence of NTA. A nearly neutral colloid is suggested by the protective action of the electrolytes.

Other derivatives of iminodiacetic acid[7] also yield green colours, *e.g.*, iminodiacetic acid, methyliminodiacetic acid, UDA, DHEG, as do other complexing agents for iron, *e.g.*, citrate, tartrate, but the most intense colour is obtained with NTA. This probably arises because of the speed of release of $[Fe(III)OH]^{2+}$ from the NTA-complex being best suited to the formation of colloidal particles of basic ferric sulphide of the shape and size appropriate to maximum absorbance.

The system approximates to the NTA complex of iron(III) acting as a hydrolytic reagent for the precipitation of a basic ferric sulphide from homogeneous solution.

Acknowledgement—We are grateful to the Universities of Baghdad and of Mosul for granting study leave and to the Gulbenkian Foundation for the award of a Fellowship to S. A. R.

Zusammenfassung—Ein absorptiometrisches Analysenverfahren für Sulfidionen wird beschrieben. Es beruht auf der grünen Farbe, die entsteht, wenn man Sulfidionen in ammoniakalischer Lösung mit Eisen(III) und einem Überschuß Nitrilotriessigsäure behandelt. Das empfohlene Verfahren kann von 1200 bis herab zu 8 ppm Sulfid verwendet werden. Es wird unter 17 untersuchten anderen Ionen nur durch Selenit ernstlich gestört. Das Farbsystem wird durch einen Überschuß von Sulfit stabilisiert. Über die Natur des Farbkörpers und über seine Entstehungsweise werden Vermutungen angestellt.

Résumé—On décrit une méthode absorptiométrique pour l'ion sulfure, basée sur la coloration verte qui se forme lorsque les ions sulfure sont traités en solution ammoniacale par le fer (III) et un excès d'acide nitrilotriacétique. On peut appliquer la technique recommandée de 1200 à 8 p.p.m. de sulfure et elle n'est sérieusement gênée que par le sélénite parmi dix sept autres anions examinés. Le système coloré est stabilisé par un excès de sulfite. On présente des suggestions sur la nature du corps coloré et son mécanisme de production.

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COLUMN CHROMATOGRAPHIC SEPARATION OF GALLIUM, INDIUM AND THALLIUM*

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Summary—Distribution ratios are given for the extraction of gallium(III), indium(III) and thallium(III) from aqueous solutions of hydrobromic acid into di-isopropyl ether and isobutyl methyl ketone. Based on the results obtained, a scheme is presented for the quantitative separation of these elements from each other by liquid–liquid partition chromatography. The effect of a number of other metal ions upon the separation is also studied. The separation method has been applied to the analysis of a series of lead–indium alloys.

METHODS for separation of gallium(III), indium(III) and thallium(III) have been reviewed in a book by Korkisch.[1] Solvent extraction methods for these elements are predominately based on extraction from different concentrations of hydrochloric or hydrobromic acid. Irving and Rossotti[2] have reviewed the extraction of these elements by diethyl ether. Gallium is nearly quantitatively extracted from 5–7*M* hydrochloric acid into diethyl ether and is partially extracted from 4–5*M* hydrobromic acid. Indium is only slightly extracted from hydrochloric acid but is strongly extracted from 4*M* hydrobromic acid. Thallium is nearly quantitatively extracted into diethyl ether from $>1M$ hydrochloric or $>1M$ hydrobromic acid.

A practical difficulty with solvent extraction is that quantitative separations are obtained only when conditions are such that one element is completely extracted while the elements from which it is separated are not extracted at all. Greater flexibility is obtained through the use of column extraction chromatography, where only a significant *difference* in extractibility is needed for quantitative separation.

In the present work conditions have been worked out for quantitative column chromatographic separation of tervalent gallium, indium and thallium. Aqueous solutions of these metal ions in hydrobromic acid are passed through a column containing isobutyl methyl ketone (IBMK) or di-isopropyl ether (IPE) on a solid granular support. Gallium comes through first; indium and thallium are then eluted successively with lower concentrations of hydrobromic acid. This separation method has also been used for the analysis of lead–indium alloys.

EXPERIMENTAL

Reagents

Aldrich "purissimum" grade IBMK and Fisher certified grade IPE were used, and equilibrated with the appropriate aqueous solvent before use.

All metal salts and inorganic acids were reagent grade and were used without further purification.

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Inert support

Amberlyst XAD-2, an inert cross-linked polystyrene polymer, was obtained from Rohm and Haas as 20–50-mesh beads. The beads were ground and sieved and 80–100-mesh fraction was used. The inert support was washed with $6M$ hydrochloric acid and methanol, and air-dried before use.

Sample solution

Solutions of metal ions were prepared by mixing 5-ml portions of the appropriate metal ion solutions and evaporating the sample solutions to near dryness. Then 2 ml of concentrated hydrobromic acid were added and the samples again taken to near dryness. The residue was then taken up in 5 ml of the appropriate eluent for transfer to the chromatographic column.

Column preparation

The column support was slurried in a portion of equilibrated organic solvent and allowed to remain in contact with the organic solvent for an hour to ensure complete saturation. The slurry was then transferred to the chromatographic column (a 150 × 10 mm column fitted with a coarse frit and a stop-cock), and a small plug of glass wool was used to prevent the top of the column from being disturbed during addition of the sample or eluent. Approximately 3 column-volumes of equilibrated acid were passed through the column to displace the interstitial organic solvent on the column. The organic phase was run down to the level of the column before the equilibrated acid was added.

Distribution ratios

Distribution ratios were obtained by shaking 20 ml of equilibrated organic phase with 20 ml of the equilibrated aqueous phase containing a known amount of solute. After equilibration in a separatory funnel, the phases were separated and the aqueous phase was analysed for metal ion content.

Methods of analysis

Most metal ions were determined by titration with EDTA by standard methods. Thallium(III) cannot be titrated in a hydrobromic acid solution because of the stability of the thallium bromide complex. Therefore, 10 ml of nitric acid were added to the thallium fraction from the column. The sample was heated very mildly to accelerate the formation of bromine, which was carefully expelled by alternately heating and cooling. After expulsion of the bromine, the sample was evaporated to a volume of 3–5 ml, 10 ml of *aqua regia* were added, and the sample was again evaporated to 3–5 ml. The *aqua regia* oxidation was repeated. A known volume of EDTA in excess was added and the solution diluted to 150 ml with water. The excess of EDTA was then titrated with thorium at pH 2·0–2·2, Xylenol Orange being used as indicator.

Antimony(III) and arsenic(III) were determined by titration with standard potassium bromate (Methyl Orange indicator). Antimony and arsenic were not evaporated with hydrobromic acid before extraction because of their tendency to volatilize.

Mercury(II) was determined by titration with thioglycerol, with the thio analogue of Michler's ketone as indicator.

Selenium(IV) was determined in a sulphuric acid solution by adding a 10-ml excess of $0{\cdot}05N$ potassium permanganate; 5 ml of phosphoric acid were added to prevent the formation of manganese dioxide. After 30 min the residual potassium permanganate was determined by adding a slight excess of iron(II) ammonium sulphate followed by a back-titration with potassium permanganate.

RESULTS

Two organic solvents, IPE and IBMK, were investigated as extractants. IPE is less soluble in the aqueous hydrobromic acid phase and is very easily volatilized prior to analysis of the aqueous phase. IBMK, however, is a more powerful extractant and is also sufficiently volatile.

Distribution coefficients for gallium, indium and thallium at various concentrations of hydrobromic acid are given in Table I for IPE and in Table II for IBMK. These data reveal that gallium is only very slightly extracted by IPE over the entire concentration range of hydrobromic acid studied. Indium is not extracted appreciably at hydrobromic acid concentration below $4M$ but is over 90% extracted from $5M$ hydrobromic acid. Thallium is essentially completely extracted from 1–$5M$ hydrobromic acid by IPE.

TABLE I.—DISTRIBUTION RATIOS AND DEGREE OF EXTRACTION OF Ga(III), In(III) AND Tl(III) FROM AQUEOUS HYDROBROMIC ACID INTO IPE

	Molar concentration HBr									
	1·0		2·0		3·0		4·0		5·0	
	Distribution ratio	Extracted, %	Distribution ratio	Extracted, %	Distribution ratio	Extracted, %	Distribution ratio	Extracted, %	Distribution ratio	Extracted, %
Ga	~0	~0	~0	~0	~0	~0	<0·01	<1·0	0·40	29
In	<0·01	<1·0	0·025	2·4	0·27	21	3·84	79	14·6	94
Tl	267	99·6	—	—	535	99·8	—	—	267	99·6

TABLE II.—DISTRIBUTION RATIOS AND PERCENTAGE EXTRACTION OF Ga(III), In(III) AND Tl(III) FROM AQUEOUS HYDROBROMIC ACID INTO IBMK

	Molar concentration HBr									
	0·25		0·5		1·0		2·0		3·0	
	Distribution ratio	Extracted, %	Distribution ratio	Extracted, %	Distribution ratio	Extracted, %	Distribution ratio	Extracted, %	Distribution ratio	Extracted, %
Ga	—	—	—	—	—	—	<0·1	<1	0·32	19
In	0·13	12	—	—	4·2	81	49	98	124	99·2
Tl	—	—	150	99·3	178	99·4	—	—	58	98·3

Column separations were performed on a column packed with 80–100 mesh Amberlyst XAD-2 impregnated with IPE. The elution curve in Fig. 1 shows excellent results for sequential elution of gallium with 5*M* hydrobromic acid, indium with 1*M* hydrobromic acid, and thallium with 3*M* nitric acid followed by IPE.

The data in Table II show significant differences in the extractability into MIBK of the elements studied. Accordingly, for separation on a column of XAD-2 impregnated with IBMK, 3*M* hydrobromic acid was selected for elution of gallium, 0·25*M* hydrobromic acid for elution of indium, and thallium was eluted with 3*M* nitric acid and IPE as before. A typical elution curve is given in Fig. 2. Quantitative results for separations on both IPE and IBMK columns are summarized in Table III.

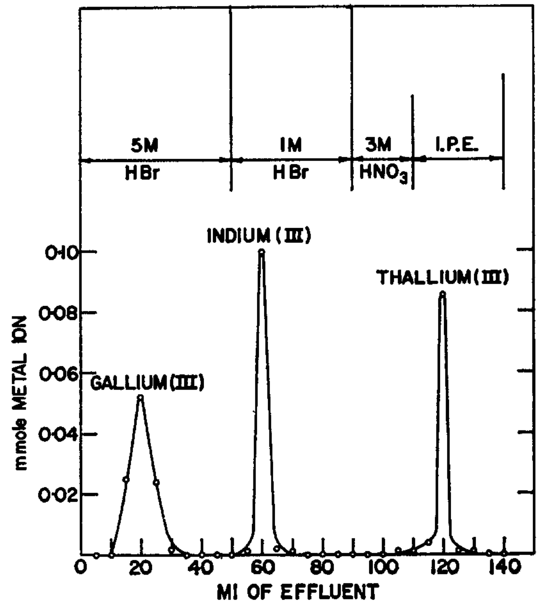

Fig. 1.—Elution of 100 μmole each of gallium(III), indium(III) and thallium(III) from a 120 × 10 mm column of 80–100 mesh Amberlyst XAD-2 impregnated with IPE. Amberlyst XAD-2 support equilibrated with di-isopropyl ether; flow-rate 1·0–1·5 ml/min.

The separation of gallium from indium on the IBMK column is also possible with 2*M* hydrobromic acid (instead of 3*M*) provided the amount of indium is small. The effect of loading on indium elution is given in Table IV.

Distribution ratios of a number of other metal ions were determined (Table V) in order to ascertain which might interfere in the column separations just described. Only selenium(IV) and iron(III) are strongly extracted by IPE from 5*M* hydrobromic acid. In the 3*M* hydrobromic acid–IBMK system, tin(IV) and mercury(II) are strongly extracted in addition to selenium(IV) and iron(III). Copper(II) and iron(III) are reduced at least partially to their lower oxidation states.

The elements most likely to interfere with the analytical separation scheme are tin(IV), iron(III), copper(II) and mercury(II). The behaviour of these elements on the column was studied by determining the break-through volume and elution volume

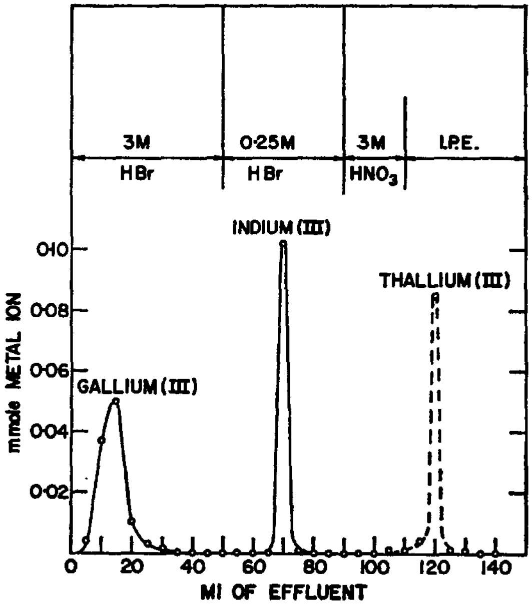

FIG. 2.—Elution of 100 μmole each of gallium(III), indium(III), and thallium(III) from a 120 × 10 mm column of 80–100 mesh Amberlyst XAD-2 impregnated with MIBK.

Amberlyst XAD-2 support equilibrated with isobutyl methyl ketone; flow-rate 1·0–1·5 ml/min.

TABLE III.—SEPARATION OF GALLIUM(III), INDIUM(III) AND THALLIUM(III). ELUTION CONDITIONS ARE AS STATED IN FIG. 1 FOR IPE COLUMN AND IN FIG. 2 FOR IBMK COLUMN

Column	Sample composition, *mmole* of each element	Recovery, %*		
		Ga	In	Tl
IPE	0·10	100·1	99·5	99·9
IPE	0·25	100·2	99·5	98·9
IBMK	0·10	100·0	99·7	99·4
IBMK	0·25	99·8	100·3	99·9

* Average of 2 or 3 individual results.

TABLE IV.—EFFECT OF COLUMN LOADING ON THE ELUTION OF 0·25 MMOLE OF INDIUM(III) FROM AMBERLYST XAD-2 IMPREGNATED WITH IBMK. COLUMN: 100 × 10 MM; FLOW RATE: 1–1·5 ML/MIN

Column loading, *mmole*	Eluent, [HBr]	Indium breakthrough, *ml*	Indium elution, *ml*
~0·25	3*M*	>120	—
~0·25	2*M*	20–30	>120
~0·025	2*M*	>120	—
~0·025	1*M*	10–20	60–70

Table V.—Distribution ratios for batch extraction of various elements from hydrobromic acid

Element	Distribution ratio			
	5*M* HBr–IPE	3*M* HBr–IBMK	2*M* HBr–IBMK	1*M* HBr–IBMK
Al(III)	0·08	0·09	—	—
Sn(IV)	0·45	25	4·2	0·59
Pb(II)	0·06	0·13	—	—
As(III)	0·27	0·04	—	—
Sb(III)	0·03	0·32	—	—
Bi(III)	~0	0·05	—	—
Se(IV)	2·5	2·1	—	—
Y(III)	0·01	0·01	—	—
VO(II)	<0·01	<0·01	—	—
Cr(III)	0·19	<0·01	—	—
Mn(II)	0·33	0·30	—	—
Fe(III)	17·5	12·1	0·70	0·03
Co(II)	<0·01	<0·01	—	—
Ni(II)	<0·01	<0·01	—	—
Cu(II)	<0·01	0·37	—	—
Zn(II)	<0·01	1·0	—	—
Cd(II)	0·05	1·0	—	—
Hg(II)	0·04	4·4	3·2	2·7
Mo(VI)	0·09	0·09	—	—
Ca(II)	~0	~0	—	—
Mg(II)	~0	0·02	—	—
Dy(III)	~0	<0·01	—	—
Yb(III)	0·02	0·04	—	—
Th(III)	0·01	0·01	—	—

(Table VI). Only iron(III) would cause difficulty on the IPE column. Both iron(III) and tin(IV) are held up on the IBMK column from 3*M* hydrobromic acid, although elution is more rapid with 2*M* hydrobromic acid.

Table VI.—The breakthrough volume and elution volume for various metal ions in hydrobromic acid. Column: 120 × 10 mm; flow-rate: 1–1·5 ml/min

	5*M* HBr–IPE		3*M* HBr–IBMK		2*M* HBr–IBMK	
Element	Breakthrough, *ml*	Elution, *ml*	Breakthrough, *ml*	Elution, *ml*	Breakthrough, *ml*	Elution, *ml*
Sn(IV)	0–5	25–30	30–35	80–90	15–20	60–70
Fe(III)	0–5	>100	5–10	>100	0–10	20–25
Cu(II)	0–5	20–25	0–5	35–40	—	—
Hg(II)	0–5	20–25	5–10	25–30	5–10	20–25

If iron(III) may be present in samples to be analysed for indium(III), a preliminary separation from hydrochloric acid on an IPE-impregnated XAD-2 column might be advantageous. Iron(III), gallium and antimony(V) have been shown previously[8] to be strongly held by such a column from 6 to 8*M* hydrochloric acid. Thallium(III) is strongly extracted by IPE from hydrochloric acid at these concentrations ($D = 100$ in 6*M* and 55 in 8*M* hydrochloric acid) and should also be strongly held. However, indium has a distribution coefficient less than 0·01 in both 6 and 8*M* hydrochloric acid and passes readily through a column. In presence of 5*M* hydrobromic acid, indium is retained by the IPE column. This sequence should result in an extremely selective separation method for indium.

ANALYSIS OF LEAD–INDIUM ALLOYS

The general method described earlier was applied to the separation of indium from lead–indium alloys. For this separation a rather high concentration of hydrobromic acid is advantageous in order to complex lead and prevent precipitation of lead bromide. In 4·4*M* hydrobromic acid the distribution ratio for indium into IBMK is approximately 200 and that for lead is only 0·06, which gives a separation factor of over 3000. A sample containing 0·1 mmole each of lead and indium in 4 ml of 4·4*M* hydrobromic acid was added to a 90 × 12 mm column of 60–80-mesh Amberlyst XAD-2 impregnated with IBMK and conditioned with 4·4*M* hydrobromic acid. Lead was eluted from the column with 15 ml of 4·4*M* hydrobromic acid at a flow-rate of 2 ml/min, and indium was then eluted with 15 ml of 0·1*M* hydrochloric acid. Titration of the separated lead and indium with EDTA gave quantitative recoveries within normal titration error.

The method was then applied to the analysis of lead-indium alloys (5–20 mole % indium). The samples (600–800 mg) were dissolved in 15 ml of hydrobromic acid, and most of the acid was evaporated after dissolution. The residue was taken up in 4·4*M* hydrobromic acid, transferred to a 25-ml volumetric flask, and diluted to volume with the same solvent. Aliquots (5 ml) were then transferred to the 90 × 12 mm IBMK column for separation. Lead and indium were eluted with 4·4*M* hydrobromic acid and 0·1*M* hydrochloric acid respectively as before, and titrated. Results for analysis of different sections of an alloy containing approximately 10 mole % of indium are given in Table VII. Although the samples were not homogeneous, the precision and material balance in each case are good enough to indicate that the analyses are correct.

TABLE VII.—ANALYTICAL RESULTS FOR LEAD–INDIUM ALLOYS

Sample number	In(III) present, *mmole*	Pb(II) present, *mmole*	Indium, *mole %*	Material balance, % of total recovered
I, aliquot a	0·0731	0·628	$10{\cdot}4_3$	100·2
I, aliquot b	0·0729	0·628	$10{\cdot}4_0$	
II, aliquot a	0·0862	0·724	$10{\cdot}6_4$	100·2
II, aliquot b	0·0860	0·723	$10{\cdot}6_3$	
III, aliquot a	0·0941	0·747	$11{\cdot}1_9$	100·4
III, aliquot b	0·0945	0·748	$11{\cdot}2_2$	

Zusammenfassung—Verteilungsverhältnisse für die Extraktion von Gallium(III), Indium(III) und Thallium(III) aus wäßrigen bromwasserstoffsauren Lösungen in Diisopropyläther und Isobutylmethylketon werden angegeben. Auf Grund der erhaltenen Ergebnisse wird ein Schema für die quantitiv Trennung dieser Elemente voneinander durch flüssig-flüssig-Verteilungschromatographie angegeben. Der Einfluß einer Anzahl anderer Metallionen auf die Trennung wird ebenfalls untersucht. Das Trennverfahren wurde auf die Analyse einer Reihe von Blei-Indium-Legierungen angewandt.

Résumé—On donne les rapports de partage pour l'extraction de gallium(III), indium(III) et thallium(III) de solutions aqueuses d'acide bromhydrique en diisopropyléther et isobutylméthylcétone. On présente un schéma, basé sur les résultats obtenus, pour la séparation quantitative de ces éléments l'un de l'autre par chromatographie de partage liquide–liquide. On étudie aussi l'influence d'un certain nombre d'autres ions métalliques sur la séparation. La méthode de séparation a été appliquée à l'analyse d'une série d'alliages plomb–indium.

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SPECTROPHOTOMETRIC DETERMINATION OF NICKEL(II) WITH MOLYBDOPHOSPHORIC ACID

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Summary—A sensitive spectrophotometric method for the determination of nickel, based on the reduction of a complex formed between molybdophosphoric acid and Ni(II) at pH 4·3 has been developed. Excess of molybdophosphoric acid is eliminated by complexation with sodium citrate. The method is rapid and the system obeys Beer's law up to 5 ppm of Ni(II). The molar absorptivity is $1{\cdot}30 \times 10^3$ $\mathrm{l.mole^{-1}.mm^{-1}}$. The technique compares favourably with existing photometric methods for nickel in sensitivity and is reasonably selective.

A SENSITIVE colorimetric technique for the determination of traces of nickel has been developed. The method is rapid and the system obeys Beer's law up to 5 ppm of nickel. The molar absorptivity is $1{\cdot}30 \times 10^3$ $\mathrm{l.mole^{-1}.mm^{-1}}$ at a wavelength of 695 nm. The limit of detection in 10-mm cells is approximately 0·1 ppm.

The method is based upon reduction of a complex formed between nickel(II) and excess of molybdophosphoric acid at pH 4·3. Since the excess of molybdophosphoric acid is also reducible under the conditions of analysis, it is rendered unreducible by complexation with citrate before reduction of the nickel-molybdophosphate by tin(II) chloride. The reduced solutions are an intense blue with maximum absorbance at 695 nm.

EXPERIMENTAL

Reagents

Demineralized distilled water was used throughout.

Sodium molybdate dihydrate solution, 0·1000*M*.

Potassium dihydrogen phosphate solution, 0·0500*M*.

Molybdophosphate reagent mixture. Prepared by mixing 600 ml of the 0·1000*M* sodium molybdate with 100 ml of the 0·0500*M* phosphate and diluting to 1 litre, to yield a solution containing molybdenum and phosphate in molar ratio 12:1.

Sodium citrate dihydrate solution, 5% *w/v*.

Stock nickel solution, 1000 *ppm*. Dissolve 4·95 g of reagent grade $Ni(NO_3)_2{\cdot}6H_2O$ in a 1-litre volumetric flask and dilute to the mark. Prepare a 100-ppm solution by appropriate dilution.

Tin(II) chloride solution. Prepare fresh daily by addition of 1·01 g of reagent grade $SnCl_2{\cdot}H_2O$ and 1·00 ml of concentrated hydrochloric to a 100-ml volumetric flask and dilution to the mark.

Keep all reagents in polyethylene bottles to avoid contamination with silicate.

Calibration curve

Add 0·00, 0·25, 0·75, 1·25, 2·00, 3·00, 4·00, and 5·00 ml of a standard 100-ppm nickel solution to a series of 150-ml beakers. To each beaker add 5·0 ml of the molybdate–phosphate reagent and 50 ml of demineralized water and adjust the pH to 4·3 by dropwise addition of 1*M* hydrochloric acid. Start a timer and simultaneously deliver rapidly 2·0 ml of 5% sodium citrate solution from a 2-ml hypodermic syringe. Exactly 5 sec later add 1·0 ml of a 1% tin(II) chloride solution by means of a 1-ml syringe. Quantitatively transfer the solutions to 100-ml volumetric flasks, dilute to the mark, and mix well. After 10–30 min, measure the absorbance at 695 nm *vs*. water. Plot absorbance *vs*. ppm of nickel.

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General procedure

Dissolve the sample and treat the solution to remove any interfering ions. Nickel may be separated from most interfering substances by ion-exchange. The sample should be neutral and diluted to about 50 ml before addition of the reagents as outlined above.

RESULTS

Preliminary studies consisted of varying the concentrations of molybdate-phosphate reagent, sodium citrate, tin(II) chloride and hydrochloric acid until the blue hue of reduced molybdophosphoric acid was more enhanced in the presence of nickel than in its absence.

The results were used in a systematic study and optimization of variables. Figure 1 shows the absorption spectrum resulting from reduction of the molybdophosphoric acid nickel complex after elimination of the excess of molybdophosphoric acid with sodium citrate. There is a broad absorption peak with its centre at 695 nm. All subsequent measurements were made at this wavelength.

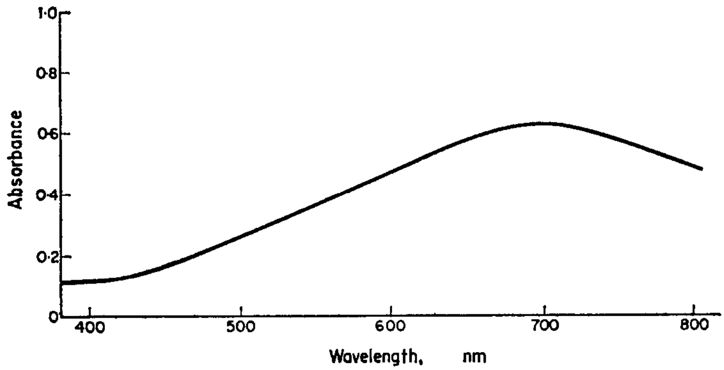

Fig. 1.—Absorption spectrum of molybdophosphoric acid—nickel complex.

Effect of pH

The effect of varying pH on the system was studied by mixing 3·00 ml of the molybdate-phosphate reagent and 2·00 ml of 100-ppm nickel solution in a 150-ml beaker, adding 50 ml of water and varying amounts of 1*M* hydrochloric acid, mixing and reading the pH; a stopwatch was then started and simultaneously 2·00 ml of 5% sodium citrate solution were delivered from a 2-ml syringe; 5 sec after addition of the citrate, 1·00 ml of the tin(II) chloride solution was added from a 2-ml hypodermic syringe. The mixture was quantitatively transferred to a 100-ml volumetric flask, diluted to the mark and mixed. After 30·0 min the absorbance at 695 nm was read. Figure 2 shows the typical pH-dependence of a heteropoly acid system. A pH of 4·3 was chosen as optimum for maximum sensitivity and minimum pH-dependence.

Choice of acid

Sulphuric, acetic and nitric acids were also tried. Sulphuric acid resulted in a lower absorbance than that obtained with hydrochloric acid, probably because a molybdophosphoric acid-sulphate complex is formed under the experimental conditions.[1–4] Acetic acid also gave lower absorbance. Though nitric acid gave slightly

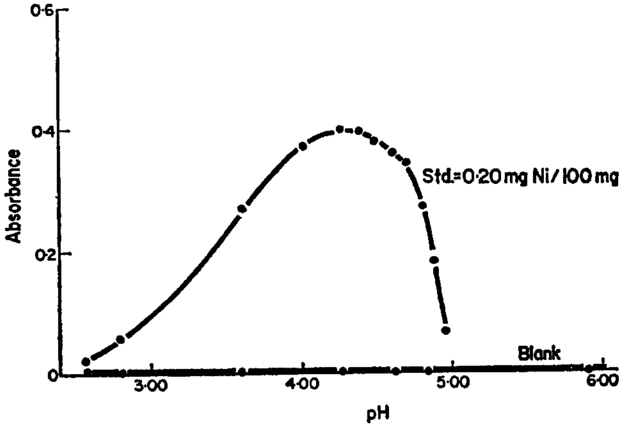

FIG. 2.—Effect of pH.

greater colour enhancement, hydrochloric acid was chosen because of its non-oxidizing nature.

Effect of molybdate–phosphate concentration

The procedure outlined under *Effect of pH* was used except that the amount of molybdate–phosphate reagent was varied, 3 ml of nickel solution were used and the pH was adjusted to 4·3. A blank was run with each sample. Figure 3 shows the results. A volume of 5 ml of molybdate–phosphate mixture was chosen as optimum. Volumes greater than 6·0 ml gave an increased absorbance in both sample and blank; this was attributed to lack of sufficient citrate to eliminate the excess of molybdophosphoric acid.

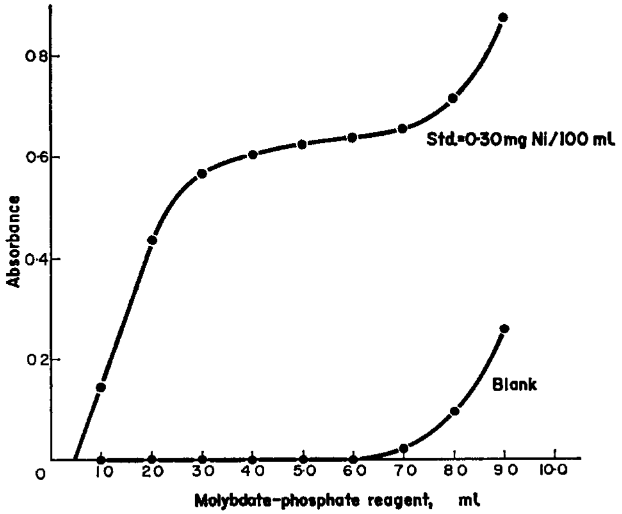

FIG. 3.—Effect of molybdate–phosphate concentration.

Choice of reductant and effect of reductant concentration

Citrate rapidly destroys the molybdate–phosphate–Ni(II) complex so a fast reductant is necessary to complete the reduction before the reducible species is destroyed. Only tin(II) chloride was found to meet this requirement. Figure 4 shows the effect of varying the reductant concentration. A volume of 2·0 ml of the 1% tin(II) chloride reductant was chosen as the most satisfactory.

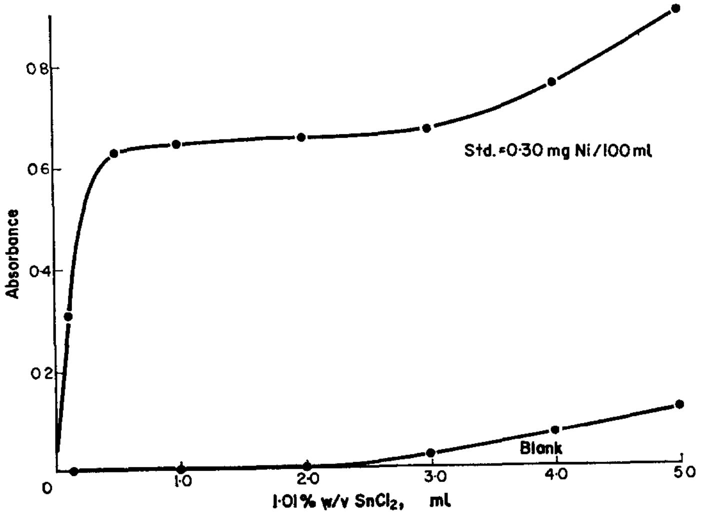

Fig. 4.—Effect of concentration of tin(II) chloride.

Effect of citrate concentration

Figure 5 shows the results of varying the citrate concentration. At low citrate concentrations, the blanks and samples show high absorbance, the difference reflecting the lack of sufficient citrate to complex the excess of molybdophosphoric acid. A volume of 2·0 ml of citrate was chosen as optimum.

Effect of varying time between addition of citrate and tin(II) chloride

The time between addition of citrate and tin(II) was varied from 5 to 100 sec. Figure 6 shows the results. Apparently, citrate almost instantaneously destroys the excess of molybdophosphoric acid but destroys the molybdate–phosphate–Ni(II) complex at a much slower rate. A time interval of 5 sec was chosen as convenient.

Effect of colour development time

Immediately following reduction, the solution exhibits its greatest absorbance. The absorbance decreases slightly for a period of 5 min, than remains constant until 30 min after the reductant has been added; after this time it decreases slowly. All studies were made with a development time of 10–30 min; 20 min is optimum, being in the middle of the absorbance *vs.* plateau, but 30 min gives greater flexibility when a series of samples is run.

Effect of diverse ions

Varying amounts of the diverse ions from 0 to 100 ppm were added to 3-ml portions of the 100-ppm nickel standard and the effect on the absorbance was noted.

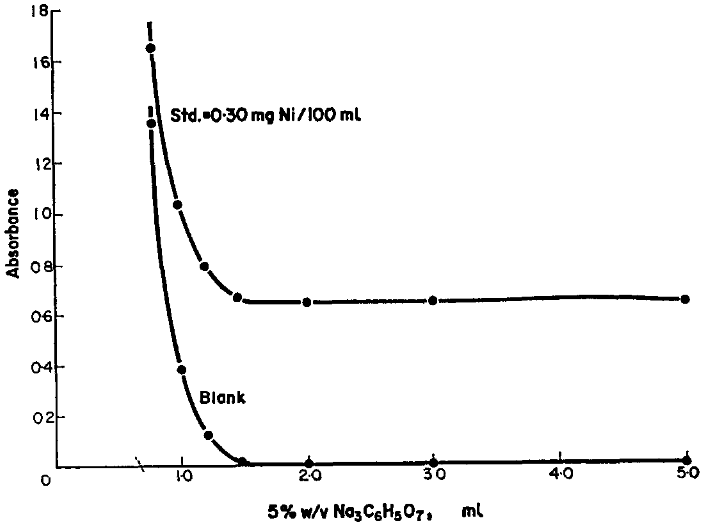

FIG. 5.—Effect of citrate concentration.

Table I shows the permitted concentrations of the diverse ions studied. A 2·0% error in the determination of nickel was considered tolerable. Besides those ions listed in the table, vanadium, titanium, silicon, germanium and tungsten interfere seriously.

Effect of temperature

The temperature of the water-bath used for storage of the samples during colour development was varied. As expected, higher temperatures result in diminished absorbance because of increased dissociation of the reducible complex. Unless the room temperature can be controlled, a thermostat controlled to ±1° should be used.

Chemistry of the system

Visible evidence for an interaction between nickel(II) and molybdophosphoric acid is manifested by a yellow colour produced on mixing the reagents, the intensity of

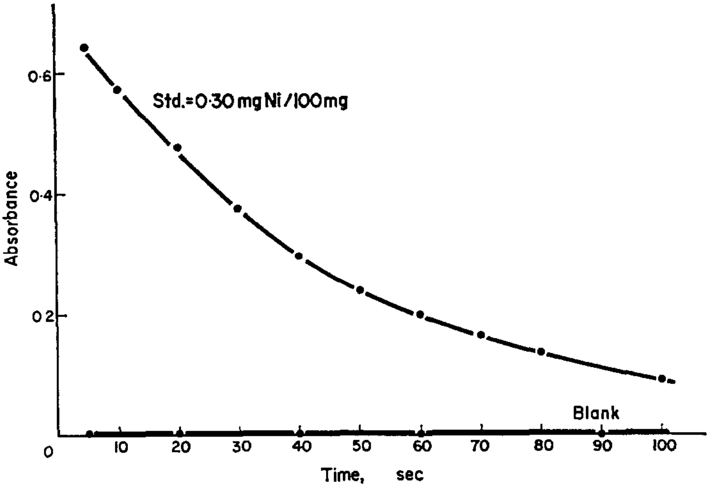

FIG. 6.—Effect of varying time between addition of citrate and tin(II) chloride.

TABLE I.—EFFECT OF DIVERSE IONS

Ion	Added as	Amount permitted, *ppm*
Co^{2+}	$Co(NO_3)_2 \cdot 6H_2O$	5
Cl^-	$NaCl$	100
SO_4^{2-}	Na_2SO_4	100
Fe^{3+}	$FeCl_3 \cdot 6H_2O$	ppte.
Cd^{2+}	$Cd(NO_3)_2 \cdot 4H_2O$	ppte.
Zn^{2+}	$ZnCl_2$	6
Mg^{2+}	$MgCl_2$	13
Al^{3+}	$Al(NO_3)_3$	ppte.
Mn^{2+}	$MnCl_2$	16
Cu^{2+}	$Cu(NO_3)_2 \cdot 3H_2O$	*
Cr^{3+}	$Cr(NO_3)_3 \cdot 9H_2O$	†
ClO_4^-	$KClO_4$	100
$S_2O_3^{2-}$	$Na_2S_2O_3 \cdot 5H_2O$	100
IO_3^-	KIO_3	100
SCN^-	$KSCN$	100
Br^-	KBr	100
NO_3^-	$NaNO_3$	100
SO_3^{2-}	Na_2SO_3	100

* Forms citrate complex.

† Complete interference.

which is proportional to the nickel concentration. Further indication of interaction is given by a bathochromic shift in the ultraviolet spectral region, proportional to the nickel concentration.

Mole-ratio studies gave contradictory results and failed to reveal the stoichiometry of the system. However, studies on the mole ratio of nickel phosphate indicated that more than one complex may exist, depending on the nickel concentration.

This behaviour leads to the conclusion that a mixed heteropoly acid of molybdophosphoric acid and nickel(II) is formed in the system.

Zusammenfassung—Ein empfindliches spektrophotometrisches Verfahren zur Bestimmung von Nickel wurde entwickelt; es beruht auf der Reduktion eines Komplexes aus Molybdophosphorsäure und Ni(II) bei pH 4,3. Ein Überschuß von Molybdophosphorsäure wird durch Komplexbildung mit Natriumcitrat entfernt. Das Verfahren geht schnell und das System erfüllt das Beersche Besetz bis zur einer oberen Grenze von 5 ppm Ni(II). Cer molare Extinktionskoeffizient betragt $1{,}30 \times 10^3$l mol^{-1} mm^{-1}. Das Verfahren schneidet im Vergleich mit bekannten photometrischen Bestimmungsmethoden für Nikkel gut ab; es ist empfindlich und hinreichend selektiv.

Résumé—On a élaboré une méthode spectrophotométrique sensible pour le dosage du nickel, basée sur la réduction d'un complexe formé entre l'acide molybdophosphorique et Ni(II) à pH 4,3. L'excès d'acide molybdophosphorique est éliminé par complexation avec le citrate de sodium. La méthode est rapide et le système obéit à la loi de Beer jusqu' à 5 p.p.m. de Ni(II). Le coefficient d'absorption molaire est de $1{,}30 \times 10^3$ l.mole^{-1}.mm^{-1}. La technique est favorablement comparable, en sensibilité, aux méthodes photométriques existant pour le nickel, et elle est raisonnablement sélective.

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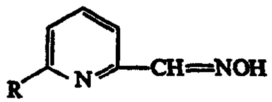
SHORT COMMUNICATIONS

Pyridine-2-aldoxime and 6-methylpyridine-2-aldoxime as gravimetric reagents for estimation of palladium(II) and uranium(VI)

(*Received* 8 *October* 1969. *Revised* 20 *February* 1970. *Accepted* 22 *March* 1970)

PYRIDINE-2-ALDOXIME (I) has already been used as a spectrophotometric reagent for the estimation of iron(II),[1] cobalt(II),[2] gold(III)[3] and palladium(II),[4] and as a gravimetric reagent for cadmium(II),[5] while its 6-methyl derivative (II) has been used as a spectrophotometric reagent for iron(II).[6] With palladium(II), (I) has been reported to form a precipitate,[4] and complexes having the composition



(I) R = H
(II) R = CH_3

PdL_2,[7] $PdL_2 \cdot HCl$,[7] $PdL_2 \cdot 2H_2O$,[8] $PdHL_2 \cdot NO_3$[8] and $PdHL_2 \cdot PdCl_4$.[8] We have confirmed that on the addition of aqueous pyridine-2-aldoxime to palladium(II) chloride solution, a shining yellow precipitate (PdL_2) is formed instantaneously and the precipitation is quantitative over the pH range 3·0–11·0, whereas from nitrate solutions (I) quantitatively precipitates a yellow complex $PdL_2 \cdot HNO_3$ over the pH range 0·5–6·0. Both complexes can be used for the gravimetric estimation of palladium(II) in presence of large quantities of Fe^{3+}, Co^{2+}, Ni^{2+} and the noble metals except Au^{3+} and Os^{4+}. With uranium(VI), (I) and (II) form yellow precipitates having the compositions $UO_2(C_6H_5N_2O)_2$ and $UO_2(C_7H_7N_2O)_2$ respectively, which can be used for the gravimetric estimation of uranium(VI) in presence of large quantities of thorium, lanthanum and cerium, even when these are present together. Pd(II) does not form any insoluble compounds with (II) under the experimental conditions used.

EXPERIMENTAL

Reagents

Pyridine-2-aldoxime. Recrystallized from water and used as 1% aqueous solution.

6-Methylpyridine-2-aldoxime. Used as 1% acetone solution.

Palladium(II) solution. The chloride or nitrate was dissolved in 1*M* hydrochloric or nitric acid respectively, and standardized gravimetrically with dimethylglyoxime.

Uranium(VI) solution. $UO_2(NO_3)_2 \cdot 6H_2O$ dissolved in water, and standardized with oxine.

Analytical grade reagents were used where possible.

Determination of palladium(II)

From palladium(II) chloride solution. To 50 ml of aqueous palladium(II) chloride solution containing 1–20 mg of Pd, add 1% pyridine-2-aldoxime solution gradually with constant stirring till 5 ml per 10 mg of Pd have been added. Adjust the pH to ~4, keep the solution at room temperature (20–30°) for 15 min and filter off on a tared sintered-glass crucible, porosity-3. Wash the precipitate free from chloride with cold water, dry it at 120–130° and weigh as $Pd(C_6H_5N_2O)_2$.

From palladium(II) nitrate solution. Add reagent as before, to the 1*M* nitric acid solution of palladium, then digest at 50–60° for ~15 min, cool to room temperature, and filter off as before. Transfer the precipitate from the beaker and wash it with 0·5*M* nitric acid till free from all ions except nitrate. Dry the precipitate at 130–140° and weigh as $Pd(C_6H_5N_2O)_2 \cdot HNO_3$.

Determination of uranium(VI)

With pyridine-2-aldoxime. To 25 ml of uranyl nitrate solution containing 6–50 mg of U, add 1% reagent solution gradually with stirring till 4 ml per 10 mg of U have been added. Adjust the pH to 4, digest the yellow precipitate at 50–60° for ~15 min, then keep it at room temperature for ~30 min to settle. Filter off on a porosity-3 sintered-glass crucible, and wash free from nitrate with cold water, dry at 120–130°, and weigh as $UO_2(C_6H_5N_2O)_2$.

With 6-methylpyridine-2-aldoxime. Add 1% acetone solution of the reagent gradually with stirring till 4 ml per 10 mg of U have been added. Leave for ~30 min for the precipitate to settle. Filter off on a porosity-3 sintered-glass crucible, and wash with hot water till free from nitrate ions and the reagent [tested with iron(II) solution]. Dry at 120–130°, and weigh as $UO_2(C_7H_7N_2O)_2$.

RESULTS AND DISCUSSION

The errors were ±0·4% for 3–20 mg of Pd(II) and ±0·2% for 12–50 mg of U. Errors up to 1% were observed for smaller amounts.

Palladium(II) is completely precipitated from chloride medium at pH 3–11 and from nitrate media between 1*N* HNO_3 and pH 6. Pyridine-2-aldoxime precipitates uranium(VI) completely at pH 3·5–10·0, and 6-methylpyridine-2-aldoxime does so at pH 3·0–10·5.

Palladium(II)

Tenfold amounts of acetate, oxalate, sulphate, tartrate, phosphate, fluoride, perchlorate, nickel, copper(II), cobalt(II), cadmium, zinc, bismuth, lead, antimony(III), iron(III), mercury(II), and fourfold quantities of platinum(IV), iridium(IV), ruthenium(III) and rhodium(III) do not interfere. Since palladium(II) can be readily separated from other platinum metals higher amounts of other platinum metals were not tested. Gold(III) and silver(I) even in minute quantities cause interference as they are reduced to the elemental state by the reagent. Osmium(IV), in more than twice the amount of palladium(II), and traces of iron(II), interfere as their complexes with pyridine-2-aldoxime are strongly adsorbed on the palladium precipitate, and cannot be washed out. Interference due to iron(II), however, can be eliminated by oxidizing it to iron(III); interference due to the platinum metals can be overcome by boiling with excess of the reagent for ~30 min to complex the platinum metals, cooling and then raising the pH to 4 (Methyl Red); the palladium(II) complex is then precipitated. If antimony is present, palladium should be precipitated from nitric acid medium in presence of tartaric acid.

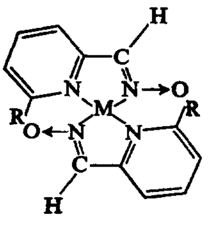
Uranium(VI)

With both reagents uranium can be successfully estimated in presence of 10-fold quantities of thorium(IV), cerium(III) and lanthanum(III), even when these are present together (maximum error + %1 for 10-fold amounts of all three), as well as in the presence of 20-fold quantities of acetate, oxalate and borate. Cerium(IV), when present in amount thrice that of uranium(VI) does not interfere; the interference due to larger quantities can be removed by reduction to cerium(III). Tartrate and citrate interfere by complexing the uranium(VI), phosphate precipitates uranium(VI) at the pH used, and titanium(IV) and zirconium(IV) salts are hydrolysed under the conditions of the estimation and hence interfere.

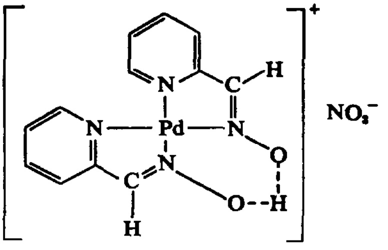
Properties of the complexes

The complex obtained from palladium(II) chloride is extractable into organic solvents such as chloroform. It does not give a positive test for chlorine after fusion with sodium and is not exchanged by either IRA 410(OH) or IRC 50(H), indicating that the complex is neutral. The complex from palladium(II) nitrate is insoluble in nitric acid and in water in presence of excess of nitrate ions, but is soluble in water, not extracted by chloroform or benzene, is exchanged by IRC 50(H) and gives a positive test for nitrate ions, indicating an ionic complex. The uranium(VI) complexes with pyridine-2-aldoxime and 6-methylpyridine-2-aldoxime, are not extracted by chloroform or benzene, but are partially extracted into higher alcohols, e.g. butanol, isopentanol, cyclohexanol. The uranium(VI) complexes are not exchanged by either the IRA 401(OH) or IRC 50(H) resins, do not give a positive test for nitrate ions, and thus are neutral.

On the basis of these observations and by analogy with the copper(II) complexes with pyridine-2-aldoxime,[9] the following structures are suggested:



$\begin{pmatrix} M = Pd; & R = H \\ M = UO_2; & R = H \text{ or } CH_3 \end{pmatrix}$



The nitrate content of the Pd(II)–(I) complex precipitated from nitrate solutions was found to be 17·1%; $Pd(C_6H_5N_2O)_2 \cdot HNO_3$ requires $NO_3^- = 15 \cdot 1\%$, supporting these conclusions.

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Summary—Pyridine-2-aldoxime (I) has been found to be a sensitive reagent for the gravimetric determination of palladium(II). From chloride medium, precipitation is complete at pH 3·0–11·0, and in solution containing $1N$ HNO_3 to pH 6·0. The compositions of the precipitates (dried at 130°) correspond to PdL_2 and $PdL_2 \cdot HNO_3$ (HL representing the reagent) respectively. Pd(II) can be estimated gravimetrically in presence of acetate, oxalate, tartrate, phosphate, fluoride borate, perchlorate, Cu(II), Cd, Co(II), Fe(III), Ni, Zn, Pb, Bi, Sb(III), Pt(IV), Ir(IV), Ru(III), Rh(III); Os(IV) in quantities more than twice that of Pd(II), and Ag(I), Au(III) and Fe(II) even in traces cause serious interference. The yellow uranium(VI) complex with (I) is precipitated quantitatively over the pH range 3·5–10·0 and, after washing and drying corresponds to the composition $(C_6H_5N_2O)_2UO_2$ The uranium(VI) complex with 6-methylpyridine-2-aldoxime (II) is precipitated quantitatively over the pH range 3·0–10·5, and after washing and drying at 120–130° corresponds to $UO_2(C_7H_7N_2O)_2$. Both (I) and (II) are suitable for the estimation of 1–50 mg of uranium(VI) in the presence of up to 10-fold quantities of Th(IV), La(III) and Ce(III) even when present together. Ce(IV) in quantities more than three times that of U must be reduced to Ce(III). Tartrate, citrate, phosphate, Ti(IV) and Zr interfere, but acetate, oxalate, and borate do not.

Zusammenfassung—Pyridin-2-aldoxim (I) hat sich als empfindliches Reagens zur gravimetrischen Bestimmung von Palladium(II) herausgestellt. Aus Chloridmedium ist die Fällung bei pH 3,0–11,0 quantitativ, aus Salpetersäure bei $1N$ HNO_3–pH 6,0. Die Zusammensetzung der (bei 130° getrockneten) Niederschläge entspricht PdL_2 bzw. $PdL_2.HNO_3$ (HL bedeutet den Liganden). Pd(II) kann in Gegenwart von Acetat, Oxalat, Tartrat, Phosphat, Fluorid, Borat, Perchlorat, Cu(II), Cd, Co(II), Fe(III), Ni, Zn, Pb, Bi, Sb(III), Pt(IV), Ir(IV), Ru(III) und Rh(III) gravimetrisch bestimmt werden; Os(IV) in mehr als doppelter Menge neben Pd(II) sowie, auch in Spuren, Ag(I), Au(III) und Fe(II) stören wesentlich. Der gelbe Uran(VI)-Komplex mit (I) fällt quantitativ im pH-Bereich 3,5–10,0 aus und hat nach Waschen und Trocknen die Zusammensetzung $(C_6H_5N_2O)_2UO_2$. Der Uran(VI)-Komplex mit 6-Methylpyridin-2-aldoxim (II) fällt im pH-Bereich 3,0–10,5 quantitativ aus und entspricht nach waschen und Trocknen bei 120–130° $UO_2(C_7H_7N_2O)_2$. (I) und (II) eignen sich zur Bestimmung von 1–50 mg Uran(VI) in Gegenwart bis zu 10-facher Mengen Th(IV), La(III) und Ce(III), auch wenn sie gemeinsam auftretsen. Ist Ce(IV) in mehr als dreifacher Menge neben U vorhanden, so muß es zu Ce(III) reduziert werden. Tartrat, Citrat, Phosphat, Ti(IV) und Zr stören, Acetat, Oxalat und Borat dagegen nicht.

Résumé—On a trouvé que la pyridine 2-aldoxime (I) est un réactif sensible pour le dosage gravimétrique du palladium (II). A partir d'un milieu chlorure, la précipitation est complète à pH 3,0–11,0 et en acide nitrique à $1N$ HNO_3–pH 6,0. Les compositions des précipités (séchés à 130°) correspondent à PdL_2 et PdL_2, NO_3H (HL représentant le réactif) respectivement. On peut doser Pd(II) gravimétriquement en présence d'acétate, oxalate, tartrate, phosphate, fluorure, borate, perchlorate, Cu(II), Cd, Co(II), Fe(III), Ni, Zn, Pb, Bi, Sb(III), Pt(IV), Ir(IV), Ru(III), Rh(III); Os(IV) en quantités supérieures à deux fois celle de Pd(II), et Ag(I), Au(III) et Fe(II) même à l'état de traces apportent une

gêne sérieuse. Le complexe jaune d'uranium(VI) avec (I) est précipité quantitativement dans le domaine de pH 3,5-10,0 et, après lavage et séchage, correspond à la composition $UO_2(C_6H_5N_2O)_2$. Le complexe d'uranium(VI) avec la 6-méthylpyridine 2-aldoxime (II) est précipité quantitativement dans le domaine de pH 3,0–10,5 et, après lavage et séchage à 120°–130°, correspond à $UO_2(C_7H_7N_2O)_2$. (I) et (II) conviennent tous deux au dosage de 1–50 mg d'uranium (VI) en la présence de quantités de Th(IV), La(III) et Ce(III) pouvant être jusqu'à 10 fois supérieures, même lorsque ces éléments sont présents ensemble. Ce(IV) en quantités supérieures à trois celle de U doit être réduit en Ce(III). Les tartrate, citrate, phosphate, Ti(IV) et Zr interfèrent, mais non les acétate, oxalate et borate.

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Separation and determination of mixtures containing *p*-aminosalicylic acid and *m*-aminophenol

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p-AMINOSALICYLIC ACID (PAS) decarboxylates to form *m*-aminophenol (MAP) as its major breakdown product. In order to study the stability of PAS and its salts in aqueous medium, a procedure has been developed for determining both components, which is based on chromatographic separation on an ion-exchange resin, followed by non-aqueous titration of the individual components.

The U.S.P. XVII method of analysis[1] is based on the diazotization reaction, which does not distinguish between PAS and MAP. The MAP content is determined separately by colorimetric analysis. Several procedures have been proposed for determining PAS alone, as salts and as pharmaceutical preparations. These have been noted earlier.[3-4] Non-aqueous titration procedures have been reviewed by Kucharsky and Safarík.[5] In our previous paper[4] a specific method was reported for PAS, its salts and preparations, and a non-aqueous differentiating titration was suggested for PAS and MAP.

EXPERIMENTAL

Reagents

p-Aminosalicylic acid and *m*-aminophenol were the best quality available from commercial sources. The *m*-aminophenol was further purified by recrystallization from hot water.

Sodium methoxide (0·1*M*) in benzene–methanol and 0·1*M* perchloric acid in glacial acetic acid were prepared and standardized as directed in U.S.P. XVII.[1]

Hydrochloric acid (2*M*) in 50% ethanol.

Mercuric acetate solution, 6%, in glacial acetic acid.

All chemicals and solvents were reagent grade.

Chromatography column

A 50-ml burette (10 mm bore) was used as a chromatographic column. It was plugged at the base with glass-wool to support the Dowex 50W-X8 (200–400 mesh) resin column, which was 30 mm in length and prepared as described earlier.[6] The column was conditioned with dimethylformamide for 24 hr before use.

gêne sérieuse. Le complexe jaune d'uranium(VI) avec (I) est précipité quantitativement dans le domaine de pH 3,5-10,0 et, après lavage et séchage, correspond à la composition $UO_2(C_6H_5N_2O)_2$. Le complexe d'uranium(VI) avec la 6-méthylpyridine 2-aldoxime (II) est précipité quantitativement dans le domaine de pH 3,0–10,5 et, après lavage et séchage à 120°–130°, correspond à $UO_2(C_7H_7N_2O)_2$. (I) et (II) conviennent tous deux au dosage de 1–50 mg d'uranium (VI) en la présence de quantités de Th(IV), La(III) et Ce(III) pouvant être jusqu'à 10 fois supérieures, même lorsque ces éléments sont présents ensemble. Ce(IV) en quantités supérieures à trois celle de U doit être réduit en Ce(III). Les tartrate, citrate, phosphate, Ti(IV) et Zr interfèrent, mais non les acétate, oxalate et borate.

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Separation and determination of mixtures containing *p*-aminosalicylic acid and *m*-aminophenol

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p-AMINOSALICYLIC ACID (PAS) decarboxylates to form *m*-aminophenol (MAP) as its major breakdown product. In order to study the stability of PAS and its salts in aqueous medium, a procedure has been developed for determining both components, which is based on chromatographic separation on an ion-exchange resin, followed by non-aqueous titration of the individual components.

The U.S.P. XVII method of analysis[1] is based on the diazotization reaction, which does not distinguish between PAS and MAP. The MAP content is determined separately by colorimetric analysis. Several procedures have been proposed for determining PAS alone, as salts and as pharmaceutical preparations. These have been noted earlier.[2–4] Non-aqueous titration procedures have been reviewed by Kucharsky and Safarík.[5] In our previous paper[4] a specific method was reported for PAS, its salts and preparations, and a non-aqueous differentiating titration was suggested for PAS and MAP.

EXPERIMENTAL

Reagents

p-Aminosalicylic acid and *m*-aminophenol were the best quality available from commercial sources. The *m*-aminophenol was further purified by recrystallization from hot water.

Sodium methoxide (0·1*M*) in benzene–methanol and 0·1*M* perchloric acid in glacial acetic acid were prepared and standardized as directed in U.S.P. XVII.[1]

Hydrochloric acid (2*M*) in 50% ethanol.

Mercuric acetate solution, 6%, in glacial acetic acid.

All chemicals and solvents were reagent grade.

Chromatography column

A 50-ml burette (10 mm bore) was used as a chromatographic column. It was plugged at the base with glass-wool to support the Dowex 50W-X8 (200–400 mesh) resin column, which was 30 mm in length and prepared as described earlier.[6] The column was conditioned with dimethylformamide for 24 hr before use.

Procedure

A series of mixtures containing varying proportions of PAS and MAP, as listed in Table I, was prepared by weight from the finely powdered compounds. The PAS was added first to a 250-ml amber, wide-mouth, screw-cap powder jar. The MAP was then added, and the bottle capped and rotated end over end until a homogeneous mixture resulted (about 5 min).

Each mixture was analysed for MAP and PAS content, the sample used containing 1 mequiv of MAP. The sample was dissolved in 20 ml of dimethylformamide and the solution was transferred quantitatively to the resin column with the aid of an additional 10 ml of dimethylformamide. The rate of flow through the column was controlled at 0·2 ml/min. The column was washed with three 10-ml portions of dimethylformamide. The eluate and washings were collected in a 50-ml volumetric flask and diluted to volume with dimethylformamide. An aliquot containing about 1 mequiv of PAS was transferred to a 150-ml beaker, dimethylformamide was added to bring the volume to about 50 ml, 1 drop of Thymol Blue indicator solution (1% in dimethylformamide) was added, and the solution, stirred magnetically and protected from carbon dioxide *etc*,[7] was titrated with 0·1*M* sodium methoxide to the first permanent blue colour. The PAS content of the mixture was determined. Results are recorded in Table I.

TABLE 1.—ANALYSIS OF MIXTURES CONTAINING VARYING PROPORTIONS OF PAS AND MAP

Composition of mixture		Found	
PAS, %	MAP, %	PAS, %	MAP, %
98·99	1·01	$98{\cdot}8 \pm 0{\cdot}0_2$	$1{\cdot}1_6 \pm 0{\cdot}0_2$
94·08	5·92	$94{\cdot}4 \pm 0{\cdot}1_4$	$5{\cdot}6_3 \pm 0{\cdot}1_7$
89·04	10·96	$88{\cdot}5 \pm 0{\cdot}2_3$	$11{\cdot}5 \pm 0{\cdot}2_8$
79·16	20·84	$77{\cdot}0 \pm 0{\cdot}1_3$	$23{\cdot}0 \pm 0{\cdot}1_9$
49·92	50·08	$49{\cdot}6 \pm 0{\cdot}8_5$	$50{\cdot}4 \pm 0{\cdot}8_5$

The resin column was washed with three 20-ml portions of ethanol and the washings were discarded. A total of 30 ml of 2*M* in 50% hydrochloric and aqueous ethanol was passed through the column at a flow-rate of 0·2 ml/min. The eluate, containing *m*-aminophenol hydrochloride, was evaporated to dryness at room temperature by passing a stream of clean air over the solution. Then 5 ml of 50% aqueous ethanol were added and the solution was again evaporated to dryness; this step was repeated. Finally, the residue was dissolved in 20 ml of glacial acetic acid, 10 ml of 6% mercuric acetate in glacial acetic acid were added,[8] followed by one drop of Methyl Violet indicator solution (1% in glacial acetic acid), and the mixture, stirred magnetically, was titrated with 0·1*M* perchloric acid to the first permanent emerald green colour. The MAP content was determined. Results are shown in Table I.

After each run the ion-exchange resin was regenerated by washing with water until the eluate pH was 7. Three 10-ml portions of ethanol were passed through the column, which was then washed with dimethylformamide and left filled with this solvent for 24 hr before re-use. Immediately before use the column was washed with a fresh 10-ml portion of dimethylformamide. The resin was used 5 times before being discarded.

DISCUSSION

Separation of PAS from MAP is readily achieved because of the stronger basic properties of MAP. Dowex 50W-X8, a sulphonic acid type resin, is a sufficiently strong acid to extract the MAP from the mixture. The PAS ($pK_a = 3{\cdot}25$) is not retained by the column because of its strongly acidic nature. It appears in the eluate and is readily titrated in non-aqueous medium with sodium methoxide. The MAP is displaced from the resin with hydrochloric acid in 50% aqueous ethanol. Ethanol is used as the solvent to solubilize the MAP hydrochloride and to facilitate the evaporation of the solvent at room temperature. The MAP hydrochloride decomposed somewhat when heated for prolonged periods. By the proposed procedure no decomposition occurred; the MAP hydrochloride was recovered as a white crystalline powder. It was readily titratable in glacial acetic acid with perchloric acid. The presence of mercury(II) acetate in the titration mixture was necessary for successful titration [undissociated mercury(II) chloride is formed and the liberated acetate acts as a base].

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Summary—A procedure is described for separating and determining *p*-aminosalicylic acid and *m*-aminophenol in mixtures. Separation is effected by passing a solution of the mixture in dimethylformamide through a column of strong cation-exchange resin. The eluate containing the *p*-aminosalicylic acid is titrated with sodium methoxide. The *m*-aminophenol is eluted from the column with ethanolic HCl. The eluate is evaporated to dryness, the residue dissolved in acetic acid, and the solution titrated with perchloric acid.

Zusammenfassung—Ein Verfahren zur Trennung und Bestimmung von *p*-Aminosalicylsäure und *m*-Aminophenol in Gemischen wird beschrieben. Die Trennung erreicht man, wenn man eine Lösung des Gemisches in Dimethylformamid durch eine Säule mit starkem Kationenaustauschharz laufen läßt. Das die *p*-Aminosalicylsäure enthaltende Eluat wird mit Natrium-methylat titriert. Das *m*-Aminophenol wird mit äthanolischer Salzsäure von der Säule eluiert. Das Eluat wird zur Trockne eingedampft, der Rückstand in Essigsäure aufgenommen und die Lösung mit Überchlorsäure titriert.

Résumé—On décrit une technique pour la séparation et le dosage de l'acide *p*-aminosalicylique et du *m*-aminophénol dans des mélanges. On effectue la séparation en passant une solution du mélange en diméthylformamide sur une colonne de résine échangeuse de cations forte. L'éluat contenant l'acide *p*-aminosalicylique est titré au méthoxyde de sodium. Le *m*-aminophénol est élué de la colonne par HCl éthanolique. L'éluat est évaporé à sec, le résidu dissous en acide acétique et la solution titrée à l'acide perchlorique.

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The complexes of bismuth(III) and nitrilotriacetic acid

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NITRILOTRIACETIC ACID [NTA, H_3X, $N(CH_2COOH)_3$] is one of the simplest aminopolycarboxylic acids which form stable complexes with metal cations. There is no full study of the reaction of bismuth(III) and NTA. Iyer, Bhat and Shankar[1] have studied the complex formation of bismuth with NTA and Tiron by potentiometry, but they do not give the stability constants.

EXPERIMENTAL

Reagents

Bismuth perchlorate solution, $1\cdot00 \times 10^{-3}M$. Dissolve an accurately weighed amount of pure metallic bismuth (99·999% purity) in the minimum quantity of nitric acid. Add perchloric acid and evaporate carefully to remove the nitric acid, and then dilute to volume with distilled water. The pH of the solution thus prepared was 1·30.

Nitrilotriacetic acid solution, $2\cdot00 \times 10^{-2}M$. Suspend a known weight of the acid (dried at 105°) in water and add sodium hydroxide to dissolve it completely. Dilute with water to volume. The pH of the solution of NTA was 5·20. Dilute precisely to $1\cdot00 \times 10^{-3}$ and $2\cdot00 \times 10^{-3}M$ for working solutions.

Summary—A procedure is described for separating and determining *p*-aminosalicylic acid and *m*-aminophenol in mixtures. Separation is effected by passing a solution of the mixture in dimethylformamide through a column of strong cation-exchange resin. The eluate containing the *p*-aminosalicylic acid is titrated with sodium methoxide. The *m*-aminophenol is eluted from the column with ethanolic HCl. The eluate is evaporated to dryness, the residue dissolved in acetic acid, and the solution titrated with perchloric acid.

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EXPERIMENTAL

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Nitrilotriacetic acid solution, 2·00 × $10^{-2}M$. Suspend a known weight of the acid (dried at 105°) in water and add sodium hydroxide to dissolve it completely. Dilute with water to volume. The pH of the solution of NTA was 5·20. Dilute precisely to 1·00 × 10^{-3} and 2·00 × $10^{-3}M$ for working solutions.

Control of pH and ionic strength ($\mu = 1$) was achieved by addition of standard solutions of perchloric acid, sodium perchlorate and sodium hydroxide.

The reagents used were *pro analysi* grade.

RESULTS AND DISCUSSION

Figure 1 shows the absorption spectra of solutions of bismuth perchlorate and NTA (in molar ratio 1:2) at different values of pH. Absorption maxima are observed at 190–195, 222, 243 and 271 nm and reach their maximum intensity in 2*M* perchloric acid, 2*M* perchloric acid, pH 1–3 and pH 4·5–7·5 media respectively. That at 222 nm is due to bismuth perchlorate, the others to bismuth–NTA complexes. Above pH 8 bismuth hydroxide precipitates. All further investigations used the absorption maxima at 243 and 271 nm.

The continuous variation and mole-ratio methods prove that the maxima at 243 nm and 271 nm are due to complex compounds with the composition Bi:NTA = 1:1 and 1:2 respectively (Figs. 2 and 3). It is more difficult to prove the existence and nature of the 1:2 complex because at pH 6, the optimum value for formation of the 1:2 complex, free bismuth hydrolyses. However, the mole ratio method (at constant concentration of NTA and pH ~6), can be employed (curves 5 and 6, Fig. 3). An increase in the ratio Bi:NTA beyond 0·7–0·8 results in the partial hydrolysis of the 1:1 complex so the method of continuous variations is not applicable to the 1:2 complex.

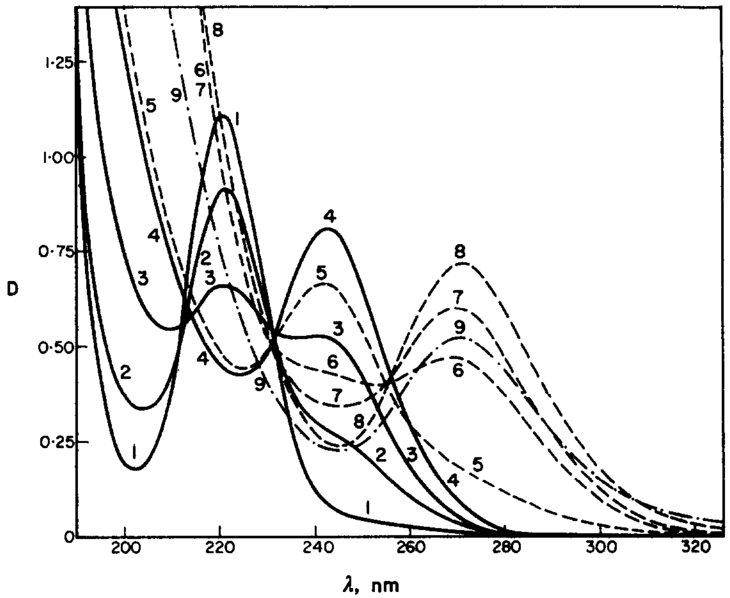

FIG. 1.—Absorption spectra.
$C_{Bi} = 1{\cdot}00 \times 10^{-4}M$. $C_{NTA} = 2{\cdot}00 \times 10^{-4}M$. pH: *1*—−0·2; *2*—0·0; *3*—0·2; *4*—1·0; *5*—3·4; *6*—4·4; *7*—4·8; *8*—6·1; *9*—7·4; water blank.

The formation of the 1:1 and 1:2 complex compounds can be seen in Fig. 4, which is a plot of the absorbance at 243 nm and 271 nm as a function of pH. It is seen that formation of the 1:1 complex begins at pH about −0·2 (1·5–1·6*M* perchloric acid) and stops at pH 0·8–1·0. On further increase of the pH the absorbance at 243 nm begins to decrease but that at 271 nm begins to increase and reaches its maximum value at pH 5·8–6·2. Under these conditions the 1:2 complex is formed, which at equivalent ratio of the two components is partially hydrolysed. If an excess of NTA is added, the hydrolysis begins at higher pH (curve 6, Fig. 4).

The formation of the 1:1 complex can be expressed by

$$\mathrm{Bi^{3+} + H_4X^+ = BiH_{4-n}X^{4-n}} + n\mathrm{H^+};$$

$$\log \frac{[\mathrm{Bi(H_{4-n}X)^{4-n}}]}{[\mathrm{Bi^{3+}}][\mathrm{H_4X^+}]} = n\mathrm{pH} + \log K_1,$$

where K_1 is the equilibrium constant. The number of protons released can be established by plotting log $[\mathrm{Bi(H_{4-n}X)^{4-n}}]/[\mathrm{Bi^{3+}}][\mathrm{H_4X^+}]$ *vs.* pH. The data for the plot were taken from curve 2 of Fig. 4 and

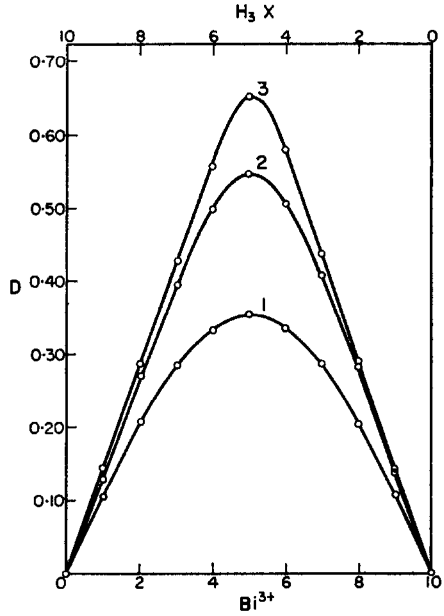

FIG. 2.—Method of continuous variation.
$C_{Bi^{3+}} + C_{NTA} = 2\cdot00 \times 10^{-4}M$; $\lambda = 243$ nm; pH: *1*—0·2; *2*—0·4 and *3*—0·6.

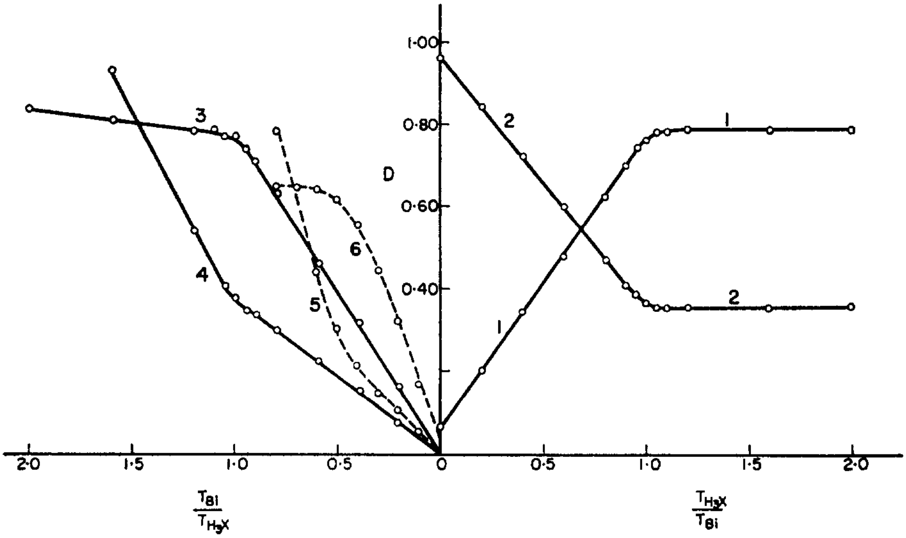

FIG. 3.—Mole-ratio method.
λ: 1, 3 and 5 at 243 nm, 2 and 4 at 222 nm and 6 at 271 nm. pH: 1, 2, 3 and 4 at 1·0, 5 and 6 at 6. $C_{Bi^{3+}}$: *1* and *2*—$1\cdot00 \times 10^{-4}M$; C_{NTA}: *3* and *4*—$1\cdot00 \times 10^{-4}M$; *5* and *6*—$2\cdot00 \times 10^{-4}M$; water blank.

from Fig. 5. The values of *n* obtained were 3·7 (for Bi:NTA = 2:1) and 3·5 (Bi:NTA = 1·1). The fractional value of *n* is explained by the fact that in the pH range used, bismuth reacts not only with H_4X^+, but also with H_3X. Therefore, the formation of the 1:1 complex can be expressed by

$$Bi^{3+} + H_4X^+ = BiX + 4H^+$$

and

$$Bi^{3+} + H_3X = BiX + 3H^+.$$

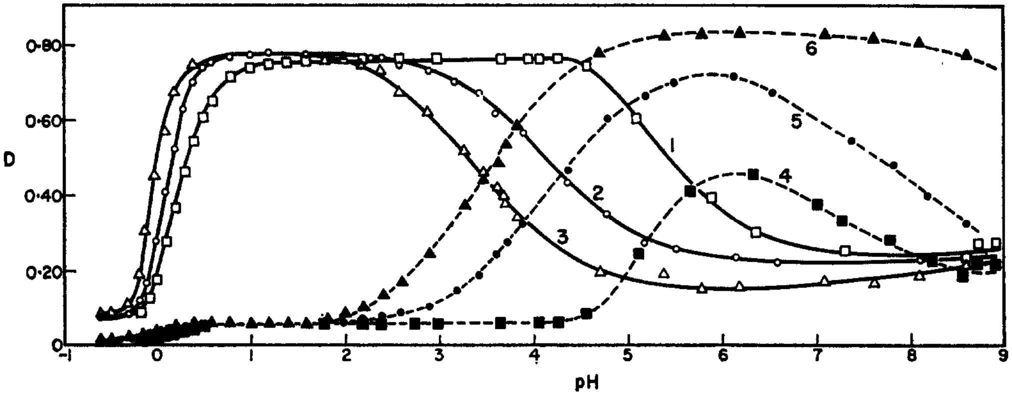

FIG. 4.—Absorbance as function of pH.
λ: *1, 2* and *3*—243 nm; *4, 5* and *6*—271 nm; $C_{Bi^{3+}} = 1{\cdot}00 \times 10^{-4}M$. C_{NTA}: *1* and *4*—$1{\cdot}00 \times 10^{-4}M$, *2* and *5*—$2{\cdot}00 \times 10^{-4}M$, *3* and *6*—$5{\cdot}00 \times 10^{-4}M$; water blank.

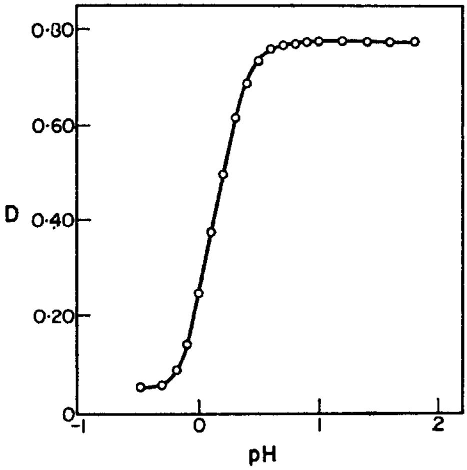

FIG. 5.—Absorbance as function of pH.
$\lambda = 243$ nm; $C_{Bi^{3+}} = 2{\cdot}00 \times 10^{-4}M$; $C_{NTA} = 1{\cdot}00 \times 10^{-4}M$; water blank.

The formation of the second complex can be expressed by

$$BiX + H_mX^{(m-3)} = BiX_2^{3-} + mH^+,$$

$$\log \frac{[BiX_2]}{[BiX][H_mX]} = m\text{pH} + \log K_2,$$

and the value of *m* obtained from the slope of a plot of log $[BiX_2]/[BiX][H_mX]$ *vs.* pH. Such a plot of the data of curves 5 and 6 (Fig. 4) at Bi:NTA ratios of 1:2 and 1:5 gave values for *m* of 1·0 and 1·1.

As can be seen from curves 1 and 4 (Fig. 4) the 1:1 complex hydrolyses at pH 4·5–6 according to

$$2BiX + 3H_2O = BiX_2^{3-} + Bi(OH)_3 + 3H^+.$$

At pH values above 6 the 1:2 complex begins to hydrolyse. Since the position of the absorption maximum does not change and a precipitate of bismuth hydroxide is formed, the hydrolysis may be expressed by

$$BiX_2^{3-} + 3H_2O = Bi(OH)_3 + 2HX^{2-} + H^+.$$

The stability constant of the 1:1 complex was calculated from the dependence of the absorbance at 243 nm on pH, for Bi:NTA ratios = 1:1, 1:2 and 2:1 at constant ionic strength $\mu = 1{\cdot}0$ (curves 1 and 2 of Fig. 4 and Fig. 5). The maximum absorbance, corresponding to complete combination of all the bismuth as the 1:1 complex, was obtained by adding a large excess of NTA at pH 1, and was found to be 0·800 in a 10-mm cell for $1{\cdot}00 \times 10^{-4}M$ bismuth, corresponding to a molar absorptivity of $8{\cdot}00 \,.\, 10^3$ l.mole^{-1}.cm^{-1}. The stability constant for BiX was calculated at every 0·1 pH unit (for the interval from −0·2 to 0·8) according to the equation:

$$\beta_{\mathrm{BiX}} = \frac{[\mathrm{BiX}]\alpha_{\mathrm{X}^{3-}}}{[\mathrm{Bi}^{3+}]C_{\mathrm{NTA}}},$$

where [BiX] and $[\mathrm{Bi}^{3+}]$ are the equilibrium concentrations of BiX and free bismuth, C_{NTA} is the total free NTA concentration irrespective of species and $\alpha_{\mathrm{X}^{3-}}$ is the side-reaction coefficient for NTA:

$$\alpha_{\mathrm{X}^{3-}} = \frac{C_{\mathrm{NTA}}}{[\mathrm{X}^{3-}]}.$$

The equilibrium concentration of the complex compound BiX was calculated from the absorbance and the molar absorptivity. The other equilibrium concentrations were calculated by difference from [BiX] and the initial total concentrations of reactants.

The constants used for the calculation of $\alpha_{\mathrm{X}^{3-}}$ were $\log k_0 = 1{\cdot}10$, $\log k_1 = 1{\cdot}98$, $\log k_2 = 2{\cdot}20$ and $\log k_3 = 8{\cdot}96$ at ionic strength $\mu = 1{\cdot}0$ and 20°.[2] The value of β_{BiX} was found to be $3{\cdot}40 \pm 0{\cdot}48 \times 10^{17}$ (30 results; 95% confidence limits).

The stepwise formation constant K_2 of $\mathrm{BiX}_2{}^{3-}$ was calculated from

$$K_2 = \frac{[\mathrm{BiX}_2{}^{3-}]\cdot\alpha_{\mathrm{X}_3-}}{[\mathrm{BiX}]C_{\mathrm{NTA}}}\ .$$

The values of K_2 were calculated from curves 5 and 6 of Fig. 4, and found to be $1{\cdot}06 \pm 0{\cdot}15 \times 10^9$ (15 results; 95% confidence limits). The overall stability constant of the 1:2 complex is therefore $3{\cdot}60 \pm 0{\cdot}62 \times 10^{26}$.

The molar absorptivities of BiX is $8{\cdot}00 \,.\, 10^3$ l.mole^{-1}. cm^{-1} at 243 nm and of $\mathrm{BiX}_2{}^{3-}$ $8{\cdot}20 \,.\, 10^3$ l.mole^{-1}.cm^{-1} at 271 nm.

ANALYTICAL APPLICATION

The two complexes can be used for the determination of both bismuth and NTA but it is better to use BiX for photometric determination in the ultraviolet, because of the higher selectivity. The conditions for this determination are: $\lambda = 243$ nm, pH about 1, concentration of bismuth (or NTA) from 1×10^{-5} to $2 \times 10^{-4}M$. The concentration of bismuth used for determination of NTA should not be higher than 2–3 times that of the NTA, and the concentration of the NTA for the determination of bismuth should be 10^{-2}–$10^{-3}M$ (all data refer to use of a 10-mm cell).

No special study of interfering elements has been made but it is obvious that ions with a high absorbance in this region of the spectrum (*e.g.* $\mathrm{NO}_3{}^-$, Fe^{3+}, to a certain degree Pb^{2+} *etc.*) will interfere. BiX can also form the basis of the spectrophotometric titration of bismuth and NTA.

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Summary—The reaction between bismuth(III) and nitrilotriacetic acid (NTA or $\mathrm{H}_3\mathrm{X}$) has been investigated by ultraviolet spectrophotometry. It has been established that bismuth(III) and NTA form two complexes with compositions bismuth(III): NTA = 1:1 and 1:2. The absorption maxima are at 243 nm (1:1) and 271 nm (1:2), the molar absorptivities being $8{\cdot}00 \times 10^3$ and $8{\cdot}20 \times 10^3$ l.mole^{-1}.cm^{-1} respectively. The stability constants (at $\mu = 1{\cdot}0$) are: $\log \beta_{\mathrm{BiX}} = 17{\cdot}53 \pm 0{\cdot}06$ and $\log \beta_{\mathrm{BiX}_2{}^{3-}} = 26{\cdot}56 \pm 0{\cdot}07$. The possibility of the analytical application of BiX is briefly discussed.

Zusammenfassung—Die Reaktion zwischen Wismut(III) und Nitrilotriessigsäure (NTA oder $\mathrm{H}_3\mathrm{X}$) wurde ultraviolettspektrophotometrisch untersucht. Es wurde festgestellt, daß Wismut(III) und NTA zwei Komplexe mit den Zusammensetzungen Wismut(III):NTA = 1:1 und 1:2 bilden. Die Absorptionsmaxima liegen bei 243 nm (1:1) und 271 nm (1:2); die molaren Extinktionskoeffizienten betragen $8{,}00 \,.\, 10^3$ bzw. $8{,}20 \,.\, 10^3$ l mol^{-1} mm^{-1}. Die Stabilitätskonstanten (bei $\mu = 1{,}0$) betragen $\log \beta_{\mathrm{BiX}} = 17{,}53 \pm 0{,}06$ und $\log \beta_{\mathrm{BiX}_2{}^{3-}} = 26{,}56 \pm 0{,}07$. Es wird kurz diskutiert, ob BiX analytische Anwendung finden kann.

Résumé—On a étudié la réaction entre le bismuth(III) et l'acide nitrilotriacétique (NTA ou H_3X) par spectrophotométrie ultra-violette Il a été établi que bismuth(III) et NTA forment deux complexes de compositions bismuth(III):NTA = 1:1 et 1:2. Les maximums d'absorption sont à 243 nm 1:1) et 271 nm (1:2), les coefficients d'absorption molaires étant $8{,}00 \times 10^3$ et $8{,}20 \times 10^3$ l.mole^{-1} cm^{-1} respectivement. Les constantes de stabilité (à $\mu = 1{,}0$) sont: $\log \beta_{\mathrm{BiX}} = 17{,}53 \pm 0{,}06$ et $\log \beta_{\mathrm{BiX}_2{}^{3-}} = 26{,}56 \pm 0{,}07$. On discute brièvement de la possibilité de l'application analytique de Bix.

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Copper(I) sulphide-impregnated silicone rubber membranes as selective electrodes for copper(II) ions

(*Received* 10 *February* 1970. *Accepted* 24 *March* 1970)

THE DEVELOPMENT of precipitate-impregnated membrane electrodes has been successful for anion-selective electrodes. Pungor[1] has developed selective membrane electrodes for chloride, bromide, iodide and sulphate ions, using silicone rubber as an inert matrix. Rechnitz[2] has summarized the responses of Pungor's electrodes toward anions.

Chatterjee and Mitra[3] prepared clay membranes that responded to copper, molybdenum and cobalt ions. Morrazzani-Pelletier and Baffier[4] examined collodion and paraffin membranes, and Buchanan and Seago[5] reported on silicone rubber membranes for nickel and cobalt. However, these membrane electrodes for cations did not exhibit the desired response, stability of potentials, analytical range, or selectivity for the ions concerned. Only the silver-selective electrode (Pungor type) has been commercially developed.

The present paper describes the development of precipitate-impregnated membranes as selective electrodes for copper(II), with copper(I) sulphide and silicone rubber as the precipitate and inert matrix respectively.

EXPERIMENTAL

Preparation of copper(I) sulphide-impregnated silicone rubber membranes

A fine powder of copper(I) sulphide was obtained by heating a mixture of copper powder and sulphur in the molar ratio of 2:1 at 600° for 2 hr in an atmosphere of hydrogen sulphide and grinding the heated mixture to a particle size of less than 10 μm. The powder was mixed with about 25% w/w of silicone rubber. A copper plate (10 × 15 × 1 mm) or the end 30 mm of a platinum wire (1 mm diameter) was coated with this mixture to a thickness of about 0·5 mm, and heated at 80° to polymerize the rubber. The membrane was then soaked in a $10^{-2}M$ solution of copper sulphate for a week. Other resins were also used as inert matrices.

Preparation of pressed epoxy resin membranes

The copper(I) sulphide powder was mixed with up to 10% by weight of epoxy resin. The mixture was compacted under a pressure of 1·50 kg/mm^2 to form a tablet with a diameter of 15 mm. After heating at 90° for 12 hr, the tablet was soaked in a $10^{-3}M$ solution of copper sulphate for a week.

Measurement of potentials

Figure 1 shows the cross-section of the membrane electrode. The end of the electrode was put into the test solution and the potentials of the membrane were measured *vs.* S.C.E. as reference electrode at 25·0 ± 0·1°. In the case of the pressed epoxy resin membrane electrodes, the measurement was made as shown in Fig. 2.

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RESULTS AND DISCUSSION

The internal electrode and solution commonly used in selective membrane electrodes as shown in Fig. 2 have been eliminated by attaching the membrane to the surface of a copper plate or platinum wire which does not react with the impregnated powder (Fig. 1). This is because their use causes contamination and mechanical weakness of the membrane. The present method of preparation makes it possible to produce selective electrodes which have arbitrary size and form, and which contain the reference electrode within themselves. They can even contain various membranes which respond toward different ions.

The potential response of copper(I) sulphide-impregnated silicone rubber membranes in a solution of copper sulphate is shown in Fig. 3. The activity was derived from the concentration by means of the ion activity coefficients tabulated by Kielland.[6] The slope was Nernstian in the concentration

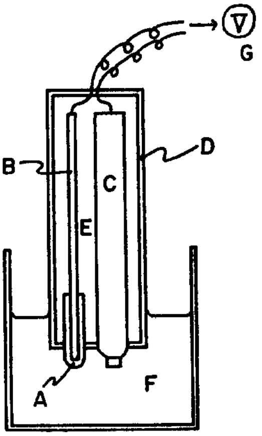

Fig. 1.—Cross-section of copper(I) sulphide-impregnated silicone rubber membrane electrode.
A. Copper(I) sulphide-impregnated silicone rubber membrane. *B*. Platinum wire. *C*. Reference electrode (S.C.E.). *D*. Plastic cover. *E*. Insulator. *F*. Test solution. *G*. pH meter.

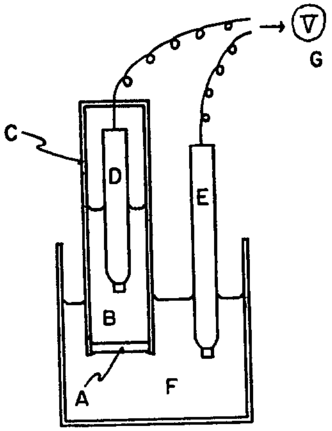

Fig. 2.—Cross-section of pressed epoxy resin membrane electrode.
A. Pressed epoxy resin membrane. *B*. Internal solution ($10^{-3}M$ copper sulphate). C. Plastic holder. *D*. Internal electrode (S.C.E.). *E*. Reference electrode (S.C.E.). *F*. Test solution. *G*. pH meter.

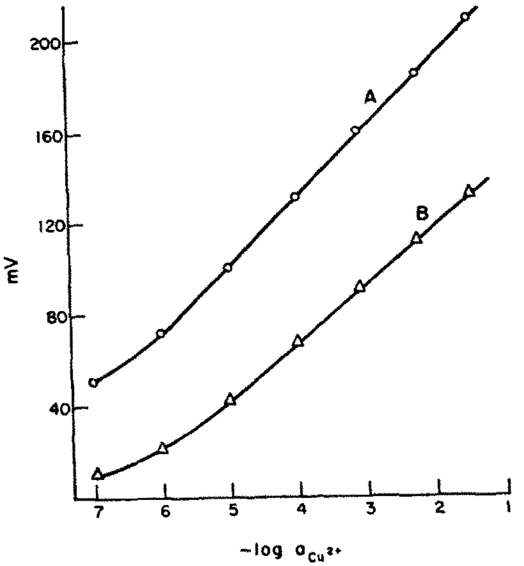

FIG. 3.—Potential responses of silicone rubber membranes impregnated with (*A*) copper(I) sulphide and (*B*) copper(II) sulphide.

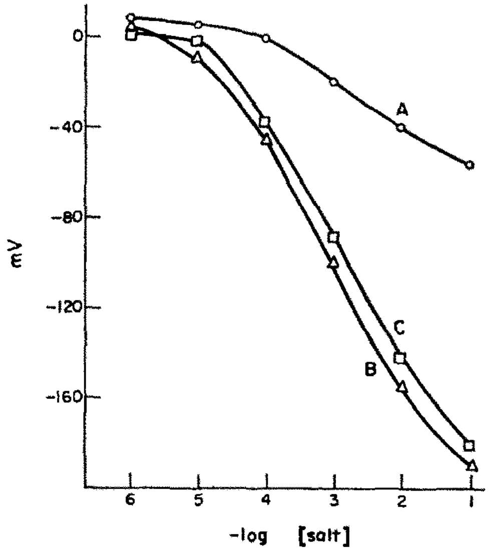

FIG. 4.—Potential responses of copper(I) sulphide-impregnated epoxy resin membranes in the solutions of (*A*) copper sulphate, (*B*) copper nitrate and (*C*) potassium chloride.

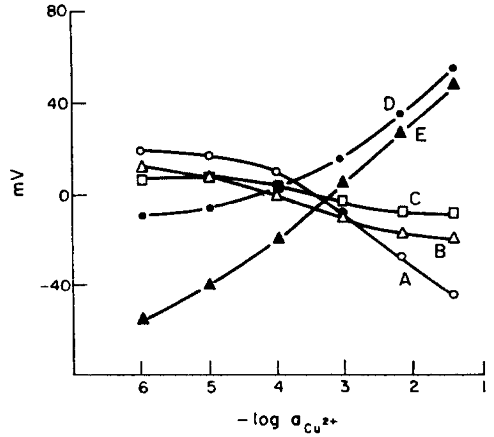

FIG. 5.—Potential responses of pressed epoxy resin membranes. *A*. 10% epoxy resin. *B*. 5% epoxy resin. *C*. 2% epoxy resin. *D*. 1% epoxy resin. *E*. Copper(I) sulphide only.

range 10^{-1}–$10^{-6}M$. The electrode can be used to determine copper in the concentration range 10^{-1}–$10^{-7}M$. The response time of the measuring cell was a few sec for $10^{-1}M$ copper(II) and about 10 min for a $10^{-7}M$ solution. The membrane had to be soaked in a $10^{-2}M$ solution of copper(II) for more than 5 days after its preparation. However, once the membrane was soaked, the potentials were stable and steady even if the membrane was exposed to air for more than two weeks. They were also stable after the membrane was soaked in the solution of copper sulphate for more than a month.

When the fraction of silicone rubber in the membrane was more than 50% by weight, the potentials were unstable and could not be measured. When it was decreased to less than 50%, the time required for soaking in the solution of copper sulphate decreased and the potentials became more stable, and potential properties similar to those shown in Fig. 3 were obtained. However, the lower the fraction of silicone rubber in the membrane, the lower is the adhesive force.

Copper(II) sulphide was used as precipitate in a silicone rubber membrane instead of copper(I) sulphide and the potential responses of this membrane in the solution of copper sulphate are also shown in Fig. 3. The slope of the potential response was about 5 mV less than that in the case of copper(I) sulphide and the chemical or mechanical stability of the membrane was less satisfactory. This is because the copper(II) sulphide powder had been treated at a temperature below 130° (for fear of decomposition).

Influence of pH

The potentials of copper(I) sulphide-impregnated silicone rubber membrane electrodes in $10^{-4}M$ copper(II) did not change at pH values below 7, but decreased sharply when the pH increased above 7, when the precipitation of copper hydroxide occurred [the pH at which the precipitation begins depends on the concentration of copper(II)].

Influence of other ions

Potassium, sodium, calcium, magnesium, aluminium, cadmium, zinc, iron(II), nickel, cobalt(II), chromium(III), lead and ammonium ions at pH values below 7 and chloride, nitrate, sulphate, bromide, perchlorate and acetate ions did not interfere with the determination of copper, and their selectivity ratios for the copper(II) ion were 10^3 or more. The selectivity ratios of iron(III) and iodide ions were 10^2. Ammonium ions (at pH greater than 7), silver, and mercury(II) interfered. The reason is that ammonium ions form stable complex ions with copper(II) in basic solution, and that silver and mercury deposit on the membrane. The sulphide ion caused interference and the membrane can be used as a selective electrode for sulphide.

Effect of temperature

Copper(I) sulphide-impregnated silicone rubber membrane electrodes could be safely used at temperatures between from 10° and 70° and the potentials of the membrane satisfied the Nernst equation within experimental error.

Inert matrices

Epoxy resin was examined as an inert matrix for a copper(I) sulphide-impregnated membrane. The fraction of epoxy resin in the membrane was varied from 10 to 70% by weight and the potential responses developed in the solutions of copper sulphate, copper nitrate and potassium chloride are shown in Fig. 4. Epoxy resin membrane electrodes responded toward anions and the slopes in Fig. 4 were almost independent of the fraction of epoxy resin within the range used. Silver chloride- or barium sulphate-impregnated epoxy resin membranes also responded to anions. In the case of pressed epoxy resin membranes which contain up to 10% of epoxy resin, the lower the fraction of epoxy resin, the smaller the slope of the potential response and the membrane responds to copper(II) when the fraction of resin is less than 2% (Fig. 5), although the Nernst equation is not satisfied.

Polyvinyl chloride, polyvinyl acetate, polyurethane and phenolic resins were examined as inert matrices, and similar results were obtained.

From these results, the membrane impregnated with copper(I) sulphide responds to copper(II)-ion only when the particles of copper(I) sulphide are in contact with each other from one surface of the membrane to the other. When the direct contact of the particles is broken, the potential of the electrode is produced by processes which do not ensure ion-selectivity.

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Summary—Silicone rubber membranes impregnated with copper(I) sulphide have been developed as selective electrodes for copper(II) ions. The internal electrode and solution were eliminated. The Nernst equation was satisfied in the concentration range from 10^{-1} to $10^{-6}M$ copper(II) and the analytical range was from 10^{-1} to $10^{-7}M$. The interference of other ions was examined. Other resins were compared with silicone rubber as inert matrices.

Zusammenfassung—Mit Kupfer(I) sulfid imprägnierte Silikongummimembranen wurden als für Kupfer(II)-Ionen selektive Elektroden entwickelt. Die innere Elektrode und die Lösung wurden weggelassen. Die Nernstsche Gleichung wurde bei Konzentrationen von 10^{-1} bis $10^{-6}M$ Kupfer(II) erfüllt; der analytische Bereich erstreckt sich von 10^{-1} bis $10^{-7}M$. Die Störung durch andere Ionen wurde geprüft. Andere Harze wurden als inerte Träger mit Silikongummi verglichen.

Résumé—On a élaboré des membranes en caoutchouc se silicone imprégnées de sulfure de cuivre(I) comme électrodes sélectives pour les ions cuivre(II). On a éliminé l'électrode et la solution internes. L'équation de Nernst a été satisfaite dans le domaine de concentrations 10^{-1} à $10^{-6}M$ en cuivre(II) et le domaine analytique va de 10^{-1} à $10^{-7}M$. On a examiné l'interférence d'autres ions. On a comparé d'autres résines avec le caoutchouc de silicone comme matrices inertes.

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Some interferences in atomic-absorption spectrometry and extraction of iron and copper

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MUCH has been written on the application of solvent extraction in atomic-absorption spectrometry to overcome interference from other metals. Takeuchi *et al.*[1] have compared the effect of complexing agents on the atomic absorption of metals and found various effects. Sastri *et al.*[2] have demonstrated that metal–oxygen-bonded species contribute to the total amount of metal oxide in flames and hence depopulate the atomic ground-state of the metal in flames.

This paper describes the interferences of the complexing agent in extracted species, in the atomic absorption determination of iron; copper was tested for comparison.

EXPERIMENTAL

Apparatus

A Nippon Jarrell-Ash Model AA-1E atomic-absorption spectrophotometer was used with a Hitachi burner-nebulizer assembly, 75 × 0·5 mm burner, HTV R-136 photomultiplier tube, and Yanagimoto Model RA-2511S recorder. The light sources were iron–chromium and copper hollow-cathode lamps.

Instrument settings

Iron. Wavelength 248·3 nm: slit-width 0·10 mm: lamp current 10 mA: burner height adjusted so that optical pass is 2, 8 or 12 mm above burner top: flow-rates, air 6·0 l./min, acetylene 0·9–1·5 l./min for air–acetylene flame; nitrous oxide 6·0 l./min, acetylene 4·0 l./min for nitrous oxide–acetylene flame: sample uptake 3·8 ml/min for isobutyl methyl ketone extracts.

Copper. Wavelength 324·8 nm: slit-width 0·10 mm: lamp current 10 mA: flame parameters as for iron.

Reagents

Iron standard solution. Dissolve 1 g of pure iron metal in a minimum excess of hydrochloric acid and oxidize with a few drops of nitric acid, boil out nitrogen oxides, and dilute to 1 litre. Prepare dilute standards just before use.

Copper standard solution. Dissolve 1 g of pure copper metal in a minimum excess of nitric acid, boil out nitrogen oxides, and dilute to 1 litre. Prepare dilute standards just before use.

8-Hydroxyquinoline solution. A 0·5% solution in isobutyl methyl ketone.

Sodium diethyldithiocarbamate solution, 2%.

Buffer solution. Acetate and borate buffer solutions for pH 5 and pH 9 respectively.

All reagents used were of analytical-reagent grade. Isobutyl methyl ketone (IBMK) was purified by distillation.

Procedure

Solvent extraction methods were used to prepare the solutions of the iron(III) complexes. The following reagents were used to produce the corresponding complexes of iron(III): potassium thiocyanate, 8-hydroxyquinoline, sodium diethyldithiocarbamate, hydrochloric acid.

Each complex was extracted with two 20-ml portions of IBMK from 30 ml of buffered solution containing 250 μg of iron(III) and the combined extracts were diluted to 50 ml with IBMK.

RESULTS AND DISCUSSION

The effects of complexing agents on iron absorption are summarized in Fig. 1. A marked depressive effect was shown in an air-acetylene flame when thiocyanate was used as complexing agent, increasing with increasing concentration of thiocyanate in the aqueous phase.

Flame conditions were also an important parameter. The fuel-lean flame (for $CO + H_2$ stoichiometry) is seen to be effective for atomization of iron from its thiocyanate complexes. The increased depression of absorption in fuel-rich flames may be derived first from incomplete dissociation and then from compound formation. Iron sulphide is a likely product from decomposition of the thiocyanate complex because the bond energy of CS (272 kJ/mole) is much lower than that of CN (865 kJ/mole) and a CN-band appears in the flame. The depressive effect was also observed when iron chloride complexes and free thiocyanic acid were separately extracted into IBMK and mixed before spraying.

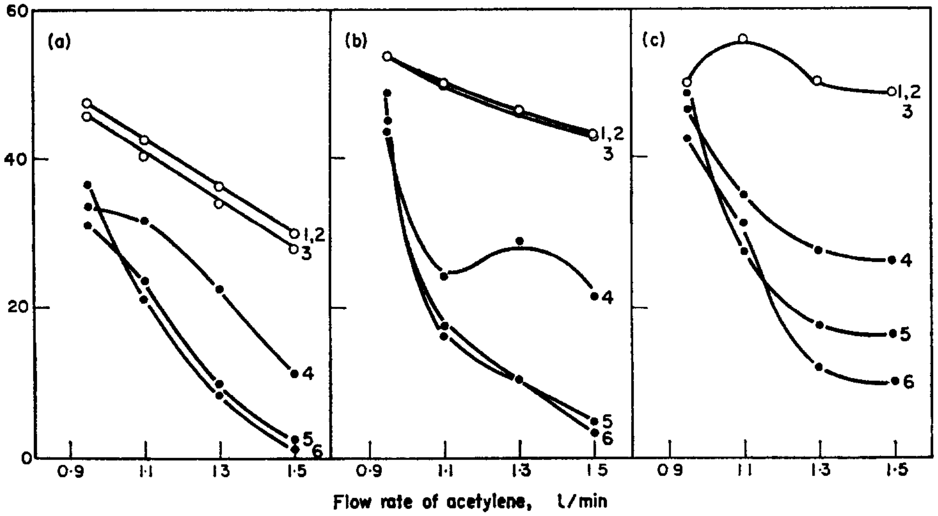

FIG. 1.—Effect of complexing agents on iron absorption.
(a) 2 mm above burner top; (b) 8 mm above burner top; (c) 12 mm above burner top; (1) chloride complex extracted from 6*M* HCl; (2) diethyldithiocarbamate complex extracted at pH 9; (3) hydroxyquinoline complex extracted at pH 5; (4) thiocyanate complex from 0·1*M* SCN⁻ 0·5*M* HCl; (5) thiocyanate complex from 2*M* SCN⁻ 0·5*M* HCl; (6) thiocyanate complex from 5*M* SCN⁻ 0·5*M* HCl.

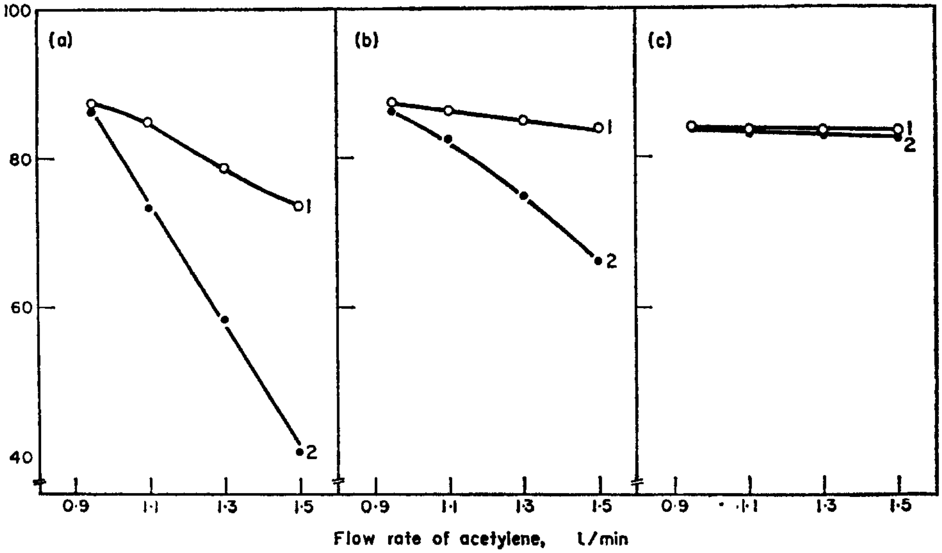

FIG. 2.—Effect of complexing agents on copper absorption.
(a) 2 mm above burner top; (b) 8 mm above burner top; (c) 12 mm above burner top; (1) diethyldithiocarbamate complex extracted at pH 5; (2) pyridine-thiocyanate complex.

Chloride, diethyldithiocarbamate and 8-hydroxyquinoline complexes of iron(III) behaved alike, but differently from thiocyanate, irrespective of flame conditions. The depressive effect of thiocyanate was reduced if a nitrous oxide–acetylene flame was used. The effect of thiocyanate on copper absorption was investigated for comparison. Copper was extracted into IBMK as the pyridine–thiocyanate complex. A depressive effect was also observed for copper absorption, but similar absorptions were found for both pyridine–thiocyanate and diethyldithiocarbamate complexes, provided the measurements were made for a fuel-lean flame or in higher regions of the flame (Fig. 2). No interference was observed on addition of pyridine to the extracted diethyldithiocarbamate complex before spraying. The depression of copper absorption may also be due to the formation of sulphide in the flame. However, copper sulphide will dissociate during the passage of the aerosol particles into the higher regions of the flame. Furthermore, copper has a higher atomic population in all regions of the flame,[3] and this may be the reason for no depressive effect occurring if measurements are made with the light-path well above the burner top.

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Summary—The effect of complexing agents on the atomic-absorption spectrometry of iron and copper extracts was investigated Thiocyanate complexes gave a marked depression of absorption by iron and copper, especially in fuel-rich flames. Chloride, diethyldithiocarbamate and hydroxyquinoline complexes of iron behaved alike, but differently from the thiocyanate complex.

Zusammenfassung—Der Einfluß von Komplexbildnern auf die Atomabsorptionsspektrometrie von Eisen- und Kupferextrakten wurde untersucht. Thiocyanatkomplexe gaben eine merkliche Verminderung der Absorption von Eisen und Kupfer, besonders in fetten Flammen. Chlorid-, Diäthyldithiocarbamat- und Hydroxychinolinkomplexe von Eisen verminderten sie ebenfalls, aber in anderem Ausmaß als der Thiocyanatkomplex.

Résumé—On a étudié l'influence d'agents complexants sur la spectrométrie d'absorption atomique d'extraits de fer et de cuivre. Les complexes du thiocyanate donnent une dépression marquée de l'absorption par le fer et le cuivre, spécialement dans des flammes riches en combustible. Les complexes chlorure, diéthyldithiocarbamate et hydroxyquinoléine du fer se comportent de la même façon, mais différemment du complexe thiocyanate.

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ANNOTATION

Mass spectrometric investigation of copper chelates with 1-(2-pyridylazo)-2-naphthol

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In a recent investigation Betteridge and John[1] (B & J) examined the mass spectra of several transition metal chelates in order to establish their stoichiometry. In the case of the copper chelate with 1-(2-pyridylazo)-2-naphthol (*o*-β-PAN) the stoichiometry was inferred to correspond to the 1:2 Cu(*o*-β-PAN)$_2$ chelate. In an earlier solution study however, Betteridge, Fernando and Freiser[2] proposed the extraction of the 1:1 Cu(*o*-β-PAN) (OH) chelate over the pH range from 4 to 10, rather than the Cu(*o*-β-PAN)$_2$ chelate which would only be formed in a solution containing a very large proportion of *o*-β-PAN relative to OH^-. Galík[3] has found that copper can be extracted as Cu(*o*-β-PAN)Z where Z^- is Br^-, SCN^- *etc*, over the pH range 4–10 and as Cu(*o*-β-PAN)$_2$ over the pH range 8–10 from solutions in which the supporting anion is sulphate. Without certain supporting anions there would be virtually no extraction below pH 8.

B & J were puzzled by the fact that the mass spectrum was like that expected for Cu(*o*-β-PAN)$_2$ except that there were no peaks corresponding to species containing copper-65, and were unable to explain this peculiarity. Being interested in the application of this chelate for quantitative determinations of copper at the ng and pg levels,[4,5] we investigated the stoichiometry as well as the isotopic abundance of this chelate in more detail.

EXPERIMENTAL

Chelates

The copper chelates were prepared from commercially obtained *o*-β-PAN samples (recrystallized from methanol) in the following ways:

(*i*) analogously to the procedure given by B & J, *i.e.*, recrystallization from the precipitate obtained by the reaction of copper(II) and *o*-β-PAN at pH 8;

(*ii*) following the same procedure as described above, in this case however, extracting the aqueous phase with chloroform until colourless, and combining the extracts;

(*iii*) in order to investigate possible extraction of the Cu(*o*-β-PAN) (OH), solutions buffered at pH 4 and 9 were extracted by a procedure analogous to that described by Betteridge, Fernando and Freiser,[2] but with a smaller PAN:Cu^{2+} ratio of 7:1 in order to obtain more evidence for the proposed Cu(*o*-β-PAN) (OH) extraction.

Apparatus

All measurements were made with an AEI MS 9 mass spectrometer fitted with an insertion lock and a direct evaporation probe. Samples were admitted by evaporating 10 μl of a solution of the chelate in chloroform (*i*, *ii*) or carbon tetrachloride (*iii*) on the tip of a quartz sample probe.

RESULTS AND DISCUSSION

The stoichiometry

Whereas the mass spectrum of the chelating agent is identical with that reported by B & J,[1] the spectrum of the chelate shows some interesting discrepancies (a part of this spectrum is given in Fig. 1). In the spectrum reported by B & J only two peaks were attributed to copper-containing ions, *viz.* the peaks at $m/e = 311$ and $m/e = 559$, corresponding to the ions CuX^+[*] and CuX_2^+ respectively. The spectrum recorded for the present work, however, shows at least nine copper-containing ions of reasonable abundance. Exact mass and isotopic abundance measurements showed the triplet at $m/e = 622$, 624 and 626[†] to correspond with the formula Cu_2X_2, yielding evidence for a 1:1 stoichiometry. Likewise, the peaks at $m/e = 559$ and $m/e = 311$ correspond with the formulae CuX_2 and CuX, indicating a 1:2 and 1:1 stoichiometry for these ions.

[*] X means *o*-β-PAN

[†] Henceforth, reference to isotopic clusters will be made by use of the lowest *m/e* value only.

[‡] 180° is the lowest temperature at which the chelate evaporates.

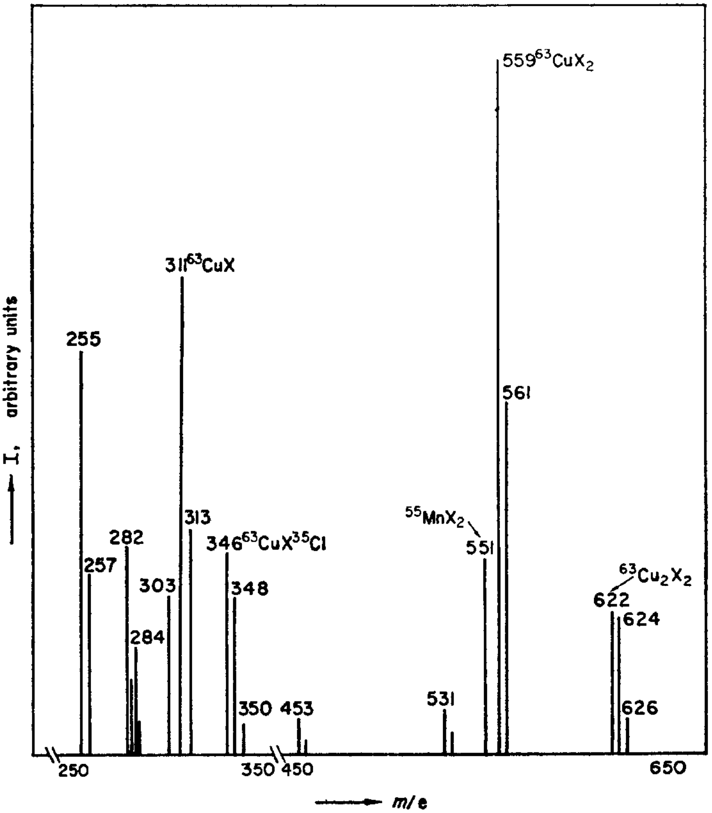

FIG. 1.—Part of mass spectrum of copper chelate with PAN. T = 200°C.

It should, however, be questioned whether these ions correspond to chelates originally present in the sample or to reactions in the mass spectrometer. Samples prepared in different ways (see experimental) showed a constant intensity ratio of the peaks at $m/e = 622$ and $m/e = 559$ during the evaporation at constant temperature. Moreover, this ratio appeared to be independent of the ion-source temperature in the region of 180–280°‡. Consequently the presence of a mixture of Cu_2X_2 and CuX_2 seems less plausible. A plot of the intensity ratio 622/559 *vs.* the electron beam energy showed the ionization potential of $Cu_2X_2^+$ to be lower than that of the CuX_2^+ ion; if we are dealing with a compound and not with a mixture, the CuX_2^+ ion is most probably formed by loss of copper from the $Cu_2X_2^+$ molecular ion. Metastable peaks originating in either field-free region of the mass spectrometer were not found, however, for this reaction.

In the work of B & J the CuX_2^+ ion is proposed to be the molecular ion, while the CuX^+ ion at $m/e = 311$ should be exclusively the result of fragmentation. This would be indicated by the close resemblance of the intensity ratio CuX_2^+/CuX^+ to the MeX_2^+/MeX^+ ratios for other metal *o*-*β*-PAN chelates, known from solution studies to have a 1:2 stoichiometry. However, apart from the fact that this ratio may vary considerably for a single component, depending on ion-source conditions, several other metal chelates, *e.g.*, acetylacetonates[6] and dibenzoylmethanates[7] of a known 1:2 stoichiometry in solution show very different MeX_2^+/MeX^+ ratios, so that no reliance can be placed upon this ratio as an indication of stoichiometry. We have found metastable transitions from the $Cu_2X_2^+$ and CuX_2^+ ions into the CuX^+ ion, while furthermore the appearance potential of the CuX^+ ion exceeds that of $Cu_2X_2^+$ and CuX_2^+, but this does not rule out the possibility that the ion at $m/e = 311$ is partly a molecular ion.

The spectra were examined for peaks due to the species CuXOH. The spectra obtained from solutions prepared at pH 4 by procedure (*iii*) had no peaks due to copper-containing species but those obtained from solutions prepared at pH 9 by the same procedure were analogous with spectra obtained by procedures (*i*) and (*ii*). It is possible indeed that in solution a chelate of the composition CuX^+OH^- is formed, which decomposes in the ion-source. However the presence of ions at $m/e = 346$, 348 and

350, which correspond (according to exact mass and isotopic abundance measurements) with the composition CuX^+Cl^- makes this less plausible. The relative intensity of this ion was strongly dependent on the temperature (elevated temperatures probably cause decompostion) and the sample. It is probably formed in solution by ion-pair formation with chloride ion impurities in the chelating agent and/or decomposition of the solvent (chloroform). In the recrystallized sample [preparation (*i*), see experimental] its presence was negligible. All other copper-containing ions in the mass spectrum can be easily understood by a comparison with the fragmentation of the pure chelating agent. Because of the results noted above we concur with B & J, that the use of mass spectrometry for the establishment of chelate stoichiometry is limited; however, we do not agree with their stoichiometric conclusions derived from the mass spectra of the copper chelate.

Isotopic abundance measurements

Copper has two stable isotopes of comparable abundance, *viz.* copper-63 (69·09%) and Copper-65 (30·91%). B & J stated that copper in $Cu(o\text{-}\beta\text{-PAN})_2$ and related chelates behaved as though copper-63 were the only stable isotope. In our investigation, the isotopic abundance of copper as measured from all copper-containing molecular and fragment ions of sufficient intensity (8), showed the expected natural abundance. This was also the case with samples prepared in a way analogous to that described by B & J.

As can be seen from Fig. 1 there are also peaks at $m/e = 551$ and $m/e = 303$. If the temperature is increased to 230–250°, the intensity of these ions is greatly enhanced with respect to that of the copper-containing ions. Exact mass measurements showed these peaks to correspond with the monoisotopic manganese chelate. At higher temperatures (280–300°) intense peaks at $m/e = 552$, 554 and 556 appear (about 5–10 times as intense as the copper ion at $m/e = 559$), which we attribute to the presence of iron and nickel. However, X-ray fluorescence analyses of the sample showed these metals only in vanishing by small quantities. We suppose these ions are the result of exchange reactions with hot metal surfaces in the ion-source, like the manganese-containing heater wires. A similar effect has been observed by Holtzclaw *et al.*[8] in their investigation of 1-methyl-3-alkyl-1,3-dione–copper(II) chelates.

Considering the (unnecessary) excessively high temperature of 380° used by B & J, we suppose the peaks, given by the dotted lines in their Figs. 12 and 13, to be merely the result of other (monoisotopic) metal chelate ions, rather than copper-containing ions.

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Summary—The mass spectra of copper chelates of 1-(2-pyridylazo)-2-naphthol, HX, prepared by different methods, are discussed. Peaks due to $Cu_2X_2^+$, CuX_2^+ and $CuXCl^+$ have been positively identified and all copper-containing species have the expected isotopic ratios. The significance of probe temperature and impurities are discussed and it is concluded that the spectra are more in accordance with the known chemical facts than those reported earlier by Betteridge and John.

Zusammenfassung—Die Massenspektren von verschieden hergestellten Kupferchelaten mit 1-(2-Pyridylazo-2-naphthol, HX, werden diskutiert. Die Peaks von $Cu_2X_2^+$, CuX_2^+ und $CuXCl^+$ wurden sicher identifiziert; alle Kupfer enthaltenden Spezies haben die erwarteten Isotopenverhältnisse. Die Bedeutung der Temperatur an der Einspritzstelle und von Verunreinigungen werden diskutiert und es wird der Schluß gezogen, daß die Spektren mit den bekannten chemischen Tatsachen besser übereinstimmen als die früher von Bettridge und John mitgeteilten.

Résumé—On discute les spectres de masse des chélates de cuivre du 1 (2-pyridylazo) 2-naphtol, HX, préparées par différentes méthodes. Les pics dûs à $Cu_2X_2^+$, CuX_2^+ et $CuXCl^+$ ont été positivement identifiés, et toutes les espèces contenant du cuivre ont les rapports isotopiques attendus. On discute l'importance de la température de

l'essai et des impuretés et l'on conclut que les spectres sont plus en accord avec les faits chimiques connus que le spectre rapporté antérieurement par Betteridge et John.

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TALANTA REVIEW*

QUANTITATIVE ANALYSIS IN PHARMACY AND PHARMACEUTICAL CHEMISTRY BY NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY

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Summary—The applications of n.m.r. to the quantitative analysis of pharmaceutical formulations and products of interest to the pharmacist and pharmaceutical analyst are reviewed. Special attention is paid to the accuracy of the method, the coefficients of variation being quoted (or calculated from data in the original paper) where possible. An elementary knowledge of n.m.r. is assumed.

SINCE the discovery of nuclear magnetic resonance (n.m.r.) spectroscopy in 1945[1,2] this spectroscopic technique has so gained in importance that, excluding those which quote n.m.r. data only as support to structural assignments, more than 250 papers a month are now appearing on the subject. Most of them, however, have not been concerned with the use of n.m.r. as a quantitative analytical tool. This may partly have been due to the relatively large quantity of sample required as compared with such analytical techniques as ultraviolet spectroscopy and gas–liquid chromatography (g.l.c.) and to the lack of n.m.r. facilities in less well equipped laboratories.

Recent advances in instrumentation have now made available cheaper n.m.r. spectrometers and time-averaging computer accessories which extend the scope of n.m.r. to microgram quantities. Thus it seems an opportune time for a comprehensive review on the work related to pharmaceutical chemistry. The basic principles of n.m.r. are described in elementary texts on physical chemistry but the needs of the pharmacist and pharmaceutical analyst are best served by current brief summaries.[3–5]

The use of n.m.r. depends on the measurement and interpretation of three parameters. These are signal position (the chemical shift or "δ" value), the splitting of that signal (the spin-spin coupling constants, J values, which reflect the number and nature of adjacent protons) and the signal intensity (expressed as a peak area or peak height). It is the signal intensity parameter which provides the quantitative measure of material in solution. A conventional proton n.m.r. experiment consists of a preliminary field sweep which establishes the proton δ and J values. For the assignment of unknown peaks in new compounds, several extensive compilations[6,7] can be consulted, and workers specially interested in nitrogen heterocyclics, alkaloids *etc*, will find of value the collected[8] proton n.m.r. shifts of 2306 proton groupings influenced

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* For reprints of this Review see Publisher's announcement near end of issue.

by a nitrogen atom in the molecule. Once a peak, or group of peaks, in the n.m.r. spectrum has been related to structural features in the compounds examined, the peak areas can be accurately measured with the electronic integrator which is built in as standard equipment on all commercially-available analytical spectrometers. Provided that the compounds are chemically stable (and that suitably rapid sweep times and non-saturating observing field parameters are selected[9]) the integrated *peak areas* are directly proportional to the number of protons causing those peaks. For absolute quantitative measurements these peak areas can then be related to that of a standard solution of a single component in the same solvent and under the same instrumental conditions or against that of a quite separate standard entity which is added to the solution under test as an internal reference. In less common analytical practice, information is obtained from the ratio of spectral peak heights. In the absence of these standard reference techniques, the n.m.r. integration method yields only *relative* quantities of components from their relative peak areas.

The armoury of the n.m.r. spectroscopist is augmented by time-averaging computers (CATS) and glass micro-cells which permit the analysis of sub-milligram quantities, *e.g.*, for the determination of 0·1 mg of barbiturate mixtures and for the analysis of 0·05-mg g.l.c. fractions from a commercial terpene fraction.[10] Spectra may often be simplified by removing interfering OH and NH proton signals through addition of a few drops of heavy water (D_2O) or gaseous acid vapour. Certain n.m.r. spectrometers can be modified to operate on nuclei other than hydrogen (*e.g.*, boron-11, carbon-13, fluorine-19, and phosphorus-31). Although much employed elsewhere[6] this has found only one application pertinent to the present review. Other techniques generally available include spectrum simplification by irradiation of the samples with a second radiofrequency (a spin-decoupling experiment) and variation of the ambient probe temperature, but these methods have not been applied in the quantitative analysis of pharmaceutical products.

The most important considerations for the purpose of quantitative analysis by n.m.r. are the precision and accuracy of integration. Several authors[9,11,12] have discussed these with regard to instrument settings of field stability and strength, integral amplitude, time of scan and the concentration of the solution. Alexander[11] concludes that the measured integral is within 1% of the theoretical value if 3–4 mequiv of protons are available (*i.e.*, about 60 mg for a compound having a molecular weight of 200 with 10 protons per molecule). Spectrum integration against a suitable reference is also used[9] for the measurement of the amount of hydrogen in organic compounds and can be at least as accurate as combustion analysis. It is disturbing to find, therefore, serious discrepancies noted[13] in an inter-laboratory collaborative n.m.r. study carried out on samples of caffeine, with hexamethylcyclotrisiloxane as internal reference standard. Six collaborators quantitatively analysed sealed aliquots supplied by an associate referee. Hence the variation in their results did not depend on initial sample preparation but only on instrumental and operator errors, and on sample stability. A relative standard deviation as high as 9·7% was recorded for the caffeine content, but there were indications that decomposition or reaction between the components had occurred. A solution of rubbing alcohol was also studied by the collaborators. In this case the stability of the sample was not in question and the results proved satisfactory, *e.g.*, for the alcohol (61·2%) and water (34·6%) contents, coefficients of variation of 0·6–1·7% were found.

ANALYSIS USING, AS REFERENCE, STANDARD SOLUTIONS OF ONE COMPONENT

In these examples the standard chosen is a solution containing a known weight of a single component from the mixture. The procedure is to calculate the integral response of the n.m.r. instrument to this standard solution and then to draw a calibration curve of integrated peak areas over the range of concentration which will be encountered in the unknown solutions.

N.M.R. has proved[14,15] a useful criterion for qualitative identification of eighteen barbiturates, deuterochloroform ($CDCl_3$) or trifluoroacetic acid (TFA) being used as solvents. Rücker[16] has used a CAT and a 0·2-ml microcell for the quantitative analysis of only 0·1–1·5 mg of six barbiturates, with a quoted coefficient of variation of 10%. The CAT operates by dividing the spectral information into 1024 sections and feeding the signal amplitude data for each section into a memory channel of the computer. The effect of repetitive scanning is to augment weak signals, from small amounts of material, at the expense of interfering noise (the improvement factor in the ratio of signal to noise height being $\sqrt{n}$ after n accumulated scans). To obtain a satisfactory spectrum from such small quantities of barbiturates Rücker found that the necessary condition was that the product of the number of protons integrated as the unknown and of the number of accumulated scans must exceed 600. As an example we can consider the analysis of a mixture of 5-ethyl-5-phenylbarbituric acid (A) and 5,5-diethylbarbituric acid (B). The peaks integrated are those due to the phenyl protons of A and the methylene protons of B as shown in Fig. 1.

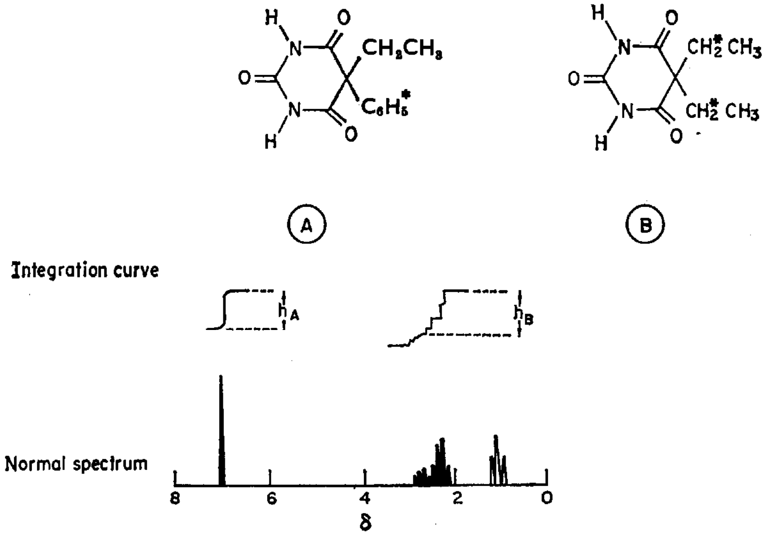


FIG. 1.—Accumulated spectrum of barbituric acids A and B. (Redrawn from *Z. Anal. Chem.*, 1967, **229**, 340 and printed by permission of the copyright holders.)

First, each component (10 mg) is dissolved in 2 ml of solvent and the spectrum of 0·2 ml of this solution accumulated 120–150 times until sufficient for integration. A constant (k) for the component and the instrument parameters is found from the equation:

$$k = \frac{h}{c.n.a.} \tag{1}$$

where h = integration height, c = concentration, n = number of protons causing the integrated peak(s) and a = number of spectra accumulated.

Quantitative analysis of a mixture (0·2 mg/ml) of A and B follows simply from integration of a 250-scan accumulated spectrum (Fig. 1) and substitution in equation (1) of the integral heights for A and B (h_A and h_B) so obtained.

Nine sedatives and hypnotics (including meclozine, methaqualone, glutethimide and ethinamate) give well defined n.m.r. spectra[17] and two ternary mixtures (containing a minimum of 3 % of each component) can be analysed with a coefficient of variation of 4 %. A microcell (without CAT) was used in this work and analyses were made on 10–15 mg quantities of the mixtures. To calibrate the integrator, each component was first made up as a solution (30–1500 mg/ml in $CDCl_3$) and the spectrum integrated to yield the relevant k values. These were then substituted into equation (1) for the calculation of mixture compositions. The author points out the advantages over other spectroscopic and chromatographic techniques, the n.m.r. method providing more specific qualitative identification and comparable quantitative accuracy.

Historically, the first application of n.m.r. to pharmaceutical formulations was the analysis[18] of aspirin, phenacetin and caffeine (APC) tablets. The analysis is based on integration of the peaks given in Table I.

Table I.—APC tablet analysis

Component	Peaks integrated	Coefficient of variation, %
Aspirin	$-OCOCH_3^*$	3·5
Phenacetin	$-OCH_2^*CH_3$	4·9
Caffeine	$—N—CH_3^*$	4·5

One analysis requires 60 mg of material with deuterochloroform (or ethanol-free chloroform) as solvent. Allowance is made in this procedure for overlap of phenacetin and caffeine peaks and for an interfering carbon-13 satellite band. Binders (starch or lactose) do not dissolve in the solvent and hence do not interfere. The integration calibration is carried out with a 50 mg/ml caffeine solution and all areas are referred to this standard measurement. The merits of this method over the United States National Formulary methods have been discussed.[18,19] Two major advantages of the n.m.r. assay procedure are simplicity of sample preparation and rapid turnover (3 samples/hr).

ANALYSIS BY *IN SITU* ADDITION OF AN INTERNAL STANDARD

Addition of a reference standard directly to the solution being analysed is a procedure preferred to that described in the previous section because it eliminates possible variations of integral amplitude with a change in temperature, tube size or instrument behaviour between measurements made on standard and unknown. It is most important, however, that there should be no adverse interactions between components in the sample and the reference. These could lead to chemical degradation or to a physical change in the peak positions, thus causing overlap of areas otherwise sufficiently separated for integration.

For qualitative analysis by n.m.r., a standard very frequently used is tetramethylsilane (TMS, $\delta = 0{\cdot}00$) which is a chemically inert material having a sharp, single n.m.r. peak well separated from "normal" C—H, O—H, S—H and N—H proton positions. The low boiling point of TMS (27°) militates against its use as a reference standard for quantitative studies and structurally similar and inert (but less volatile) materials have been investigated. Barcza[20] has calculated molecular weights accurate to within 3% by n.m.r. integration of peaks from the unknown and relation of this to the integration of the single peak of the reference material hexamethylcyclotrisiloxane ($\delta = 0{\cdot}15$, m.p. 64·5°). The recently introduced[21] cyclosilane-d_{18} ($\delta = -0{\cdot}33$, b.p. 208°) also seems very suitable as a non-volatile, inert standard.

Tranquillizers and analgesics have been studied by n.m.r. methods. Neville[22] reported the identification of the salts of procaine, larocaine and lidocaine. Turczan and Kram[23] have presented simple, rapid and specific quantitative analyses of meprobamate tablets and of carisoprodol and mebutamate. Meprobamate (80 mg/ml) is measured by comparing the integration of the carbamate methylene group (H_2N—CO—O—CH_2^*—) at 3·8δ with the methylene signal ($\delta = 3{\cdot}3$) of malonic acid, the standard added (80 mg/ml). Acetone (which need not be deuterated) is the solvent of choice. For seven synthetic meprobamate preparations a coefficient of variation of 1·3% was found and the authors report no interference from other active ingredients which may be present in various meprobamate formulations (*e.g.*, amphetamine salts, dexamethasone or aspirin).

The fast analysis (30 min) of hypoglycaemic agents by n.m.r.[24] compares well in accuracy with classical acidimetric and bromometric methods, without the necessity of preliminary, time-consuming separation. Glycodiazine (C), carbutamide (D) and tolbutamide (E) have easily interpreted n.m.r. spectra in trifluoroacetic acid; maleic acid ($\delta = 6{\cdot}62$) serves as the reference standard for all of these. The spectra in the 6–10δ region are given in Fig. 2 together with the coefficients of variation for five measurements on 500-mg samples. The protons used for integration are those indicated as c, d, d^1, e and e^1 and the vinylic protons of maleic acid.

It is also possible[24] to analyse a mixture of the three components by integration of the signals for the protons shown in Fig. 2 together with the aromatic methyl proton signal ($\delta = 2{\cdot}50$) of compound E. Twenty-one measurements made on synthetically prepared ternary mixtures of C, D and E with maleic acid gave coefficients of variation of 1·2% (C) and 1·7% (D and E).

A similar method[25] can be applied to the methylxanthine stimulants theophylline (F), theobromine (G) and caffeine (H) in mixtures with sodium benzoate (I) and sodium salicylate (J). *p*-t-Butylbenzoic acid is a satisfactory reference compound, with a single, very intense absorption ($\delta = 1{\cdot}40$) for the nine protons of the t-butyl group. Each component in the mixture is detectable down to 3%. N.M.R. integration has been carried out on twenty-seven synthetic mixtures (60–100 mg) of the five components and the standard (10–15 mg) in trifluoroacetic acid (0·4–0·6 ml). Coefficients of variation for the methylxanthines and the sodium salts were 1·5% (F), 2·9% (G), 3·3% (H), 1·1% (I) and 1·0% (J). Thus the n.m.r. method "brings one step nearer the goal of complete complex tablet analysis in one working process."[25]

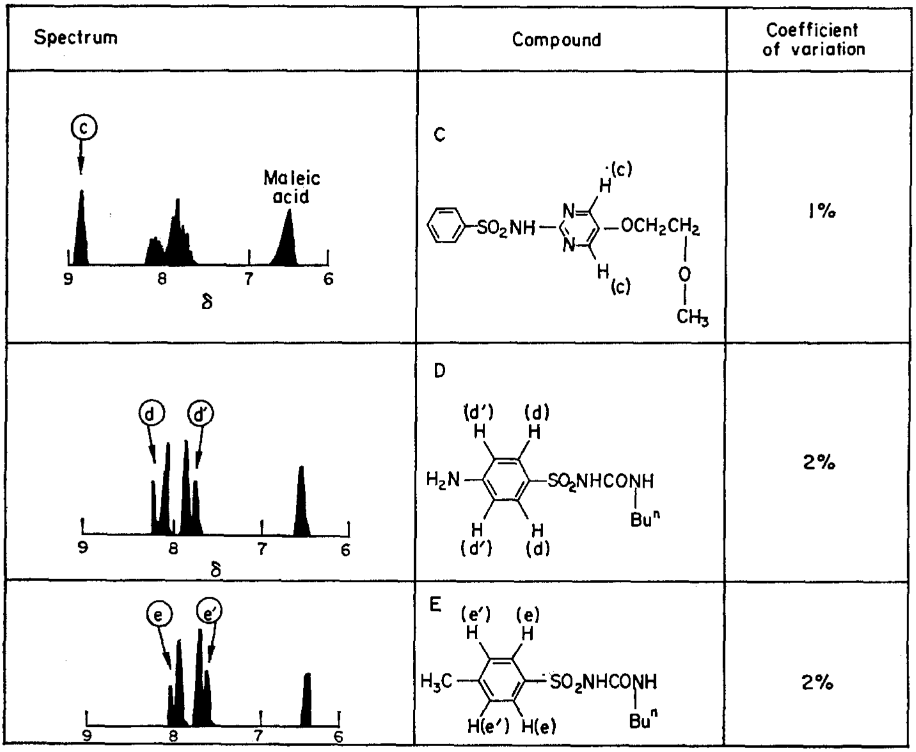


Fig. 2.—N.M.R. spectra of hypoglycaemic preparations. (Redrawn from *Z. Anal. Chem.*, 1969, **246**, 22 and printed by permission of the copyright holders.)

A contaminant sometimes found in human and veterinary preparations is dimethylsulphoxide (DMSO) which can be quantitatively assayed[26] in the range 20·0–0·05% by use of the sharp single peak in the n.m.r. spectrum. Integration of the spectrum is satisfactory for 20·0–2·0% concentration but below this level (*i.e.*, 2·0–0·05%) the integrator is insufficiently sensitive and a measurement of peak heights is made. The reference compound chosen is methanol and the method allows the use of non-deuterated water or chloroform as solvent; their n.m.r. peaks do not interfere in the region of importance. If measurements are made at room temperature (23·3°) and equal volumes of solution and methanol standard are used, the calculation of DMSO content reduces to the simple expression

$$\%\,\text{DMSO (v/v)} = 87{\cdot}83 \times \frac{\text{DMSO area at } 2{\cdot}7\delta}{\text{methanol area at } 3{\cdot}3\delta}.$$

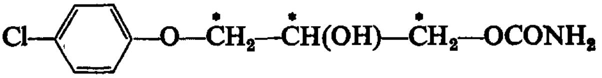
Coefficients of variation are not available for the integration method but the relative error quoted lies between 0·1 and 1·2%.

ANALYSIS BY PEAK HEIGHT OR PEAK POSITION MEASUREMENTS

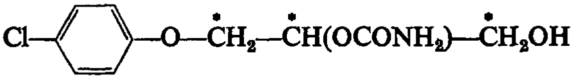
In cases where a satisfactory separation of peaks (or a sufficiently high concentration) for an accurate integration of peak areas cannot be achieved, it may be advantageous to work on the measurement of the peak heights (of readily assigned signals from each component but it should be noted that this is valid only when the line widths, and multiplicities, are identical) or of peak positions (when a rapid proton exchange process occurs between the components, causing coalescence of their signals).

During the manufacture of the muscle relaxant maolate, a second isomer is formed in low yield

Maolate



Secondary isomer



Slomp *et al.*[27] have tested n.m.r. as a quantitative analytical method for this binary mixture. Considerable simplification can be brought about by moving —OH and —NH type protons from positions in which they will interfere with the integration of the remainder of the spectrum. This is accomplished by purging the solution (10% in hexadeuteroacetone) with hydrochloric acid vapour, which causes a rapid exchange of the OH and NH protons and a shift in their δ values. Unfortunately a small, broad interfering absorption due to OH or NH protons still remains and this has a highly unfavourable effect on the integral areas. The problem has been resolved by measurement of relative peak heights at $\delta = 3{\cdot}75$ (mainly secondary isomer) and $\delta = 4{\cdot}08$ (wholly maolate) in the region where the starred protons of the two isomers absorb, the very broad NH or OH proton residue having little effect on peak height. Data from the n.m.r. spectra were processed by an IBM 1620 which computed composition and standard deviation thus saving 80% of operator calculating time. The method of assay is considered significant to a few tenths of 1% and the coefficient of variation for 15 assays is 1–2%.

Antihistamines can be analysed qualitatively by n.m.r.[28] Koch *et al.*[29] have used n.m.r. quantitatively to estimate the ratio of salt to free base in chloroform extracts of these amines from aqueous acidic solutions. Analyses were made by measuring the time-averaged n.m.r. shift of an *N*-methyl group in base/salt mixture and comparing

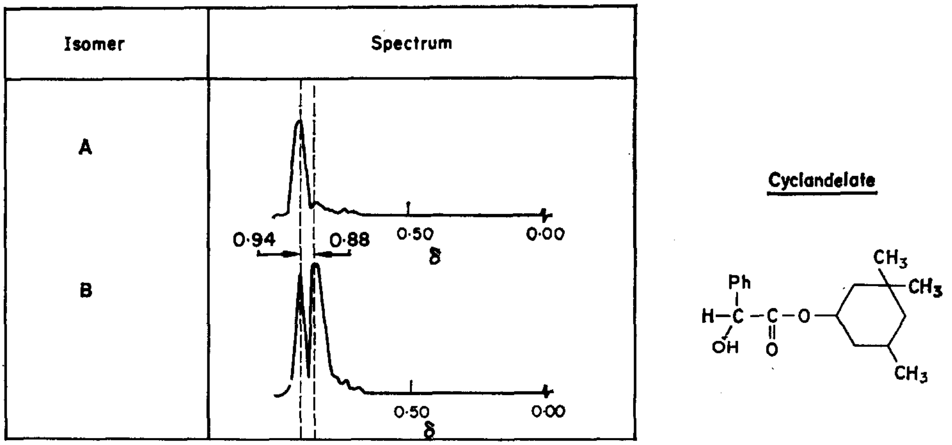


FIG. 3.—Spectra of isomers of cyclandelate. (Redrawn from *Pharm. Weekblad*, 1966, 101, 93 and printed by permission of the copyright holders.)

this with its position in the pure free amine and amine salt components alone. The maximum shifts obtained between —N—CH_3 and $\text{—}\overset{+}{\text{N}}\text{—CH}_3$ were 10–100 Hz (*e.g.*, 36·6 Hz for diphenhydramine). Linear calibration curves were constructed for known mixtures by a least-squares analysis, with a standard deviation of 0·05–0·13 Hz. The n.m.r. technique is faster and requires less material than the alternative method of ultraviolet spectrometry followed by silver nitrate titration.

The vasodilator cyclandelate consists of a mixture of 4 isomeric esters which can be separated into two diastereoisomeric pairs of optical antipodes. The ratio of these pairs determines the final properties of the commercial material and this can be measured[30] with a coefficient of variation of 3% by n.m.r. from the peak heights. The spectra of the diastereoisomeric pairs (A, m.p. 84° and B, m.p. 55·5°) differ slightly (in their methyl proton regions only). They cannot be analysed by integration but quantitative determination of the isomeric ratio is possible from the relative peak heights of the methyl signals at 0·88 and 0·94δ (Fig. 3). A calibration graph for peak heights is first established for mixtures of known composition in deuterochloroform.

As a final example in this section we refer to the problem of dimethylsulphoxide assay.[26] When the quantities of DMSO are too small for accurate integration to be carried out (<2%), peak height measurements are made. In this case the coefficient of variation (1·4–5·4%) is greater than the relative error stated for the integration method (0·1–1·2%). A simple expedient would seem to be to use a CAT for spectrum accumulation until the peaks are of sufficient amplitude for normal integration processing.

ANALYSIS WITHOUT A REFERENCE STANDARD

When information from peak areas or peak heights is not referred to a standard compound in the manner previously described, only a *relative* measure of quantities in solution is obtained.

The opium alkaloid thebaine is naturally accompanied by small quantities of cryptopine, and Rüll[31,32] has estimated the relative proportions of these by n.m.r., down to 2% of cryptopine. This small quantity is not revealed by paper chromatography, infrared or visible spectrophotometry or by electrophoresis. Rüll found that the methoxyl signals in mixtures of the two alkaloids are not always sufficiently resolved but that an accurate integration could be achieved by considering the aromatic, olefinic, methylenedioxy and methine protons in the region 4·8–7·15δ (Table II). No coefficient of variation is available but a precision of 0·5% is stated for the cryptopine content.

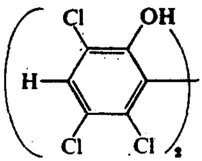
TABLE II.—OPIUM ALKALOIDS

Compound	Protons at 4·8–5·75δ	Protons at 5·75–7·15δ
Thebaine	3	2
Cryptopine	0	6

Dietrich[33] has pointed out the deficiencies of colorimetry and ultraviolet spectrophotometry in the qualitative identification and quantitation of binary mixtures of six commercial soap and detergent bacteriostats. The requirements for quantitative analysis are met by an n.m.r. method[33] based on the spectral integration of 10%

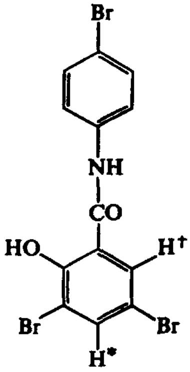
solutions of the materials (50 mg) in dimethylsulphoxide. For a mixture of hexachlorophene (K) and 3,4′,5-tribromosalicylanilide (L), the peaks integrated are those due to the methylene protons of K and the aryl protons of L (shown starred below).

Hexachlorophene (K)



*4·38δ

3,4′,5-Tribromo-salicylanilide (L)



*8·00δ
†8·27δ

All possible binary mixtures can be measured by n.m.r. integration. Coefficients of variation are not given but the authors estimate a precision and error of about 3%. It is suggested that the method can also be extended to certain three-component systems. Other detergent chemicals have been studied by n.m.r. There are reports[34,35,36] of the quantitative analysis of ionic and non-ionic detergents (*e.g.*, ethylene oxide/alkylphenol condensates). In these, n.m.r. has yielded unique information regarding olefin distributions, *ortho–para* substitution ratios and average alkyl chain lengths and molecular weights.

Very recently the n.m.r. method has been used in the analysis of pesticides. Organophosphorus materials frequently have simple spectra permitting facile qualitative analysis.[37,38] The use of an n.m.r. spectrometer operating at high magnetic fields and frequencies (100 or 220 MHz instead of 60 MHz) often simplifies complex spectra. Keith *et al.* revise some of the assignments made[38] at 60 MHz for these pesticides, on the basis of a 100 MHz study.[39] A further 26 DDT-like pesticides are the subject of a paper[40] which includes the quantitative analysis of a technical DDT preparation (a mixture of the 2,4′ and 4,4′ isomers). The benzylic protons of these are well separated for integration. Typical results showed a fourfold excess of the 4,4′ isomer.

The systemic insecticide Systox consists of two isomers (M and N—see Fig. 4), in approximately equal quantities together with a small amount (1–5%) of a dithionopyrophosphate (Q). Since they differ in toxicity a method was required which would yield the quantities of M and N (in the presence of Q). A combination of g.l.c. and n.m.r.[41] is rapid, low in material requirement (100 mg) and non-degradative.

Samples of Systox are made up as 20% solutions in carbon tetrachloride. The protons of M, N and Q fall conveniently into three regions (Fig. 4) according to the adjacent C, S or O atom and the integration is measured at 1·1–1·5, 2·3–3·1 and

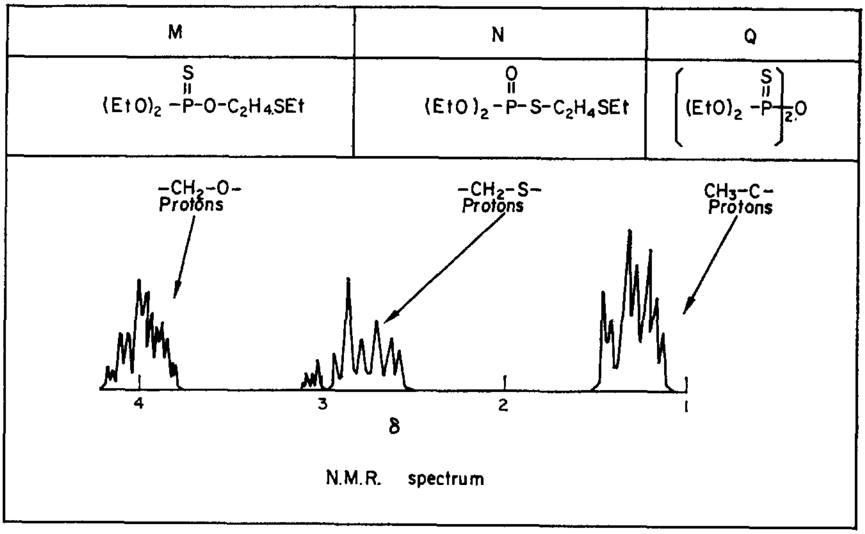


FIG. 4.—Constituents and n.m.r. spectrum of Systox. (Redrawn from *Anal. Chim. Acta*, 1968, 40, 387 and printed by permission of the copyright holders.)

3·8–4·3δ. The weight of material taken and the ratio of the integrated areas give a relative measure of the composition. An independent determination of the Q content is made by the known g.l.c. method[42] and this leads directly to the weight of isomers M and N in technical Systox. Insufficient data are given in the paper for a calculation of the coefficient of variation but the authors quote an error of 1·5%.

Muller[43] previously employed phosphorus-31 magnetic resonance for investigating the rate law for the isomerism of M and N in Systox free from component Q. Although absorption peaks in phosphorus-31 resonance are much broader than in proton resonance, chemical shifts are frequently an order of magnitude greater. For M and N the phosphorus chemical shifts are 41·8 ppm apart and thus ideally separated for integration (contrast 1–2 ppm for the —CH_2—O— and —CH_2—S— proton chemical shifts). Unfortunately, the dearth of phosphorus-31 n.m.r. equipment means that this attractive alternative nucleus is unlikely to find wide application in quantitative pharmaceutical analysis for many years.

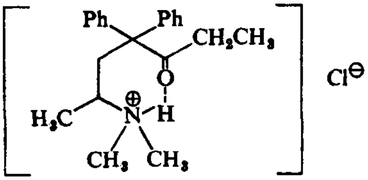
When the spectra are sufficiently resolved, the relative composition of certain stereoisomeric mixtures may be quantitatively analysed by integration of their n.m.r. spectra. Casy has found this method applicable for determining the *cis*/*trans* ratio of some piperidinols[44] and for the mixture of α- and β-propoxyphene carbinols.[45] In the latter a clear separation of peaks is noted for the secondary methyl doublets of the α- and β-isomers (16 Hz for the free bases and 22 Hz for their hydrochlorides).

ISOMERISM AND COMPLEXATION

In the final section brief mention will be made of some of the potentialities of n.m.r. for the identification and analysis of certain isomers and of interactions difficult to study by other physical methods. It is hoped that the analyst will thus be encouraged to consider how n.m.r. may be of assistance in problems beyond the range of those discussed so far.

Mention has already been made of the quantitative analysis of diastereoisomeric pairs of optical isomers by n.m.r. and peak height measurement. In very fortuitous examples, it is also possible to resolve the peaks due to the *optical isomers* themselves. Burlingame[46] found that the asymmetric carbinol $PhCH(OH)CF_3$ gives the expected doublet for the hydroxyl group proton in normal solvents but that this is split into a pair of doublets when an optically active naphthylethylamine is used as the solvent. This splitting is attributed to the (+) and (—) carbinols and was measured as 1·6 Hz at 60 MHz. A similar splitting (of 5 Hz) has also been noted[47] for propanol esters derived from R-*O*-methylmandelic acid.

Many examples can be found in which separate n.m.r. signals are obtained from *conformational isomers*. These need not necessarily be ring structures, *e.g.*, the straight-chain analgesic methadone hydrochloride shows two singlets in the n.m.r.[48] for its *N*,*N*-diethylamino group. This has been explained by hydrogen bonding between the ketonic group and the basic centre which can cause two different quasi-ring conformations.



Apart from pharmaceutical analysis the n.m.r. method has also found extensive use for the identification of *geometrical isomers* about an olefinic double bond (*e.g.*, in the carotenoids[49]) and in the quantitative measure of *keto–enol tautomerism* (as in acetylacetone[50]). To the pharmacologist n.m.r. has become an attractive tool for examination of the sites of complexation between drugs and protein materials. Jardetzky has shown that n.m.r. line-broadening[51] and signal decay time[52] parameters offer otherwise unobtainable information about the sites of bonding of sulphonamides to egg albumin and of NAD to enzymes.

There is no doubt that the types of n.m.r. approach described in this and previous sections will find increasing application in quantitative pharmaceutical practice when a single-step, rapid, accurate and non-destructive assay procedure is needed.

Acknowledgement—I wish to thank Dr. A. F. Cockerill and Dr. N. C. Franklin for their valuable advice in the preparation of this manuscript.

Zusammenfassung—Die Anwendungen von N.M.R. auf die quantitative Analyse von pharmazeutischen Formulierungen und Produkten, die für den Pharmazeuten und pharmazeutischen Analytiker von Interesse sind, werden besprochen. Besondere Aufmerksamkeit wird der Richtigkeit der Methode gewidmet; die Koefizienten der Variation, die zitiert (oder von Daten im ursprünglichen Referat kalkuliert) werden, waren möglich. Elementare N.M.R.-Kenntnisse werden vorausgesetzt.

Résumé—On passe en revue les applications de la RMN à l'analyse quantitative de formulations pharmaceutiques et de produits intéressant le pharmacien et l'analyste en pharmacie. On porte une attention particulière à l'exactitude de la méthode, les coefficients de variation étant fournis (ou calculés des données du mémoire original) lorsque cela est possible. On admet une connaissance élémentaire de la RMN.

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THERMOMETRIC TITRATION STUDIES OF MIXED LIGAND COMPLEXES OF THORIUM

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Summary—Mixed-ligand chelates consisting of two different multidentate ligands linked to a central thorium(IV) ion have been prepared in aqueous solution and their heats of formation studied thermometrically. Pyrocatechol, tiron, chromotropic acid, potassium hydrogen phthalate, 8-hydroxyquinoline-5-sulphonic acid, iminodiacetic acid, 5-sulphosalicylic acid and salicylic acid were used as the secondary ligands, while ethylenediaminetetra-acetate and 1,2-diaminocyclohexane-*N*,*N*,*N*′,*N*′-tetra-acetate were used as primary ligands. ΔH values for the overall reactions are given, and where possible, the ΔH and ΔS values for the specific secondary ligand addition were calculated. The overall stability of the mixed-ligand chelates and the enhanced stability of EDTA mixed chelates relative to the analogous DCTA chelates were found to be due to entropy rather than enthalpy effects.

MIXED-LIGAND chelates of thorium(IV) were first prepared in solution and studied potentiometrically by Carey, Bogucki and Martell.[1] These bi-ligand chelates are formed by the reaction of various bidentate secondary ligands with thorium(IV) chelates of multidentate primary ligands such as EDTA and DCTA (1,2-diaminocyclohexane-*N*,*N*,*N*′,*N*′-tetra-acetic acid). Since thorium(IV) has a co-ordination number of eight[2] and EDTA is hexadentate, the metal ion in the simple 1:1 Th-EDTA chelate has two unused co-ordinating sites available for hydrolysis, olation or polymerization reactions. Filling these two vacant sites by the addition of a bidentate secondary ligand results in the formation of a 1:1:1 mixed-ligand chelate which is found to be quite stable and more resistant towards hydrolysis than the simple EDTA chelate. Previously,[1] only free energy (log K) values were reported for such secondary ligand addition reactions. These data, though important, were of limited usefulness in explaining why mixed-ligand chelate formation occurs. The present paper provides ΔH and ΔS values for these systems in order to supply information concerning the energetics of mixed-ligand chelate formation.

Usefulness of thermometric titration techniques as an easy, rapid and accurate method to obtain enthalpy values for metal chelate systems has been amply demonstrated in the literature.[3–7] Jordan[3] has described the theory and instrumentation of thermometric titrations. Using this method Jordan and Alleman[4] have obtained heats of formation for a number of transition metal–EDTA chelates by titration of EDTA with metal ions at constant pH. Raffa *et al.*[5] determined ΔH for the dissociation of ephedrinium and pseudoephedrinium ions by titration of the ligand with sodium hydroxide or hydrochloric acid, and Freeburg[6] obtained heats of formation for bivalent metal–nitrilotriacetate chelates. Zenchelsky[7] has reviewed the field of thermometric titrations.

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EXPERIMENTAL

Reagents

Fischer "certified" thorium nitrate was used. Solutions were standardized gravimetrically by evaporation and ignition to thorium dioxide. Tiron (disodium 1,2-dihydroxybenzene-3,5-disulphonate) was obtained from the La Motte Chemical Products Co., Chestertown, Md., and was used without further purification after the establishment of its purity and standardization of an aqueous solution by potentiometric titration. "Baker Analyzed" samples of the disodium salt of EDTA were used. The 5-sulphosalicylic acid (SSA), salicylic acid (SA), chromotropic acid salt (1,8-dihydroxynaphthalene-3,6-disodium sulphonate) (CS), pyrocatechol (1,2-dihydroxybenzene) (PY), and 8-hydroxyquinoline-5-sulphonic acid (HQS) were purchased from the Eastman Kodak Co.; the iminodiacetic acid (IMDA) and DCTA were obtained through the courtesy of the Dow Chemical Co. The DCTA was converted into its disodium salt before use. The potassium hydrogen phthalate (KHP) was Fischer "certified."

Instrumentation

The pH measurements and titrations were made with a Beckman Research pH Meter Model 1019, and recorded on a Sargent multi-range precision recorder. The pH meter was calibrated with various standard buffers.

Procedure

Thermometric measurements were made by recording the temperature changes in the reaction system, contained in an adiabatic reaction vessel (Dewar flask fitted with a cork stopper), using a thermistor sensing device which served as one arm of a Wheatstone bridge. The Dewar flask contained 100 ml of a $4{\cdot}0 \times 10^{-3}M$ solution of ligand and/or metal ion, with ionic strength kept constant at 0·10 by the addition of potassium nitrate. The solution was stirred by a constant speed magnetic stirrer, and a nitrogen atmosphere was maintained over the solution in order to exclude carbon dioxide and to avoid aerial oxidation. Sodium hydroxide solution, $0{\cdot}5M$, was supplied through a finely drawn capillary at the rate of 1 ml/min by a Sargent Automatic Constant Flow Rate Buret, Model C. All titrations were carried out at a nominal temperature of 25° in a constant temperature room, after the solutions had achieved thermal equilibrium with their surroundings. A diagram of the apparatus is shown in Fig. 1. The titrant concentration was about 100 times that of the titrand, so that the reaction was complete on addition of about 1 ml, and thus the volume change and consequent heat capacity change were kept to a minimum.

Figure 2 shows a typical titration curve for a two-step titration. Portion ABC represents the temperature change of the system, due to two consecutive exothermic reactions. Portion CD represents the effect of excess of titrant, and the slope of this line is due to any non-isothermality

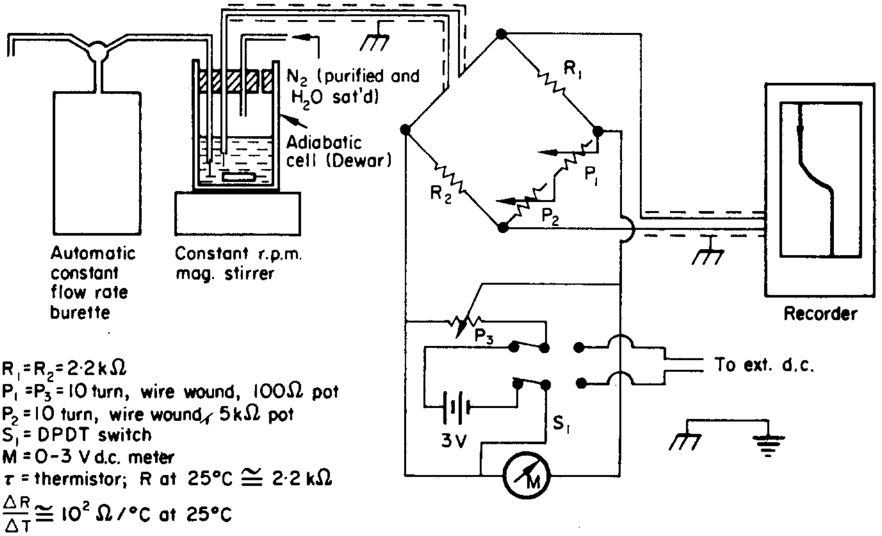

FIG. 1.—Thermometric titration apparatus.

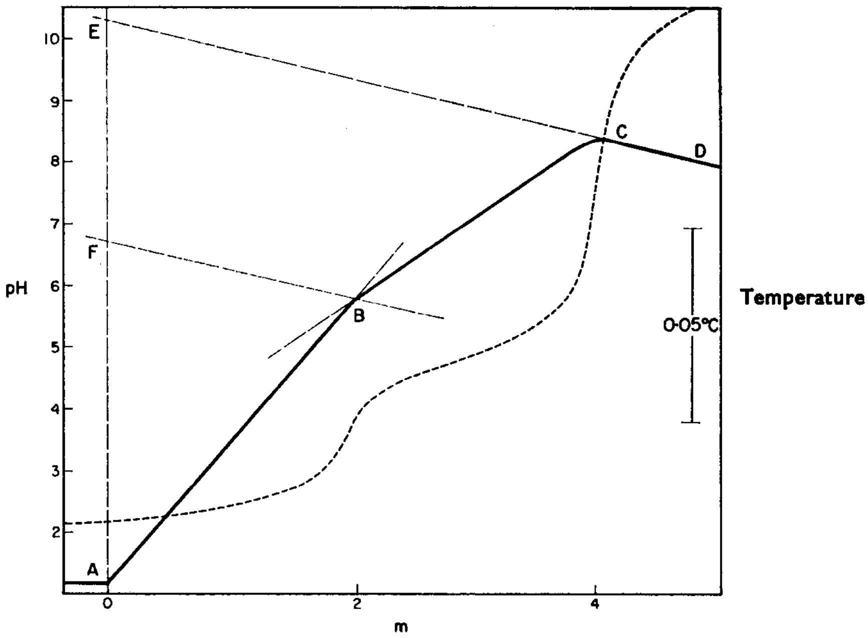

FIG. 2.—Potentiometric titration (broken line) and thermometric titration of a 1:1:1 Th(IV)-DCTA-CS mixed-ligand chelate system $4{\cdot}0 \times 10^{-3}M$ in Th(IV), DCTA, and CS. $\mu = 0{\cdot}10$, T = 25°C, and m = number of moles of base added per mole of metal ion.

between the titrant and titrand, heats of dilution, heats of stirring, heat loss from the system to the surroundings, and any other constant thermal interchange exclusive of the heat of reaction. Extrapolation of this line back to the start of the titration cancels out these effects, provided the line is straight and of relatively small slope. A line parallel to this extrapolation is drawn through the first break-point of the titration curve, B, located if necessary at the intersection of the extrapolated lines AB and BC. The two parallel extrapolations are carried back to intersect with a vertical line at the point corresponding to the start of the titration. The vertical distances EF and FA then correspond to the temperature increase resulting from the second and first titration steps, respectively, and after correction for the small volume change can be translated into enthalpy changes by means of a calibration curve for a standard system.

The thermometric apparatus was standardized by utilizing a system of known enthalpy change (titration of hydrochloric acid *vs.* sodium hydroxide), and constructing a calibration curve of corrected enthalpogram step height *vs.* joules liberated. A value of $-56{\cdot}51$ kJ/mole for the heat of neutralization of hydrochloric acid by sodium hydroxide at 25° and $\mu = 0{\cdot}10$ was obtained by extrapolating the data of Hale *et al.*[8] The enthalpogram step heights were plotted *vs.* the calculated amount of heat liberated. This procedure yielded points exactly collinear, with a slope of $3{\cdot}04_4$ mm/J The calibration curve was checked periodically and was found not to vary over a period of six months. Substitution of a $0{\cdot}1M$ potassium chloride medium for the $0{\cdot}10M$ potassium nitrate medium was found to have no effect on the calibration curve.

For the mixed-ligand chelate experiments, 100 ml of $4{\cdot}0 \times 10^{-3}M$ thorium, containing primary ligand and secondary ligand, was placed in the adiabatic titration vessel after the ionic strength had been adjusted with potassium nitrate. Time was allowed for thermal equilibrium to be attained, and the solution was titrated with a concentrated solution of sodium hydroxide.

RESULTS AND CALCULATIONS

Determination of ΔH for the deprotonation of the secondary ligands

Before the ΔH due to the actual coupling of the secondary ligand onto the simple metal–primary ligand chelate (ΔH_{MLA}) could be calculated, values of ΔH for the various deprotonation steps of the secondary ligand species ($\Delta H_{\mathrm{H}_n\mathrm{A}}$) had to be known. Since the free ligands were dissolved in aqueous solution and titrated with base, the actual ΔH_{EXP} value experimentally obtained from the thermometric titration was for the reaction:

$$(a - b)\mathrm{HA} + b\mathrm{A} + b\mathrm{H}^+ + a\mathrm{OH}^- \rightarrow a\mathrm{A} + a\mathrm{H_2O} \qquad (\Delta H_{\mathrm{EXP}}). \tag{1}$$

Consequently, in order to obtain the desired ΔH for the simple deprotonation reaction:

$$\mathrm{HA} \rightarrow \mathrm{A} + \mathrm{H}^+ \qquad (\Delta H_{\mathrm{H}_n\mathrm{A}}) \tag{2}$$

the ΔH_{EXP} value had to be adjusted to account for the neutralization of the released hydrogen ions by the hydroxide, and also in some cases for the partial dissociation of the free ligand before the start of the titration. Hale *et al.*'s[8] value of −56·51 kJ/mole was used for the heat of neutralization. Log K values which had been potentiometrically determined[1] at 25° and $\mu = 0{\cdot}10$ were used to calculate the degree of dissociation of the free ligand.

Table I shows the thermodynamic values obtained for the free secondary ligands used in the present investigation. The inflection points in the thermometric curves are noted and the ΔH_{EXP} and $\Delta H_{\mathrm{H}_n\mathrm{A}}$ values are listed for the stepwise deprotonation of the individual ligands. In the case of some ligands (Tiron, CS, PY, and SSA), no $\Delta H_{\mathrm{H}_n\mathrm{A}}$ values are given for the loss of the second proton, since this dissociation occurs only to a small extent or not at all in aqueous solution titrations. The ΔG values for the same deprotonation reactions were calculated by using the appropriate ligand log K values and the relationship: $\Delta G = -RT \ln K$. $\Delta S_{\mathrm{H}_n\mathrm{A}}$ values were obtained from the $\Delta H_{\mathrm{H}_n\mathrm{A}}$ and the corresponding $\Delta G_{\mathrm{H}_n\mathrm{A}}$ values through use of the standard relationship $\Delta G = \Delta H - T\Delta S$.

Comparison of potentiometric and thermometric titration curves for the same mixed-ligand chelate systems

The potentiometric as well as the thermometric titration curves for the 1:1:1 Th(IV)–DCTA–CS mixed-ligand chelate system [$4{\cdot}0 \times 10^{-3}M$ in thorium(IV)] are shown in Fig. 2. An explanation for the potentiometric curve follows. The 1:1 Th–DCTA chelate is completely formed at the start of the titration, and the buffer region up to $m = 2{\cdot}00$ represents the titration of the two hydrogen ions freed from the chelated disodium salt of DCTA. The second buffer region from $m = 2$ to $m = 4$ is due to the attachment of the two hydroxyl groups on the chromotropic salt onto the 1:1 chelate to form the 1:1:1 mixed-ligand chelate. This buffer region terminates in a sharp inflection at $m = 4$ indicating that complete formation of the mixed-ligand chelate has occurred at this point.

The thermometric curve for the same system may be similarly explained. Thus, the highly exothermic constant slope region from $m = 0$ to $m = 2$ is due to the heat liberated by the neutralization of the two hydrogen ions freed from the 1:1 Th–DCTA chelate. At $m = 2$ the slope changes and we obtain another, slightly less, exothermic constant slope region from $m = 2$ to $m = 4$ due to the formation of the 1:1:1 mixed-ligand chelate. The overall heat change observed in this region is due to three factors: the heat of formation of the mixed-ligand chelate, the heat of neutralization of the two hydrogen ions freed from the chromotropic salt, and the heat of deprotonation when these two hydrogen ions are removed from the chromotropic salt. At

TABLE I. —THERMODYNAMIC DATA FOR THE DEPROTONATION OF FREE SECONDARY LIGANDS ACCORDING TO THE REACTION $HA \rightarrow A + H^+$ AT 25°C AND $\mu = 0{\cdot}1$ (KNO_3)

Ligand	Values* of inflection points	Range* over which H was calculated	pK†	ΔH_{EXP} kJ/mole	ΔH_{H_nA} kJ/mole	ΔG_{H_nA} kJ/mole	ΔS_{H_nA} J/mole.K
Na_2EDTA	1(w) 2(g)	0–1	6·16	−41·7	+18·2 (+18·2)§	+35·2	−57 (−56)§
		1–2	10·26	−33·1	+23·4 (+23·7)§	+58·6	−118 (−116)§
Na_2DCTA	1(w) 2(vw)	0–1	6·16	−46·3	+10·3 (+8·6)§	+35·2	−83 (−88)§
		1–2¶	12·35	−18·6	+37·9 (+27·8)§	+70·6	−109 (−142)
Tiron (H_2A)	1(g)	0–1	7·61	−35·6	+21·0	+43·5	−75
CS (H_2A)	1(g)	0–1	5·32	−43·4	+13·6	+30·4	−57
PY (H_2A)	1(g)	0–1	9·19	−31·4	+25·1	+52·5	−92
HQS (H_2A)	2(g)	0–2	3·97	−77·5	+38·5 (+35·0)‡	+70·9	−108 (−118)‡
SSA (H_3A)	2(g)	0–2	2·62	−95·5	+25·5	+15·0	+35
SA	1(g) 2(w)	0–1	2·89	−54·3	+3·8	+16·5	−43
(H_2A)		1–2	13·6	+1·3	+55·2	+77·8	−75
IMDA	1(g) 2(g)	0–1	2·52	−53·6	+6·8	+14·4	−26
(H_2A)		1–2	9·30	−23·3	+33·1	+53·1	−67
KHP (HA)	1(g)	0–1	5·00	−56·1	+0·3	+28·6	−95

* Moles of base added per mole of ligand ($=a$).

† $\mu = 0{\cdot}10$ (KNO_3), $T = 25$°C, reference 1.

§ $\mu = 0{\cdot}10$ (KNO_3), $T = 25{\cdot}3$°C, reference 9.

‡ $\mu = 0{\cdot}10$, $T = 25{\cdot}0$°C, $\Delta H_{H_2A} = +18{\cdot}3$ kJ/mole, $\Delta H_{HA} = +16{\cdot}7$ kJ/mole, $\Delta S_{H_2A} = -13$ J/mole.K, $\Delta S_{HA} = -105$ J/mole.K, reference 10.

¶ Enthalpogram is rounded between $a = 1$ and $a = 2$. At $a = 2$ there is no well defined end-point, and the curved region continues.

g—good inflection
w—weak inflection
vw—very weak inflection

$m = 4$, the curve reverts to that for addition of excess of reagent. In some instances there is a slight delay or curvature at this point, indicating minor hydrolysis.

The other mixed ligand chelate systems (not shown) in the present study exhibit the same correspondence as seen in Fig. 2, between the thermometric and potentiometric curves. The 1:1:1 Th–EDTA-secondary ligand chelate systems exhibit potentiometric curves having inflections at $m = 2$ and $m = 4$ for PY, CS Tiron and HQS; $m = 3$ and $m = 4$ for SA and IMDA: $m = 4$ and $m = 5$ for SSA; and $m = 2$ and $m = 3$ for KHP. Mixed-ligand chelate formation occurs in the regions between these inflection points.

Determination of ΔH for the formation of the mixed ligand chelates

The ΔH due to the actual coupling of the secondary ligand onto the simple metal–primary ligand chelate according to the reaction:

$$ML + A \rightarrow MLA \qquad (\Delta H_{MLA}). \tag{3}$$

was sought. The actual reaction, however, has a heat output which is due, as explained earlier, to three separate factors, and is represented by the equation:

$$\mathrm{ML} + \mathrm{H}_n\mathrm{A} + n\mathrm{OH}^- \rightarrow \mathrm{MLA} + n\mathrm{H_2O} \qquad (\Delta H_{\mathrm{EXP'}}). \tag{4}$$

Thus the $\Delta H_{\mathrm{EXP'}}$ includes: (*a*) the heat of neutralization; (*b*) the heat of deprotonation; and (*c*) the heat of the actual mixed-ligand complex formation, ΔH_{MLA}. The heat of neutralization (*a*) is easily accounted for, but as stated above, not all the $\Delta H_{\mathrm{H}_n\mathrm{A}}$ values were obtainable. Thus in some cases only a value for the combination of (*b*) and (*c*) ($\Delta H_{\mathrm{MLA+H}_n\mathrm{A}}$) could be obtained. This value is the result of the reaction:

$$\mathrm{ML} + \mathrm{H}_n\mathrm{A} \rightarrow \mathrm{MLA} + n\mathrm{H}^+ \qquad (\Delta H_{\mathrm{MLA+H}_n\mathrm{A}}). \tag{5}$$

In the cases for which the $\Delta H_{\mathrm{H}_n\mathrm{A}}$ values could be obtained, ΔH_{MLA} values were calculated.

The thermodynamic results obtained from the thermometric titrations of the various mixed-ligand chelate systems are presented in Table II. The *m*-values between which mixed-ligand chelate formation occurs, and from which the thermometric data were taken, is noted for each system. The $\Delta H_{\mathrm{EXP'}}$ and $\Delta H_{\mathrm{MLA+H}_n\mathrm{A}}$ values for each secondary ligand as well as the ΔH_{MLA} values are listed. ΔG_{MLA} was calculated from the log K values reported previously[1] for mixed ligand chelates. ΔS_{MLA} for mixed ligand chelate formation was obtained from ΔH_{MLA} and ΔG_{MLA} values.

DISCUSSION

Comparison of literature values and thermometric values for secondary ligand deprotonation

Calorimetrically determined values of $\Delta H_{\mathrm{H}_n\mathrm{A}}$ and ΔS for the deprotonation of the free ligands EDTA and DCTA have been reported by Anderegg,[9] while those for HQS have been reported by Gutnikov and Freiser.[10] These values compare favourably with those obtained thermometrically (see Table I). Agreement is good for all the ligands except disodium DCTA. This discrepancy is due to a kinetically slow step, indicated by a curved region on the enthalpogram. Adjustment of the thermometric value to compensate for the slow step would yield a value close to that reported by Anderegg. Thus, to apply thermometric titrations successfully to the determination of such values, one must carefully consider the speed of reaction *vs.* titrant addition rates, heat leak rates, and subsequent reactions.

The agreement between the literature values and thermometric values for $\Delta H_{\mathrm{H}_n\mathrm{A}}$ shown in Table I demonstrates the validity of the thermometric method to obtain thermodynamic data of this type.

The energetics of mixed-ligand chelate formation

Table II reveals that the favourable ΔG for the formation of mixed ligand chelates results principally from favourable positive ΔS_{MLA} values. ΔH_{MLA} is seen to vary from favourable to unfavourable with apparently little effect upon ΔG. The large entropy value is primarily due to the release of hydrated water molecules from both

TABLE II.—THERMODYNAMIC DATA FOR THE FORMATION OF MIXED LIGAND CHELATES FROM THE ADDITION OF ONE MOLE OF SECONDARY LIGAND (H_nA) TO THE 1:1 PRIMARY LIGAND CHELATE AT 25°C AND $\mu = 0{\cdot}10$ (KNO_3)

Secondary ligand	*m* values between which mixed ligand complex occurs	Primary ligand EDTA					Primary ligand DCTA				
		ΔH_{EXP} kJ/mole	ΔH_{MLA+H_nA} kJ/mole	ΔH_{MLA} kJ/mole	ΔG_{MLA} kJ/mole	ΔS_{MLA} J/mole.K	ΔH_{EXP} kJ/mole	ΔH_{MLA+H_nA} kJ/mole	ΔH_{MLA} kJ/mole	ΔG_{MLA} kJ/mole	ΔS_{MLA} J/mole.K
CS	2–4	−68·2	44·8	—	−78·1	—	−65·2	47·8	—	−75·1	—
Tiron	2–4	−97·2	15·8	—	−76·6	—	−84·6	28·4	—	−72·4	—
PY	2–4	−61·8	51·1	—	−73·7	—	−59·5	53·5	—	−70·1	—
SA	3–4	−20·7	35·8	−19·4	−61·1	140	−20·5	36·0	—	—	—
SSA	4–5	−24·8	31·7	—	−53·1	—	−21·5	35·0	—	−50·7	—
HQS	2–4	−81·2	31·8	−6·8	−39·9	111	−93·0	20·0	−18·5	−38·3	66
IMDA	3–4	−13·4	43·2	+10·0	−38·3	162	−19·9	36·6	+3·5	−34·9	129
KHP	2–3	−32·7	23·8	+23·5	−17·7	138	−35·5	21·0	+20·7	−15·0	120

m = moles of base added per mole of metal ion present.
* At 25·3°C, $\mu = 0{\cdot}10$ (KNO_3), reference 11.

the free ligand and the metal ion in the simple 1:1 chelate upon mixed-ligand chelate formation.

The inability to obtain explicit ΔH_{MLA} values for certain secondary ligand systems does not prevent a meaningful comparison between the ΔH_{MLA+H_nA} values of the EDTA and DCTA mixed ligand chelates of the same secondary ligands. This is so because the heat of deprotonation for a given secondary ligand is constant during mixed-ligand formation, even though in certain cases it may be indeterminable. Thus, for any given secondary ligand the effective heats of mixed-ligand addition for the EDTA system may be compared with those for the DCTA system.

The EDTA mixed-ligand chelates were previously[1] found to be more stable than the analogous DCTA mixed-ligand chelates, as is evidenced in the comparison of the ΔG_{MLA} values for the various secondary ligand additions. The buffer region in which the mixed-ligand chelate is formed occurs at a higher pH with DCTA than with EDTA.

This enhanced stability of the EDTA system cannot be accounted for by enthalpy effects, since the ΔH values for the two systems can be seen to show no definite trend in relation to each other; the ΔH_{MLA+H_nA} values involving the secondary ligands CS, PY, Tiron and SSA are more positive for the DCTA system, while the opposite is true for the ligands HQS, IMDA and KHP. Consequently, the greater stability of the EDTA mixed-ligand chelates must depend on entropy effects, which is evidenced by the more favourable positive ΔS_{MLA} values. This effect is probably due to less saturation of the co-ordinating tendencies (less effective shielding of the charge) of the thorium(IV) ion in the simple 1:1 Th–EDTA chelate. This leads to greater hydration and subsequent release of a greater number of water molecules upon mixed-ligand chelate formation.

Zusammenfassung—Chelate mit verschiedenen Liganden, die aus zwei verschiedenen, an ein Thorium(IV)-Zentralion gebundenen mehrzähnigen Liganden bestehen, wurden in wäßriger Lösung hergestellt und ihre Bildungswärmen thermometrisch untersucht. Brenzcatechin, Tiron, Chromotropsäure, Kaliumhydrogenphthalat, 8-Hydroxychinolin-5-sulfonsäure, Iminoessigsäure, 5-Sulfosalicylsäure und Salicylsäure wurden als Zweitliganden, Äthylendiamintetraacetat und 1,2-Diaminocyclohexan-*N*, *N*, *N'*, *N'*-tetraacetat als Erstliganden eingesetzt. ΔH-Werte für die Bruttoreaktionen werden angegeben und, soweit möglich, ΔH- und ΔS-Werte speziell für den Eintritt des Zweitliganden berechnet. Die Bruttostabilität der gemischten Chelate und die erhöhte Stabilität der gemischten Chelate mit EDTA, verglichen mit den analogen DCTA-Chelaten, beruht offenbar eher auf Entropie- als auf Enthalpieeffekten.

Résumé—On a préparé en solution aqueuse des chélates de ligands mixtes consistant en deux ligands différents à multicoordination liés à un ion thorium (IV) central, et l'on a étudié thermométriquement leurs chaleurs de formation. Les pyrocatéchol, tiron, acide chromotropique, phtalate acide de potassium, acide 8-hydroxquinoléine 5-sulfonique, acide iminoacétique, acide 5-sulfosalicylique et acide salicylique ont été utilisés comme ligands secondaires, tandis que l'éthylènediaminetétracétate et le 1,2-diaminocyclohexane *N*, *N*, *N'*, *N'*-tétracétate ont été utilisés comme ligands primaires. On donne les valeurs ΔH pour les réactions globales et, lorsque c'était possible, les valeurs ΔH et ΔS pour l'addition spécifique du ligand secondaire ont été calculées. On a trouvé que la stabilité d'ensemble des chélates de ligands mixtes et la stabilité accrue des chélates mixtes d'EDTA par rapport aux chélates analogues de DCTA sont dues à des influences d'entropie plutôt que d'enthalpie.

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VERWENDUNG VON ALKYLPHOSPHORSÄUREN IN DER ANALYTISCHEN CHEMIE

EXTRAKTION VON GALLIUM(III) AUS LÖSUNGEN SAUERSTOFFHALTIGER SÄUREN MIT LÖSUNGSMITTELGEMISCHEN

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Zusammenfassung—Gallium(III) kann durch kombination zweier Extraktionsmittel (M2EHPS mit TBP, oder M2EHPS mit Methylhexylketon) aus schwefel- oder bromwasserstoffsauren Lösungen von Aluminium abgetrennt werden, wobei Gallium in der organischen Phase verbleibt. Alle andere extrahierten Metallen werden mittels selektiver Waschlösungen abgetrennt.

Gallium(III) kann durch Extraktion mit Pyroalkylphosphorsäuren (PAPS) von den meisten Begleitstoffen außer Aluminium abgetrennt werden.[1] Zur Galliumbestimmung wird dann die organische Phase mit Oxalsäure extrahiert und Gallium mit Malachitgrün photometrisch bestimmt,[2] wobei Aluminium nicht stört. Bei der komplexometrischen Galliumbestimmung jedoch müssen Aluminium und Oxalsäure abwesend sein. In der folgenden Arbeit wird daher ein Verfahren zur gleichzeitigen Abtrennung des Galliums(III) von Aluminium(III) und Begleitelementen beschrieben. Als Extraktionsmittel dient Mono-2-äthylhexylphosphorsäure (M2EHPS)* sowie ein Gemisch von M2EHPS mit verschiedenen Antagonisten.

Galliumbestimmungen im Milligrammbereich wurden komplexometrisch mit dem Indikator Xylenolorange[4] und im Mikrogrammbereich photometrisch mit Malachitgrün[2] ausgeführt.

Abtrennung von Ga(III) *und* Al(III) *mit Monoalkylphosphorsäure*

Es wurde (Abb. 1–3) die Abtrennung des Ga mit M2EHPS aus mineralsauren Lösungen verschiedener Konzentration untersucht. Es zeigt sich, daß durch Änderung der Säurekonzentration in der wäßrigen Phase eine getrennte Extraktion von Ga(III) und Al(III) mittels M2EHPS unmöglich ist. Auch das Zusammenwirken von Trialkylphosphaten S, wobei S auch Alkohole oder Ketone sein können und Säuren (HX = Schwefel- oder Salpetersäure) im System Me(III)–M2EHPS–S–HX bewirkt keinen Trenneffekt (Abb. 4).

Jedoch läßt sich Gallium(III) von Alkoholen, Trialkylphosphaten und Ketonen aus Lösungen verschiedener Halogenwasserstoffkonzentration (Abb. 5) sehr gut extrahieren. In diesem System liegen die Trennfaktoren

$$\beta_{Ga/Al} = D_{Ga}/D_{Al}$$

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* Die extraktive Galliumabtrennung mit Dialkylphosphorsäuren ist wegen zu niedriger Verteilungskoeffizienten unmöglich.[3] Monoalkylphosphorsäuren sind nach einem bereits beschriebenen Verfahren zugänglich.[5] Zur Herstellung von Galliumlösungen wurde Gallium hoher Reinheit in den entsprechenden Säuren aufgelöst.

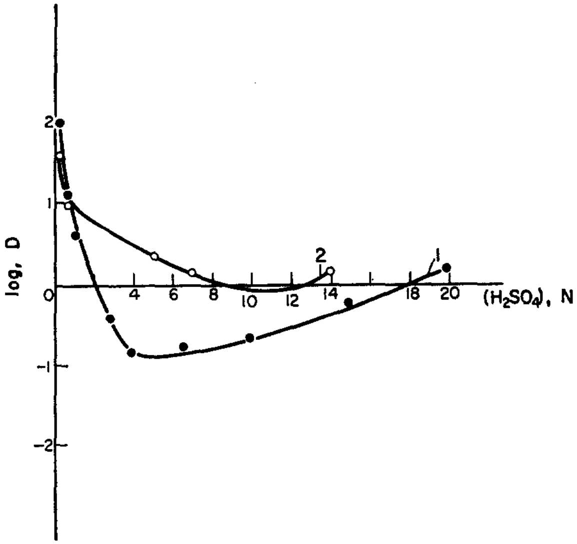

Abb. 1.—Verteilungskoeffizienten von Ga(III) und Al(III) in Abhängigkeit von der H_2SO_4-Konzentration in der wäßrigen Phase.
Organische Phase: 1,5*N* M2EHPS in Heptan
Kurve 1: Ga, 1,18 mg/ml
Kurve 2: Al, 4 mg/ml.

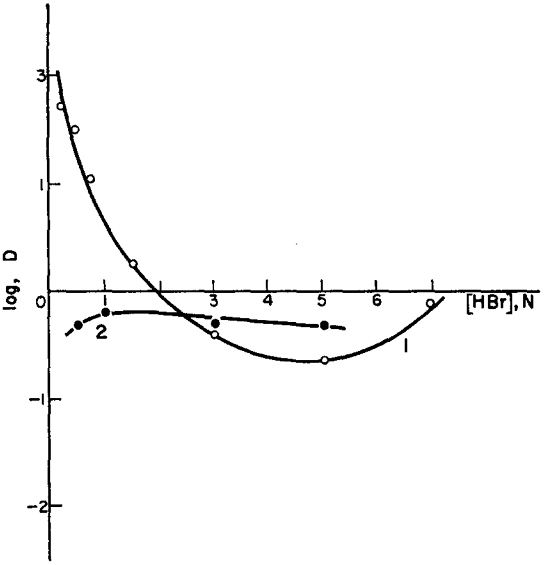

Abb. 2.—Verteilungskoeffizienten von Ga(III) und Al(III) in Abhängigkeit von der HBr-Konzentration in der wäßrigen Phase.
Organische Phase: 1,5*N* M2EHPS in Heptan
Kurve 1: Ga, 1 mg/ml
Kurve 2: Al, 3 mg/ml.

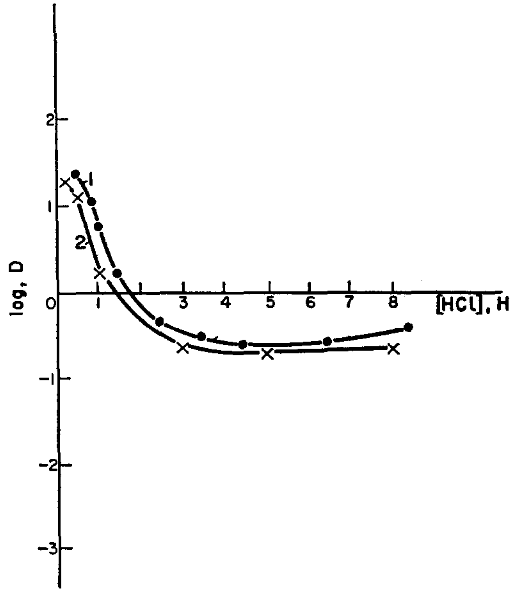

ABB. 3.—Verteilungskoeffizienten von Ga(III) und Al(III) in Abhängigkeit von der HCl-Konzentration in der wäßrigen Phase.
Organische Phase: 1,5*N* M2EHPS in Heptan
Kurve 1: Ga, 1 mg/ml
Kurve 2: Al, 3 mg/ml.

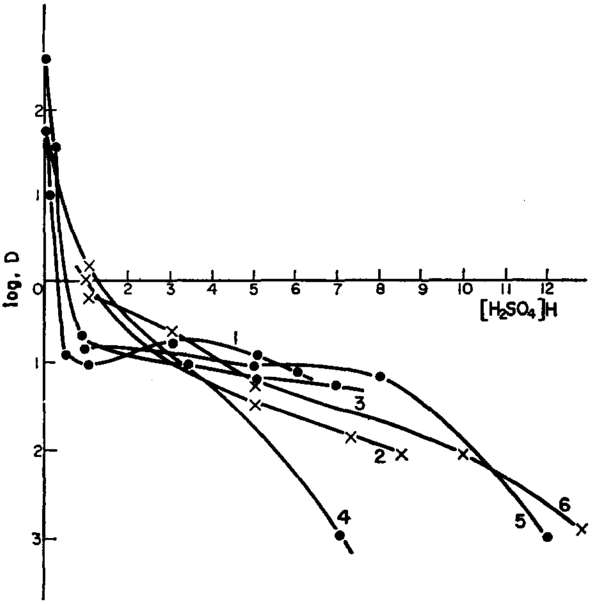

ABB. 4.—Verteilungskoeffizienten von Ga(III) und Al(III) in Abhängigkeit von der H_2SO_4-Konzentration in der wäßrigen Phase.
$c_{Ga} = 1{,}77$ mg/ml; $c_{Al} = 2{,}1$ mg/ml
I. Org. Phase: M2EHPS (0,75*N*) und TBP (1,88*N*) in Heptan
Kurve 1: Ga; Kurve 2: Al
II. Org. Phase: M2EHPS (0,75*N*) und 2EHA (3*N*) in Heptan
Kurve 3: Ga; Kurve 4: Al
III. Org. Phase: M2EHPS (0,75*N*) und MHK (3,2*N*) in Heptan
Kurve 5: Ga; Kurve 6: Al.

(D = entsprechende Verteilungskoeffizienten) bei etwa 10^2. Im System Me(III)–M2EHPS–S–HX, wobei HX = HCl oder HBr, ist die Komponente S von großer Wichtigkeit.

Untersucht wurden die Systeme

Ga(III)–M2EHPS–TBP–HBr (TBP = Tributylphosphat)
Ga(III)–M2EHPS–2EHA–Hbr (2EHA = 2-Ethylhexylphosphat)
Ga(III)–M2EHPS–MHK–HBr (MHK = Methylhexylketon)

als Funktion der Bromwasserstoffsäurekonzentration (Abb. 6). Es zeigt sich, daß in diesen Systemen M2EHPS die Rolle eines Antisynergentenmittels spielt. M2EHPS allein vermag Ga(III) nur in geringem Umfang aus HBr-Lösungen zu extrahieren. Durch Erhöhung der Acidität (Zugabe von Schwefelsäure) jedoch wird D_{Ga} merklich größer (Abb. 7), während Al(III) unter diesen Bedingungen kaum extrahiert wird.

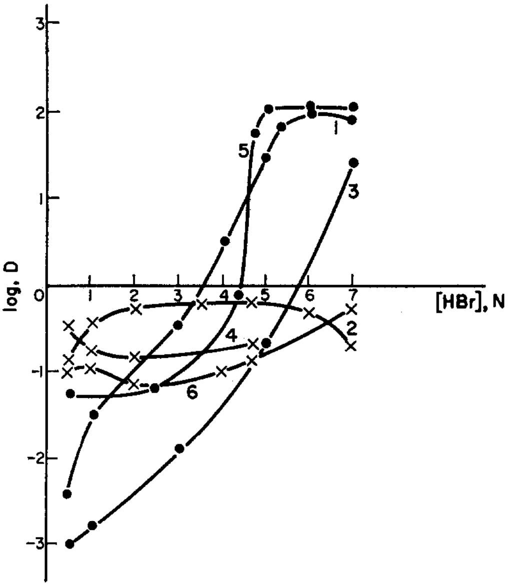

ABB. 5.—Verteilungskoeffizienten von Ga(III) und Al(III) in Abhängigkeit von der HBr-Konzentration in der wäßrigen Phase.
$c_{Ga} = 1{,}77$ mg/ml; $c_{Al} = 2{,}1$ mg/ml
I. Org. Phase: TBP (3,76*N*) in Heptan
Kurve 1: Ga; Kurve 2: Al
II. Org. Phase: 2EHA (6*N*) in Heptan
Kurve 3: Ga; Kurve 4: Al
III. Org. Phase: MHK (6,4*N*) in Heptan
Kurve 5: Ga; Kurve 6: Al.

Abbildung 8 zeigt den gemeinsamen Einfluß von M2EHPS und TBP auf das Extraktionsverhalten von Ga(III) und Al(III). Die Verteilungskoeffizienten ergeben für dieses System Trennfaktoren von 10^3 bis 10^5.

Bei Verwendung ein Semisch von TBP + M2EHPS wird bereits durch ein- bis zweimalige Extraktion eine Ga/Al-Trennung erreicht. Aber wie aus Tabelle I zu ersehen ist, hat die Aluminium-konzentration in der wäßrigen Phase einen Einfluß auf der Verteilungskoeffizient D_{Ga}. Diese Störung kann durch Einstellung der zu

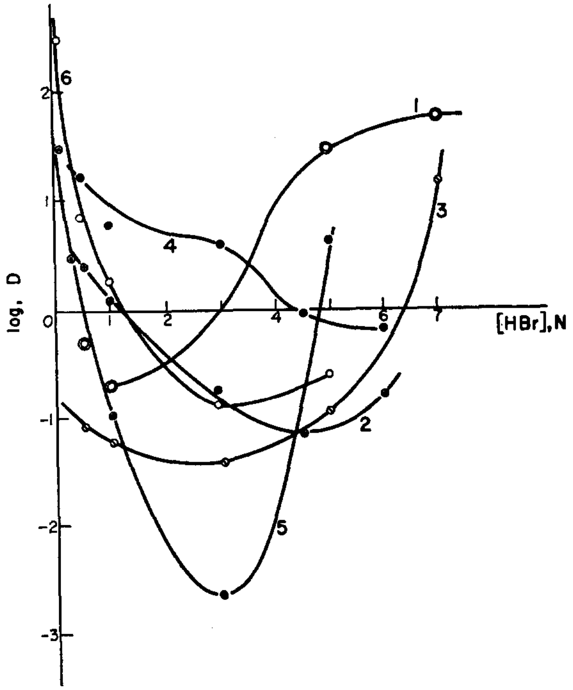

ABB. 6.—Verteilungskoeffizienten von Ga(III) und Al(III) in Abhängigkeit von der HBr-Konzentration in der wäßrigen Phase.
$c_{Ga} = 1{,}77$ mg/ml; $c_{Al} = 2{,}1$ mg/ml
I. Org. Phase: M2EHPS (0,75*N*) und TBP (1,88*N*) in Heptan
Kurve 1: Ga; Kurve 2: Al
II. Org. Phase: M2EHPS (0,75*N*) und 2EHA (3*N*) in Heptan
Kurve 3: Ga; Kurve 4: Al
III. Org. Phase: M2EHPS (0,75*N*) und MHK (3,2*N*) in Heptan.
Kurve 5: Ga; Kurve 6: Al.

extrahierenden Lösung auf pH 4–5 behoben werden, wobei der pH so gewählt wird, daß die Ausfällung von Hydroxiden unterbleibt.

DISKUSSION

Im folgenden wird ein allgemeines Verfahren zur Abtrennung von Ga(III) aus Lösungen, die Beimengungen an Kupfer, Zink, Cadmium, Kobalt, Eisen u.a. enthalten, beschrieben.

Fe(III) wird zunächst zu Fe(II) reduziert und verbleibt bei der Extraktion mit M2EHPS in der wäßrigen Phase. Dabei geht Tl(III) in Tl(I) auch über. Die Begleitelemente, die bei der Extraktion mit M2EHPS in geringem Umfang in der organischen Phase nachzuweisen sind (Tabelle III), werden durch Waschen mit konzentrierter Perchlorsäure entfernt.

Nach Abtrennung dieser schlecht extrahierbaren Elemente mit Perchlorsäure läßt sich Aluminium durch Zugabe des Schwefelsäure-Bromwasserstoffsäure-Gemisches nur schwer wieder aus der organischen Phase extrahieren. Vermutlich verbleibt Al(III) in Form von gemischten Ga–Al-Komplexen in der organischen Phase. Für diese Annahme spricht die ungestörte Al(III)-Abtrennung aus galliumfreien Lösungen.

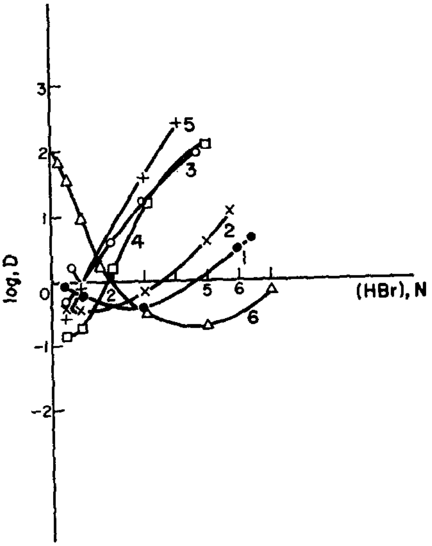

ABB. 7.—Verteilungskoeffizient von Ga(III) in Abhängigkeit von der H_2SO_4–HBr-Konzentration in der wäßrigen Phase.
Organische Phase: M2EHPS bzw. TBP in Heptan
$c_{Ga} = 1{,}77$ mg/ml; $c_{M2EHPS} = 1{,}5N$, $c_{TBP} = 3{,}76N$
Kurve 1: M2EHPS, $3N\ H_2SO_4$ Kurve 4: TBP, $3N\ H_2SO_4$
Kurve 2: M2EHPS, $7N\ H_2SO_4$ Kurve 5: TBP, $7N\ H_2SO_4$
Kurve 3: M2EHPS, $12N\ H_2SO_4$ Kurve 6: M2EHPS

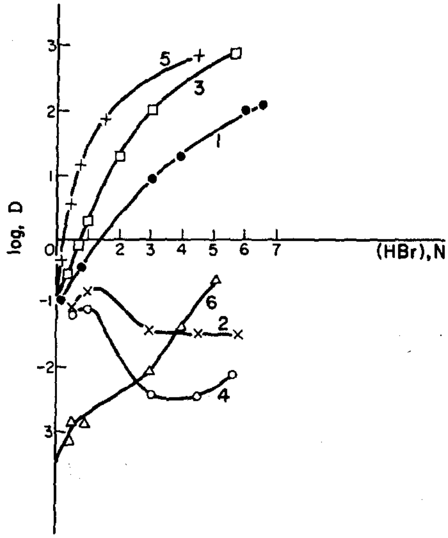

ABB. 8.—Verteilungskoeffizienten von Ga(III) und Al(III) in Abhängigkeit von der H_2SO_4–HBr-Konzentration in der wäßrigen Phase.
Organische Phase: M2EHPS + TBP in Heptan.
$c_{Ga} = 1{,}77$ mg/ml, $c_{Al} = 2{,}1$ mg/ml, $c_{M2EHPS} = 0{,}75N$ und $c_{TBP} = 1{,}88N$
Kurve 1: Ga, $3N\ H_2SO_4$ Kurve 4: Al, $7N\ H_2SO_4$
Kurve 2: Al, $3N\ H_2SO_4$ Kurve 5: Ga, $12N\ H_2SO_4$
Kurve 3: Ga, $7N\ H_2SO_4$ Kurve 6: Al, $12N\ H_2SO_4$

Tabelle I.—Einfluss des Aluminiums auf der Extraktion von Gallium mit TBP und M2EHPS

[Ga] In der wäßrigen Phase, *mg/l.*	[Al] *g/l.*	[Ga] in der wäßrigen Phase nach einer Extraktion, *mg/l.*	D_{Ga}
925	0	6	153
925	6	73	11,7
925	12	145	5,38
926	18	162	4,71
927	24	166	4,58
93	0	2	45,5
93	6	13	6,15
94	12	28,4	2,29
94	18	38,4	1,45
95	24	43	1,20

Tabelle II.—Trennung des Galliums von Aluminium durch Extraktion mit TBP und M2EHPS

[Al], *g/l.*	[Ga], *g/l.*	Al:Ga	Ga, gefunden im Reextrakt, *g/l.*	Al, gefunden bei Wäschen, *g/l.*
24	1,42	17	1,44	
24	0,142	170	0,142	
25,6	1,42	18	1,45	
31,4	0,142	220	0,136	
25,6	0,07	370	0,08	
0,19	6,8	0,03	6,58	0,178
0,98	5,68	0,2	5,39	0,102
2	6,8	0,3	6,71	2,11

$V_0:V_B = 1{\cdot}5:1$, [M2EHPS] = 0,75*N*, [TPB] =1,88*N*.

In Anwesenheit von Ga(III) werden 45–65% Al ausgewaschen. Yedoch, wenn man die organische Phase vorläufig mit Wasser auswascht, wird das al leicht durch Zugalee des Schwefelsäure = Bromwasser — stoffsäure = Gemisches reextrahiert.

Zusammen mit Gallium(III) befinden sich In, Tl(III), Sb(III), Bi, Sn(II), Sn(IV) U, Th, Zr, Hf, Sc, Seltene Erden, Ti u.a. in dem M2EHPS-Extrakt. Davon sind Ti, Zr, Hf, Sc nur schwer wieder aus der organischen Phase zu entfernen. Liegen in der galliumhaltigen Lösung In(III), Sb(III), Sn(II) und Bi(III) vor, dann können sie, wie Abb. 9 zeigt, durch zusätzliche Extraktion mit 2-Äthylhexanol und Salzsäure aus der organischen Phase abgetrennt werden.[6]

Isolierung von Ga(III) *aus Lösungen vorgegebener Zusammensetzung*

Der in Abb. 9 gezeigte Trennungsgang wurde an einer Lösung folgender Zusammensetzung geprüft:

Element	Konzentration (*g/l.*)
Ni	2,84
Hg	1,42

usw.

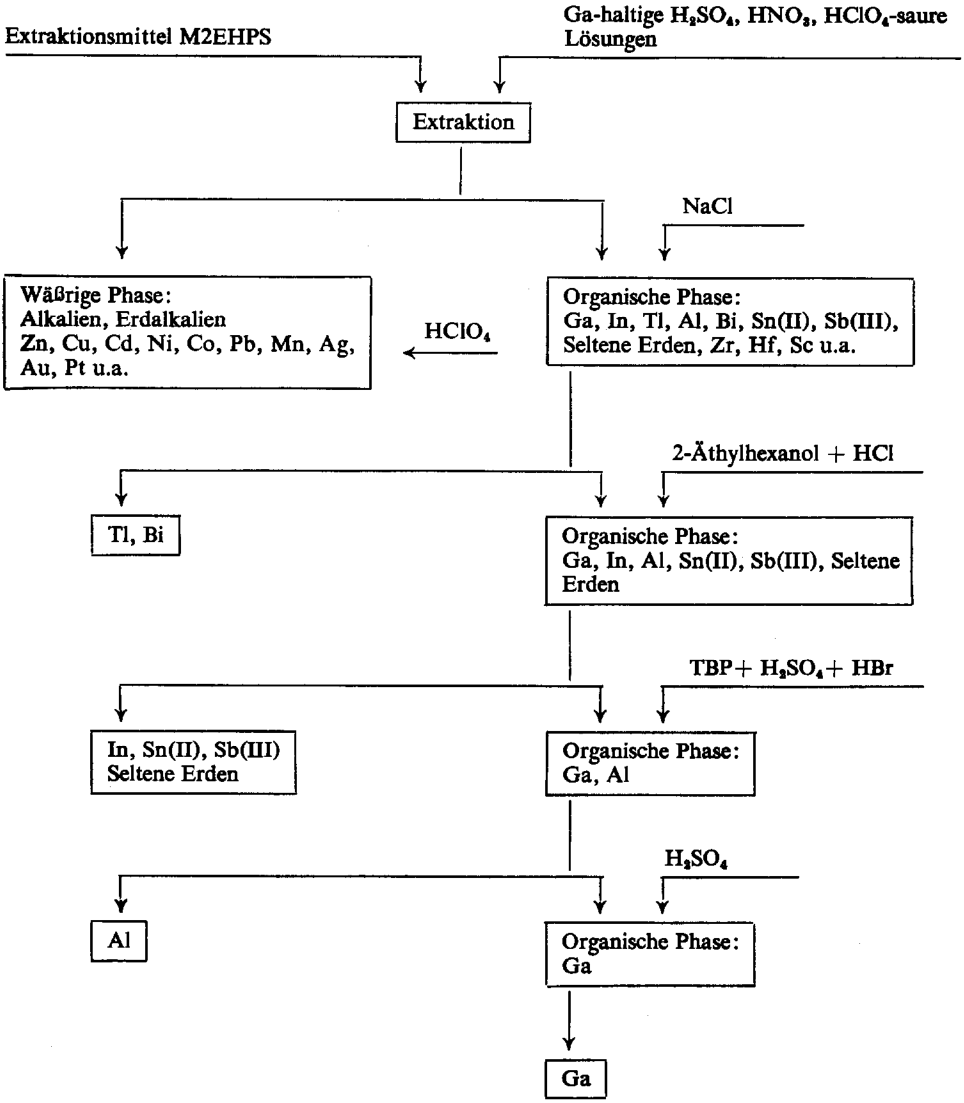

ABB. 9.—Extraktionsschema zur Isolierung von Ga.

Die Galliumkonzentration nach Ausführung des Trennungsganges betrug 1,15 g/l., die der vorgegebenen Lösung 1,18 g/l.

EXPERIMENTELLER TEIL

Galliumhaltige Zwischenprodukte aus Tonerdebetrieben werden zunächst nach den üblichen Verfahren aufgeschlossen. Dann stellt man mit Lauge in den schwach salpeter- oder perchlorsauren Lösungen einen pH-Wert zwischen 4 und 5 ein und extrahiert mit dem 1,5-fachen Volumen einer Lösung von 2*N* M2HPS* in Heptan. Sollte die ursprüngliche Lösung Fe(III) enthalten, dann wird zunächst mit fester Ascorbinsäure reduziert. Die Vollständigkeit der Reaktion wird durch das Ausbleiben der Eisen(III)-thiocyanatreaktion auf Filterpapier geprüft.

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* M2HPS ist ein Gemisch aus 92–93% M2EHPS und 7–8% D2EHPS. Dieses Extraktionsmittel entsteht[5] bei der Einwirkung von P_2O_5 auf ROH nach $P_2O_5 + 2\,ROH \rightarrow R_2H_2P_2O_7$ und nachfolgender sechsstündiger Hydrolyse mit HCl (1:1).

TABELLE III.—ABTRENNUNG DES GALLIUMS VON SCHLECHT EXTRAHIERBAREN METALLEN

Me	[Me], *g/l.*	[Ga], *g/l.*	[Me]: [Ga]	Ga in Reextrakt, *g/l.*
Ni	40	1,42	28,2	1,39
Co	40	0,142	282	0,140
	40	1,42	28,2	1,42
	40	0,142	282	0,146
	40	1,42	28,2	1,37
Cu	40	0,142	282	0,150
	40	1,42	28,2	1,15
Cd	40	0,142	282	0,146
Mn(II)	16	1,42	11,3	1,44
	16	0,142	113	0,143
Pb	7,79	1,42	5,5	1,40
	7,79	0,142	55	0,144
Hg	20	1,42	14	1,39
	20	1,142	140	0,136
Zn	64	1,42	45	1,41
	64	0,142	450	0,146

$V_o : V_a = 1{,}5 :1$, [M2EHPS] = $2N$, Lösungsmittel Heptan.

Die Extraktion erfolgt unter Schütteln (Schütteldauer 1 Minute). Die organische Phase wird zweimal mit konzentrierter Perchlorsäure und dann einmal mit Wasser gewaschen, wobei die wäßrigen Phasen jeweils verworfen werden. Zur Abtrennung des Aluminiums wird die organische Phase mit dem gleichen Volumen TBP versetzt und Aluminium durch Ausschütteln mit demselben Volumen einer Lösung, die $7N$ an Schwefelsäure umd $7N$ an Bromwasserstoffsäure ist, entfernt. Zur Isolierung des Galliums wird die verbleibende organische Lösung zweimal mit $4N$ Schwefelsäure extrahiert und Gallium dann in den vereinigten Lösungen komplexometrisch bestimmt.

Dazu wird die gallliumhaltige Lösung mit Wasser auf 60–70 ml gebracht, ein Überschuß an $0{,}01M$ Komplexonlösung zugegeben, auf 70° erhitzt und dann mit Ammoniak bis zur Rotfärbung von Kongorot neutralisiert. Nach Zugabe des Acetatpuffers vom pH 5 wird die Lösung mit wenigen Tropfen Xylenolorange versetzt und mit $0{,}01M$ Zinknitratlösung bis zum Farbton rosa titriert.

Die Galliummenge errechnet sich nach

$$\mathrm{Ga} = 0{,}697(V_1 - V_2)\,\mathrm{mg}$$

wobei V_1 (ml) das zugesetzte Komplexonvolumen und V_2 (ml) der Verbrauch an Zinknitrat bedeuten.

Anwendung fand das Verfahren bei der Analyse von Zwischenprodukten, wie sie in Tonerdebetrieben vorkommen. Diese Produkte enthalten nach anderen Bestimmungsmethoden[7] ermittelte Galliumbeimengungen von 0,48%. Nach dem hier beschriebenen Verfahren wurde aus 10 Bestimmungen ein Galliumgehalt von 0,49 ± 0,02% ermittelt.

Summary—Gallium(III) can be separated from aluminium in sulphuric or hydrobromic acid medium by synergic extraction with a combination of mono(2-ethylhexyl)phosphoric acid and tributyl phosphate, or of mono(2-ethylhexyl)phosphoric acid with hexyl methyl ketone. All other metals extracted are removed by selective stripping reactions.

Résumé—Le Gallium(III) peut être séparé de l'aluminium en milieu d'acide sulphurique ou hydrobromique par extraction synergique avec une combinaison d'acide mono(2-ethylhexyl) phosphorique et de phosphate de tributyl ou avec une combinaison d'acide mono(2-ethylhexyl)phosphorique et de ketone d'hexyl methyl. Tous les autres métaux extraits sont prélevés par réactions lamellisantes sélectives.

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PHOTOCHEMICAL PRECIPITATION OF THORIUM AND CERIUM AND THEIR SEPARATION FROM OTHER IONS IN AQUEOUS SOLUTION

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Summary—Thorium was precipitated from homogeneous solution by exposing solutions of thorium and periodate in dilute perchloric acid to 253·7 nm radiation from a low-pressure mercury lamp. Periodate is reduced photochemically to iodate which causes the formation of a dense precipitate of the basic iodate of thorium(IV). The precipitate was redissolved, the iodate reduced, the thorium precipitated first as the hydroxide, then as the oxalate and ignited to the dioxide for weighing. Thorium(IV) solutions containing 8–200 mg of ThO_2 gave quantitative results with a standard deviation (s) of 0·2 mg. Separations from 25 mg each of iron, calcium, magnesium, 50 mg of yttrium and up to 500 mg of uranium(VI) were quantitative (s = 0·25 mg). Separations from rare earths, except cerium, were accomplished by using hexamethylenetetramine rather than ammonia for the precipitation of the hydroxide. Cerium(III) was similarly precipitated and converted into CeO_2 for weighing. Quantitative results were obtained for 13–150 mg of CeO_2 with a standard deviation of 0·2 mg. Separations from 200 mg of uranium were quantitative. Other rare earths and yttrium interfered seriously. The precipitates of the basic cerium(IV) and thorium iodates obtained are more compact than those obtained by direct precipitation and can be handled easily. Attempts to duplicate Suzuki's method for separating cerium from neodymium and yttrium were not successful.

PRECIPITATION from homogeneous solution (PFHS) has been effected by a number of methods,[1] but until recently, photochemical oxidation or reduction had not been applied. Yen and Yang[2] produced non-quantitative precipitation of tantalum selenite from homogeneous solution by the photo-induced oxidation of oxalate by bromine in the presence of manganese(II) chloride. The tantalum was originally complexed by the oxalate and after oxidation of the oxalate, the tantalum precipitated as the selenite. Suzuki[3] reported a method for the photochemical separation of cerium from some other rare-earth elements by a photochemical method which involved the IO_4^-–IO_3^- system. We did not become aware of his work until after the publication of our preliminary communication.[4]

Thorium and some other elements are frequently precipitated as the iodates. Stine and Gordon[5] introduced a PFHS method for thorium, based on the reduction of periodate by 2-hydroxyethyl acetate, resulting in the precipitation of thorium iodate. In order to achieve a separation from rare earths, a 2·5–3M nitric acid solution had

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to be used. Meyer and Speter[6] had used 7*M* nitric acid in the direct precipitation of thorium iodate, but Stine and Gordon recognized that such a high concentration of acid caused an intolerable loss of thorium which appeared to be partially compensated by co-precipitation of silica. On the other hand, too low a concentration of nitric acid allowed the co-precipitation of cerium. Inasmuch as Stine and Gordon's method does not provide for a separation from cerium, a lower acid concentration was used. Meyer and Speter had to add a very large excess of the expensive iodate in order to decrease the solubility of thorium iodate. In all these methods, the thorium iodate precipitates as a mixture of different iodates. Consequently, it is necessary to convert the thorium into a weighable form such as ThO_2. However, direct ignition of the iodate to ThO_2 does not succeed, requiring the precipitate to be dissolved and thorium precipitated as the oxalate. Special modifications were used in the separation from rare earths and from uranium to decrease interferences.

The work reported here applies the photochemical reduction of periodate to the *in situ* precipitation of thorium. Head and co-workers[7,8] have demonstrated that metaperiodate is readily reduced to iodate by the action of ultraviolet radiation. Periodate shows an absorption maximum at 220 nm ($\varepsilon = 980\ \mathrm{l.mole^{-1}.mm^{-1}}$) and an absorptivity of 180 $\mathrm{l.mole^{-1}.mm^{-1}}$ at 253·7 nm. Because of the high absorbance of the nitrate ion in the ultraviolet and the low absorbance of perchlorate, perchloric acid solutions have been used throughout this work. It has been found that for thorium the optimum perchloric acid concentration range is 1·0–1·8*M*, the solubility of thorium iodate then being very low, requiring only a small excess of iodate.

We modified the procedure involving the *in situ* generation of iodate from the photoreduction of periodate so that it could be applied to cerium. It is known[9] that cerium(III) in perchlorate solution is photochemically oxidized to the quadrivalent form, albeit with a low quantum yield. Furthermore, in dilute acidic solutions, periodate does not oxidize cerium(III) to (IV). It was, therefore, of interest to see whether cerium(III) perchlorate solutions in the presence of periodate would undergo photochemical oxidation–reduction with the formation of insoluble ceric iodates. Inasmuch as ceric periodate is only sparingly soluble, it would be preferable to start with the more soluble cerium(III) periodate and, after irradiation, obtain the insoluble ceric iodate.

Brinton and James[10] utilized the low solubility of cerium(IV) iodate in developing a method for the precipitation of cerium in dilute nitric acid solution. Willard and Yu[11] oxidized cerium(III) to (IV) with peroxydisulphate or bromate in 0·5*M* nitric acid in the presence of iodate and obtained a dense precipitate of ceric iodate by this PFHS method. Reprecipitation of the cerium was required, however, in order to accomplish satisfactory separations from equal amounts of rare earths.

In order to avoid the precipitation of the cerium(IV) periodate, Suzuki,[8] who started with cerium(IV), added potassium periodate in small portions during the irradiation period. By starting with cerium(III) and sodium periodate, we avoided the formation of cerium(IV) periodate, and the disadvantages of the low solubility of potassium periodate. Suzuki carried out the photochemical reduction in 0·7–0·8*M* sulphuric acid. He claimed excellent separations of cerium from neodymium and yttrium. We have made repeated attempts to duplicate his results, using his method, but have found that neodymium is co-precipitated to the extent of 5–8% and yttrium to an even greater extent.

EXPERIMENTAL

Equipment and reagents

Lamp. A helical-coil low-pressure mercury resonance lamp with a quartz envelope, Nester/Faust Co. Model NFUV-100, was used. Approximately 85–90% of the output is at 253·7 nm. An inexpensive Sylvania lamp, H 37-5 KB/RS which is used for street illumination, was modified by cutting an opening into the external glass envelope. It was used for some of the work and gave equivalent results with one-half the irradiation times. The larger heat generation from this lamp was dissipated with a slow stream of air.

Thorium perchlorate. Reagent grade $Th(NO_3)_4 \cdot 4H_2O$ was repeatedly evaporated with a small excess of 60% perchloric acid. After dilution, the solution contained approximately 0·56 g of ThO_2 and 1 g of 60% perchloric acid per 100 ml. The thorium content was determined by the modification of Vogel's method.[12] A volume of solution containing about 100 mg of ThO_2 was mixed with 225 ml of water and 5 ml of concentrated hydrochloric acid and heated to boiling. With stirring, 55 ml of hot 10% oxalic acid dihydrate solution were added slowly. The hot solution was digested for 2 hr and then allowed to stand overnight at room temperature. The solutions were filtered through a medium ashless filter paper; the precipitate was washed with 150–200 ml of wash solution, dried, ashed, and ignited at 700–800° in an electric muffle and weighed as ThO_2. The wash solution consisted of 2·5 g of oxalic acid dihydrate dissolved in 3·5 ml of concentrated hydrochloric acid diluted to 100 ml.

Cerium(III) perchlorate solution. The calculated amount of $Ce(ClO_4)_3 \cdot 6H_2O$ was dissolved in 1% perchloric acid to make a 0·025*M* solution. The solution was standardized gravimetrically by precipitating cerium(III) oxalate; 25 ml of the perchlorate solution were diluted to 75 ml, heated to boiling, and 25 ml of 10% oxalic acid solution were added slowly with constant stirring. The precipitate was allowed to stand for 2 h, filtered off on ashless paper, washed with cold 2% oxalic acid solution, dried, ashed, and ignited to CeO_2 at 900°, following the recommendations of Brinton and James.[10]

Solutions of rare earths, uranium, and yttrium. Appropriate amounts of the nitrates were dissolved and heated to fumes with a small excess of perchloric acid, or alternatively, the carbonates were treated with a small excess of dilute perchloric acid. The rare-earth and yttrium compounds were of at least 99·9% purity, and were examined spectrographically for the presence of interfering elements. The solutions were analysed by precipitation of the rare earths or yttrium as the oxalates and ignition to the oxides by the standard procedures. Reagent grade uranyl nitrate was used. Uranium was determined by the precipitation of ammonium diuranate and ignition to U_3O_8 by standard procedures.

All other reagents used were A.C.S. reagent grade.

Procedures

Photochemical precipitation of thorium. The exposures were carried out by placing the solution to be photolysed in a 100 × 50 mm crystallizing dish under the mercury lamp which was held in a horizontal position about 50 mm above the level of the solution. Aluminium foil over the top of the lamp increased the available radiation by reflection and shielded the operator from the direct radiation when the opaque fume-cupboard window was opened for inspection (protective ultraviolet-absorbing goggles must be worn).

The solution consisted of an appropriate volume of the thorium perchlorate solution, 60 ml of water, 10 ml of 60% perchloric acid and 4 g of sodium periodate. The range of thorium was equivalent to 8–210 mg of ThO_2. Photolysis times of 4 hr were found to be adequate.

After it was cooled to room temperature, the solution was decanted and the precipitate transferred to Schleicher and Schüll 589 Blue Label (high retention) filter paper. The precipitate on the filter paper and that adhering to the crystallizing dish was dissolved in 100 ml of 1*M* hydrochloric acid. The iodate was reduced to iodide by the addition of solid sodium sulphite until the tri-iodide color was discharged. The solution was heated to 60–70° and filtered ammonia solution added until there was a slight excess. The resulting thorium hydroxide was filtered off on medium ashless filter paper and washed with water until the excess of ammonia was removed. The precipitate was dissolved with 0·5*M* hydrochloric acid. After dilution to 250 ml, the thorium was determined by the oxalate method given above.

Hexamine precipitation of thorium hydroxide. The solution obtained from the dissolving of the thorium iodate was neutralized, after reduction of the iodate, with filtered ammonia solution until a slight turbidity appeared; a few drops of hydrochloric acid were then added to remove the turbidity. The solution (300 ml) was heated to 70–80° and a 10% hexamethylenetetramine solution was added dropwise with stirring until a white turbidity appeared, after which an additional 7 ml of the reagent solution were added. The mixture was digested for 1 hr at 70°, filtered, and the precipitate washed with water, then dissolved in the dilute hydrochloric acid and precipitated as the oxalate, as above.

Determination of thorium in the filtrates. In order to evaluate any thorium loss in these precipitations, the thorium in the filtrates was extracted with thenoyltrifluoroacetone in benzene in the presence of calcium nitrate at a pH of about 2. The thorium was stripped with $2M$ nitric acid, and the nitric acid removed by evaporation after the addition of a few ml of perchloric acid. Thorium was determined by adding 2 ml of concentrated hydrochloric acid and 0·1% thoron solution ([*o*-(2-hydroxy-3,6-disulpho-1-naphthyl)azo]benzene arsonic acid disodium salt) and measuring the absorbance at 545 nm. Aliquots of a standard thorium solution were similarly extracted to obtain a standard curve. The extraction was omitted in the case of the filtrate from the oxalate precipitation; instead, the oxalate was destroyed by careful evaporation with nitric acid followed by repeated evaporation with perchloric acid.

Analysis of the thorium iodate precipitates. The photochemically prepared thorium iodate was filtered off on a sintered-glass crucible, washed with alcohol and dried at 25° for 3 hr. Thorium was determined by the oxalate method after the precipitate was dissolved in concentrated hydrochloric acid. Iodate was determined by dissolving the precipitate in $2M$ sulphuric acid, adding an excess of potassium iodide and titrating the tri-iodide with standard thiosulphate. The precipitate was also analysed spectroscopically, and was shown to contain less than 0·05% sodium.

Photochemical precipitation of cerium. Samples containing an appropriate amount of cerium(III) perchlorate, 3 ml of 60% perchloric acid and 4 g of sodium periodate in 75 ml total volume were irradiated as for thorium. The precipitate of the basic cerium(IV) iodate was allowed to stand for 30 min, then the supernatant liquid was decanted through No. 589 Blue Label filter paper. The precipitate was washed 3–4 times by decantation and transferred to the filter paper with cold water, after which the filter was punctured and the precipitate in the filter transferred into a beaker. The punctured filter was added and the mixture was heated with 6 g of solid oxalic acid until no more iodine was evolved. An additional 1 g of oxalic acid was added and the mixture heated for a further 5 min. About 50 ml of hot water were added, the precipitate was allowed to settle for several hours (usually overnight) and the precipitate of cerium(III) oxalate was filtered off on No. 589 Blue Label filter paper, washed with 2% aqueous oxalic acid solution, dried, ashed and ignited to CeO_2 at 800° to constant weight. The decomposition of the iodate, conversion to cerium(III) oxalate, and ignition essentially follows the precedure in Scott's *Standard Methods.*[13]

Determination of lamp efficiency. The lamp efficiency, and therefore the appropriate exposure times, were found by irradiating a solution containing 4 g of sodium periodate and 3 ml (for cerium analysis) or 10 ml (for thorium analysis) of 60% perchloric acid and analysing it volumetrically for iodate by the method in Scott's *Standard Methods.*[14] Sufficient iodate must be formed to provide a 50% excess.

It was found that the amount of iodate produced with a 4-hr exposure sufficed for precipitating up to 240 mg of thorium or 145 mg of cerium. Such exposures were therefore used in all runs, except for those using the Sylvania lamp, in which case a 2-hr exposure was sufficient.

The quantum yield of the process was determined by irradiating uranyl oxalate solutions, using the same experimental geometry. A quantum yield of 0·37 was obtained for the periodate reduction in $0{\cdot}9M$ perchloric acid solution.

RESULTS AND DISCUSSION

Results for thorium are shown in Tables I–V and for cerium in Tables VI–IX.

Thorium

Acidity. With $3{\cdot}6M$ perchloric acid the thorium loss was about 5·1 mg of ThO_2 out of 147 mg, as compared to 0·0 mg in solutions which were up to $1{\cdot}8M$ in perchloric acid. A maximum acidity of $1{\cdot}8M$ perchloric acid was therefore chosen.

Excess of iodate. The method of Meyer and Speter[6] requires 15 g of potassium iodate in the 250 ml of solution in order to keep the solubility of the thorium iodate sufficiently low in the presence of $7M$ nitric acid. In perchloric acid, the solubility losses are low and only a small excess of iodate is required. The PFHS method of Stine and Gordon[5] uses 2·5–$3M$ nitric acid but still suffers a slight solubility loss requiring the use of 14 g of sodium periodate followed by the addition of 2 g of potassium iodate after the initial reduction, in order to ensure complete precipitation. In the photochemical method, only 4 g of sodium periodate are required. This presents an appreciable economy, in view of the high cost of periodates.

Determination of thorium in the filtrates. Table I shows the weight of ThO_2 in the filtrates from the three methods (as determined by the thoron method) and also in the

TABLE I.—THORIUM IN THE FILTRATE (140·0 mg OF ThO$_2$ TAKEN)

Method	ThO$_2$ in filtrate		
	average, *mg*	No. of detns., *n*	Std. devn., *s*,
Meyer and Speter[6]	1·45	4	0·11
Stine and Gordon PFHS[5]	0·14	4	0·06
Photochemical PFHS	0·04	4	0·02
Oxalate precipitation[13]	0·13	5	0·08

filtrate of the oxalate precipitation. The photochemical PFHS method shows the lowest thorium loss. No thorium could be found in the filtrates of the thorium hydroxide precipitation, which is to be expected in view of its known very low solubility.

Composition of the precipitate. Chernikov and Uspenskaya[15] gave the composition of the precipitate obtained by the method of Meyer and Speter as $4Th(IO_3)_4 \cdot KIO_3 \cdot 18H_2O$, giving an IO_3^-:Th mole ratio of 4·25:1; Moeller and Fritz[16] found a ratio of 4·02:1 and based a volumetric method for thorium on this value. The precipitate produced by the photochemical method has an IO_3^-:Th ratio of 2·26:1. The precipitate apparently consists mostly of basic thorium iodate, $ThO(IO_3)_2$, containing a small portion of the normal iodate. Inasmuch as the precipitation is used for separation, this non-stoichiometric composition does no harm. The composition of the precipitate is not surprising in view of the low acid concentration used.

Determination of thorium. Because of the non-stoichiometric composition of the thorium iodate precipitate, direct weighing of the precipitate was not attempted. In addition, the presence of non-volatile electrolytes made direct weighing or ignition to thorium dioxide impractical at this stage. Water-washing to remove the electrolytes would have resulted in excessive solubility losses. The precipitation as the hydroxide removes interfering electrolytes and makes the application of the oxalate precipitation possible. Although a PFHS of the oxalate could have been applied at this point, little would have been gained by doing so. Results for solutions containing known amounts of thorium in the absence of interfering ions are given in Table II. Table III shows the results obtained in the presence of possible interfering ions introduced as the perchlorate salts. It is seen that calcium, magnesium, iron, yttrium and uranium

TABLE II.—DETERMINATION OF THORIUM

ThO$_2$ taken, *mg*	Error in ThO$_2$ found,† *mg*			
8·10*	−0·1;	0·0;	+0·2;	+0·1
15·05*	+0·1;	0·0;	0·0;	+0·2
26·8*	−0·3;	−0·1;	0·0;	+0·2
39·5*	−0·1;	0·0;	0·0;	−0·1
81·1	+0·2;	0·0;	+0·2;	0·0
122·7	+0·1;	−0·4;	−0·3;	0·0
163·1		0·0;	−0·2	
164·7	−0·4;	+0·1;	−0·1;	−0·4
206·1		+0·2;	+0·4	

* 12 hr digestion used.

† S 0·20 *mg*, $n = 32$. A regression-line analysis yielded a straight line with no significant differences in the slope and intercept from the expected values of 1·000 and 0·00, respectively (95% probability).

TABLE III.—EFFECT OF FOREIGN IONS ON DETERMINATION OF THORIUM

Element added, *mg*		ThO$_2$, *mg*		
		Taken	Found, error	
Ca	25	143·2	−0·3	$n = 10$ $s = 0{\cdot}24$ mg
Mg	25	143·2	−0·1	
Fe	7	143·2	0·0	
	14	143·2	0·0	
	28	143·2	−0·5	
Y	25	143·2	−0·3	
	50	143·2	0·0	
U	25	142·7	+0·1	
	50	142·7	+0·2	
	100	143·2	−0·1	
La	24	142·8	+0·2	$n = 11$ $s = 1{\cdot}71$ mg
Nd	25	142·7	+0·5	
	50	142·7	+1·1	
Pr	25	142·7	+0·8	
	50	142·7	+2·0	
Mixture*	87	113·7	+1·3; +0·8	
	174	113·7	+1·3; +2·0	
	261	113·7	+2·6; +2·9	

* Approximately equal amounts of Sm, Eu, Gd, Dy, Er.

do not interfere at the levels shown. The standard deviation in these cases does not differ significantly from that for the results in Table II. It is seen that some of the rare earths are apparently co-precipitated to a certain extent, giving up to 2·9 mg error for ThO$_2$. The rare-earth interference is expected to be more serious in the photochemical method, in accordance with the findings of Moeller and Fritz,[16] who pointed out that a high nitric acid concentration prevents such interference. In the photochemical method the concentration of free acid, as well as of iodate, was much lower than in the other methods. The increased co-precipitation of rare earths was overcome, however, by precipitating the thorium hydroxide by the hexamine procedure of Ismail and Harwood.[17] Table IV shows the results obtained by introducing this modification. It can be seen that the precision of the thorium determinations does not differ significantly whether these other metals or the rare earths are present or not.

TABLE IV.—DETERMINATION OF THORIUM, RARE EARTHS PRESENT, HEXAMINE PROCEDURE

Element added, *mg*		ThO$_2$, *mg*	
		Taken	Found, error†
Mixture*	87	112·1	−0·4; −0·4
	174	112·1	0·0; +0·1
	261	112·1	−0·1; 0·0
	435	109·3	−0·1
	610	109·3	0·0; +0·3
	870	109·3	−0·2

* Approximately equal amounts of: Sm, Eu, Gd, Dy, Er.
† $n = 10$; $s = 0{\cdot}23$ mg.

Although uranium co-precipitates to a slight extent during the photochemical precipitation (Table V), the uranium remains complexed by the oxalate and thus is

TABLE V.—DETERMINATION OF THORIUM, URANIUM(VI) PRESENT

	Uranium taken, *mg*	ThO_2, *mg*		
		Taken	Found, error	
Method I	100	48·2	−0·1; −0·1	
	300		−0·1; +0·1	
	500		0·0; 0·0	*n* = 10
	750		−0·5; −0·5	*s* = 0·31 mg
	1000		−0·4; −0·4	
	1500		−1·0; −1·1	
Method II	100	48·0	+1·1; +0·6	
	200		+2·3; +1·7	
	300		+2·5; +2·5	*n* = 9
	400		+3·0; +3·4	*s* = 2·5 mg
	500		+3·3	

Method I: Final precipitation of thorium from oxalate solution (usual method).
Method II: Final precipitation of thorium as hydroxide; no oxalate present.

separated from thorium in the final precipitation. Owing to the absorbance of the uranyl ion, however, incomplete precipitation of thorium(IV) could result in the presence of very large amounts of uranyl ion because of the lower ultraviolet flux which would be available for the periodate reduction.

Cerium must be removed prior to the determination because cerium(IV) iodate is similarly precipitated.

No photochemical system can be truly concentration-homogeneous, as Fitzgerald[18] pointed out, because of the decrease in the intensity of radiation with thickness of the solution; absorption of the photochemically effective radiation is required in order to have a photochemical change. Yet the described method is much closer to the gradual formation of the precipitate typical for PFHS than is direct addition of a reagent.

Cerium

Acidity. The original method of precipitating cerium(IV) iodate, by Brinton and James,[10] made use of 8*M* nitric acid solution. Other rare-earth iodates are sufficiently soluble in this highly acidic solution to permit separations from cerium. Solubility errors due to the increased solubility of cerium(IV) iodate in this high concentration of nitric acid were decreased by keeping an extremely large excess of iodate in solution.

TABLE VI.—DETERMINATION OF CERIUM, SULPHITE PROCEDURE

CeO_2 taken, *mg*	Error in CeO_2 found, *mg*†
12·7	−0·3, −0·2, −0·2, −0·2
25·5	0·0, 0·0, +0·1, 0·0
43·0	+0·2, +0·2, +0·1, 0·0
66·6	0·0, −0·1, 0·0
97·6	−0·3, −0·3, −0·3, −0·4
104·6	−0·2, −0·1
133·0	+2·1, +2·2, +0·4, +1·2, +0·9
148·1*	+0·2, +0·4

* Oxalate procedure.

† *n* = 23 (excluding 133·0-mg determinations); *s* = 0·20 mg.

The method described here makes use of only dilute acid solutions (0·13–0·50*M* perchloric acid) and requires only a modest excess of the iodate. This lower acidity causes a decrease in solubility errors due to cerium(IV) iodate (Table VIII), but at the expense of separations from rare earths and yttrium (Tables VII and IX). Willard and Yu[11] found much less interference by other rare earths; nitric acid is apparently more effective in preventing the precipitation of rare earth iodates than is perchloric acid. However, because of the strong absorption of ultraviolet radiation by nitric acid, we could not use this acid.

TABLE VII.—DETERMINATION OF CERIUM, RARE EARTHS PRESENT

Rare earth added, *mg*		60% $HClO_4$, *ml*	CeO_2, *mg*	
			Taken	Found, error
Gd_2O_3	15	3	62·7	+9·1, +10·0
	30	3	62·7	+14·2, +14·8
	60	3	62·7	+22·6, +22·3
	50	1	74·2	+43·5
	100	1	74·2	+92·4
Dy_2O_3	30	3	62·7	+6·6
	50	1	74·2	+45·5
	100	1	74·2	+91·8
Pr_2O_3	30	3	62·7	+24·8, +26·0
	50	1	74·2	+47·7
	100	1	74·2	+95·0
Ho_2O_3	50	1	74·2	+42·2
	100	1	74·2	+85·3
La_2O_3	100	1	74·2	+101·4
	200	1	74·2	+200·4
Yb_2O_3	30	3	62·7	+11·3
	60	3	62·7	+15·7
Nd_2O_3	60	3	62·7	+33·3
	57·6	1	148·5	+56·3
	57·6	2	148·5	+57·6
	57·6	3	148·5	+53·0
	57·6	4	148·5	+45·5
	57·6	6	148·5	+41·7
	57·6	8	148·5	+21·9

TABLE VIII.—EFFECT OF ACIDITY ON THE RECOVERY OF CERIUM (107·1 mg OF CeO_2 TAKEN)

Perchloric acid, *M*	Error in CeO_2 found, *mg*
0·28	−0·1
0·56	−3·6
0·94	−7·4

Composition of the precipitate. The composition of the precipitate shifts progressively in favour of basic iodates as the acidity is lowered. Our analysis gave a ratio of 3·6 for the molar ratio of $CeO(IO_3)_2:Ce(IO_3)_4$. It is interesting to note that despite our use of perchloric acid, this composition of the precipitate corresponds exactly to that shown by Willard and Yu (Fig. 1 of Ref. 11) for 0·3*M* nitric acid. The amount of iodate found was 89% of that in normal cerium(IV) iodate. Suzuki[8] obtained a mixed iodate of cerium and potassium, but our precipitates contained no

TABLE IX.—EFFECT OF FOREIGN IONS ON DETERMINATION OF CERIUM

Foreign species present, *mg*		60% $HClO_4$, *ml*	CeO_2, *mg*	
			Taken	Found, error
Y_2O_3	100	1	74·2	44·9
	200	1	74·2	+63·9
	32	3	62·6	+7·1
	64	3	62·6	+8·3
U_3O_8 [as U(VI)]	69·6	2	148·4	+0·1
	139·2	2	148·4	0·0
	208·8	2	148·4	+0·1
MgO	356	1	74·2	0·0
	712	1	74·2	+0·6
Fe_2O_3	287	1	74·2	+1·0*
	575	1	74·2	+1·6*
CaO	342	1	74·2	+220·9
	683	1	74·2	+291·7

* Precipitates were brownish due to the contamination by Fe.

more than traces of sodium or potassium. The presence of the basic iodate does not affect the analytical result inasmuch as it is at least as insoluble as the normal iodate and, in any case, the precipitate is converted into the dioxide for weighing.

Determination of cerium. In our re-examination of the system, the cerium(IV) iodate was initially decomposed as given in our method for thorium, by adding sulphite, heating until all the iodine was volatilized, and then precipitating cerium(III) hydroxide with ammonia, followed by ignition to the dioxide. In view of the high results obtained for larger samples (Table VI) we used oxalate to decompose the cerium(IV) iodate as discussed in the experimental section above. We attempted direct ignition of cerium(IV) iodate to CeO_2, following the method of Willard and Yu,[11] but found that the loss due to sputtering was significant.

To compare the density of the precipitates obtained by the photochemical method and the direct addition method of Brinton and James,[10] precipitates were allowed to settle for 24 hrs after transfer into graduated cylinders. The precipitate from magnetically stirred photochemically reduced solution showed the least volume but even an unstirred solution gave a volume of the precipitate significantly less than that from the direct addition method. The volume ratios of precipitate were found to be approximately 1:2:4 for the same amounts of cerium precipitated by the photochemical method with stirring, without stirring, and by the direct addition method, respectively. Photomicrographs of the ceric iodate precipitates obtained by these methods showed that the particles obtained by the photochemical method were more compact and appeared less gelatinous than those obtained by the direct addition method of Brinton and James.[10] It was apparent that the more dense particles should be more easily washed than the almost gelatinous aggregates obtained by direct precipitation.

In view of the low acidity of the solution, it is not surprising that the rare earths and yttrium interfere seriously with the determination of cerium although separations from uranium (as uranyl ion) were accomplished. It was found that the initial iodate precipitate contained some uranium but that the oxalate precipitation step kept the uranyl ion in solution as the oxalato complex. Separation from much larger amounts of uranium necessitated modification of the procedure and will be reported elsewhere together with data on the separation of thorium from uranium. Further, Table IX shows that cerium can be separated essentially quantitatively from magnesium and almost quantitatively from iron(III), although the precipitate appears to retain a small amount of iron which gives a brownish colour to the precipitate and causes slightly high results. Calcium is co-precipitated to a large extent, but not quantitatively. Thorium, of course, behaves similarly to cerium and will be co-precipitated quantitatively. The results in Table VII suggest that the photochemical precipitation method should give quantitative results for neodymium and lanthanum; some preliminary results have been reported.[9]

We were never able to reproduce the exceedingly good separations which Suzuki reported in Table 6 of his paper.[3] Samples containing 71·3 mg of cerium dioxide and 15·2 and 30·4 mg of neodymium oxide were treated by Suzuki's procedure and gave recoveries which were high by 4·2 and 6·2 mg, respectively. The presence of 100 mg of yttrium oxide in the cerium gave results which were 44·5 mg too high.

The method of Willard and Yu[11] is to be preferred if separation from other rare earths is desired, and the method reported here is to be preferred if it is desired to carry out the cerium precipitation at room temperature or if uranium is present, which seriously interferes with the non-photochemical precipitation procedure.[11]

Zusammenfassung—Thorium wurde aus homogener Lösung gefällt, indem Lösungen von Thorium und Perjodat in verdünnter Überchlorsäure der 253,7 nm-Strahlung einer Niederdruck-Quecksilberlampe ausgesetzt wurden. Perjodat wird photochemisch zu Jodat reduziert; dieses führt zur Bildung eines dichten Niederschlags von basischem Thorium(IV) jodat. Der Niederschlag wurde wieder gelöst, das Jodat reduziert, das Thorium zuerst als Hydroxid, dann als Oxalat gefällt, zum Oxid verglüht und gewogen. Thorium(IV)-Lösungen mit 8–200 mg ThO_2 gaben quantitative Ergebnisse mit einer Standardabweichung (*s*) von 0,2 mg. Abtrennungen von je 25 mg Eisen, Calcium, Magnesium, 50 mg Yttrium und bis zu 500 mg Uran(VI) waren quantitativ ($s = 0{,}25$ mg). Abtrennungen von seltenen Erden außer Cer wurden erreicht, wenn zur Fällung des Hydroxids Hexamethylentetramin statt Ammoniak verwendet wurde. Cer(III) wurde ähnlich gefällt und zur Wägung in CeO_2 überführt. Quantitative Erebnisse wurden für 13–150 mg CeO_2 mit einer Standardabweichung von 0,2 mg erhalten. Abtrennungen von 200 mg Uran waren quantitativ. Andere seltene Erden und Yttrium störten erheblich. Die Niederschläge der basischen Jodate von Cer(IV) und Thorium sind kompakter als die, die man bei direkter Fällung erhält, und leichter zu handhaben. Versuche, das Verfahren von Suzuki zur Trennung von Cer von Neodym und Yttrium nachzuarbeiten, blieben ohne Erfolg.

Résumé—On a précipité le thorium en solution homogène en exposant des solutions de thorium et de periodate en acide perchlorique dilué à la radiation 253,7 nm d'une lampe à mercure à basse pression. Le periodate est réduit photochimiquement en iodate qui provoque la formation d'un précipité dense de l'iodate basique de thorium(IV). Le précipité est redissous, l'iodate réduit, le thorium précipité d'abord à l'état d'hydroxyde, puis d'oxalate et calciné en dioxyde pour pesée. Les solutions de thorium(IV) contenant 8–200 mg de ThO_2 ont donné des résultats quantitatifs avec un écart type (*s*) de 0,2 mg. Des séparations de 25 mg de chacun des métaux fer, calcium, magnésium, de 50 mg d'yttrium et jusqu'à 500 mg d'uranium(VI) ont été quantitatives ($s = 0{,}25$ mg). Les séparations de terres rares, à l'exception du cérium, ont été réalisées en utilisant l'hexaméthyléne tétramine

plutöt que l'ammoniaque pour la précipitation de l'hydroxyde. Le cérium(III) a été précipité de manière semblable et converti en CeO_2 pour la pesée. On a obtenu des résultats quantitatifs pour 13–150 mg de CeO_2 avec un écart type de 0,2 mg. Des séparations de 200 mg d'uranium ont été quantitatives. Les autres terres rares et l'yttrium interfèrent sérieusement. Les précipités d'iodates basiques de cérium (IV) et de thorium obtenus sont plus compacts que ceux obtenus par précipitation directe et peuvent être manipulés aisément. Des essais pour reproduire la méthode de Suzuki de séparation du cérium du néodyme et de l'yttrium n'ont pas réussi.

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COULOMETRIC DETERMINATION OF URANIUM WITH A PLATINUM WORKING ELECTRODE

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Summary—Experimental conditions have been established which enable uranium to be determined coulometrically by the reduction of uranium(VI) to uranium(IV) at a platinum working electrode, by controlled-potential or controlled-potential-limit techniques. The procedure has been used successfully as a subsidiary method in the routine determination of uranium in pure uranyl nitrate solutions. The platinum electrode has several important practical advantages over the well established mercury-pool electrode for the coulometric determination of uranium. The consecutive determination of iron(III) and uranium(VI), or plutonium(IV) and uranium(VI) can be carried out with the same working electrode in the same solution and the coulometric oxidation of uranium(IV) to uranium(VI) is practicable. The rate of stirring of the cell liquor is much less critical in the case of the platinum electrode. Two main problems had to be overcome before a practical procedure could be achieved; hydrogen evolution during the uranium(VI)–(IV) reduction had to be eliminated so that 100% current efficiency could be obtained for the desired reaction and electrode-surface poisoning phenomena had to be controlled so that reaction times could be kept reasonably short. It was found that selection of a hydrochloric acid base solution containing a small amount of bismuth(III) enabled hydrogen evolution to be avoided: also electrode-surface poisoning with this base solution was not particularly serious and could be maintained at a satisfactorily low level by occasionally anodizing the electrode in dilute sulphuric acid. Bismuth(III) forms a complex with chloride ions and its presence increases the hydrogen overvoltage at the working electrode: no visible deposit of bismuth metal forms on the electrode during the uranium reduction. Samples containing nitrate can be analysed provided sulphamic acid is added to this hydrochoric acid base solution.

THE DETERMINATION of uranium by controlled-potential coulometry, employing a mercury-pool working electrode at which uranium(VI) is reduced to uranium(IV), is a well established technique. Analytical procedures have been described by Booman *et al.*,[1] Goode *et al.*[2] and McColm *et al.*[3]

There are, however, two main disadvantages associated with the application of the mercury-pool electrode to coulometric analyses in general. One is that, for optimum performance, the experimental arrangements for mixing the contents of the working compartment of the coulometric cell are somewhat critical; both aqueous and mercury phases need to be efficiently stirred without producing detached droplets of one phase within the other. The other main disadvantage is that mercury dissolves under mildly oxidizing conditions: for example, it is impracticable to perform coulometric oxidations of uranium(IV), iron(II) and plutonium(III) in the usual mineral-acid base electrolytes.

These two disadvantages do not apply to the platinum-gauze working electrode,

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and it appeared that a useful improvement in coulometric technique would be accomplished if the mercury pool could be replaced by a platinum electrode in the case of uranium determinations. Such a change of working electrode is not a straightforward matter, since difficulties due to hydrogen evolution and surface-poisoning effects arise at the platinum electrode at the potentials needed for the reduction of uranium(VI) to uranium(IV).

This paper describes how these difficulties were overcome and how a practical procedure for the coulometric determination of uranium at a platinum working electrode was achieved.

EXPERIMENTAL

Apparatus

Coulometer. The constant-current potential-limit coulometer described by McColm *et al.*[3] was used for this work. This instrument contains sixteen constant current sources providing currents of 512, 256, 128, 64, 32 . . . 0·16 mA. When the working electrode voltage reaches the set potential limit, the current is automatically halved until a pre-set maximum current is reached. Hence the conditions of controlled-potential coulometry are approximated to by a series of discrete controlling steps, rather than the continuous control normally used.

Cell and electrodes. Figure 1 depicts the cell employed in the later stages of the investigational work and for the final recommended procedure. The body of the cell was made from borosilicate glass. The ion-exchange membranes were sealed with picein wax into ground-in ledges made inside standard glass cone-and-socket joints. The working electrode consisted of a strip of platinum gauze about 30 mm wide and 300 mm long, formed into a cylinder two to three layers thick: it fitted loosely in the working compartment and when in position needed about 20 ml of liquid to cover it. The liquor in the working compartment was stirred by a compressed-air operated glass stirrer running in PTFE bearings. The reference electrode compartment contained an E.I.L. type RJ.23 "saturated calomel" element immersed in saturated potassium chloride solution. The dimensions and construction of the platinum auxiliary electrode were not critical. The purpose of the conducting bridge was to isolate the auxiliary electrode reaction products from the working compartment. The total resistance of the cell was such that a potential difference between the working and auxiliary electrodes of 12 V would cause a current of about 0·6 A to flow. The working compartment liquor was de-aerated by passing nitrogen over its surface, with the stirrer in operation.

The cells employed for the earlier work differed from the one described above mainly in being slower in operation because of their inferior electrode area : solution volume ratios.

Preliminary work

Amount of uranium per determination. The amount of uranium added in most of the trials was about 200 mg per determination. This amount was rather larger than that normally taken by other workers: it was selected to make it easier to obtain high precision of measurement and to decrease the "blank" and other corrections. The uranium was added as an aqueous uranyl chloride or uranyl nitrate solution of known concentration. Sulphamic acid was always added to the base electrolyte when the nitrate was employed.

Use of gold electrodes. Because information already available indicated that it was probably impracticable to use a platinum working electrode for the uranium(VI)–(IV) reduction, and because our preliminary experiments appeared to confirm this, most of our early experimental work, aimed at replacing the mercury pool, was done with gold electrodes. It was hoped that gold would prove to be more satisfactory than platinum. These gold electrodes were prepared by gold-plating platinum gauze from a cyanide plating bath.

Initially $1M$ sulphuric acid was employed as base electrolyte in the trial uranium determinations. Experiments showed that uranium(VI) could in fact be determined precisely by reduction to uranium-(IV) at a gold-plated working electrode, but that the time required for the determination of fixed amounts of uranium under apparently identical conditions varied widely, in the worst cases becoming prohibitively long.

The variation in time required per determination was explicable by assuming that the electrode surface became increasingly "poisoned" with use, so that its effective area became less. In one particular instance it was shown that a molybdenum concentration less than 0·1 % of that of the uranium was sufficient to produce a very marked effect, under the conditions described above.

It was found that the gold surface could be cleaned by anodizing in dilute sulphuric acid, thus enabling the time of determination of uranium in fairly pure solutions to be kept near the minimum. In addition, trials with hydrochloric acid base electrolytes were made, and it became clear that the

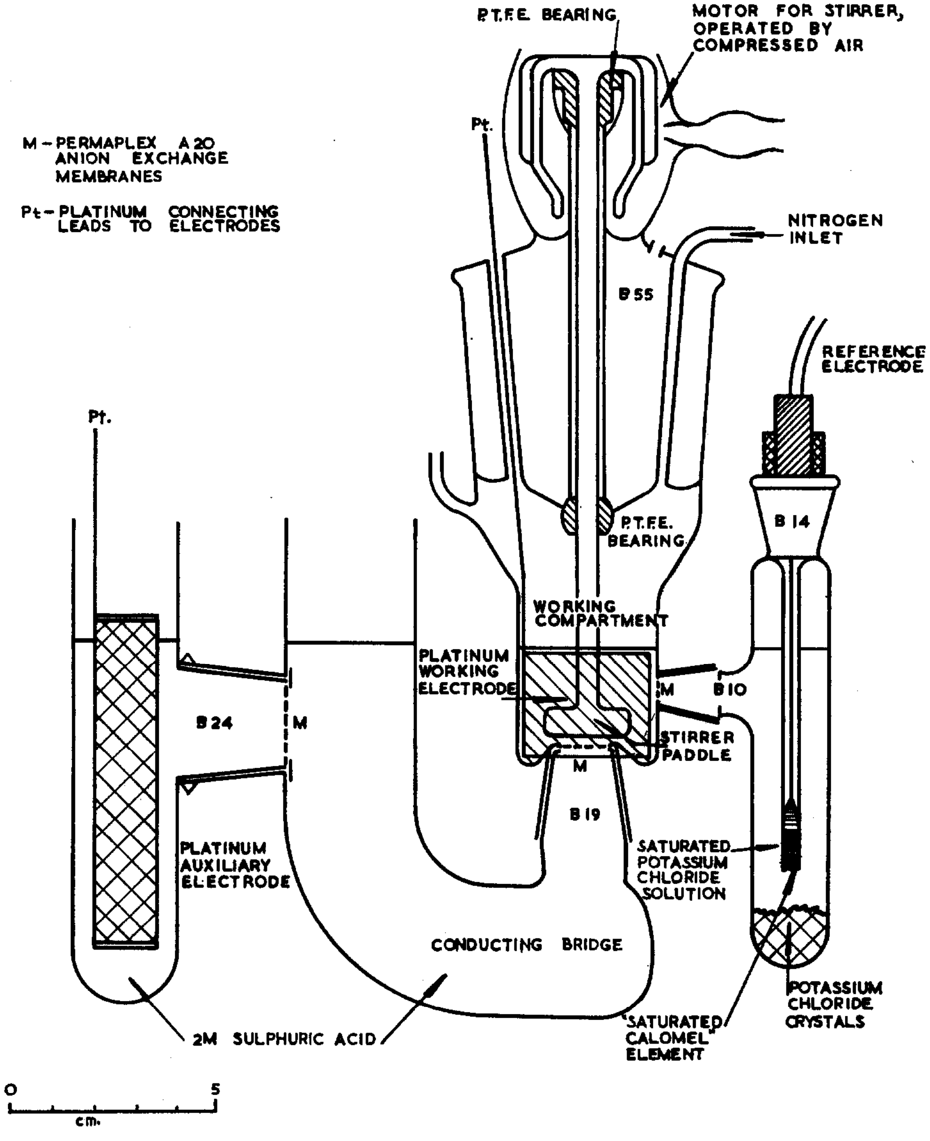

FIG. 1.—Diagram of coulometer cell.

electrode-poisoning effects were substantially less serious in hydrochloric acid than in sulphuric acid.

Application of the platinum working electrode. The combined effect of the anodizing pretreatment in dilute sulphuric acid and the use of $3M$ hydrochloric acid as base solution on the determination of uranium was so beneficial in the case of the gold electrode that it was decided to try the same procedure with a platinum working electrode.

It was shown to be practicable to reduce uranium(VI) to uranium(IV) quantitatively in either $1M$ or $3M$ hydrochloric acid, using a platinum electrode which had previously been anodized in $2M$ sulphuric acid, though the conditions for the avoidance of hydrogen evolution seemed more critical than with the gold cathode; also the minimum time required per determination was somewhat longer than with a gold electrode of the same apparent area.

Despite these drawbacks, the work on platinum electrodes was continued because it had become evident by this time that the gold-plated electrode would be unsuitable for use in a routine procedure, owing to difficulties in preparation and maintenance of the gold deposit.

Effects of foreign metal ions. The effects of foreign metals on the performance of a platinum working electrode in the reduction of uranium(VI) were systematically investigated. Because it seemed possible that optimum performance in previous trials might have depended on the presence of some metal impurity, desirable effects such as the suppression of hydrogen evolution were looked for as well as undesirable electrode-poisoning phenomena. The investigation covered those metals known to be present as impurities in the plutonium/uranium oxides and nitrates received for analysis, and also those easily reducible metals which could be electro-deposited at potentials near those used for the uranium reduction.

The first most important finding was the beneficial effect of copper. It was found that with the $3M$ hydrochloric acid base solution the presence of 1–2 mg of copper(I) per 20 ml could enable potentials as negative as $-0{\cdot}30$ V *vs.* S.C.E. to be used for the uranium reduction (compared with $-0{\cdot}15$ V without copper) without appreciable hydrogen evolution. [The addition of copper as copper(II) entailed a pre-reduction to a limit of $+0{\cdot}10$ V *vs.* S.C.E. to produce copper(I)]. This effect enabled uranium reductions to be performed more rapidly and rendered electrode-poisoning troubles less important. At $-0{\cdot}30$ V, the electrode was not quite negative enough to produce a visible deposit of copper metal.

In addition, it was shown that comparatively large amounts of iron(III), nickel(II), cobalt(II), chromium(III), copper(I) and cadmium(II) had little or no electrode-poisoning effect on a uranium reduction in $3M$ hydrochloric acid.

It was later found that the inhibition of hydrogen evolution at the platinum working electrode, already observed with copper(I), was also shown by lead, tin, antimony, arsenic and bismuth ions to varying extents. Metal ions which begin to electro-deposit at potentials slightly more negative than the desired working electrode potential promoted this inhibition most effectively, although no visible deposit was formed in use.

In some cases this beneficial action was more than outweighed by an electrode-poisoning effect which increased the time required for a uranium determination, and complications also arose when the metal ion had two or more oxidation states, especially when the redox systems behaved irreversibly.

Selection of bismuth(III) as additive. Of the metal ions studied, bismuth(III) appeared to be the most suitable to add to the base solution to improve the performance of the platinum electrode in the reduction of uranium. Bismuth was preferred to copper because of the absence of interfering oxidation states, and because the uranium(VI) reduction could proceed with the working electrode appreciably less negative in the presence of bismuth(III). As in the case of copper the addition of bismuth made electrode-poisoning effects less serious.

Base electrolyte composition. Because of the promising performance of a hydrochloric acid base solution with bismuth(III) added, in conjunction with the platinum electrode, the effects of varying the hydrochloric acid and bismuth concentrations were studied more closely. This work showed that neither concentration was very critical, but that $4{\cdot}5M$ was probably the optimum concentration of hydrochloric acid. Halving or doubling the concentration of bismuth finally chosen made little difference to the effectiveness of the bismuth.

Cell design. A substantial effort was devoted to optimizing the design of the coulometer cell. Importance was attached to making the ratio of area of electrode to solution volume as large as practicable, to keep the time required per determination as short as possible: this would minimize mechanical losses of the cell liquor by spray and through membranes, and the undesirable effects of background currents.

Before conditions for the reliable reduction of uranium(VI) were established, it was found very worthwhile to make use of the highly-reversible iron(II)/iron(III) system to evaluate the performance of experimental designs of cell.

Procedure for the coulometric determination of uranium in uranyl solutions

Reagents. Bismuth(III) solution, $0{\cdot}01M$. Add 20 ml of concentrated hydrochloric acid to 2·8 g of sodium bismuthate. Warm to dissolve, then boil the solution to expel chlorine, cool, and dilute to 1 litre with $4{\cdot}5M$ hydrochloric acid.

Hydrochloric acid, $4{\cdot}5M$.

Sulphamic acid, $1{\cdot}5M$.

Sulphuric acid, $2M$.

Method. Add about 10 ml of $4{\cdot}5M$ hydrochloric acid to the working compartment of the coulometer, followed by 1 ml of $1{\cdot}5M$ sulphamic acid and 1 ml of $0{\cdot}01M$ bismuth(III). Add the sample [not more than 5 ml in volume, containing 150–300 mg of uranium(VI) and less than 10 mmole of nitric acid], then dilute the cell contents to about 20 ml with $4{\cdot}5M$ hydrochloric acid, so that the electrode will just be covered by the solution.

With the working electrode in position, deaerate by passing nitrogen over the surface of the solution for 15 min while the solution is being stirred.

Reduce the solution, to a potential limit of $+0{\cdot}15$ V *vs.* S.C.E., until the current falls below

2 mA. [Any iron(III) and plutonium(IV) present are reduced to iron(II) and plutonium(III) respectively: for "pure" uranyl solutions this step takes less than 30 sec and less than 0·3 C are required.]

Reduce the solution, to a potential limit of −0·20 V *vs.* S.C.E., until the current falls below 2 mA. Note the number of coulombs required. [The total time required for the reduction of 200 mg of uranium(VI) to uranium(IV) is about 7 min: almost 95% of the uranium(VI) is reduced at the maximum available current of 512 mA and thereafter the current is halved about every 20 sec until it drops below 2 mA.]

Calculate the amount of uranium in the portion of sample added as follows:-

$$\begin{matrix}\text{mg of uranium}\\ \text{in sample}\end{matrix} = G\left[\begin{matrix}\text{coulombs required,}\\ \text{extrapolated}\\ \text{to zero current}\end{matrix} - \begin{matrix}\text{blank}\\ \text{correction}\end{matrix}\right]$$

where G is the number of mg of uranium equivalent to 1 C (1·2335 for natural uranium).

When the current falls below 2 mA, the reaction is normally only 0·05–0·1 C short of completion. The blank correction is experimentally determined and normally amounts to about 0·2 C.

Anodizing the platinum working electrode. Cleaning the electrode surface by anodizing in sulphuric acid is essential. It is recommended that it should be carried out when the speed of a uranium(VI) reduction decreases to about one half that with a freshly anodized electrode, *i.e.*, after about eight determinations of uranium in "pure" uranyl nitrate solutions.

For the anodizing process, the cell is filled with $2M$ sulphuric acid, care being taken to exclude chloride, and a current of about 0·5 A passed for 5–10 min with the platinum working electrode acting as anode, so that oxygen is evolved. The cell and electrode are then washed thoroughly with water followed by $4{\cdot}5M$ hydrochloric acid before use.

New electrodes should be ignited at red heat for a few minutes before the anodizing process.

DISCUSSION

Variations on the final procedure

Reoxidation of uranium(IV) to obtain a confirmatory value. This may be usefully carried out in the case of pure uranium solution samples by first adding 1 ml of $1M$ iron(III) (a ferric alum solution is suitable) to the cell contents and then oxidizing the mixture to a potential limit of +0·65 V *vs.* S.C.E.

When calculating the uranium content from the number of coulombs used in the oxidation step, allowance must be made for any iron found to be present in the sample in the pre-reduction step, the incompleteness of the uranium reduction step, and the oxidation step "blank." These corrections should be comparatively small.

Without the iron(III) addition, the coulometric oxidation of uranium(IV) to (VI) does not proceed sufficiently rapidly.

Successive determination of plutonium and uranium in the same sample. Although the basic method can be used satisfactorily for the successive determination of plutonium(IV) and uranium(VI), in practice it is the determination of "total"—*i.e.*, all oxidation states—plutonium and "total" uranium that is usually required for fuel solutions. Since the plutonium may not be all in a single oxidation state in the sample received, all the plutonium must first be reduced to plutonium(III). Shults[4] has discussed this in detail. The plutonium(III) thus obtained is coulometrically oxidized to plutonium(IV) to obtain one estimate of the total plutonium. A confirmatory estimate is obtained on reduction back to plutonium(III), which must be done before the uranium can be determined. [Uranium is all present as uranium(VI) in fuel solutions normally encountered.]

To make this sequence of events practicable it was found necessary to add sulphuric acid to the base electrolyte. This makes the formal potential of the plutonium(III)/plutonium(IV) more negative, owing to complexing of the plutonium(IV) by sulphate, and enables cycling between the plutonium oxidation states to be accomplished without attack of the working electrode during the oxidation step.

The recommended changes to the experimental conditions of the basic method, to enable plutonium and uranium to be determined successively, are as follows:

Replace the 4·5*M* hydrochloric acid reagent recommended in the basic procedure by a mixture of equal volumes of 4*M* hydrochloric acid and 2*M* sulphuric acid.

Reduce to a potential limit of +0·20 V *vs*. S.C.E. to convert all the plutonium into plutonium(III).

Oxidize to a potential limit of +0·80 V *vs*. S.C.E. to convert all the plutonium into plutonium(IV).

Repeat the reduction to +0·20 V to reconvert all the plutonium into plutonium(III).

Determine the uranium(VI) by reduction to a potential limit of −0·20 V *vs*. S.C.E. as before.

The effects of bismuth(III)

From the work on electrodeposition from extremely dilute solutions described by both Haissinsky[5] and Rogers *et al.*[6,7], it is known that the deposition of sub-monatomic layers of metals on platinum and other "inert" metal cathodes can occur at potentials appreciably more positive than those predicted by the version of the Nernst equation applicable to an electrode entirely covered with the metal being deposited. The potential chosen for the uranium(VI)–(IV) reduction is about 50 mV more positive than that required to deposit macro-amounts of bismuth metal, and it would seem that a similar sub-monatomic layer of bismuth could be formed on the platinum working electrode under the conditions selected for the uranium reduction. The platinum surface will be non-uniform to some extent at the microscopic and submicroscopic levels, and it is likely that any bismuth which is deposited would first form a monatomic layer on the more reactive parts of the surface. It seems possible that this could provide the platinum electrode with protection against the occurrence of hydrogen evolution at its most vulnerable points by increasing the hydrogen overpotential at these locations. The same argument could of course be used to explain the inhibition of hydrogen evolution at the platinum electrode, caused by copper(I) and some of the other metal ions investigated.

It was also observed that the addition of bismuth or copper ions made electrode-surface poisoning effects less serious. This beneficial effect could be due to the formation of monatomic layers of bismuth or copper over some of the poisoned areas, thus increasing the usable surface area for the uranium(VI) reduction. [Comparative reductions of iron(III) and uranium(VI), made in the earlier work, indicated that it was possible for the same platinum surface to be apparently much more poisoned for the uranium(VI) reduction than for the iron(III) reduction. It seems feasible that a similar state of affairs might hold for the bismuth(III) and uranium(VI) reductions, enabling bismuth to be deposited on regions of the surface which were poisoned with respect to the uranium(VI) reduction.]

It is worth mentioning that bismuth(III) would not have the same effect in coulometric uranium reductions made in chloride-free perchloric, nitric or sulphuric acid base electrolytes. Macro-amounts of bismuth metal would electro-deposit from these base electrolytes at too positive a potential, *i.e.*, at about 0·0 V *vs*. S.C.E., interfering with the uranium(VI) reduction step. The usefulness of bismuth(III) in hydrochloric acid base electrolytes depends on the complexing of the bismuth(III) ion by chloride. This complexing shifts the potential at which macro-amounts of bismuth deposit, to the more negative values encountered in the procedure developed.

Interferences

A preliminary study indicated that appreciable amounts of phosphate, fluoride, molybdenum and mercury ions must be absent from the sample. Substantial amounts of iron, plutonium, nickel, cobalt, chromium(III), copper, cadmium, nitrate, sulphate, perchlorate and sulphamate ions may be present in the sample without effect on the uranium(VI) reduction in the final procedure.

Performance

Scrutiny of many past results from the analysis of uranium standard solutions showed that, for sample aliquots containing about 200 mg of uranium, the coefficient of variation applicable to a single determination is about 0·1% under "development" conditions and about 0·2% under routine analysis conditions, and results have less than 0·1% bias when the coulometer calibration is based on electrical measurements.

The procedure developed has been used successfully as a subsidiary method in the routine determination of uranium in pure uranyl nitrate solutions for uranium-accounting purposes during the past four years: several hundred samples have been analysed. A simplified controlled-potential-limit coulometer was employed for this routine work.

The amount of uranium taken and the cell design are important factors in determining the performance of the method. Under the recommended experimental conditions the "blank" correction needed amounts to less than 0·2% of the total number of coulombs used. If it was desired to scale down the procedure to enable much smaller amounts of uranium to be determined without undue loss of performance it would probably be necessary to decrease the cell volume while maintaining the electrode area : electrolyte volume ratio at the original value.

Zusammenfassung—Die experimentellen Bedingungen zur coulometrischen Bestimmung von Uran wurden ermittelt; man reduziert Uran(VI) zu Uran(IV) an einer Platin-Arbeitselektrode mit geregelter Spannung oder geregelter Grenzsapunnung. Dieses Verfahren wurde mit Erfolg als ergänzende Methode bei der Routinebestimmung von Uran in reinen Uranylnitratlösungen verwendet. Die Platinelektrode hat mehrere wichtige praktische Vorteile gegenüber der wohlbekannten Quecksilber-Sumpfelektode bei der coulometrischen Bestimmung von Uran. Die Bestimmungen von Eisen(III) und Uran(VI) oder von Plutonium(IV) und Uran(VI) nacheinander können mit derselben Arbeitselektrode in derselben Lösung ausgeführt werden; auch die coulometrische Oxidation von Uran(IV) zu Uran(VI) ist möglich. Die Rührgeschwindigkeit in der Zellflüssigkeit ist bei der Platinelektrode viel weniger kritisch. Zwei Hauptprobleme mußten gelöst werden, ehe ein praktisch verwertbares Verfahren zustande kam: die Wasserstoffentwicklung während der Reduktion mußte verhindert werden, damit die gewünschte Reaktion auf 100% Stromausbeute kam; ferner mußten Vergiftungserscheinungen der Elektrodenoberfläche unter Kontrolle gebracht werden, sodaß die Reaktionszeit hinreichend kurz gehalten werden konnte. Es zeigte sich, daß eine salzsaure Grundlösung mit ein wenig Wismut(III) die Wasserstoffentwicklung verhinderte; auch die Vergiftung der Elektrodenoberfläche war mit dieser Grundlösung nicht erheblich und ließ sich gering halten, wenn die Elektrode gelegentlich in verdünnter Schwefelsäure anodisch behandelt wurde. Wismut(III) bildet einen Komplex mit Chlorid; dessen Gegenwart erhöht die Wasserstoffüberspannung an der Arbeitselektrode. Während der Uranreduktion findet keine sichtbare Wismutabscheidung an der Elektrode statt. Nitrathaltige Lösungen können analysiert werden, wenn der salzsauren Grundlösung Amidosulfonsäure zugesetzt wird.

Résumé—On a établi les conditions expérimentales qui permettent la détermination coulométrique de l'uranium par réduction de l'uranium-(VI) en uranium(IV) sur une électrode de travail en platine, par des techniques de potentiel contrôlé ou de limite de potentiel contrôlé. La

technique a été utilisée avec succès comme méthode subsidiaire dans le dosage de routine de l'uranium dans des solutions de nitrate d'uranyle pures. L'électrode de platine a plusieurs avantages pratiques importants sur l'électrode de masse de mercure bien établie pour le dosage coulométrique de l'uranium. La détermination consécutive des fer(III) et uranium(VI), ou plutonium(IV) et uranium(VI) peut être menée avec la même électrode de travail dans la même solution et l'oxydation coulométrique de l'uranium(IV) en uranium(VI) est réalisable. La vitesse d'agitation de la liqueur de la cellule est beaucoup moins critique dans le cas de l'électrode de platine. Deux problèmes principaux ont dû être surmontés avant qu'une technique pratique ne puisse être réalisée; le dégagement d'hydrogène durant la réduction U(VI)–U(IV) a dû être éliminé de sorte qu'une efficacité de courant de 100% puisse être obtenue pour la réaction désirée, et les phénomènes d'empoisonnement de la surface d'électrode ont dû être contrôlés de sorte que le temps de réaction puisse être maintenu raisonnablement court. On a trouvé que la sélection d'une solution de base d'acide chlorhydrique contenant une petite quantité de bismuth(III) permet d'éviter le dégagement d'hydrogène: également, l'empoisonnement de la surface d'électrode avec cette solution de base n'est pas particulièrement sérieux et peut être maintenu à un bas niveau satisfaisant en anodisant occasionnellement l'électrode en acide sulfurique dilué. Le bismuth(III) forme un complexe avec les ions chlorure et sa présence accroît la surtension de l'hydrogène à l'électrode de travail: il ne se forme pas de dépôt visible de bismuth sur l'électrode durant la réduction de l'uranium. On peut analyser des échantillons contenant du nitrate, étant entendu que l'on ajoute de l'acide sulfamique à cette solution de base d'acide chlorhydrique.

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AMPEROMETRIC COMPLEX-FORMATION TITRATIONS OF TRACES OF COPPER

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Summary—Copper has been determined in the submicrogram range by means of a complexometric titration with triethylenetetramine (TRIEN), the end-point being detected by following the anodic wave of the chelating agent at a rotating mercury electrode. The influence of the presence of other metals has been investigated both from the theoretical and the experimental point of view. Because of its higher selectivity TRIEN is preferred to other reagents of the EDTA group. The results show that copper can be determined in the presence of large amounts of most other metals.

IN A PRELIMINARY communication[1] the principles of the amperometric complex-formation titration of metal ions with indication by means of the anodic wave of the excess of ligand, have been presented. The work of Campbell and Reilley,[2] who used a dropping mercury electrode, can be extended to a higher sensitivity by using a rotating mercury electrode as the indicator electrode. In the present paper the theoretical background of this type of titration will be treated more thoroughly. The theory will be illustrated by the determination of copper(II) with triethylentetramine (TRIEN).

THEORETICAL

Titration curves

Considering the titration reaction

$$M + L \rightleftharpoons ML$$

we suppose that changes in volume will be negligible and define $f = c_L/c_M$ as the titration parameter, which is a measure of the progress of the titration, having the value $f_e = 1$ at the equivalence point.

The formula for the titration curve can be derived from

$$K_M' = \frac{[ML]'}{[M]'[L]'} \tag{1}$$

$$c_M = [M]' + [ML]' \tag{2}$$

$$f = \frac{c_L}{c_M} = \frac{[L]' + [ML]'}{[M]' + [ML]'}. \tag{3}$$

Concentrations are primed according to Ringbom,[3] so that all side-reactions are taken into account, K_M' being the conditional constant.

In order to facilitate the handling of these formulae, we propose the use of relative concentrations, dimensionless numbers, defined as

$$m = \frac{[M]'}{c_M}; \qquad l = \frac{[L]'}{c_M}; \qquad ml = \frac{[ML]'}{c_M}.$$

The equations (1), (2) and (3) can now be written as

$$Z_M = K_M'c_M = \frac{ml}{m\,.\,l} \tag{4}$$

$$1 = m + ml \tag{5}$$

$$f = l + ml. \tag{6}$$

Z_M is another dimensionless quantity in which the effects of the analytical concentration of M and the conditional stability constant are combined.

As the experimental part of this paper describes titrations with monitoring of the ligand L, it is useful to find f as a function of l. The titration curve can easily be derived from (4), (5) and (6):

$$f = l + \frac{Z_M l}{1 + Z_M l} = f_1 + f_2. \tag{7}$$

So for the graphical construction of f as a function of l we have to add the linear $f_1 = l$ and the orthogonal hyperbola $f_2 = (Z_M l/1 + Z_M l)$, illustrated in Fig. 1.

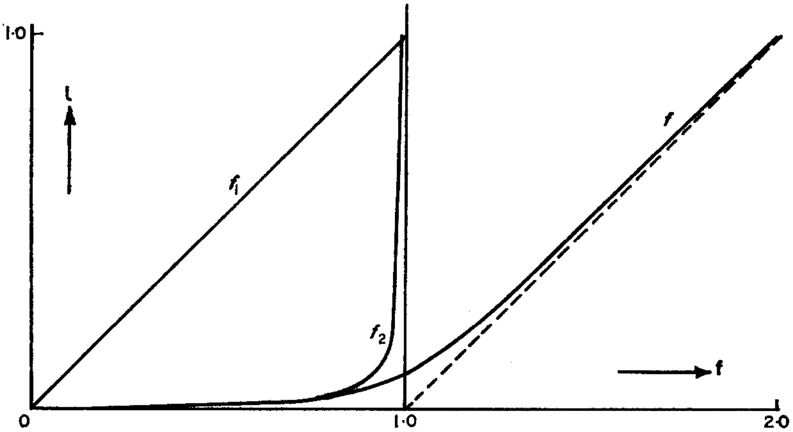

FIG. 1.—l-f curve:

$$f = f_1 + f_2 = l + \frac{Zl}{1 + Zl} \quad \text{for} \quad Z = 100.$$

It is obvious that the shape of the (f–l)-curve and the (f–[L])-curve will be identical. For the calculation of the titration error we will assume that the end-point of the titration will be found graphically by intersecting the tangents for $l = 0$ and $l = 1$ (Fig. 1). As $\mathrm{d}f/\mathrm{d}l = 1 + Z_M/(1 + Z_M l)^2$, these tangents are given by:

$$f = \left(\frac{\mathrm{d}f}{\mathrm{d}l}\right)_0 l = (1 + Z_M)l \sim Z_M l \tag{8}$$

and

$$f = \left(\frac{\mathrm{d}f}{\mathrm{d}l}\right)_1 (l - 1) + f_1,$$

where f_1 is the value of f in the titration curve (7) for $l = 1$, or

$$f = \left\{1 + \frac{Z_M}{(1 + Z_M)^2}\right\}(l - 1) + 1 + \frac{Z_M}{1 + Z_M}$$

which for $Z_M \gg 1$ simplifies to

$$f \sim \left\{1 + \frac{1}{Z_M}\right\} l + 1 - \frac{2}{Z_M}. \tag{9}$$

The tangents (8) and (9) intersect in f_s. It can easily be found that $f_s = 1 - 1/Z_M$. The systematic titration error is therefore,

$$\Delta = -\frac{1}{Z_M}. \tag{10}$$

In earlier work[4] it has been suggested to take $1/\sqrt{Z_M} = m_{f=1} = l_{f=1}$ as a measure of the sharpness. As $1/Z_M$ is directly related to the systematic titration error we propose to use this value as the measure of sharpness. If we accept a systematic error of 1% the value of $Z_M = K'c_M$ has to be greater than 100.

Titration of mixtures of metals

The titration curve for the complexometric titration of two metals M and N has been derived in a previous paper. When the metal N is considered to be an interfering metal it is better to use $f = c_L/c_M$ instead of $f = c_L/(c_M + c_N)$ as was done in the previous paper.[5] With introduction as before of the relative concentration $n = [N]'/c_M$, the titration curve will, in the new notation, change to

$$f = l + \frac{Z_M l}{1 + Z_M l} + \frac{c_N}{c_M} \cdot \frac{Z_N l}{(1 + Z_N l)} \tag{11}$$

$$= f_1 + f_2 + f_3. \tag{12}$$

As we consider the metal N as an interference in the titration of M the complex NL will be much weaker than ML. The titration curve will only have the required linear shape when f_3 is pseudolinear. If we accept a deviation from linearity of 1% we can consider f_3 to be pseudolinear if

$$Z_N l < 10^{-2}. \tag{13}$$

We can then write (11) as

$$f = (1 + K_N'c_N)l + \frac{Z_M l}{1 + Z_m l}. \tag{14}$$

The factor $(1 + K_N'c_N)$ is the side-reaction coefficient of the side-reaction of L caused by the presence of N. Taking into account this side-reaction coefficient $\alpha_{L(N)}$ in Z_M, equation (14) can be written as

$$f = l' + \frac{Z_M'l'}{1 + Z_M'l'} \tag{15}$$

in which $l' = (1 + K_N'c_N)l = \alpha_{L(N)}l$
and

$$Z_M' = \frac{Z_M}{\alpha_{L(N)}}.$$

The new sharpness criterion will be

$$Z_M' = \frac{K_M' c_M}{1 + K_N' c_N} \geqslant 100. \tag{16}$$

The largest value of l' in practical work will be $l' = 1$. The largest value of l therefore will be

$$l = \frac{1}{1 + K_N' c_N}.$$

Substitution in equation (13) leads to the condition for linearity

$$Z_N l = \frac{K_N' c_M}{1 + K_N' c_N} \leqslant 10^{-2}. \tag{17}$$

The presence of the interfering metal N causes a decrease in the slope of the titration curve after the equivalence point by a factor $\alpha_{L(N)}$ and therefore a decrease in the sensitivity of the determination of M. In trace determinations of M we will often work near the limit of sensitivity of the indication system, in which case only a relatively small reduction of the slope can be tolerated.

When a reduction of 50% in the slope is allowed, we get the condition

$$K_N' c_N < 1 \tag{18}$$

and when a decrease of sensitivity by a factor n can be allowed, the sensitivity condition becomes

$$K_N' c_N \leqslant (n - 1). \tag{19}$$

Recapitulating, we may conclude that the titration of M in the presence of a metal N can be carried out when three conditions are fulfilled, a sharpness criterion, *cf.* equation (16), a condition for linearity, *cf.* equation (17) and a sensitivity condition, mentioned in equation (19).

Up to now we have supposed that the indication signal was perfectly linear in l. In the titrations that will be described the linearity is limited to values of l smaller than 0·1.

It can easily be shown that drawing the tangent at $l = 0{\cdot}1$ will change the sharpness condition to

$$Z_M' = \frac{K_M' c_M}{1 + K_N' c_N} \geqslant 2 \times 10^3 \tag{20}$$

and the linearity condition to

$$\frac{K_N' c_M}{1 + K_N' c_N} \leqslant 10^{-1}. \tag{21}$$

The sensitivity condition, *cf.* equation (19) remains unaltered. The conditions derived above for a sharp indication can only be applied under equilibrium conditions. At low concentrations the conditions for sharp end-points will sometimes be kinetically determined. As our knowledge of the complex-formation and the corresponding stability constants is still incomplete, predictions may sometimes fail.

Anodic indication of L

The reaction at the indicator electrode used for the indication of the excess of ligand is the oxidation of mercury from the electrode according to the reaction

$$\mathrm{Hg^0 + L - 2e \rightarrow HgL}$$

The equation of the corresponding reversible polarographic wave at an ordinary DME is

$$E_{\mathrm{L}} = E_0 - 0{\cdot}03 \log K_{\mathrm{HgL}} + 0{\cdot}03 \log \alpha_{\mathrm{L(N)}} + 0{\cdot}03 \log \frac{\bar{k}_{\mathrm{L}}}{k_{\mathrm{HgL}}} + 0{\cdot}03 \log \frac{i}{i_{\mathrm{d}} - i} \qquad (22)$$

The ligand will be present as a mixture of several protonated forms. In equation (21) it is assumed that all these forms have the same diffusion coefficient $\bar{k}_{\mathrm{L}}$. The limiting current i_{d} will be proportional to the sum of the concentrations of all these forms.

The useful potential range for the indication can be found by comparing the wave of the free ligand [equation (22)] with the current–voltage curve for the anodic dissolution of mercury in the absence of the free ligand, which can be represented by

$$E_{\mathrm{Hg}} = E_0 - 0{\cdot}03 \log \alpha_{\mathrm{Hg}} - 0{\cdot}03 \log \bar{k}_{\mathrm{Hg}} + 0{\cdot}03 \log i \qquad (23)$$

where α_{Hg} is the side-reaction coefficient taking into account all side-reactions of mercury(II) with the exception of the reaction between mercury(II) and L.

Two possible current voltage curves are given in Fig. 2. The suitable potential range ΔE can be found by subtracting E_{L} from E_{Hg} for a suitable value of i. We then get

$$\Delta E = E_{\mathrm{Hg}} - E_{\mathrm{L}} = 0{\cdot}03 \log K_{\mathrm{HgL}} - 0{\cdot}03 \log \alpha_{\mathrm{L(H)}} - 0{\cdot}03 \log \alpha_{\mathrm{Hg}}$$

$$+ 0{\cdot}03 \log \frac{k_{\mathrm{HgL}}}{\bar{k}_{\mathrm{Hg}} \bar{k}_{\mathrm{L}}} + 0{\cdot}03 \log (i_{\mathrm{d}} - i)$$

$$\Delta E = 0{\cdot}03 \log K'_{\mathrm{HgL}} + 0{\cdot}03 \log \frac{k_{\mathrm{HgL}}}{\bar{k}_{\mathrm{Hg}} \bar{k}_{\mathrm{L}}} + 0{\cdot}03 \log (i_{\mathrm{d}} - i). \qquad (24)$$

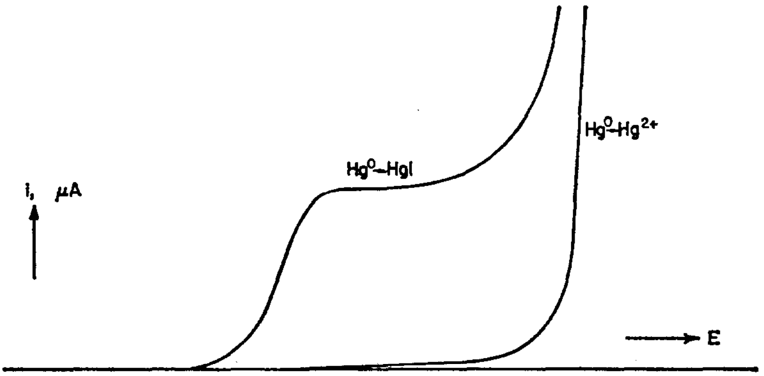

FIG. 2.—Anodic dissolution wave of mercury in the presence and in the absence of the ligand.

The result, as could be expected, is that the useful potential range is directly related to the conditional constant K'_{HgL} of the complex HgL.

The main advantages of anodic amperometry for indication in complexometry are that the method can be used for the titration of nearly all metal ions giving stable complexes, independent of the cathodic behaviour, and the possibility of using a working potential more positive than the half-wave potential of the first reduction wave of oxygen. Reilley and Campbell[2] have given a table of the potential ranges for anodic amperometry in several buffered media.

A rotating mercury electrode has the advantage over a dropping electrode that currents are appreciably larger, that no capacity currents occur, and that there are no current fluctuations due to the growth and fall of the drop. These effects result in a lower limit of determination.

The useful potential range has been discussed above on the basis of reversibility of the reaction at the electrode. However, reactions reversible at the DME might be irreversible at a rotating mercury electrode. In general it can be stated that polarograms at the rotating mercury electrode are not as well developed as at the DME. Moreover the shape of the polarograms depends on the condition of the mercury electrode. Especially when an acid solution is used, a diffusion plateau can hardly be observed. In these and a number of other cases a working potential has to be chosen in a rising part of the current–voltage curve of the free ligand.

As part of the applied voltage is lost in the *iR*-drop, which is not constant, but rises after the end-point of the titration, the potential of the mercury anode shifts to more negative values, resulting in a deviation of the titration curve from linearity. The ascending part of the titration curve bends towards the *f*-axis, as illustrated in Fig. 3. This is the reason why the titrations at a rotating mercury electrode are generally not carried further than to about 10% beyond the end-point.

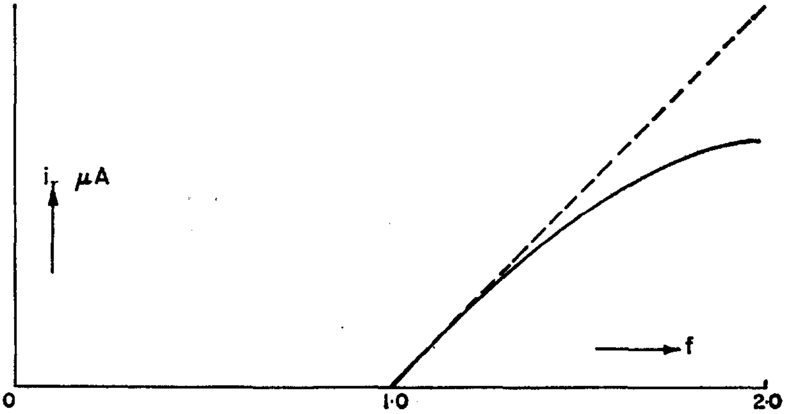

FIG. 3.—Effect of *IR*-drop on indication current after the end-point.

EXPERIMENTAL

Chemicals

Pro analysi chemicals were used. Impurities in the buffer solutions were determined by means of a blank titration. The water used was singly distilled and traces of copper still present were removed by ion-exchange.

Apparatus

Polarograms necessary for the selection of the suitable potential of the indicator electrode were registered with the Metrohm polarograph E 261, using the rotating electrode as working electrode. The titrations were performed in a 10-ml compartment of an H-cell, containing the rotating mercury electrode. The titrant was added from a Metrohm 1-ml syringe burette. The other compartment of the H-cell, separated from the first by a fritted glass disc, was filled with the same supporting electrolyte solution as was the titration compartment, and contained a calomel electrode.

The amperometric titrations were carried out by means of a simple polarographic circuit with a Philips d.c. microammeter PM 2436 for current measurements. As this meter has a higher sensitivity than the polarograph it was preferred for the titrations of low concentrations.

The rotating mercury electrode (750 rpm) consisted of a small piece of platinum wire (25 mm length; 0·75 mm diameter) sealed into glass. The platinum microelectrode is covered with mercury, either by direct electrolysis in a mercury(I) nitrate solution for 1 hr at a current of 10 mA, or by successive electrolyses in a solution of a gold(III) salt and a mercury(I) nitrate solution, both for 1 hr at a current of 10 mA. The electrodes last for a few weeks, after which the mercury layer has to be renewed.

RESULTS

TRIEN was preferred for the determination of copper(II) because of the high value of the stability constant of the complex and the relatively high selectivity compared with the polyaminopolycarboxylic acids. In general, titrations of copper(II) in acid solution are preferred because of the higher selectivity. Determinations in alkaline solution in the presence of other metals will generally require masking. However the anodic wave of TRIEN in a tris-buffer [tris(hydroxymethyl)methylamine] in alkaline solution at pH 9 is much better developed than in acid solution, so that a number of determinations have been carried out at this pH.

For the determinations in acid solution a pH-value of 5 was chosen. At pH 5 $\log K'_{\mathrm{CuL}} = 9{\cdot}4$. According to equation (18) the limit of determination would be somewhat less than $10^{-6}M$.

In Table I some results are given for determinations of copper(II) in $0{\cdot}01M$ acetate buffer at pH 5. The results agree very well with the theoretical predictions.

In Table II some results are given for determinations of $6 \times 10^{-6}M$ copper(II) in the presence of other metals, and in Table III the corresponding results are given for $6 \times 10^{-7}M$ copper(II). The buffer concentration was $0{\cdot}01M$ in all cases.

The amounts of other metals present, mentioned in Tables II and III, are about the maximum allowable limits found experimentally. The interference of more than 1000-fold amounts of metals such as nickel(II), zinc(II) and cadmium(II) can be explained by means of equation (17) derived in the theoretical part.

At pH 5, $\log K'_{\mathrm{NiL}} = 3{\cdot}0$, so when $c_{\mathrm{Ni}} = 6 \times 10^{-3}M$ as in the first experiment of Table II, the product $K'_{\mathrm{NiL}} \cdot c_{\mathrm{Ni}} = 6$ which is not in agreement with condition (18). In this experiment the decrease of the slope after the equivalence point was indeed more than 50%. The maximum allowable amounts of zinc(II), cadmium(II) and cobalt(II)

TABLE I.—DETERMINATION OF Cu(II) WITH TRIEN IN $0{\cdot}01M$ ACETATE BUFFER AT pH 5, VOLUME 5 ml

Cu(II)			Error	Std. devn., %	Titrant concentration
	Amount, μg				
Concentration	Present	Found	%	(no. of detns.)	M
6×10^{-6}	1·90	1·91	0·5	1·3 (8)	10^{-4}
6×10^{-7}	0·190	0·188	−2	1·3 (8)	10^{-5}
6×10^{-8}	0·019	0·021	+10	20 (8)	10^{-6}

TABLE II.—DETERMINATION OF 1·9 μg OF Cu(II) WITH $10^{-4}M$ TRIEN; VOLUME 5 ml

Amount of other metal relative to that of copper		Error, %	Std. devn., % (no. of detns.)	Buffer, masking
Ni	1000	−1·7	1·3(8)	acetate pH 5
Zn	1000	0·0	1·3(8)	acetate pH 5
Cd	1000	−1·2	0·7(8)	acetate pH 6
Cr(III)	1000	−0·6	1·0(8)	acetate pH 6
Pb	10000	0·0	0·6(8)	acetate pH 5
Pb	100000	+2·2	0·7(8)	acetate pH 5
Co	10000	−1·3	1·0(8)	acetate pH 5
Mg	100000	−1·0	1·3(8)	acetate pH 6
Mn(II)	100000	+0·6	0·7(8)	acetate pH 6
Ca	100000	+2·2	1·0(8)	acetate pH 6
Zn	100	−0·6	1·0(8)	Tris pH 9, $10^{-3}M$ NTA
Pb	1000	+1·2	2·0(8)	Tris pH 9, $10^{-3}M$ NTA
Mg	10000	−1·2	1·0(8)	Tris pH 9
Fe(III)	1000	+2·2	1·0(8)	Tris pH 9, citrate
Fe(III)	1000	0·0	0·3(8)	Tris pH 9, oxalate + NTA
Al 1000 + Fe(III) 1000		−0·6	0·7(8)	Tris pH 9, oxalate + NTA

TABLE III.—DETERMINATION OF 0·19 μg OF Cu(II) WITH $10^{-5}M$ TRIEN: VOLUME 5 ml

Amount of other metal relative to that of copper		Error, %	Std. devn., % (no. of detns.)	Buffer, masking
Ca	100000	−0·6	4·0(8)	acetate pH 6
Pb	100000	+4·5	3·3(8)	acetate pH 6
Mg	100000	+2·0	3·7(8)	acetate pH 6
Cd	100000	−1·0	3·7(8)	acetate pH 6
Mn	100000	−2·7	2·0(8)	acetate pH 6
Co	100000	−5·4	7·0(8)	acetate pH 6
Zn	1000	−8·0	3·3(6)	acetate pH 6
Zn	500	−3·3	3·7(8)	acetate pH 6
Ni	1000	+5·0	7·7(4)	acetate pH 6
Ni	200	−1·4	1·3(8)	acetate pH 6
Al	10000	+6·0	4·0(8)	Tris pH 9, oxalate + NTA
Fe(III)	1000	+8·0	2·7(8)	Tris pH 9, oxalate + NTA

TABLE IV.—TITRATION OF 1·9 μg OF Cu(II) ($6 \times 10^{-6}M$) WITH $10^{-4}M$ TRIEN; VOLUME 5 ml

Interference	Error, %	Std. devn., %	Buffer solution
0·01M chloride	−0·7	0·7	0·01M acetate, pH 6
1M chloride	+2·2	1·0	0·8M Tris, pH 9
0·01M bromide	+2·6	0·7	0·01M Tris, pH 9

Note: The time required for all titrations mentioned above is only a few minutes for each.

can be roughly explained in the same manner. The condition given by equation (20) is fulfilled in all experiments mentioned in Tables II and III.

In some cases sample solutions may contain compounds forming complexes with mercury(II), resulting in a current during the whole titration. When such a current is small, titrations can be carried out when the interfering current is electrically compensated. In this way it is possible to carry out the titrations of copper(II) with TRIEN as mentioned above, even in the presence of large amounts of chloride and bromide. Table IV shows some results of such titrations.

Zusammenfassung—Kupfer wurde im Submikrogrammbereich durch komplexometrische Titration mit Triäthylentetramin (TRIEN) bestimmt. Der Endpunkt wurde durch Beobachtung der anodischen Stufe des Chelatbildners an einer rotierenden Quecksilberelektrode ermittelt. Der Einfluss anderer Metalle wurde vom theoretischen und experimentellen Standpunkt aus untersucht. Wegen seiner höheren Selektivität ist TRIEN anderen Reagentien aus der EDTA-Gruppe vorzuziehen. Die Ergebnisse zeigen, dass Kupfer in Gegenwart grosser Mengen der meisten anderen Metalle bestimmt werden kann.

Résumé—On a dosé le cuivre dans le domaine du submicrogramme au moyen d'un titrage complexométrique avec la triéthylènetétramine (TRIEN), le point de fin de dosage étant détecté en suivant la vague anodique de l'agent chelatant sur une électrode de mercure rotative. On a étudié l'influence de la présence d'autres métaux, tant du point de vue théorique qu'expérimental. A cause de sa plus haute sélectivité, on préfère le TRIEN aux autres réactifs du groupe EDTA. Les résultats montrent que l'on peut doser le cuivre en la présence de grandes quantités de la plupart des autres métaux.

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SILICA GEL AS A SUPPORT FOR INORGANIC ION-EXCHANGERS FOR THE DETERMINATION OF CAESIUM-137 IN NATURAL WATERS

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Summary—The preparation and characteristics of ammonium molybdophosphate and potassium or ammonium hexacyanocobalt ferrate supported in silica gel, and their application to the determination of ^{137}Cs in natural waters are described. Use of columns of these materials gives better recovery of ^{137}Cs from natural waters (in comparison with co-precipitation with ammonium molybdophosphate), requires less exchanger, so raising the γ-counting efficiency of ^{137}Cs, and permits elimination of other radionuclides by washing with hydrofluoric acid.

SINCE Smit[1] revealed the excellent ion-exchange properties of ammonium molybdophosphate, especially for potassium, rubidium, caesium, silver, mercury(I) and thallium(I), this exchanger has been used for the separation of alkali metals and especially for the radiochemical determination of ^{137}Cs in biological materials, natural waters, sea-water, *etc*,[2-5] but recovery of caesium from sea-water was only 70–80% in large-scale operations.[4,5] If an appropriate column method is available, ^{137}Cs can be concentrated from large volumes of natural waters more efficiently and conveniently. Smit has proposed a column consisting of a physical mixture of the heteropoly acid salt and asbestos fibre[6,7] or filter paper pulp,[8] and of coarse particles of the insoluble ammonium salt of 12-molybdophosphate (AMP),[9] because asbestos or filter paper pulp would reduce the bed capacity per unit volume. The difficulty was to prepare the coarse AMP since it was usually accompanied by a substantial proportion of very fine crystals.

Prout, Russel and Groh[10] have recently described potassium hexacyanocobalt ferrate (KCFC) as an inorganic exchanger and the material was employed by Boni[11] to concentrate radiocaesium from biological and environmental samples such as milk, urine, sea-water and fresh water. Petrow and Levine[12] have recommended ammonium hexacyanocobalt ferrate (NCFC) as an improved exchange material for radiocaesium, because the ammonium salt can obviate the interference by the decay of the potassium in KCFC, in the ^{137}Cs region of the γ-spectrum.

The lack of any satisfactory procedure for elution of the adsorbed caesium made it impossible to reduce the volume of the counting sample and to raise the counting efficiency for γ-activity with an NaI crystal detector. Moreover, a large amount of exchanger had to be thrown away after only one use, since a simple regeneration procedure had not been found. A more convenient material for enrichment of ^{137}Cs from large volumes of natural waters would therefore be desirable.

The present paper describes a simple method of preparing such materials, which will be called AMP-SiO_2, KCFC-SiO_2 or NCFC-SiO_2, and their successful application to natural waters, including sea-water.

EXPERIMENTAL

Reagents

Radioactive nuclides. Caesium-137 as caesium chloride, and cerium-144, cobalt-60, ruthenium-106, strontium-90, zinc-65 and zirconium-95.

Silica gel. Chromatographic grade (WAKOGEL C-100).

Other chemicals. Caesium sulphate used as carrier was of guaranteed reagent-grade, and ammonium molybdate, ammonium monohydrogen phosphate, ammonium nitrate, nitric acid, sodium hexacyanoferrate, potassium hexacyanoferrate and cobalt(II) nitrate were of chemically pure reagent-grade.

Apparatus

Scintillation counter. Well-type, with 45 × 50 mm NaI(Tl) crystal.

G-M counter. Mica-window tube, 28 mg/mm^2, 11·7% counting efficiency for ^{90}Sr(^{90}Y).

γ-Ray spectrometer. Low-background model with transistorized single-channel pulse-height analyser, high-speed scaler and printing scaler.

Glass chromatographic columns. Internal diameter 9·8, 12 and 17 mm, length 140 mm, with a coarse sintered-glass disc and a stop-cock at the bottom.

Preparation of AMP-SiO$_2$

About 240 g of silica gel (42–60, 60–80 and 80–100 mesh) were put into a solution of 100 g of ammonium molybdate and 6 g of ammonium monohydrogen phosphate in 400 ml of distilled water and stirred occasionally. After standing for about 2 hr the contents were heated in an electric air-bath at 105° for a day. The dried material was transferred into a beaker containing a solution of 10 g of ammonium nitrate in 300 ml of 3*M* nitric acid and heated to about 80° on a hot water-bath (with occasional stirring) and digested at that temperature for 3 hr, then the mixture was filtered (coarse cotton cloth spread over a 2-l. beaker) and the residue was washed with distilled water to remove free AMP as thoroughly as possible. The material was transferred on the cloth to a Buchner funnel and covered with another piece of cloth, and was left under suction till almost dry. Finally, the dried material was heated at about 105° for a day and was sieved into 42–60, 60–80 and 80–100 mesh fractions.

Preparation of KCFC-SiO$_2$

About 100 g of silica gel (42–60 and 60–80 mesh) were put into a beaker containing about 200 ml of 0·5*M* potassium hexacyanoferrate and stirred occasionally. After standing for about 2 hr the supernatant liquid was decanted. The impregnated silica gel was then transferred (glass spoon) into a beaker containing about 500 ml of 0·3*M* cobalt(II) nitrate solution, with continuous stirring. A dark green precipitate appeared immediately on the surface of the silica gel. The contents of the beaker were stood for about 2 hr with occasional stirring, then the supernatant liquid and free KCFC were poured off and the remaining KCFC-SiO$_2$ was washed with distilled water; this treatment was repeated until the supernatant liquid became clear. Finally, the product was dried at 115° in an electric air-bath for about 20 hr until it changed colour to purple. The product was sieved (42–60 and 60–80 mesh) and stored in polyethylene bottles.

Preparation of NCFC-SiO$_2$

About 100 g of silica gel (42–80 mesh) were put into a beaker containing about 200 ml of 0·5*M* sodium hexacyanoferrate solution, with occasional stirring. After standing for about 2 hr the supernatant liquid was decanted. The impregnated silica gel was transferred (glass spoon) into a beaker containing about 500 ml of 0·3*M* cobalt nitrate in 0·1*M* ammonium nitrate solution, with continuous stirring. The contents were then treated in the same way as KCFC-SiO$_2$.

Ion-exchange column preparation

The chromatographic tube was filled with a water slurry of 10 g of water-washed 60–80 mesh exchange material. A piece of absorbent cotton was placed on top of the material so that the bed was not disturbed during sample addition. The cotton should be changed several times if a sample contains suspended matter.

Procedure for the determination of ^{137}Cs in a large volume of sample

A volume of water sample to which had been added 70 μg (15 μg for KCFC- or NCFC-SiO$_2$) of Cs$^+$ as carrier and about 1 ml of nitric acid per litre to keep strontium in solution, was passed through the column at a flow-rate of 6–8 l./hr under slight suction from a water-pump, and the effluent was stored in a polyethylene bottle for strontium-90 measurement.

After all the sample had passed through the column, the cotton plug was removed and most of the exchanger was pushed out of the column under air-pressure, then the rest was washed out with a small amount of distilled water. The exchanger was collected in a 50-ml polyethylene centrifuge tube. The water was decanted and *ca.* 30 ml of 46% hydrofluoric acid were added dropwise with occasional shaking. After complete dissolution of the silica the tube was centrifuged for about 20 min at 3000 rpm. The supernatant liquid was rejected and the residue was washed with distilled water and centrifuged twice more. The final residue was transferred with a small amount of ethyl alcohol into a shallow plastic dish having a cover (i.d. *ca.* 60 mm) and was dried under an infrared lamp; its γ-activity was counted with a low-background γ-ray spectrometer.

RESULTS AND DISCUSSION

Characteristics of the exchange materials

AMP-SiO$_2$. The amount of AMP on the silica gel was calculated from the phosphorus content, determined spectrophotometrically as molybdenum blue after dissolution of the AMP in aqueous ammonia (1 + 9). The results obtained are shown in Table I. The increase in loading as the particle-size decreases is probably due to the increase in surface area.

TABLE I.—CHARACTERISTICS OF THE EXCHANGE MATERIALS

Material (M)	Mesh size	M supported, *g* of M/*g* of M-SiO$_2$	Exchange capacity, *mequiv* of Cs/*g* of M-SiO$_2$	Max. flow-rate, *l./hr*
AMP-SiO$_2$	42–60	0·113	0·069 (9·5 mg)	9·0
	60–80	0·187	0·079 (10·8 mg)	7·2
	80–100	0·204	0·101 (13·8 mg)	2·5
KCFC-SiO$_2$	42–60	0·025	0·014 (1·9 mg)	11·5
	60–80	0·029	0·019 (2·6 mg)	8·6
NCFC-SiO$_2$	60–80	0·028	0·018 (2·5 mg)	8·1

The exchange capacity for caesium was measured by passing 100 ml of sea-water, containing about 1·7 mequiv of caesium sulphate, ^{137}Cs tracer and 0·1 ml of nitric acid, at 1 drop/min through a column containing 2 g of the material, dissolving the exchanger with 10 ml of 5*M* sodium hydroxide and heating, making up to standard volume and measuring the γ-activity of an aliquot with a well-type scintillation counter.

KCFC-SiO$_2$ or NCFC-SiO$_2$. The amount of KCFC or NCFC supported on silica gel (Table I) was calculated from the cobalt, iron and potassium or ammonium content of the materials, after removal of silica with hydrofluoric and sulphuric acids. Iron was determined as iron(III) oxide after extraction with IBMK–pentyl acetate solvent mixture, and cobalt as cobalt(III) oxide after precipitation of its 1-nitroso-2 naphthol salt from the aqueous phase. Potassium was determined flame-photometrically and ammonium spectrophotometrically.

The exchange capacity of the KCFC- or NCFC-SiO$_2$ for caesium was measured in the same way as for AMP-SiO$_2$. The exchanger was completely decomposed by hydrofluoric and sulphuric acid treatment and the residue dissolved with hydrochloric acid.

The exchange capacities of AMP-, KCFC- and NCFC-SiO$_2$ for caesium are considered large enough for caesium to be collected by them from large volumes (*e.g.*, 80 or 100 l.) of sea-water, the caesium contents of which have been reported as 0·3–0·8 μg/l.[13–16] This means that the operating capacity of 10 g of AMP-SiO$_2$ (60–80 mesh) is about 19 times the total amount of caesium in 80 l. of sea-water (to which 5·6 mg of Cs+ have been added as carrier) and that of 10 g of KCFC- or NCFC-SiO_2 (60–80 mesh) is at least 17 times the total amount of caesium in 100 l. of sea-water (to which 1·5 mg of Cs+ have been added as carrier). In the case of fresh water the situation will be more favourable since its caesium content is supposed to be comparable to or less than that of sea-water.

The last column in Table I shows the maximum attainable flow-rate for columns containing 5 g of adsorbing material of different sizes. Exchanger of 60–80 mesh size is the most suitable for treatment of large volumes of sample because the exchange capacity for caesium is higher than that of 42–60 mesh material and the maximum attainable flow-rate is higher than that of 80–100 mesh material.

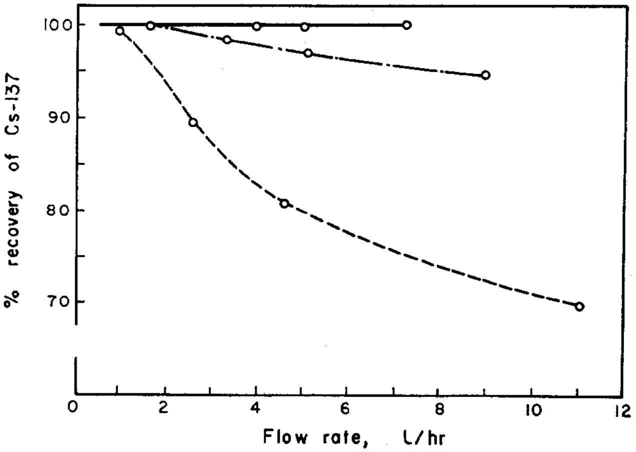

FIG. 1.—Relationship between the flow-rate and recovery of ^{137}Cs.
—O— 5 g of AMP-SiO_2
--O-- 2 g of AMP-SiO_2
—O-— 1 g of AMP-SiO_2
Sample, 3 l. of sea-water; 12-mm diameter column.

It was also confirmed that ^{137}Cs is not adsorbed by silica gel itself from a water sample containing the specified amount of nitric acid.

Effect of flow-rate

It was expected that the operating capacity of the exchanger would be related to the flow-rate of water sample. The results for 1, 2, 3 and 5 g of 60–80 mesh exchange material are shown in Figs. 1 and 2. The maximum attainable flow-rates for 1, 2, 3 and 5 g of the exchanger were about 15, 11, 9 and 7·2 l./hr respectively for AMP-SiO_2, and 30, 18, 13 and 8·6 l./hr for KCFC-SiO_2. Quantitative adsorption might be expected if 5 g of either exchanger were used with a flow-rate less than 7 l./hr.

Effect of volume of sample

Two exchanger columns (12 mm bore, 80 mm length, 5 g of 60–80 mesh exchanger), were connected vertically in series and sea-water containing caesium carrier and tracer was passed through them. After passage of each 20 l. of sample, a fresh lower column was substituted and the flow was continued until 100 l. of sample had passed through. Then the ^{137}Cs adsorbed on each exchanger was measured as described above. The

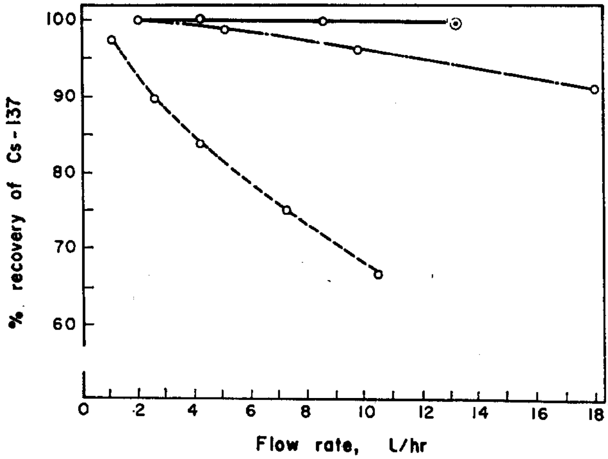

FIG. 2.—Relationship between the flow-rate and the recovery of ^{137}Cs.
—O— 5 g of KCFC-SiO$_2$
—⊙— 3 g of KCFC-SiO$_2$
—O— 2 g of KCFC-SiO$_2$
---O--- 1 g of KCFC-SiO$_2$
Sample, 3 l. of sea-water; 12-mm diameter column.

results are illustrated in Fig. 3. Adsorption was nearly quantitative for the first 40 l. of sample and then decreased rapidly. Larger amounts of sample may be treated if a wider column is used with a larger amount of exchanger; *e.g.*, 80–100 l. (60–80 mesh) of sea-water and tap-water were treated with 10 g of exchanger in a 17 × 80 mm column and the yield was satisfactory at a flow-rate of about 10 l./hr for AMP-SiO$_2$, and also for KCFC-SiO$_2$ (Fig. 3).

Effect of caesium carrier

Although the caesium content of sea-water is reported to be 0·3–0·8 μg/l., it was found that addition of caesium carrier enhanced the adsorption yield of ^{137}Cs on the exchanger. The effect of caesium sulphate as carrier was therefore examined. The results are shown in Table II. For sea-water the effect of the carrier was not remarkable, but for tap-water it was very appreciable, *e.g.*, the recovery of caesium by AMP-SiO$_2$ increased from 87·6 to 98·8% on addition of 0·07 ppm of caesium carrier. However, larger amounts of carrier decreased the adsorption of ^{137}Cs. Consequently, the amount of caesium carrier, especially in fresh water, is critically important.

Other factors affecting adsorption of ^{137}Cs

When sea-water is passed through AMP-SiO$_2$, the yellow colour of the material fades gradually as AMP dissolves, but the addition of 1 ml of nitric acid per litre of water prevents this, the pH of the sample becoming about 2, the most favourable for formation of ammonium molybdophosphate. When the acidified sample is introduced into the column through an ordinary rubber tube, reduction of AMP occasionally occurs and the exchanger becomes dark blue. A polyethylene tube

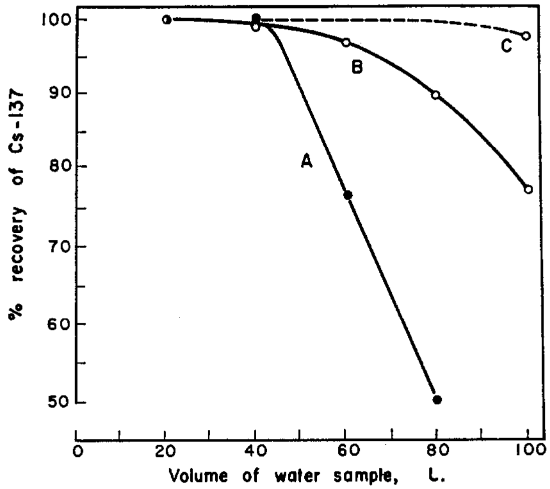

FIG. 3.—Relationship of the volume of sample and recovery of ^{137}Cs.
A: AMP-SiO_2, 5 g; column 12-mm bore.
B: KCFC-SiO_2, 5 g; column 12-mm bore.
C: KCFC-SiO_2, 10 g; column 17-mm bore.
Flow-rate 6 l./hr.

TABLE II.—EFFECT OF ADDITION OF CAESIUM CARRIER ON RECOVERY OF ^{137}Cs

Exchanger (5 g)	Cs added (as Cs_2SO_4),* ppm	Recovery of ^{137}Cs, %	
		Sea-water†	Fresh water
AMP-SiO_2	0	97·3	87·6
	0·07	98·6	98·8
KCFC-SiO_2	0	98·9	86·7
	0·015	99·1	98·7

* 40-l. samples; flow-rate 7 l./hr.
† Sea-water contained 0·0005 ppm Cs originally.

has no such effect and should therefore be used. The temperature of the sample water has no effect in the range 5–35°.

Adsorption properties for other radionuclides

As a check, recovery experiments for other radionuclides believed to exist in sea-water were carried out after addition of a known amount of each to 3 l. of sea-water which contained the amounts of caesium carrier and nitric acid mentioned above. The samples were processed with 5 g of exchanger. at a flow-rate of 3 l./hr. It was found that AMP-SiO_2 scarcely adsorbed other radionuclides except for radiozirconium–niobium, about 12% of the original amount being adsorbed, but KCFC-SiO_2 can concentrate not only ^{137}Cs, but 34% of radiocerium, 29% of radiocobalt, 15% of radioruthenium–rhodium, 26% of radiozinc and 24% of radiozirconium–niobium as shown in Table III. However, it was thought that the degree of adsorption of these nuclides might decrease considerably when a large volume of sea-water was treated, and this was confirmed by the 3·5% adsorption of radiozirconium–niobium when

40 l. of doped sea-water were passed through the AMP-SiO_2 column. Table III shows that AMP-SiO_2 is more selective than KCFC-SiO_2 for ^{137}Cs. Radiostrontium was not adsorbed at all. NCFC-SiO_2 behaved similarly to KCFC-SiO_2.

TABLE III.—RECOVERY OF VARIOUS RADIONUCLIDES

Radionuclide	Adsorbed by		Remaining after HF treatment	
	AMP-SiO_2 (5 g) %	KCFC-SiO_2 (5 g) %	AMP-SiO_2 %	KCFC-SiO_2 %
^{137}Cs	99*	100	95	100
^{144}Ce–^{144}Pr	0·2	34	0	0
^{60}Co	0·3	29	0	0
^{106}Ru–^{106}Rh	0·4	15	0	0
^{90}Sr–^{90}Y	0	0	0	0
^{65}Zn	0·7	26	0	0
^{95}Zr–^{95}Nb	12·1	24	0	0
^{95}Zr–^{95}Nb	3·5	—	0	0

* Sample: 40 l. of sea-water.

However, as it was impossible to match the chemical forms of the active species used in these experiments with those present in sea-water, the results given in Table III are not in themselves conclusive evidence of recovery of the radionuclides in a sample. Either way, these adsorbed radionuclides have to be removed from the exchanger before the activity measurement of ^{137}Cs. After several tests it was found that the interfering nuclides adsorbed could be easily eliminated by dissolution of the silica in hydrofluoric acid, whereby the nuclides other than ^{137}Cs went into solution while ^{137}Cs was held on the AMP and KCFC or NCFC because these adsorbents are not readily attacked by hydrofluoric acid. As shown in Table III, during the treatment with hydrofluoric acid about 4% of the caesium was lost from the solid phase (AMP-SiO_2), but the other nuclides could be eliminated completely from the exchanger. The loss of ^{137}Cs from KCFC- or NCFC-SiO_2 was negligible. Furthermore, this procedure reduces the volume of the counting sample, and the counting efficiency for Cs-137 is increased by about 20%.

Effect of the potassium in KCFC

According to Petrow *et al.*,[12] the contribution of potassium-40 γ-radiation in 8 g of KCFC to the caesium region of the spectrum was equivalent to 10 pCi of ^{137}Cs. The counting system used by us is closely similar to theirs, but the amount of KCFC used is only about 250 mg, which should produce a response of about 0·3 pCi of Cs-137 in the caesium region. However, the blank value for KCFC-SiO_2 was less than 0·1 pCi, which was only about 0·5% of the total count, so the exchanger itself was regarded as without effect on the results.

Determination of ^{137}Cs in surface sea-water

Table IV shows the results of ^{137}Cs analyses, by the present method, of four surface water samples collected from the Japan Sea. Counting was done with a gamma-ray spectrometer for about 20 hr to obtain sufficient total counts to minimize the statistical counting error. These values are in satisfactory agreement with those determined by Miyake *et al.*[17] (who employed the ordinary co-precipitation method with

TABLE IV.—CS-137 CONTENT OF SURFACE WATER OF JAPAN SEA (AUGUST, 1967)

St. No.	Lat. N	Long. E	Cs-137, pCi/l.* a	b	c
5	38°06′	134°27′	0·26 ± 0·01	0·23 ± 0·01	0·24 ± 0·04
12	41°02′	132°15′	0·22 ± 0·01	0·22 ± 0·01	0·21 ± 0·04
15	40°14′	135°12	0·22 ± 0·01	0·20 ± 0·01	
18	39°31′	138°11′	0·23 ± 0·01	0·23 ± 0·01	

* a Data obtained with AMP-SiO_2 method.
b Data obtained with KCFC-SiO_2 method.
c Data obtained by Miyake *et al.*

ammonium molybdophosphate) for surface water samples collected from the same station of the Japan Sea at the same time.

CONCLUSION

Caesium-137 can be separated almost quantitatively from large volumes of natural waters with AMP-SiO_2 and KCFC- or NCFC-SiO_2 chromatographic columns. AMP-SiO_2 is more easily prepared than coarse AMP crystals and more convenient to use than AMP-asbestos, because of its mechanical strength and homogeneity. In spite of their exchange capacity being smaller than that of ordinary AMP and KCFC, AMP-SiO_2 and KCFC-SiO_2 can catch ^{137}Cs quantitatively even at high flow-rate of sample. This fact seems to indicate a highly effective adsorption surface and a rapid ion-exchange process in the columns.

The apparatus for the enrichment of ^{137}Cs is so simple that it is readily used on board ship, for freshly collected samples.

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Zusammenfassung—Darstellung und Eigenschaften von auf Silicagel aufgezogenem Ammoniummolybdophosphat und Kalium- oder Ammoniumhexacyanokobaltferrat sowie ihre Anwendung auf die Bestimmung von ^{137}Cs in natürlichen Wässern werden beschrieben. Säulen aus diesen Materialien geben bessere Ausbeuten an ^{137}Cs aus natürlichen Wässern (verglichen mit der Mitfällung mit Ammoniummolybdophosphat), erfordern weniger Austauscher, wodurch die γ-Zählausbeute von ^{137}Cs ansteigt, und ermöglichen die Entfernung anderer Radionuklide durch Wachen mit Flußsäure.

Résumé—On décrit la préparation et les caractéristiques de molybdophosphate d'ammonium et d'hexacyanocobalt-ferrate de potassium ou d'ammonium supportés en gel de silice, et leur application au dosage de ^{137}Cs dans les eaux naturelles. L'emploi de colonnes de ces produits donne une meilleure récupération de ^{137}Cs d'eaux naturelles (par comparaison à la co-précipitation avec le molybdophosphate d'ammonium), nécessite moins d'échangeur, élevant ainsi l'efficacité du comptage γ de ^{137}Cs, et permet l'élimination d'autres radionucléides par lavage à l'acide fluorhydrique.

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ATOMIC-FLUORESCENCE CHARACTERISTICS AND ANALYTICAL DETERMINATION OF MANGANESE IN AN AIR-ACETYLENE FLAME

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Summary—The atomic-fluorescence characteristics of manganese atoms in a premixed nitrogen-shielded air–acetylene flame are described. Excitation is obtained at 280 nm from a microwave-excited electrodeless discharge tube. A detection limit of 0·001 ppm for the determination of manganese by atomic-fluorescence spectroscopy is obtained by measurement of the resonance fluorescence observed at this wavelength. In addition to several other weaker atomic-fluorescence signals observed from manganese atoms in the flame, weak resonance fluorescence at 258 and 260 nm from manganese ions stimulated by ion line-emission from the source has been recorded. Linear calibration graphs for atomic-fluorescence measurement at 280 nm are obtained over the range 0·0025–10 ppm of manganese in aqueous solution. Of 26 foreign anions and cations examined for interference at the 1000-fold weight excess level only four produced interference. Large amounts of Si, Th and V interfere by scattering of the incident radiation, while Mg causes depression of the atomic fluorescence by a chemical effect.

Atomic fluorescence has been observed for manganese at 279·5 nm, a 150-W xenon arc source being used for excitation, in air–hydrogen, air–propane and hydrogen–oxygen–argon flames, with detection limits of 0·15, 0·3 and 1 ppm respectively.[1,2] Ellis and Demers[3] reported a detection limit of 0·004 ppm at 279·5 nm for the atomic fluorescence of manganese, and used a 450-W xenon arc source. In the general application of electrodeless discharge tubes and particular instrumental detection systems to the detection of atomic fluorescence for a range of elements, both Winefordner *et al.*[4] and West and co-workers[5] have observed the atomic fluorescence of manganese at 279·5 nm, the detection limits being 0·006 and 0·014 ppm in an argon–hydrogen diffusion flame[4] and an air–hydrogen flame[5] respectively.

The detection and determination of manganese by flame emission spectroscopy (FES) and atomic-absorption spectroscopy (AAS) is well established. Recently, several very low detection limits have been obtained for manganese by FES: 0·1 ppm in an oxy-acetylene flame, (Fassel and Golightly[6]), 0·1 ppm in an air–acetylene flame and 0·024 ppm in a premixed oxygen-enriched air–acetylene flame (Chapman and Dale[7]), and 0·005 ppm in a premixed nitrous oxide–acetylene flame (Pickett and Koirtyohann[8]); all at 403·1 nm. Hobbs, Kirkbright and West[9] have reported detection of manganese by FES in a nitrogen-shielded air–acetylene flame; the detection limit obtained in the conventional air–acetylene flame at 403·3 nm was 0·1 ppm, while with the shielded flame a detection limit of 0·01 ppm was obtained. Several workers have studied the determination of manganese by AAS. Beyer[10] and Slavin[11] obtained detection limits (at 279·4 nm) of 0·05 and 0·005 ppm respectively. The manganese line at 403·3 nm is less sensitive and Allen[12] reports spectral interference at the manganese 403·3073 nm line from the gallium line at 403·2982 nm. Silicon appears to be the only major chemical interference, and the addition of lanthanum has been reported to suppress this.[13] To the best of our knowledge no study of the atomic-fluorescence spectral characteristics of manganese has been reported, nor one of the analytical utility of manganese atomic fluorescence in an air–acetylene flame. This paper describes the preparation and properties of the microwave-excited electrodeless discharge tubes employed as sources, and the sensitive and selective determination of manganese by atomic-fluorescence spectroscopy in a nitrogen-shielded air–acetylene flame. A comparison has been made with flame emission spectroscopy, the same detector system being used.

EXPERIMENTAL

Apparatus

A Unicam SP 900A flame spectrophotometer was employed. The use of this instrument for AFS has been described elsewhere.[1] The indirect cyclone nebulizer unit of this instrument was employed without modification. The nebulizer spray rate was 3 ml/min at the pressures used. An EMI 9601B photomultiplier was fitted in place of the standard EMI 9529B supplied with this instrument, to obtain higher sensitivity in the ultraviolet region.

The manganese electrodeless discharge tube was operated at 2450 MHz with a 200-W Microtron 200 Mark II power generator and three-quarter wave Broida-type resonant cavity (Electromedical Supplies, Ltd., Wantage, Type 210L). The cavity was modified by the addition of a side-wall tuning stub. The tube output was modulated at 50 Hz as previously described.[14]

A premixed air–acetylene flame was used throughout this investigation. Nitrogen shielding was used to separate the secondary diffusion zone from the primary reaction zone, the burner being the type described by Hobbs, Kirkbright and West.[9] The burner head was placed 50 mm in front of the monochromator entrance slit. The rim of the flame-shield device was raised so that the monochromator did not view the primary zone. In fluorescence measurements the source was positioned at 90° to the burner–monochromator axis and in the same horizontal plane, so that the distance between the electrodeless discharge tube and the centre of the flame was 50 mm.

Reagents

Manganese stock solution. A 1000-ppm stock solution was prepared by dissolving 3·60 g of crystalline manganese(II) chloride (analytical grade) in 1 litre of $0{\cdot}5M$ hydrochloric acid. This solution was diluted as required immediately before use.

Diverse ions. Solutions were prepared from analytical-reagent grade salts.

ATOMIC FLUORESCENCE SPECTROSCOPY

Preparation of electrodeless discharge tube

The preparation of manganese electrodeless discharge tubes from manganese(II) iodide and manganese,[4] manganese(II) iodide,[15] manganese(II) chloride[5] and the element and chlorine[16] has previously been reported. In this study these methods of preparation were examined in an attempt to produce the most stable and intense tubes which had good operating life times. The tubes were prepared by the general procedure described elsewhere.[16] Argon-filled tubes were found to be more stable and to have a longer operating life time than those containing helium. The most satisfactory results were obtained for tubes which contained *ca.* 1 mg of manganese(II) chloride (analytical-reagent grade $MnCl_2 . 4H_2O$ dehydrated under vacuum) and an argon filler-gas pressure of 4 mbar.

Operation and spectral characteristics of manganese discharge tube

The electrodeless discharge tubes were operated in the three-quarter wave resonant cavity with a power input of 50 W. After an initial running-in period of between 1 and 2 hr, only a 5-min warm-up period was required after initiation of the discharge. After this warm-up and under these operating conditions, the line-to-background ratios at 279·4 nm and 403·1 nm were typically greater than 100:1, while the short term output stability of the radiation at these wavelengths was ±3%. The discharge obtained exhibits the lines of the resonance spectrum of manganese. The tubes also emit the most intense lines of the Mn(II) spectrum, *i.e.*, from the $3d^5$ $4s^1$ $a\,{}^7S_3$ ion. The presence of these ionic lines does not appear to impair the analytical usefulness of the tubes for atomic-fluorescence work. The relative intensities of the most useful manganese lines obtained with these operating conditions are shown in Table I.

TABLE I.—AFS RELATIVE SOURCE AND FLUORESCENCE INTENSITIES AND DETECTION LIMITS

Wavelength, *nm*	Spectrum*	Transition† (refs. 18, 19)	Relative intensities from source§	Relative fluorescence intensities§	Limit of detection for manganese, *ppm*
257·6	II	$a\,{}^7S_3 - z\,{}^7P_4{}^0$	34	12	1·5
259·4	II	$a\,{}^7S_3 - z\,{}^7P_3{}^0$	33	8	12
260·6	II	$a\,{}^7S_3 - z\,{}^7P_2{}^0$	32	8	12
279·5	I	$a\,{}^6S_{5/2} - y\,{}^6P_{7/2}{}^0$	100‡	100‡	0·001‡
279·8	I	$a\,{}^6S_{5/2} - y\,{}^6P_{5/2}{}^0$			
280·1	I	$a\,{}^6S_{5/2} - y\,{}^6P_{3/2}{}^0$			
293·3	II	$a\,{}^5S_2 - z\,{}^5P_1{}^0$	2	4‡	90‡
293·9	II	$a\,{}^5S_2 - z\,{}^5P_2{}^0$	5		
294·9	II	$a\,{}^5S_2 - z\,{}^5P_3{}^0$	6	3	90
304·5	I	$a\,{}^6D_{5/2} - v\,{}^6P_{7/2}{}^0$	4	11	30
357·8	I	$a\,{}^6D_{5/2} - x\,{}^6P_{7/2}{}^0$	8	7	50
383·4	I	$a\,{}^6D_{5/2} - z\,{}^6F_{7/2}{}^0$	6	8	67
403·1	I	$a\,{}^6S_{5/2} - z\,{}^6P_{7/2}{}^0$	312‡	49‡	0·02‡
403·3	I	$a\,{}^6S_{5/2} - z\,{}^6P_{5/2}{}^0$			
403·4	I	$a\,{}^6S_{5/2} - z\,{}^6P_{3/2}{}^0$		30‖	

* Normal state of valence electrons: Mn(I) $3d^5\,4s^2\,{}^6S_{5/2} = 0$; Mn(II) $3d^5\,4s^1\,{}^7S_3 = 0$.

† Lowest state of Mn(I) is $a\,{}^6S_{5/2}$ and of Mn(II) $a\,{}^7S_3$.

‡ Unresolved lines.

§ Relative to 280-nm triplet, and uncorrected for response characteristics of photomultiplier.

‖ Relative intensity at 403 nm with 280-nm source radiation filtered out.

Atomic fluorescence measurements

When 10-ppm manganese solutions were nebulized into the air-acetylene flame with the electrodeless discharge tube in operation, atomic-fluorescence signals were observed at each of the wavelengths shown in Table I. The most intense fluorescence was obtained from the 280- and 403-nm triplet lines which arise from transitions to the ground state. The individual lines of these triplets were unresolved with the spectral band-pass available. The use of an optical wide-band filter to prevent irradiation of the flame by the 280 nm radiation from the source revealed that the fluorescence emission signal at 403 nm orginated from both resonance fluorescence and some stepwise fluorescence from deactivation of the excited $y\,{}^6P_{3/2}{}^0$, $y\,{}^6P_{5/2}{}^0$ and $y\,{}^6P_{7/2}{}^0$ state atoms by radiationless transitions to the $z\,{}^6P_{3/2}{}^0$, $z\,{}^6P_{5/2}{}^0$ and $z\,{}^6P_{7/2}{}^0$ excited states. The use of an optical filter to prevent irradiation of the flame by the 403-nm radiation from the source, revealed as expected that excitation at 403 nm did not contribute to the fluorescence radiation observed at 280 nm.

The suitability of both fluorescence signals (280 and 403 nm) for the analytical determination of manganese was investigated. Lower flame background intensity, lower thermal emission intensity for manganese and freedom from spectral interference[12] is observed at 280 nm, however, and all analytical AFS measurements were made at this wavelength.

The emission at 260 nm for the most intense lines of the Mn(II) spectrum has been observed to stimulate ionic resonance fluorescence from manganese in the $3d^5\,4s^1$, $a\,^7S_3$ ionic state in the air–acetylene flame. Assuming that thermal equilibrium prevails in the air–acetylene flame, the calculated degree of ionization produced when a 10-ppm manganese solution is nebulized into a nitrogen-shielded air–acetylene flame at 2450 K is $0{\cdot}6 \times 10^{-3}\%$. Although the population of ions is low, the *gf* values (*i.e.*, products of the statistical weights and oscillator strengths) and source intensities of the 257·6, 259·4 and 260·6 Mn(II) lines are high. The net result is a resonance ionic fluorescence signal of appreciable intensity. Although the *gf* values of the Mn(II) lines at 293·3, 293·9 and 294·9 nm are high, the source intensities at these lines are low and they are not due to transitions to the ground state. For this reason, and because of the relatively high background at these wavelengths, only very weak ionic fluorescence was observed at these wavelengths. The fluorescence from manganese ions was suppressed at all the observed lines on addition of 1000 ppm of potassium as potassium chloride to the solutions nebulized.

Optimum operating conditions

The use of both conventional unshielded and nitrogen-shielded air–acetylene flames was investigated. At 280 nm the atomic-fluorescence signal intensity was reproducibly 30% greater in the shielded flame and the signal noise levels obtained were decreased by a factor of 2 on shielding. The nitrogen-shielded air–acetylene flame was chosen for all further measurements and a nitrogen flow-rate of 14 l./min was employed.

The most intense fluorescence at 280 nm was obtained with an air flow-rate of 6·5 l./min and an acetylene flow-rate of 1·1 l./min (the ranges investigated were 5–7·5 and 0·9–1·4 l./min respectively). De Waele and Harjadi[17] have reported the relation of the optimum burner height to concentration of manganese in atomic-absorption spectroscopy. Although we found an optimum height of observation in the flame, it was not markedly dependent on concentration. With the optimum burner height the monochromator views the interconal region of the flame between *ca.* 6 and 26 mm above the burner head.

The effect of variation of the monochromator slit-width on the atomic-fluorescence signal-to-background noise ratio was investigated under otherwise optimum conditions. The optimum slit-width at 280 nm was 0·4 mm; this corresponds to a spectral bandwidth of approximately 1·6 nm. The use of a lens to focus radiation from the source into the flame did not improve the attainable detection limit for manganese.

Calibration data and detection limits

With the optimum operating conditions established, linear atomic-fluorescence calibration graphs were obtained at 280 nm over the range from 0·0025 to 10 ppm of manganese in aqueous solution. The fluorescence at 280 nm suffers self-absorption above 10 ppm and at above this concentration the calibration graphs curve towards the concentration axis. Linear atomic-fluorescence calibration graphs were obtained over the range 0·1 to 15 ppm of manganese in aqueous solution when fluorescence measurements were made at 403 nm.

The detection limits obtained at each of the ten wavelengths for which atomic fluorescence was observed are shown in Table I. The detection limit was defined as that concentration of manganese in aqueous solution which produced a signal equivalent to twice the standard deviation of the background noise measured near the limit of detection.

Interference studies

The effect, on the atomic fluorescence intensity produced at 280 nm by a 0·5-ppm manganese solution, of the presence of a 1000-fold excess by weight of a range of cations and anions has been examined. The results of this investigation are summarized in Table II. Of the 26 ions studied at this concentration only 4 produced serious interferences; three of the most refractory elements (thorium, silicon and vanadium) gave a positive interference by particulate scattering of incident radiation from the source. Two of these, thorium and silicon, gave negligible interferences when only a 100-fold weight excess was employed. Magnesium seriously reduced the fluorescence signal even when only a 100-fold weight excess was present. Magnesium similarly depressed the manganese atomic-absorption signal and apparently interferes by reducing the population of manganese atoms in the flame. The interference of silicon in the atomic-absorption spectrophotometry of manganese has previously been reported and the use of lanthanum as a releasing agent proposed.[13]

TABLE II.—EFFECTS OF FOREIGN IONS ON FLUORIMETRIC DETERMINATION OF 0·5 ppm OF MANGANESE AT 280 nm

Effect on AFS signal	Foreign ion (1000-fold weight excess)
No interference	Cr^{3+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Al^{3+}, Mo^{6+}, Cd^{2+}, Pb^{2+}, PO_4^{3-}, SO_4^{2-}, NO_3^-, NH_4^+, Na^+, Th^{4+*}
Negligible interference (<3%)	K^+, Ca^{2+}, Ba^{2+}, W^{6+}, Hg^{2+}, Si^{4+*}, Sn^{2+}, Ta^{5+}, Ga^{3+}
Interference	Th^{4+}(+4%), Si^{4+}(+5%), V^{5+}(+16%), V^{5+*}(+8%), Mg^{2+}(−39%), Mg^{2+*}(−11%)

* 100-fold weight excess.

FLAME EMISSION SPECTROSCOPY

Investigation of the detection of manganese by flame emission spectroscopy was made both in the conventional and nitrogen-shielded flames, and the optimum operating conditions established. The effect of variation of acetylene flow-rate between 0·9 and 1·2 l./min on the emission intensity at 403 nm was investigated. The optimum acetylene flow-rate was found to be 1·07 l./min for both unshielded and shielded flames. The effect of varying the air-flow rate between 6·5 and 7·5 l./min was also investigated. For the unshielded flame an optimum air flow-rate of 7·0 l./min was used, while for the nitrogen-shielded flame the optimum flow-rate was 7·5 l./min. The optimum flow-rate for the nitrogen shielding gas for this latter flame was found to be 14 l./min.

With these optimum conditions, the optimum height of observation was found to be in the region 13–33 mm above the burner head for both flames.

The optimum slit-widths and the detection limits at each wavelength are shown in Table III. The use of the most intense line emission, at 403 nm, gives rise to the lowest detection limit.

TABLE III.—SUMMARY OF DETECTION LIMITS BY FLAME EMISSION

Wavelength*, *nm*	Unshielded flame		Shielded flame	
	Slit width, *mm*	Limit of detection, *ppm*	Slit width, *mm*	Limit of detection, *ppm*
279·5 279·8 280·1	0·175	0·08	0·19	0·05
354·78 354·80	0·08	1·5	0·13	1·2
356·95 356·98	0·08	1·0	0·12	1·0
403·1 403·3 403·4	0·04	0·02	0·09	0·01

* All lines were unresolved.

ATOMIC ABSORPTION

Reference has already been made to the many studies of the atomic-absorption spectrophotometry (AAS) of manganese. A brief study of the AAS of manganese was made with the same apparatus as described here for fluorescence measurements, adapted as reported in an earlier paper from this laboratory.[14] The limits of detection for an aqueous manganese solution were found to be 0·1 and 0·4 ppm at 279·5 and 403·1 nm respectively.

CONCLUSION

This study indicates that manganese may be determined with extremely high sensitivity by atomic-fluorescence spectroscopy when a high-intensity source of radiation is used. The apparatus we have employed was originally designed for flame emission spectroscopy. Consequently, while this apparatus permits the sensitive detection of manganese by atomic-emission spectroscopy, the attainable sensitivities for manganese by atomic-absorption spectroscopy are poorer than those reported by other workers using instrumentation specifically designed for atomic-absorption work. The atomic-fluorescence detection limit obtainable is *ca.* one order of magnitude lower than the best attainable flame emission detection limit. Good selectivity is also available in the determination of manganese by atomic-fluorescence spectroscopy using the flame and nebulizer system described. Some physical scattering interference in the presence of high concentrations of elements which form refractory oxides in the air–acetylene flame has been observed, and chemical interference from magnesium has also been recorded.

TABLE IV.—DETECTION LIMITS FOR MANGANESE

Wavelength, *nm*	Detection limits, *ppm*		
	Atomic fluorescence	Atomic absorption	Flame emission
280	0·001	0·1	0·05
403	0·02	0·4	0·01

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Zusammenfassung—Die Atomfluoreszenzeigenschaften von Manganatomen in einer vorgemischten Luft-Acetylen-Flamme mit Stickstoffmantel werden beschrieben. Eine mit Mikrowellen erregte elektrodenlose Entladungsröhre dient zur Anregung bei 280 nm. Messung der Resonanzfluoreszenz bei dieser Wellenlänge führt zu einer Nachweisgrenze von 0,001 ppm für die atomfluoreszenzspektrometrische Bestimmung von Mangan. Außer mehreren anderen schwächeren Atomfluoreszenzsignalen von Manganatomen in der Flamme wurde schwache Resonanzfluoreszenz bei 258 und 260 nm an Manganatomen registriert, die durch Linienemission von Ionen aus der Lichtquelle angeregt wurde. Im Bereich 0,0025 bis 10 ppm Mangan in wäßriger Lösung werden bei 280 nm lineare Eichkurven bei der Atomfluoreszenzmessung gefunden. Unter den 26 bei 1000-fachen Überschuß untersuchten fremden Anionen und Kationen störten nur vier. Große Mengen Si, Th und V stören durch Streuung der einfallenden Strahlung, während Mg die Atomfluoreszenz durch einen chemischen Effekt vermindert.

Résumé—On décrit les caractéristiques de fluorescence atomique d'atomes de manganèse dans une flamme air–acétylène préalablement mélangés et protégée à l'azote. On obtient l'excitation à 280 nm à partir d'un tube à décharge sans électrode excité aux micro-ondes. On obtient une limite de détection de 0,001 p.p.m. pour la détermination du manganèse par spectroscopie de fluorescence atomique en mesurant la fluorescence de résonance observée à cette longueur d'onde. En addition à plusieurs autres signaux de fluorescence atomique plus faibles observés à partir d'atomes de manganèse dans la flamme, on a enregistré une faible fluorescence de résonance à 258 et 260 nm à partir d'ions manganèse provoqués par émission de raie d'ion de la source. On obtient des graphiques d'étalonnage linéaires pour la mesure de fluorescence atomique à 280 nm dans le domaine 0,0025–10 p.p.m. de manganèse en solution aqueuse. Des 26 anions et cations étrangers examinés pour leur interférence en quantité 100 fois supérieure, quatre seulement apportent une gêne. De grandes quantités de Si, Th et V interfèrent par dispersion de la radiation incidente, tandis que Mg cause un abaissement de la fluorescence atomique par une influence chimique.

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REDOXAUSTAUSCHER UND IHRE ANWENDUNGEN—XV

REDUKTION VON EISEN(III) AN REDOXITEN UND ANSCHLIEẞENDE OXYDIMETRISCHE BESTIMMUNG*

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Zusammenfassung—Als Beispiel für die Reduktion von Kationen an Redoxiten wird die quantitative Reduktion von 50 bis 200 mg Eisen(III) in schwefelsaurer Lösung an einem Leukomethylenblau- und Ferrocen-Harz auf Polystyrolbasis beschrieben. Im Durchlauf wird Eisen(II) potentiometrisch mit 0,1*N* Cer(IV)-sulfatlösung bestimmt. Unter optimalen Bedingungen ergibt sich im Bereich von 100 bis 200 mg Eisen eine Standardabweichung von ±0,04 bis ±0,14 mg. Im Gegensatz zu Metallreduktioren stören Cu^{2+}, Bi^{3+}, TiO^{2+}, Sn^{4+}, Ce^{4+} und AsO_4^{3-} nicht. Die Methode wurde zur Direktbestimmung von Eisen in Erzen, Martinschlacke und Spezialstählen angewendet.

OXYDIMETRISCHE Bestimmungen behaupten sich in der Makro- bis Halbmikroanalyse neben photometrischen Methoden, da sie zuverlässig sind und oft weniger durch Begleitelemente gestört werden.[1,2] Die ihnen vorausgehende Reduktion des zu bestimmenden Stoffes erfolgt meist in einer Säule mit aufgeschichteten Metallkörnern (Jones-Reduktor),[3,4] gelegentlich flüssigen Amalgamen[1,5] und seltener durch gelöste Reduktionsmittel. Bekannteste Beispiele sind die Reduktionen von Eisen(III) oder Transuranen am Cadmiumbzw. Blei-Reduktor für anschließende quantitative Bestimmungen oder Trennungen.

Im Jahre 1952 haben Sansoni[6] und Cassidy[7] unabhängig voneinander die von ihnen entwickelten Redoxaustauscher[7,8,9] als unlösliche Jones-Reduktoren vorgeschlagen. Die erste analytische Anwendung[10] beschrieb einen mit Anthrahydrochinon beladenen Anionenaustauscher, an dem von 50 bis 100 mg Eisen(III) in schwefelsaurer Lösung 96% als Eisen(II) im Durchlauf wiedergefunden wurden.[10,11] Später verwendeten Erdey, Inczédy und Markovits[12] am Anionenaustauscher gebundenes Chlorostannat(II) in 3*M* Salzsäure bei erhöhter Temperatur. Inczédy[13] arbeitete im Citratpuffer bei pH 6 mit 0,025–1 mg Eisen am Variaminblau-Kationenaustauscher.

Wesentlich allgemeiner anwendbar sind jedoch unlösliche Redoxite mit kovalent eingebauten Redoxsystemen. Sie sind auch für stark saure bis stark alkalische Medien geeignet und verunreinigen die Lösung nicht mit eluierten Redox-Ionen.

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* XIV. Mitteilung R. Winkler, B. Sansoni, K. Starke, *Chem. Zvesti*, 1967, **21**, 571. XII. Mitteilung B. Sansoni, R. Winkler, K. Starke, *Angew. Chem.* 1966, **78**, 645. Vorgetragen GDCH-Fachgruppe "Analytische Chemie," Stuttgart 1960 (Referat *Angew. Chem.*, 1961, **72**, 569) sowie XX. IUPAC-Kongreß Moskau 1965 (Abstracts E/F, S. 94). Herrn Prof. Dr. R. Klement, München, zum 70. Geburtstag.

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§ Publication delayed at authors' request.

Störungen durch ionenaustauschende Gruppen entfallen. Aus diesen Gründen hatten wir bereits im Jahre 1953 ein Polystyrolharz mit nachträglich chemisch eingebautem Leukomethylenblau eingesetzt.[10,11] Jedoch war die anschließende oxydimetrische Titration mit Permanganat zu ungenau,[14] da etwas Leukomethylenblau ausblutete und die Erkennung des Farbumschlags des Permanganates störte.

Im folgenden wird die quantitative Reduktion von Eisen(III) zu Eisen(II) an verbesserten Redoxiten beschrieben. Die anschließende Eisenbestimmung erfolgt mit Cer(IV) und potentiometrischer Endpunktsanzeige. Im Verlauf der Arbeit werden die allgemeinen Arbeitsbedingungen analytischer Anwendungen von Redoxiten studiert und mit denen bei Ionenaustauschern verglichen.

THEORETISCHER TEIL

Als Redoxite standen das Tonmineral Nontronit[15] sowie Polystyrolharze mit chemisch eingebautem Ferrocen,[16] Leukomethylenblau[10,11] und Anilinohydrochinon[17] nach Sansoni und Sigmund zur Verfügung. Die beiden ersteren übertragen nur Elektronen, die beiden letzteren zusätzlich Protonen. Eisen(III) wird an den genannten Redoxiten in schwefelsaurer Lösung nach dem Schema

$$\mathrm{Fe^{3+}} + \boxed{\mathrm{R}} \rightleftharpoons \boxed{\mathrm{R^+}} + \mathrm{Fe^{2+}} \qquad \text{oder} \tag{1}$$

$$2\mathrm{Fe^{3+}} + \boxed{\mathrm{H_2R}} \rightleftharpoons \boxed{\mathrm{R}} + 2\mathrm{Fe^{2+}} + 2\mathrm{H^+} \tag{2}$$

reduziert.

Die Gleichgewichtskonstante K für die Reduktion von Eisen(III) am Redoxit in beliebigem Medium ergibt sich nach

$$-\Delta G = RT.\ln K = n \cdot F \cdot \Delta E_{50\%} \tag{3}$$

unter den üblichen thermodynamischen Voraussetzungen für 25° zu

$$\log K = \frac{n}{0{,}0591} \cdot \Delta E_{50\%}$$

$$\text{bzw. } K = 10^{(n/0{,}0591)\cdot \Delta E_{50\%}}. \tag{4}$$

Darin bedeutet ΔG die Änderung der Freien Energie während eines Formelumsatzes, n die Anzahl der übertragenen Elektronen, F die Faradaykonstante und $\Delta E_{50\%}$ [Volt] die Differenz der Realpotentiale $E_{50\%}$ beider Teilreaktionen im jeweiligen Medium:

$$\Delta E_{50\%} \equiv E_{50\%,\mathrm{Fe^{2+}/Fe^{3+}}} - E_{50\%,\mathrm{Redoxit}}. \tag{5}$$

Die Reduktion sollte freiwillig ablaufen, wenn

$$-\Delta G = n \cdot F \cdot \Delta E_{50\%} > 0. \tag{6}$$

$E_{50\%}$ kann aus Abb. 1 als Ordinatendifferenz entnommen werden. Dort sind die von Bock und Herrmann[18] gemessenen Realpotentiale des $\mathrm{Fe^{2+}/Fe^{3+}}$-sulfates für verschiedene Mineralsäuren in Abhängigkeit von deren Konzentration und die Realpotentiale der Redoxite in Abhängigkeit von der Schwefelsäurekonzentration aufgetragen.[9,19] In erster Näherung wird dabei angenommen, daß die Potentiale der Redoxite unter reversiblen Bedingungen gemessen wurden und unabhängig von der

Art der verwendeten Mineralsäuren sind.[19] Da diese Bedingungen nicht streng erfüllt sind, sind hier nur halbquantitative Aussagen möglich.

Danach läßt sich voraussehen, daß Eisen(III) in Perchlorsäure an allen vier Redoxiten vollständig, in Schwefelsäure und Salzsäure nur an den drei Redox-Harzen glatt, an Nontronit teilweise, in Phosphorsäure auch an den Harzen unvollständig und in der hier nicht eingetragenen Flußsäure fast nicht mehr reduziert wird.

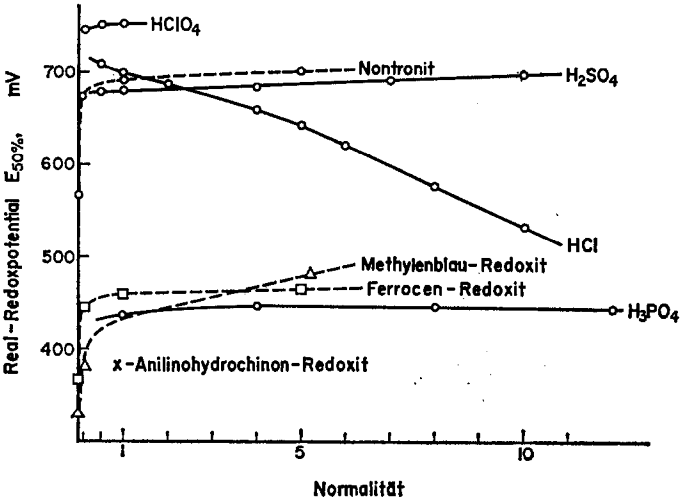

ABB. 1.—Vergleich der Realpotentiale $E_{50\%}$ von Fe^{3+}/Fe^{2+} und Redoxiten in verschiedenen Mineralsäuren bei 20,0°.
——— Realpotentiale des Eisensystems[18]
- - - - - Realpotentiale des Redoxites in Schwefelsäure.[17,19]

Nach einem Potentialvergleich zwischen Redoxiten und elektrochemischer Spannungsreihe sollten an Nontronit außer Eisen(III) nur Chrom(VI), Thallium(III), Selen(VI), Vanadin(V), Quecksilber(II); am Ferrocen-Harz zusätzlich Arsen(V), Molybdatosilikat und Molybdän(VI); am Leukomethylenblau-Harz unter Umständen noch Uran(VI) reduziert werden. Diese Näherung vernachlässigt allerdings Unterschiede zwischen Real- und Normalpotentialen. Bei Arsen(V) lassen höhere Aktivierungsenergien nur langsame Reaktionsgeschwindigkeiten voraussehen.

Als Ergebnis der Betrachtung ist das Anilinohydrochinon-Harz wegen seines tiefen Redoxpotentiales zu unspezifisch. Der wesentlich selektivere Nontronit hingegen ist in 1*N* Schwefelsäure nicht mehr ausreichend stabil. Daher werden in vorliegender Arbeit die schnell reagierenden Leukomethylenblau- und Ferrocen-Harze (gelegentlich auch das Anilinohydrochinon-Harz) verwendet.

EXPERIMENTELLER TEIL

Geräte

Säulen. Es werden Säulen nach Abb. 2 mit den Abmessungen 240 × 12 bzw. 340 × 12 mm (Kapillarrohr innen 2-mm Durchmesser) verwendet.

Säulenaggregat. Jeweils 5 Säulen stehen in einem Plexiglasgestell nach Abb. 3 und werden durch ein gemeinsames Verteilerrohr mit Schliffhähnen undansätzen verbunden. In gleicher Weise werden 4 dieser so erhaltenen Aggregate zusammengeschaltet. Damit können dann insgesamt 20 Säulen

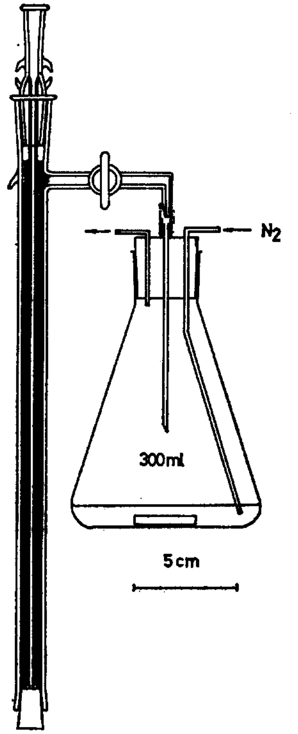

ABB. 2.—Austauschersäule mit aufsteigender Flüssigkeitsströmung.[27,28] Dazu ein 100-ml Vorratsbecher mit 12,5 NS Schliff; Quarz- oder Polyacrylfaserwatte ist schraffiert.

gleichzeitig, unter Luftabschluß und halbautomatisch über Nacht über eine gemeinsame Leitung gewaschen werden.

Waschwasser. Eine Redoxaustauscheranlage[9,20] liefert pro Regeneration etwa 2500 Liter sauerstoffarmes Leitfähigkeitswasser mit $\leqslant 40\ \mu g\ O_2/l$, $\approx 2 \cdot 10^{-8} \Omega^{-1} \cdot mm^{-1}$, pH 6,6 – 6,8 (21 ± 1°). Bei Verwendung von nur ausgekochtem und mit Inertgas gespültem oder auch normalem Ionenaustauscherwasser wird ein entsprechender Anteil Reduktionskapazität der zu waschenden Säule verbraucht. Diese Arbeitsweise ist jedoch bei etwas geringeren Ansprüchen durchaus möglich. Eine ausführliche Beschreibung der Anlage wird in Mitteilung XVIII dieser Reihe erfolgen.

Meßgeräte. Präzisions-pH-Meter 35 (Knick); Pt-Kalomel-Einstabmeßkette 480 NS (Ingold); justierbare Spritzpipetten 5 bis 15 ± 0,002 ml (Jacobs, Kopenhagen); 10 ml-Kolbenbürette (Ströhlein). Strahlungsmeßgerät FH 90 und Szintillationszählrohr FH 421 (Frieseke & Höpfner).

Redoxite. Die Redox-Harze werden aus Poly-4-aminostyrol der Korngröße 0,3–0,5 mm hergestellt.[9] Es befinden sich jeweils 8 g Methylenblau-Harz in den 240-mm Säulen und 11 g Ferrocen-Harz bzw. 11 g Anilinochydrochinon-Harz in den 340-mm Säulen. Alle Redoxite werden vor der ersten Anwendung mehrmals reduziert und oxydiert. Das Leukomethylenblau-Harz war bereits etwa 150mal einem Redox-Cyclus unterworfen worden. Von der Synthese der noch gebundene und unerwünschte kationenaustauschende Gruppen sind in 1*N* Schwefelsäure ohne Wirkung. Einzelne wenige Chargen der selbst hergestellten Redox-Harze halten nach der Regeneration durch Anionenaustausch gelegenlich Spuren Dithionit fest. Diese müssen dann durch kurzes Waschen mit schwach sauerstoffhaltigem Wasser oxydiert oder durch Blindbestimmungen berücksichtigt werden. Meist erübrigte sich dies jedoch.

Lösungen

Ammoniakalische Dithionitlösung. 25 bis 50 g $Na_2S_2O_4$ (gereinigt, Riedel-DeHaen, werden in 30 ml konz. Ammoniaklösung sowie 500 ml Wasser gelöst.

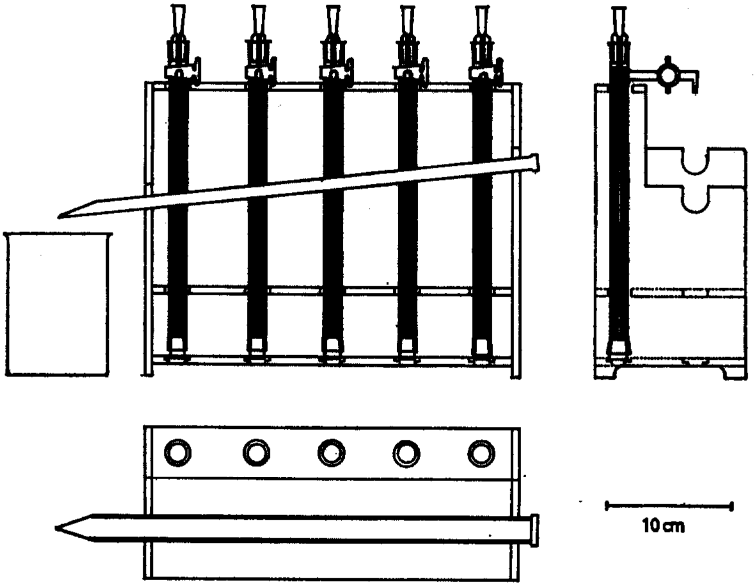

ABB. 3.—Aggregat für 5 Säulen.
Plexiglasgestell für gemeinsames Waschen nach Aufsetzen eines gemeinsamen Verteilerstückes auf die 5 Säulen.

Schwefelsaure Eisen(III)*-sulfatlösung*. Die erforderliche Menge $NH_4Fe(SO_4)_2 \cdot 12\,H_2O$ (*p.a.*) wird in 1*N* Schwefelsäure gelöst, mit dieser Säure auf 2 Liter aufgefüllt und komplexometrisch (Indikator Sulfosalicylsäure) eingestellt.[21]

0,1*N Cer*(IV)*-sulfatlösung* in 1*N* H_2SO_4, wird mit potentiometrischer Endpunktsanzeige[2] bei 40–50° gegen As_2O_3 unter Zugabe von 2 Tropfen OsO_4-Lösung eingestellt.

Osmiumtetroxidlösung: 250 mg OsO_4 werden in 100 ml Wasser gelöst.

0,1*N Permanganatlösung* wird gegen Natriumoxalat eingestellt.

Markierte Eisen(III)*-lösung*: 2 mCi einer fast trägerfreien ^{59}Eisen(III)-sulfatlösung (Harwell, mit Spur Citronensäure stabilisiert) mit Eisen(III)sulfatlösung in 1*N* Schwefelsäure auf 100 ml aufgefüllt (Träger 15 mg Fe/ml).

Regeneration

Die Redoxite werden mit Wasser vorgequollen, in die Säulen gefüllt und mit je 100 ml Dithionitlösung bei einer Durchlaufgeschwindigkeit von etwa 1,5 ml/min bis zum vollständigen Farbumschlag reduziert. Dann wird das Säulenaggregat zusammengesetzt und über Nacht mit etwa 2 Liter Waschwasser pro Säule bei etwa 2,2 ml/min (1 Tropfen/5 sec) sorgfältig dithionitfrei gewaschen. Die letzten 100 ml Durchlauf dürfen 1 Tropfen 0,01*N* Permanganatlösung innerhalb einer Minute nicht entfärben. Andernfalls muß noch weiter gewaschen werden.

Reduktion von Eisen(III)

Man versieht die regenerierten Säulen mit 100-ml Schliff-Vorratsbechern und befestigt am Säulenauslauf jeweils einen dreifach durchbohrten Gummistopfen mit Ein- und Ausleitungsrohr für Inertgas. In die zum Auffangen des Durchlaufes bestimmten 300-ml Erlenmeyerkolben gibt man zuvor je 25 ml konz. Schwefelsäure, 25 ml sirupöse Phosphorsäure (beide *p.a.*) und 50 ml Wasser. Dann werden sie an dem Gummistopfen des Auslaufrohres der Säulen befestigt und gemeinsam mit nachgereinigstem Stickstoff (Linde) gespült. Die zu reduzierende Eisen(III)-lösung gibt man mit der Kolbenbürette oder Spritzpipette in den unteren Teil des Vorratsbechers, ohne dessen Wand zu berühren, läßt die Lösung mit 2,2 ml/min durchlaufen und wäscht dreimal mit je 1,5 ml und dann insgesamt 250 ml Schwefelsäure nach. Bei dieser Anordnung bleibt die Luft weitgehend ausgeschlossen.

Eisenbestimmung. Auf die Erlenmeyerkolben wird nun ein anderer Gummistopfen mit Einstabmeßkette sowie Gasein- und ausleitungsrohr gesetzt und unter magnetischem Rühren mit Cer(IV)-sulfatlösung titriert. Gelegentlich ergaben unvollständig ausgewaschene Spuren Dithionit bei der Titration kleine Vorstufen, die vom Gesamtverbrauch abgezogen werden müssen. Deren Berücksichtigung bereitete jedoch im allgemeinen keine Schwierigkeit.

Optimale Reduktionsbedingungen

Da es sich um das erste Beispiel einer analytischen Anwendung von Redoxiten handelt, wurde der Einfluß verschiedener Faktoren auf die Reduktion von Eisen(III) näher untersucht.

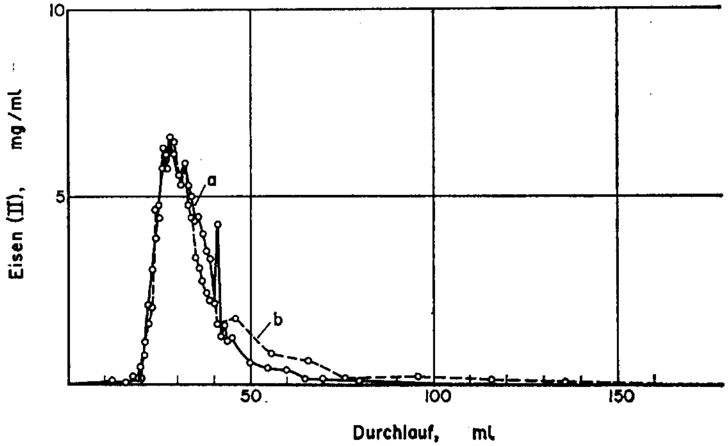

ABB. 4.—Reduktionskurven für Eisen(III) am Leukomethylenblau-Redoxit. Reduktion von(*a*) 109,0 mg und(*b*) 117,3 mg Fe(III) in 6,70 ml 1*N* Schwefelsäure mit 0,5 ml/min an 8,00 g Leukomethylenblau-Harz; Säulen 240 × 12 mmi, Waschen mit 250 ml 1*N* Schwefelsäure.

Stabilität der Redoxite

Die verwendeten Redoxite sind ausreichend stabil. So wurden durch 55 g Ferrocen-Harz 13 Liter 1*N* Schwefelsäure innerhalb von 260 Stunden (etwa 0,8 ml/min) filtriert, auf 300 ml eingeengt und neutralisiert. Weder mit Thiocyanat noch mit α,α'-Dipyridyl oder Sulfosalicylsäure konnte Eisen nachgeweisen werden. Das vorher schon etwa 150mal zu verschiedenartigen Reduktionen verwendete Leukomethylenblau-Harz gab selbst nach zwei Jahren Stehen unter 1*N* Schwefelsäure keine Farbstoffspuren ab. Indessen ließ seine Reaktionsgeschwindigkeit nach etwa 300 Redox-Umwandlungen merklich nach. Das Anilinohydrochinon-Harz färbte die überstehende 1*N* schwefelsaure Lösung nach einigen Wochen leicht braun.

Reduktionsverlauf von Eisen(III)

Der Verlauf der Reduktion von Eisen(III) zu Eisen(II) und dessen Auswaschen in der Säule ist den Reduktionskurven in Abb. 4 und 5 zu entnehmen. Etwa Hundert mg Eisen(III) werden in wenig 1*N* Schwefelsäure an 8 g Leukomethylenblau-Harz reduziert, mit der gleichen Säure gewaschen und im Durchlauf Eisen(II) portionsweise mit Permanganat titriert. Nach Abb. 4 gelangt der Hauptanteil an Eisen(II) bereits in die ersten 80 ml Durchlauf. Zum vollständigen Auswaschen genügen 150 ml. Zwei gleiche, hintereinander geschaltete Säulen mit der doppelten Harzmenge brauchen kaum mehr Waschflüssigkeit. Die Übereinstimmung der zwei Reduktionskurven aus getrennten Versuchen in Abb. 4 zeigt die gute Reproduzierbarkeit der Reduktion in der Säule.

Das Ferrocen-Harz ermöglicht noch etwas schärfere Elutionsbanden (Abb. 5, Kurve *d*). Hier benötigt die doppelte Eisenmenge in einer um 40% längeren Säule mit 11 g Harz (Kurve *c*) etwa 40 ml Waschlösung mehr. In allen Fällen genügen 250 ml vollauf.

Durchbruchskurven für Gesamteisen

Die entsprechenden Versuche mit radioaktiv markierter Eisen(III)-lösung ergaben nach Abb. 6 im Durchlauf des Leukomethylenblau-, Ferrocen-, bzw. Anilinohydrochinon-Harzes nur mehr analytisch vernachlässigbare Konzentrationen von 0,03; 0,06; 0,6 μg Gesamteisen pro ml. Auch hier ist die Elutionsbande am Ferrocen-Harz schärfer, hingegen läßt sich das Leukomethylenblau-Harz etwas schneller eisenfrei waschen.

Adsorption von Eisenspuren

In einem weiteren Versuch verblieben im ungünstigsten Fall des Anilinohydrochinon-Harzes nach Waschen mit 250 ml 1*N* Schwefelsäure nur etwa 0,07 μg Eisen auf der Säule. Damit ist nachgewiesen, daß eine Übertragung des Verfahrens auch in den Mikromaßstab möglich ist. Unter vorliegenden Bedingungen sind Reste von ionenaustauschenden Gruppen am Redox-Harz ohne Wirkung. Die Konzentration der gebundenen Eisenspuren steigt zum Säulenende linear an. Das läßt den Schluß zu, daß längeres Auswaschen noch weitgehende Elution erlaubt. Auch am oberen Quarzwattebauch, gefetteten Schliff sowie Auslaufrohr verblieben nur ≤0,09; ≤0,06; ≤0,02 μg Eisen.

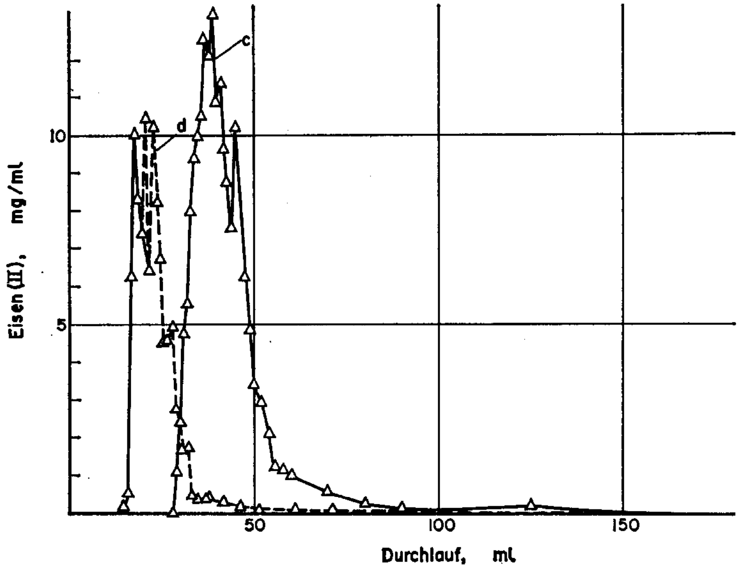

ABB. 5.—Reduktionskurven für Eisen(III) am Ferrocen-Redoxit.
Reduktion von(*c*) 203,2 mg Fe(III) an 11,0 g Ferrocen-Harz in 6,70 ml 1*N* Schwefelsäure (Säule 340 × 12 mm), (*d*) 101,6 mg Fe(III) an 7,50 g Harz (Säule 240 × 12 mm) i jeweils 0,5 ml/min.

Durchlaufgeschwindigkeit

Sie darf maximal für das Leukomethylenblau-Harz 0,5 ml/min und für das Ferrocen-Harz 0,8 ml/min betragen. Das wesentlich langsamer reagierende Anilinohydrochinon-Harz erlaubt nur Durchlaufgeschwindigkeiten von unter etwa 0,2 ml/min.

Eisenkonzentration

Sie hat einen untergeordneten Einfluß. Jedoch ergaben bei 200 mg Fe an 11 g Ferrocen-Harz Volumina der aufgegebenen Eisen(III)-lösung von 90 ml an aufwärts zunehmende Minusfehler.

Nutzbare Reduktionskapazität

Sie beträgt für die angegebene Säule mit 8 g Leukomethylenblau-Harz etwa 120 mg Eisen(III), entsprechend 0,23 mMol/g oder 85% ihrer Gesamt-Kapazität. Dieser Wert liegt im Vergleich zu 60–80% bei Ionenaustauschern[11] günstig.

Temperatur

Änderungen zwischen +10 und +25° waren ohne sichtbaren Einfluß. Stärkere Temperaturerhöhung läßt jedoch bei langsamen Redoxreaktionen eine merkliche Erhöhung der Reaktionsgeschwindigkeit und damit Verbesserung des Säulenbetriebes erwarten.

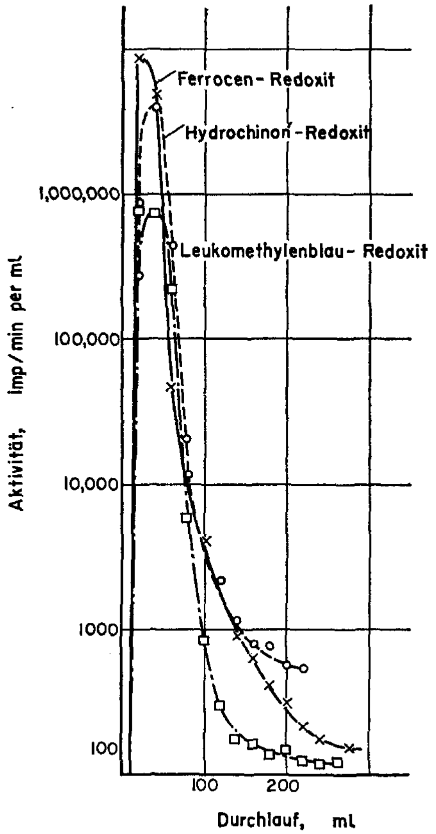

ABB. 6.—Durchbruchskurve für Eisen(II + III) einer mit ^{59}Fe markierten Eisen(III)-Lösung.
Leukomethylenblau- (8,0 g), Ferrocen- (7,5 g) und Anilinohydrochinon- (11 g) Redoxite in 240 × 11 mm Säulen; 6,70 ml 1*N* schwefelsure, radioaktiv markierte Eisen(III)-sulfatlösung (15 mg Fe/ml) jeweils mit 0,5 ml/min filtriert und mit 250 ml 1*N* Schwefelsäure gewaschen. 10^3 Impulse entsprechen 0,61 μg Eisen.

pH-*Wert und Lösungsmittel*

Die für die Reduktion der Eisen(III)-Lösung maßgebenden Redoxpotentiale ändern sich mit pH-Wert, Komplexbildung oder Fällung in der Lösung. Das zeigt deutlich der Unterschied zwischen verschiedenen Mineralsäuren:

Schwefelsäure. Unter Versuchsbedingungen lassen sich 100 mg Eisen(III) am Leukomethylenblau-Harz in 0,5 bis 10*N* oder 200 mg am Ferrocen-Harz in 0,5 bis 5*N* Schwefelsäure quantitativ reduzieren und damit bestimmen. Höhere Säurekonzentrationen führten im zweiten Fall zu Überwerten.

Salzsäure. Unter sonst gleichen Bedingungen gelingt hier die quantitative Bestimmung nur in dem schmalen Bereich von 1 bis 2*N*. Ober- und unterhalb treten starke Minusfehler auf. Oberhalb von 7 bis 8*N* wird auch die cerimetrische Titration unmöglich, über 10*N* beginnt Chlorentwicklung in der Säule. Weitergehende Reduktion gelingt jedoch auch hier in längeren Säulen. Salzsäure ist aber grundsätzlich infolge der Bildung von Chloroferrat(III)-Komplexen ungünstiger als Schwefel- oder Perchlorsäure.

Phosphorsäure. Unter analogen Bedingungen bewirkt 0,5 bis 15*N* Phosphorsäure von 25 bis 51% ansteigende Minusfehler. Sie beruhen auch hier auf zunehmender Bildung von Phosphatoferrat(III)-Komplexen. In der Säule vorübergehend ausfallende weiße Niederschläge—vermutlich Eisenphosphat—lösen sich beim Waschen mit 1*N* Schwefelsäure wieder auf. 15*N* Phosphorsäure greift das Leukomethylenblau-Harz an. Infolgedessen liefert hier die cerimetrische Bestimmung falsche Werte.

Kanalbildung

Die in Ionenaustauschersäulen auftretenden Kanäle sind meist zunächst nicht sichtbar. Sie können jedoch am Leukomethylenblau-Harz infolge des starken Farbumschlages während der Oxydation von hellbraun nach blauschwarz mit dem Auge gut beobachtet werden. Die grün (Mischfarbe) gefärbten Kanäle wandern der Front des oxydierten Harzes mehr oder weniger stark voraus. Bei den untersuchten Fällen verringerte sich die störende Kanalbildung einmal mit steigender H^+-Konzentration und zum anderen bei konstanter H^+-Konzentration mit zunehmender Bildung von Ferrat(III)-Komplexen. So traten bei 0,05*N* Schwefelsäure in der Übergangsschicht bis zu mehrere Zentimeter lange Bänder auf, bei 10*N* Phosphorsäure war die wandernde Front bis auf 1–2 mm scharf zusammengezogen. Die Kanalbildung läßt sich außerdem herabsetzen durch Verwendung kleinerer Korngrößen des Redoxites, gleichmäßigere Packung und sorgfältigere Justierung der Säule, Aufteilung einer überlangen Säule in mehrere kleine, ferner langsamere Durchlaufgeschwindigkeit und möglicherweise Beschleunigung der Reaktion durch Temperaturerhöhung.

Modellbestimmungen

Unter den vorausgehend ermittelten optimalen Reduktionsbedingungen wurden oxydimetrische Modellbestimmungen reiner Eisen(III)-Lösungen ohne und mit Zusatz von Fremdelementen ausgeführt.

Reine Eisen(III)-Lösungen

Die potentiometrische Titration des in den Durchlauf gelangten Eisen(II) mit 0,1*N* Cer(IV)-sulfat ergab für reine Lösungen von Eisen(III)-sulfat in 1*N* Schwefelsäure für jeweils *n* Bestimmungen folgende Standardabweichungen *s* und Variationskoeffizienten *V* (relative Standardabweichung):[23]

TABELLE I.—CERIMETRISCHE BESTIMMUNG REINER EISEN(III)-LÖSUNGEN

Redoxit	Gegeben, *mg*	Eisen(III) gefunden, *s, mg*	*V*%	*n*	Bemerkungen
Leukomethylenblau-Harz	100,1	±0,14	±0,14	12	
	200,2	±0,25	±0,12	4	(a)
Ferrocen-Harz	101,6	±0,04	±0,04	6	(b)
	194,5	±0,10	±0,05	4	(a, b)
	203,2	±0,09	±0,04	21	(a, b)

8 g Leukomethylenblau-Harz (240 × 12 mm), 11 g Ferrocen-Harz (350 × 11 mm) i Eisen (III)-sulfat in 1*N* Schwefelsäure (15,2 mg Fe/ml); 2,2 ml/min; 250 ml 1*N* Schwefelsäure; 20 – 23°C
(a) 2 Säulen hintereinander; (b) Dosierung der Eisenlösung mit Kolbenpipette.

Die scheinbar höhere Präzision der Bestimmung am Ferrocen-Harz ist dadurch bedingt, daß die relativ konzentrierte Eisen(III)-Lösung mit einer Kolbenpipette anstatt einer normalen 10 ml-Bürette vorgelegt wurde. Sie ist grundsätzlich auch am Leukomethylenblau-Harz zu erreichen. Gelegentliche Korrekturen für Blindbestimmungen an einzelnen Harz-Chargen sind bereits vorgenommen. Zwei Bestimmungen von 100 mg Eisen(III) an 11 g Anilinohydrochinon-Harz ergaben bei entsprechend verringerter Durchlaufgeschwindigkeit Fehler von etwa + 0,2%.

Einfluß von Fremdelementen

In Übereinstimmung mit den Aussagen des theoretischen Teiles wird die Eisenbestimmung (Tabelle II) nicht gestört durch Alkali- und Erdalkali-Ionen, Zink, Mangan(II), Nickel(II), Kobalt(II), Aluminium, Seltene Erden, Chrom(III), Cadmium, Thallium(I), Zirkon und Thorium sowie bemerkenswerterweise auch Kupfer-(II), Wismut(III), Titan(IV), Zinn(IV), Cer(IV) und Arsen(V). Die letztgenannten 6 Elemente werden durch Metallreduktoren ebenfalls reduziert und stören daher dort die oxydimetrische Bestimmung von Eisen.

TABELLE II.—EISEN(III)-BESTIMMUNG NEBEN NICHT STÖRENDEN BEGLEITELEMENTEN

Eisen, *mg*		Fehler, %	Fremdionenzusatz	
Gegeben	Gefunden		Ion	Salz
8 g Leukomethylenblau-Redoxit, Säule 240 × 10 mm:				
150,0	150,3	+0,2	Na^+	750 mg Na_2SO_4
150,0	150,4	+0,3	Na^+	5000 mg Na_2SO_4
150,0	150,1	+0,1	Mg^{2+}	150 mg $MgSO_4 \cdot 7\,H_2O$
150,0	150,3	+0,2	Zn^{2+}	150 mg $ZnSO_4 \cdot 7\,H_2O$
150,0	149,9	−0,1	Mn^{2+}	750 mg $MnSO_4 \cdot H_2O$
150,0	150,6	+0,4	Co^{2+}	750 mg $CoSO_4 \cdot 7\,H_2O$
150,0	149,8	−0,1	Ni^{2+}	750 mg $NiSO_4 \cdot 7\,H_2O$
100,1	100,2	+0,2	Cr^{3+}	750 mg $KCr(SO_4)_2 \cdot 12H_2O$
150,0	150,5	+0,3	Cr^{3+}	750 mg $KCr(SO_4)_2 \cdot 12H_2O$
150,0	150,1	+0,1	Al^{3+}	750 mg $AlCl_3 \cdot 6\,H_2O$
100,1	100,3	+0,2	TiO^{2+}	750 mg $TiO\,(SO_4)_2$
150,0	150,2	+0,1	Cd^{2+}	750 mg $CdSO_4 \cdot 8/3\,H_2O$
150,0	150,0	0,0	Cu^{2+}	750 mg $CuSO_4 \cdot 5\,H_2O$
150,5	150,2	−0,1	Bi^{3+}	750 mg $Bi(NO_3)_3 \cdot 5\,H_2O$
150,0	150,1	+0,1	Sn^{4+}	750 mg $Sn(SO_4)_2 \cdot 4\,H_2O$
100,1	100,0	−0,1	As(V)	750 mg Na_2HAsO_4
100,1	100,0	−0,1	Ce^{4+}	750 mg $Ce\,(SO_4)_2 \cdot 4\,H_2O$
11 g Ferrocen-Redoxit, Säule 340 × 10 mm:				
194,46	194,51	+0,03	Na^+	500 mg $Na_2SO_4 \cdot 10\,H_2O$
	194,57	+0,06	K^+	500 mg K_2SO_4
	194,51	+0,03	NH_4^+	500 mg $(NH_4)_2SO_4$
			Mg^{2+}	500 mg $MgSO_4 \cdot 7\,H_2O$
			Li^+	500 mg LiCl
194,46	194,51	+0,03	Mn^{2+}	500 mg $MnSO_4 \cdot 7\,H_2O$
	194,68	+0,08	Zn^{2+}	500 mg $ZnSO_4 \cdot 7\,H_2O$
	194,57	+0,06	Ni^{2+}	500 mg $NiSO_4 \cdot 7\,H_2O$
			Co^{2+}	500 mg $CoSO_4 \cdot 7\,H_2O$
194,46	194,51	+0,03	Al^{3+}	500 mg $Al_2(SO_4)_3 \cdot 18\,H_2O$
	194,62	+0,08	Cu^{2+}	500 mg $CuSO_4 \cdot 5\,H_2O$
	194,51	+0,03	Cd^{2+}	500 mg $CdSO_4 \cdot 8/3\,H_2O$
0,0	0,0	—	Ti(IV)	500 mg $Ti(SO_4)_2$
			Zr^{4+}	500 mg $ZrO(NO_3)_2$
			Th^{4+}	500 mg $Th(NO_3)_4$
			Tl^+	500 mg Tl_2SO_4
0,0	0,0	—	Nd^{3+}	100 mg Nd_2O_3
			Pr^{3+}	100 mg Pr_2O_3
			Sm^{3+}	100 mg Sm_2O_3
			Y^{3+}	100 mg Y_2O_3
0,0	0,0	—	As(V)	250 mg Na_2HAsO_4
0,0	0,0	—	Be^{2+}	250 mg $Be(CH_3COO)_2$
0,0	0,0	—	Cr^{3+}	500 mg $Cr_2(SO_4)_3 \cdot aq$

(Versuchsbedingungen wie in Tabelle I.).

Zusammen mit Eisen(III) werden durch die Redoxite Vanadin(V) zu (III/IV), Molybdän(VI) zu (V/VI), Spuren von Uran(VI) zu (IV) und Cer(IV) zu (III) reduziert. Mit Ausnahme des letzteren stören diese Begleitelemente die Bestimmung von Eisen(III).

ANWENDUNGEN

Analyse von Schlacke und Erz[14]

Die untersuchten Stoffe, je eine Martinschlacke, ein Schwedenerz und ein Agglomerat enthielten nach Werksangaben 13,4; 62,6; 61,0% Eisen. Die Reduktion am Zink-Reduktor mit anschließender Titration mit Permanganat ergab 13,7; 62,8; 61,6% Eisen. Reduktion an dem früher verwendeten, noch ausblutenden Leukomethylenblau-Harz und Titration mit Permanganat[14] führten im Mittel von jeweils 3 Bestimmungen zu 13,8; 63,1; 62,0% Eisen.

Eisenbestimmung in Stahl

Der als Beispiel gewählte hochlegierte Stahl X 10 Cr, Ni, Nb 18/9 (AISI Nr. 347) enthält etwa 70% Eisen, ferner u.a. Chrom, Nickel und Niob. Die cerimetrische Bestimmung nach der Redoxaustauschermethode führte zu folgendem Ergebnis:

TABELLE III.—BESTIMMUNG DES EISENS IN STAHL

Redoxit	Einwaage, *mg*	Eisengehalt, *mg*		Fehler %	
		theor.	gefunden	abs.	rel.
Leukomethylenblau-Harz (2 × 8,0 g)	113,54	69,05	$69{,}3_0$	+0,25	+0,4
	113,54	69,05	$69{,}2_5$	+0,20	+0,3
Ferrocen-Harz (11 g)	113,54	69,05	$69{,}2_5$	+0,20	+0,3
	113,54	69,05	$69{,}3_0$	+0,25	+0,4

Die gefundenen Eisenwerte liegen scheinbar um 0,3 bis 0,4% zu hoch. Da jedoch der theoretische Gehalt nach einer der üblichen Restmethoden bestimmt worden war, entsprechen die nach vorliegender Direktmethode gefundenen Werte dem tatsächlichen Gehalt wahrscheinlich besser.

Arbeitsvorschrift

Man löst 500–600 mg Metallspäne in 50 ml 6*N* Salzsäure unter Zugabe von 10 Tropfen 30% igem H_2O_2 und 10—20 Tropfen konz. Salpetersäure bei Siedetemperatur. Ausgeschiedene Kieselsäure und Kohlenstoff werden abfiltriert. Das auf 10 bis 15 ml eigeengte Filtrat wird dann in eine Lösung von etwa 15 g Natriumhydroxid (*p.a.*) und 3 g Natriumperoxid in 100 ml Wasser gegeben und 10 Minuten mit Siedestäbchen gekochrt. Hierauf filtriert man das evtl. noch $TiO_2 \cdot xH_2O$ enthaltende Eisen(III)-hydroxid ab und wäscht dreimal mit 20–30 ml 60°-heißem Wasser. Der Niederschlag wird vom Filter mit etwa 80–100 ml heißer 6*N* Saltsäure gelöst und dieses mit 50 ml heißem Wasser nachgespült. Das auf 10–15 ml eingeengte Filtrat wird nochmals wie oben gefällt und der Niederschlag gelöst. Man wäscht mit 50 ml heißem Wasser nach und engt mit 5 ml konz. Schwefelsäure bis zum Auftreten von SO_3-Nebeln ein. Dann füllt man auf 100 ml auf. Die etwa 1*N* schwefelsaure Eisenlösung wird nun mit einer Spritzpipette entnommen und nach der allgemeinen Arbeitsvorschrift in zwei hintereinander geschalteten Säulen mit je 8,0 g Leukomethylenblau-bzw. einer Säule mit 11 g Ferrocen-Harz reduziert. Im Durchlauf wird Eisen(II) potentiometrisch mit 0,1*N* Cer (IV)-sulfat titriert.

DISKUSSION

1. Elutionsstabile Redoxite ermöglichen oxydimetrische Bestimmungen von gelösten Redoxsystemen. Im Gegensatz zu Metallreduktoren und den meisten Redox-Ionenaustauschern wird die Lösung tatsächlich nicht durch Ionen des Reagenz verunreinigt. Für das untersuchte Beispiel der Reduktion von Eisen(III) zu (II) in 1*N* Schwefelsäure ($E_{50\%} = +0{,}68$ V) eignen sich auf Grund von Realpotential, Reaktionsgeschwindigkeit, Stabilität sowie deutlich sichtbarem Farbumschlag vor allem das Leukomethylenblau- und Ferrocen-Harz ($E_{50\%} = +0{,}42$ bzw. $+ 0{,}47$ V).

2. Nach Lage ihrer Redoxpotentiale sind die meisten bisher bekannten Redoxite (Abb. 27 in Citat 9) mildere und damit wesentlich selektivere Reduktionsmittel als Metallreduktoren. Im vorliegenden Fall wird die Reduktion von Eisen(III) am Redoxit im Gegensatz zum Metallreduktor nicht durch Kupfer(II), Wismut(III), Titan(IV), Zinn(IV) und Arsen(V) gestört. Ein Redoxit mit dem Redoxpotential des Nontronites ($E_{50\%} = +0{,}65$ V) sollte selektiv nur Eisen(III) und Vanadin(V) neben allen anderen in Zitat[25] (dort Abb. 27) aufgeführten Redoxsystemen reduzieren.

3. Ein Potentialvergleich zwischen Redoxiten und gelösten Redoxsystemen der elektrochemischen Spannungsreihe erlaubt qualitative Vorhersagen über störende Fremdionen und halbquantitative über den Grad der Reduzierbarkeit beliebiger Redoxsysteme in unterschiedlichem Medium. Beim betrachteten System Eisen (III/II) stimmten Vorhersage und Experiment durchweg gut überein. Das zeigt den Wert[9,24] der Messung von Realpotentialen $E_{50\%}$ der Redoxite auch dann, wenn sie wegen irreversibler Oxydationsanteile, teilweise nicht streng reversibler Gleichgewichtseinstellung und etwas unterschiedlichem Medium für thermodynamische Berechnungen nicht brauchbar sind.

4. Geeignete Redoxite eröffnen wegen ihrer höheren und gut abgestuften Redoxpotentiale vielleicht die Möglichkeit, Transurane aus höheren Oxydationsstufen in einem Schritt sofort in mittlere zu überführen. Metallreduktoren reduzieren fast immer zur niedrigsten Stufe.

5. Im untersuchten Beispiel wird die Reduktion von Eisen(III) in der Reihenfolge Perchlor-, Schwefel-, Salz-, Phosphor-, Flußsäure sowie für jeweils eine dieser Mineralsäuren mit steigender H^+-Konzentration schwieriger. Das ist durch Stabilisierung von Fe(III) infolge Komplexbildung bzw. Verschiebung des Redoxgleichgewichtes (2) durch steigende H^+-Konzentration zu erklären. Die Selektivität der Redoxite läßt sich somit auch durch geeignete Komplexbildung und Einstellung des pH-Wertes der jeweiligen Aufgabe anpassen.

6. Die allgemeinen Arbeitsbedingungen der analytischen Anwendung von Redoxaustauschern entsprechen in vorliegendem Falle hinsichtlich Säulenbetrieb, Gestalt der Durchbruchskurve, Austauschkapazität, optimaler Korngröße und Kanalbildung denen der Ionenaustauscher. Ähnliche Durchlaufgeschwindigkeiten erfordern jedoch die Verwendung etwas längerer Säulen mit einer größeren Austauschermenge. Allerdings reagierte das Redox-Harz vom Hydrochinon-Typ langsamer.

7. Im Gegensatz zum Ionenaustausch erfordert die Regeneration der Säulen nur wenig mehr als die stöchiometrische Menge an Reduktions-bzw. Oxydationsmitteln.[11] Der beim Ionenaustausch erforderlichen hohen Konzentration an Regenerationsmittel entspricht hier ein ausreichend hohes bzw. niedriges Redoxpotential.

Das Auswaschen des Reduktionsmittels muß verständlicherweise im allgemeinen unter Ausschluß von Luftsauerstoff in Waschwasser und Apparatur erfolgen, wobei sich die mit aufsteigendem Flüssigkeitsstrom arbeitende Austauschersäule nach Abb. 2 besonders bewährt hat.[11]

Organische Redox-Harze sind zwar gegen so starke Reduktionsmittel wie Dithionit ausreichend stabil, werden jedoch von starken Oxydationsmitteln leicht irreversibel angegriffen.[20,25] Demgegenüber sind rein anorganische Redoxaustauscher auch gegen starke Oxydationsmittel vollständig stabil.[15,26]

8. Reste von ionenaustauschenden Gruppen stören häufig die analytische Anwendung von Redoxaustauschern. Die coulometrisch und radiometrisch bestimmten

Kapazitäten für derartige unerwünschte, bei der Synthese verbleibende Gruppen, lagen bei den verwendeten Redox-Harzen in der Größenordnung von nur 0,04 mEq/g.[9] Bei der Reduktion von Eisen(III) machte sich in 1*N* Schwefelsäure jedoch keinerlei störender Kationenaustausch bemerkbar. Anionenaustauschende Restgruppen können dagegen während der Regeneration und des Waschens Spuren Regenerationsmittel, z.B. Dithionit-Anionen binden. Bei der späteren Elution wird dadurch die anschließende oxydimetrische Titration gestört. Soferne man daher bei der Synthese von Redox-Harzen nicht vermeiden kann, daß das Harzgerüst unerwünschte positiv oder negativ geladene Gruppen enthält, kann man wie oben beschrieben, versuchen, Dithionitspuren durch Waschen mit schwach sauerstoffhaltigem Wasser rasch weg zu oxydieren oder man muß—wie bei Metallreduktoren—Blindbestimmungen ausführen.

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Summary—As an example of the reduction of cations on redox exchangers, the reduction of 50–200 mg of iron(III) on leucomethyleneblue- and ferrocene-resin of a polystyrene type, is described. The iron(II) was titrated potentiometrically with cerium(IV). Under optimum conditions, the standard deviation was 0·04–0·14 mg. In contrast to their behaviour on metal reductors, there is no interference from Cu^{2+}, Bi^{3+}, TiO^{2+}, Sn^{4+}, Ce^{4+} and AsO_4^{3-}. The method has been used for the direct determination of iron in ores, slags and special steels.

Résumé—Comme exemple de la réduction de cations sur des échangeurs redox, on décrit la réduction de 50–200 mg de fer(III) sur une résine bleu de leucométhylène et ferrocène d'un type polystyrène. Le fer(II) a été titré potentiométriquement au cérium(IV). Dans les conditions optimales, l'écart type est de 0,04–0,14 mg. En contraste avec leur comportement sur des réducteurs métalliques, il n'y a pas d'interférence de Cu^{2+}, Bi^{3+}, TiO^{2+}, Sn^{4+}, Ce^{4+} et AsO_4^{3-}. On a utilisé la méthode pour le dosage direct du fer dans les minerais, scories et aciers spéciaux.

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REDOXAUSTAUSCHER UND IHRE ANWENDUNGEN—XVI

ENTFERNUNG VON WASSERSTOFFPEROXID AUS WÄSSERIGER LÖSUNG AN REDOX- UND IONENAUSTAUSCHERN*

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Zusammenfassung—Wasserstoffperoxid läßt sich aus wässeriger Lösung durch Reduktion an einem mit Dithionit oder vor allem Sulfit beladenem Anionenaustauscher (Lewatit M 600) sowie durch katalytische Zersetzung am OH^--Anionenaustauscher halbkontinuierlich und automatisch entfernen. Dazu werden einfache Säulenanordnungen beschrieben, die sowohl den Ausschluß störender Labordämpfe als auch einen quasi-Säulenbetrieb bei durch Gasentwicklung stark aufgewirbelter Austauscherschicht ermöglichen.

WASSERSTOFFPEROXID stört die Weiterverarbeitung von Lösungen in Strahlenchemie, Kerntechnik und Analytik.[1] Es bildet sich durch Enzymeinwirkung, hemmt aber das Wachstum anaerober Bakterien und kann den zur Bildung von Carcinomen führenden krankhaften Gärungsstoffwechsel der Zelle auslösen. Nicht zuletzt beruht die Strahlenschädigung des Organismus teilweise mit auf intermediär gebildeten Peroxiden und OH^--Radikalen.[2]

Wasserstoffperoxid kann durch Reduktion, Oxydation, katalytische Zersetzung oder Abtrennung aus Lösungen entfernt werden.[2] Im folgenden interessierte die Reduktion des Wasserstoffperoxides an Redoxaustauschern als Teilschritt der Entfernung von gelöstem Sauerstoff aus Wasser. Dabei wurde die katalytische Zersetzung an OH^--Anionenaustauschern beobachtet.

Daraus ergeben sich Anregungen für die Entfernung radiolytisch gebildeter Peroxide im Kühlwasserkreislauf von Atomreaktoren. Verschiedene Membranen der physiologischen Zelle haben den Charakter von Redoxaustauschern.[3] Overberger[4] hat Redoxite als unlösliches Prophylaktikum für Strahlenschäden im Organismus zur Reduktion von $.OH^-$-Radikalen und Peroxiden verwendet.

Wasserstoffperoxid hat eine negative Bildungsenergie von −134 kJ/Mol bei 25°. Seine Aktivierungsenergie von etwa 75 kJ/Mol hindert den Zerfall. Die kathodische Reduktion verläuft in saurer Lösung[5,6] nach

$$H_2O_2 + 2H^+ + 2e^- \rightleftharpoons 2H_2O \qquad E^\circ = +1{,}77\,V, \qquad (1)$$

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* XV. Mitteilung B. Sansoni W. Wiegand, *Talanta*, 1970, **17**, 973. Vorgetragen Chemische Gesellschaft Marburg/Lahn (Januar 1960) und GDCH-Hauptversammlung Aachen, 1961 (Referat, *Angew. Chem.*, 1961, **73**, 763).

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und in alkalischer[7] nach

$$HO_2^- + H_2O + 2e^- \rightleftharpoons 3OH^- \qquad E^\circ = +0{,}88\ V. \qquad (2)$$

Die katalytische Zersetzung

$$H_2O_2 \rightarrow H_2O + \tfrac{1}{2}O_2 \qquad (3)$$

erfolgt besonders leicht in alkalischem Medium. Die Reaktionen (1) bis (3) verlaufen über Radikale.[7] Wasserstoffperoxid ist in wässeriger Lösung eine sehr schwache Säure[8] mit $K = 2{,}24 \cdot 10^{-12}$.

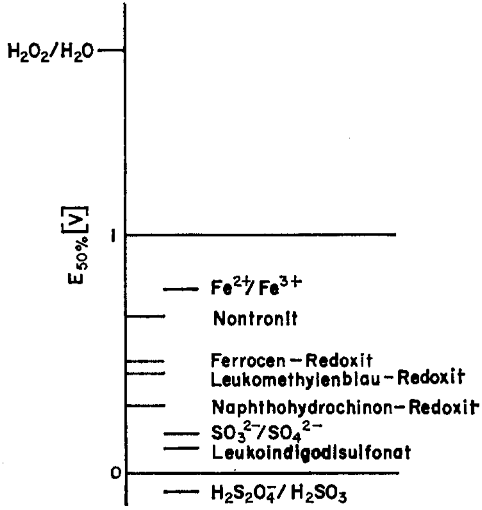

ABB. 1.—Vergleich der Redoxpotentiale von H_2O_2/H_2O und Redoxaustauschern. Normalpotentiale für H_2O_2/H_2O und gelöste Ionen,[5,6] Realpotentiale für Redox-Harze in 1N und für Nontronit in 0,01N Schwefelsäure.[11]

Nach Abb. 1 sollte Wasserstoffperoxid durch alle angegebenen Redoxaustauscher zu Wasser reduziert werden können. Für Anwendungen in salzfreier-Lösung genügen einfache Redox-Ionenaustauscher. Ihr Gerüst ist relativ beständig. Anionen wie Dithionit, Sulfit, Thiosulfat, Phosphit vermeiden die bei verschiedenen Kationen[9] sowie Redoxiten beobachtete störende katalytische Zersetzung.[10] Durch Oxydation gebildetes Sulfat ist indifferent und stört bei Elution durch salzhaltige Lösungen weniger als entsprechende Redox-Kationen. Die an den Reaktionen (1) bis (3) beteiligten Radikale können organische Redoxgruppen an Redoxiten irreversibel angreifen und diese unbrauchbar machen.

EXPERIMENTELLE TEIL

Geräte

Die Reduktionsversuche wurden in Schliffsäulen (180 × 10 mm nach Abb. 2) unter Ausschluß störender Laborluft ausgeführt. Die 300 ml-Erlenmeyerkolben stehen auf einem in entsprechender Höhe angebrachten Plexiglasstreifen. Die katalytische Zersetzung erfolgte in den Apparaturen nach Abb. 3 und 4. Sie erlauben bei nicht zu schneller Durchlaufgeschwindigkeit und etwas Übung auch bei starker Gasentwicklung einen quasi-Säulenbetrieb. In der Anordnung Abb. 3 entweichen die Gasblasen durch das Kapillarrohr. In Abb. 4 soll der schräg eintauchende Glasstab (1–2 mm Durchmesser) das Aufsteigen der Gasblasen erleichtern. In beiden Fällen dient das untere Drittel der Säulenfüllung als Sicherheit für etwa durchgebrochene Peroxidspuren.

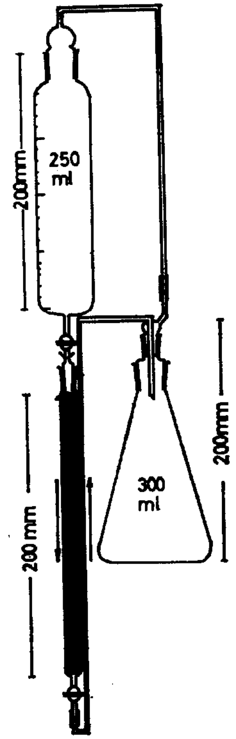

Abb. 2.—Schliffsäule mit Ausschluß störender Laborluft.

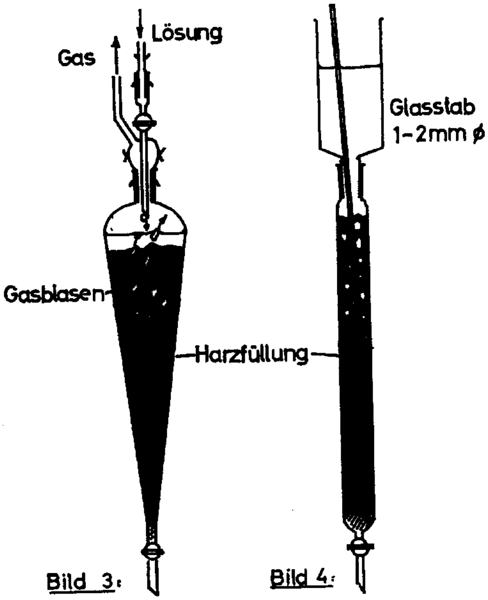

Abb. 3 und 4.—Apparaturen für quasi-Säulenbetrieb bei starker Gasentwicklung.

Außerdem wurden verwendet: Fraktionsteiler RadiRac (LKB) mit 10-ml Syphon, Polarograph Polarecord (Metrohm), Leitfähigkeitsmesser CDM II mit 0,2-ml Durchflußzelle(Radiometer).

Die Redoxaustauscheranlage[9,11] lieferte sauerstoffarmes Wachwasser mit $\sim 0{,}2 \cdot 10^{-7}\ \Omega^{-1}.\ \mathrm{mm}^{-1}$ $\leqslant 40\ \mu g\ O_2/l$ und pH 6,6–6,8 (bei 21 ± 1°). Gegebenenfalls kann auch ausgekochtes und mit N_2 gespültes vollentsalztes Waschwasser verwendet werden.

Redox-Ionenaustauscher

Ionenaustauscher. Stark saurer Lewatit S100 und stark basischer Lewatit M 600 werden wie üblich mit 4*M* Salzsäure in die H^+-bzw. Cl^--Form gebracht, sorgfältig eisenfrei, anschließend neutral gewaschen, an der Luft getrocknet und gesiebt. Ein Teil des Anionenaustauschers wird anschließend mit 2*M* Natriumlauge unter CO_2-Ausschluß in die OH^--Form übergeführt.

Die Anionenaustauschkapazität von Cl^--Lewatit M 600 ergab sich für die Siebfraktion 0,1–0,2 mm zu 3,27 mEq Cl^-/g Trockengewicht; 0,6–0,75 mm zu 3,18; 0,75–1,00 mm zu 3,22; ungesiebt zu 3,22 und ist damit innerhalb der Fehlergrenzen befriedigend konstant. Dagegen nahm der Feuchtigkeitsgehalt bei konstanter Luftfeuchtigkeit mit steigender Korngröße etwas zu: Korngröße 0,1–0,2 mm 16,5%; 0,2–0,3 mm 21,2%; 0,3–0,4 mm 22,7%; 0,4–0,5 mm 23,5% 0,5–0,6 mm 23,7%; 0,6–0,75 mm 23,5%; 0,75–1,00 mm 24,5%.

$S_2O_4^{2-}$-Anionenaustauscher. Jeweils 7,00 g lufttrockener Cl^--Lewatit M 600 (0,6–0,75 mm) werden in der Säule nach Abb. 2 mit 200 ml ammoniakalischer Dithionitlösung bei etwa 1 Tropfen/sec (3–4 ml/min) in die Dithionit-Form übergeführt und mit etwa 300 ml sauerstoffreiem Wasser dithionitfrei gewaschen. Dabei soll die oberste Harzschicht nicht mit Luft in Berührung kommen. Andernfalls muß mit jeweils konstantem Kapazitätsverlust gearbeitet werden. Die Sulfat-Form des Austauschers wird unmittelbar mit frischer Dithionitlösung regeneriert.

SO_3^{2-}-Anionenaustauscher. Entsprechend werden 7,00 g Cl^--Lewatit M 600 (0,6–0,75 mm) mit etwa 100 ml Sulfitlösung in die Sulfit-Form gebracht. Nach Oxydation wird das gebundene Sulfat ebenfalls mit 10%iger Natriumsulfit-Lösung ausgetauscht.

Reagenzien

Ammoniakalische Dithionitlösung. Jeweils kurz vor Gebrauch werden etwa 50 g $Na_2S_2O_4$ (gereinigt, Riedel-DeHaen in 1 Liter 1*M* Ammoniaklösung (chem. rein) gelöst.

Sulfitlösung. 100 g Na_2SO_3 (*p.a.*) in 1 Liter vollentsalztem Wasser.

Wasserstoffperoxidlösung. 30%iges H_2O_2 (Perhydrol, *p.a.*) wird kurz vor Gebrauch verdünnt und mit 0,1*N* Thiosulfat jodometrisch eingestellt.

Analytische Bestimmungen

Ionenaustauschkapazitäten wurden volumetrisch,[12] Redoxkapazitäten mit Eisen(III)-sulfat[11,13,14] Wasserstoffperoxid jodometrisch nach Kolthoff[15] und gelegentlich im Durchlauf auch polarographisch bestimmt.[16]

ERGEBNISSE

Nach Vorversuchen mit einer größeren Anzahl von Redox-Ionenaustauschern wurden die mit Dithionit und Sulfit beladenen Anionenaustauscher eingehender untersucht.

Reduktion am $S_2O_4^{2-}$-Anionenaustauscher

Der Dithionit-Anionenaustauscher ist nach Abb. 5 ausreichend stabil. Sene Reduktionskapazität verändert sich in der gut verschlossenen Säule während 24 Stunden kaum und sinkt nach 100 Stunden auf etwa die Hälfte.

In drei Versuchsreihen wurden zunehmende Volumina wässerige 0,1*N* Wasserstoffperoxidlösung an $S_2O_4^{2-}$-Lewatit M 600 in Säulen nach Abb. 3 unter möglichst konstanten Bedingungen reduziert. Abbildung 6 enthält das Ergebnis der Einzelversuche als Durchbruchskurve. Dabei wurde (*a*) die in der Säule entfernte und (*b*) im Durchlauf gefundene Wasserstoffperoxidmenge gegen die vorgegebene aufgetragen und jeweils als mEq H_2O_2 auf das Trockengewicht (g) des Austauschers bezogen. Der Sättigungswert von (*a*) ergibt eine Gesamt-Reduktionskapazität[17] von 2,6–2,7 mEq H_2O_2/g, der Durchbruchspunkt von (*b*) eine nutzbare Durchbruchskapazität[17] von 2,5 mEq H_2O_2/g. Die Abszissendifferenz des Sättigungs- und Durchbruchspunktes entspricht einer ausgenutzten Gesamt-Kapazität der Säule von etwa 95%. Für Ionenaustauscher werden 60–80% angegeben.[18] Dieser hohe Wert deutet auf rasche und vollständige Gleichgewichtseinstellung in jedem Säulenabschnitt.

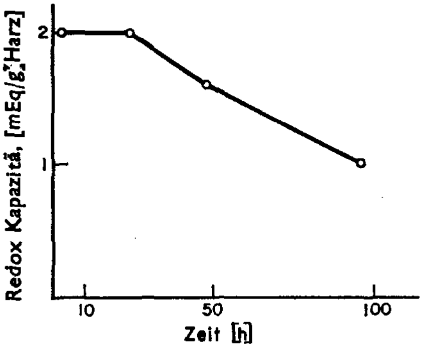

ABB. 5.—Stabilität von $S_2O_4^{2-}$-Permutit ES (5).
Säule 180 × 10 mm; 10 g Cl^--Permutit ES (0,3–0,5 mm) in $S_2O_4^{2-}$-Form; 20–25°C; diffuses Sonnenlicht.

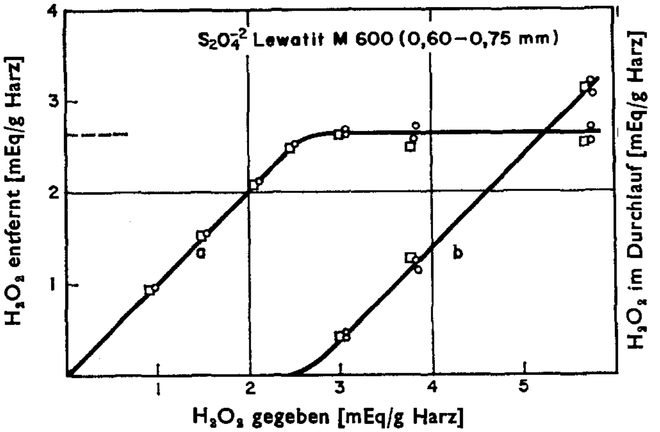

ABB. 6.—Reduktion von Wasserstoffperoxid an $S_2O_4^{2-}$-Lewatit M 600.
Säulen 180 × 10 mm (Abb. 2) mit 7,00 g lufttrockener Harzeinwaage an Cl^--Lewatit M 600; (0,6–0,75 mm); 1,1 ml/min; 24–25°C; diffuses Sonnenlicht.

Die gefundene Gesamt-Reduktionskapazität ist erheblich kleiner als die theoretisch für den Übergang von S(III) zu S(IV) zu erwartende von etwa 9,5 mEq/g. Das hat mehrere Gründe. Erstens enthielt frisch der Originalflasche entnommenes $Na_2S_2O_4$ (gereinigt, Riedel-DeHaen) nur etwa 74 Gew.-% des theoretischen Gehaltes an Dithionit, daneben 11% Thiosulfat und 12% Sulfit. Zweitens sinkt der Reduktionswert des am Austauscher gebundenen Dithionites infolge Oxydation der obersten Schichten durch den Luftsauerstoff in Apparatur und Waschwasser. Drittens ist im angewendeten schwach ammoniakalischen Medium die Beladung des Lewatit M 600 nicht mehr ganz vollständig. So führte eine Beladung mit wässriger, also schwach saurer Dithionitlösung zu Gesamt-Redoxkapazitäten von 3,4–3,8 $mEqFe^{3+}/g$. Viertens entstehen aus 1 Mol $S_2O_4^{2-}$, 2 Mol SO_3^{2-} bzw. SO_4^{2-}. Das bedeutet notwendigerweise eine teilweise Elution von Sulfit- bzw. Sulfat. Der an der Luft aufgefangene Durchlauf einer wässerigen Wasserstoffperoxidlösung enthielt je nach

Basizität des Anionenaustauschers 18 bis 24 Äquivalent-% der mit H_2O_2 gemessenen Gesamt-Reduktionskapazität als Sulfat bzw. Schwefelsäure. Damit erfolgt die Oxydation von Dithionit am Anionenaustauscher zwar sehr schnell, jedoch unübersichtlich.

In der ersten Versuchsreihe (o) von Abb. 6 wurde Cl^--Lewatit M 600 zunächst mit $2M$ Natronlauge in die OH^-- und dann erst mit ammoniakalischer Dithionitlösung in die $S_2O_4^{2-}$-Form übergeführt; in der zweiten und dritten wurde direkt in die $S_2O_4^{2-}$-Form gebracht. Die Übereinstimmung ist in Anbetracht der etwas erhöhten Raumtemperatur sowie des diffusen Sonnenlichtes (geringe katalytische Peroxidzersetzung an der Glaswandung) befriedigend. Das zeigt, daß auch ein Überspringen der OH^--Form vollständige Regeneration ermöglicht. Außerdem hat sich die Kapazität des Anionenaustauschers nach dreimaliger Oxydation–Reduktion nicht merklich verändert.

Reduktion am SO_3^{2-}-Anionenaustauscher

Der Sulfit-Anionenaustauscher reagiert nach

$$SO_3^{2-}\text{-Iat.} + H_2O_2 \rightleftharpoons SO_4^{2-}\text{-Iat.} + H_2O. \qquad (4)$$

Die Reaktion ist langsamer, aber einfacher und übersichtlicher als bei Dithionit. Infolge konstant bleibender Anionenladung wird die Lösung grundsätzlich nicht verunreinig. Sulfit erfordert überdies geringere Betriebskosten.

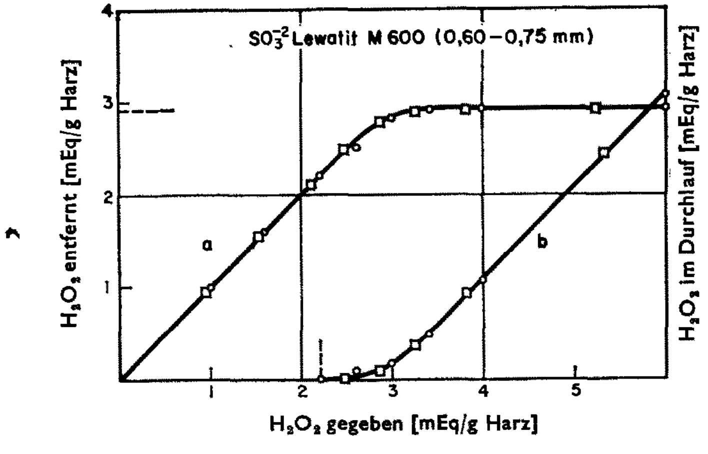

ABB. 7.—Reduktion von Wasserstoffperoxid an SO_3^{2-}-Lewatit M 600. 7,00 g lufttrockene Harzeinwaage an Cl^--Lewatit M 600; Korngröße; ungesiebt; sonst wie für Abb. 6.

Der Sulfit-Anionenaustauscher ist gegen Autoxydation so stabil wie eine entsprechend verschlossen aufbewahrte wässerige Sulfitlösung. Die Gesamt-Reduktionskapazität nimmt innerhalb von 44 Tagen nur um 6% ab. Auch das Gerüst des Anionenaustauschers ist ausreichend beständig. So blieb die Anionenaustauschkapazität von Lewatit M 600 nach 6 Redoxumwandlungen mit Sulfit bzw. $0{,}1N$ Wasserstoffperoxid mit 3,18 bis 3,19 $mEqCl^-$ g konstant. Die unter gleichen Bedingungen wie beim Dithionit-Anionenaustauscher aus Einzelversuchen zusammengesetzte *Durchbruchskurve* für etwa $1M$ Wasserstoffperoxidlösung zeigt Abb. 7. Die Gesamt-Reduktionskapazität beträgt nach Kurve (*a*) etwa 240 mg H_2O_2 pro Säule oder 2,9 mEq H_2O_2/g. Durchlauf erfolgt nach (*b*) ab 165 mg H_2O_2, entsprechend knapp 70% der Gesamt-Reduktionskapazität. Letzterer Wert entspricht durchaus denen des Ionenaustauschers, liegt aber niedriger als beim Dithionit-Anionenaustauscher. Das ist eine Folge der langsameren Oxydation des Sulfites.

Die gemessene *Gesamt-Reduktionskapazität* stimmt gut mit dem aus der Anionenaustauschkapazität berechneten Wert von 3,2 mEq H_2O_2/g überein. Die geringe Differenz ist durch teilweise Autoxydation des festen bzw. im oberen Säulenteil gebundenen Sulfites durch Luftsauerstoff sowie geringe Peroxidverluste infolge Zerfalls an den Glaswänden bedingt.

Die Werte aus zwei Versuchsreihen (Abb. 7) streuen erheblich weniger als beim Dithionit-Anionenaustauscher (Abb. 6). Das ist durch den übersichtlicheren Reaktionsverlauf und die geringere Reaktionsgeschwindigkeit der Sulfitoxydation mit Luftsauerstoff zu erklären. Auch hier kann die erschöpfte Sulfat-Form mit 5–10%iger Natriumsulfitlösung direkt regeneriert werden.

Eine Erhöhung der *Durchlaufgeschwindigkeit* von 0,1 auf 5 ml/min hat kaum Einfluß auf die mit einem H_2O_2-Überschuß bestimmte Gesamt-Reduktionskapazität. Ein schwacher Anstieg unterhalb von 0,5 ml/min wird nur durch die bei längerer Wartezeit spürbar werdende Selbstzersetzung des Wasserstoffperoxides an Gefäßwänden und Harzoberfläche vorgetäuscht. Andererseits hängt die wirklich nutzbare Durchbruchskapazität stärker von der Durchlaufgeschwindigkeit ab. Es kann aber auch hier die beim Ionenaustausch übliche von 1 ml/min angewendet werden.

Die *Korngröße* des Anionenaustauschers ist von 0,1 bis 1,0 mm praktisch ohne Einfluß auf die wie vorher bestimmte Gesamt-Reduktionskapazität. Streuungen sind wiederum durch langsam beginnende Selbstzersetzung des Peroxides bedingt.

Die *Konzentration* der Wasserstoffperoxidlösung ist im Bereich von 0,1–2,5*M* nach drei Versuchsreihen ohne Einfluß auf die in der Säule reduzierte Peroxidmenge.

Geringe Mengen an *Stabilisatoren* wie Diphosphat, Barbitursäure, Harnstoff, ferner Zusatz von 1% Phosphorsäure sowie 0,04*N* Schwefelsäure, aber auch 0,02*M* Natronlauge zeigten praktisch keinen Einfluß auf die Reduktion in der Säule.

Die störende Gasentwicklung durch Selbstzersetzung des Wasserstoffperoxides beginnt oberhalb etwa 25° deutlich zu werden. Bei $<$23–24° wurde nur gelegentlich schwache Gasentwicklung beobachtet. Sie störte den Säulenbetrieb nicht wesentlich.

Wasserstoffperoxid kann ohne Störungen am Sulfit-Anionenaustauscher nur in dem pH-Bereich von etwa 4,5 bis 7 reduziert werden. Im stärker sauren Gebiet wird Schwefeldioxid abgespalten, im stärker alkalischen tritt Selbstzersetzung des Peroxides unter deutlicher Gasentwicklung ein. Ebenso stören Fremdsalzkonzentrationen ab etwa 0,01*N* durch Elution von Sulfit.

Abbildung 8 zeigt die Durchbruchskurve für die Reduktion von fast 2 Liter 0,15*M* Wasserstoffperoxidlösung im kontinuierlichen Säulenbetrieb an etwa 100 g Sulfit-Anionenaustauscher. Es trat während der Reduktion praktisch keine Gasentwicklung in der Säule auf.

Reduktion und katalytische Zersetzung an Redoxiten

Steigender Salzgehalt der Wasserstoffperoxidlösung bewirkt, von einigen Ausnahmen abgesehen, zunehmende Elution des reduzierenden Ions vom Anionenaustauscher. In diesem Fall sind Redoxite mit elutionsstabil eingebauter Redox-Gruppe geeigneter.

Als Beispiel wurde eine 0,3%ige Wasserstoffperoxidlösung in 1*M* Natriumsulfat an einem Leukomethylenblau-Polystyrol-Redoxit[13] quantitativ reduziert, ohne daß die Lösung verunreinigt wurde. Der gleiche Redoxit war früher zur Prüfung seiner Stabilität nach jeweils vorherigen Reduktionen mit Dithionit über hundert Male mit 0,1%iger wässeriger Wasserstoffperoxidlösung oxydiert worden. Dabei nahm die Reduktionskapazität um weniger als 15% ab.

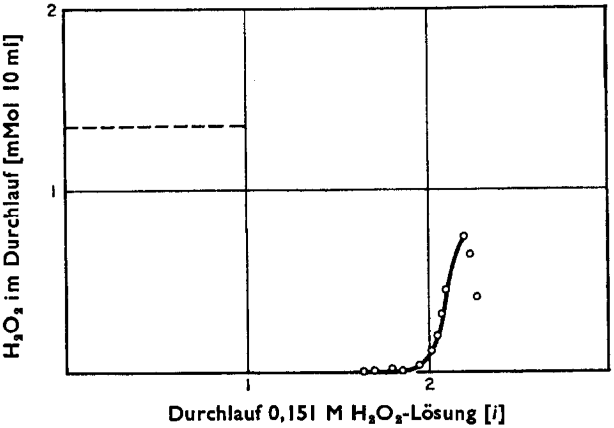

ABB. 8.—Kontinuierliche Entfernung von 0,151*M* Wasserstoffperoxid durch Reduktion an SO_3^{2-}-Lewatit M 600.
100 g Cl^--Lewatit M 600 (0,6–0,75 mm; 22,6% Feuchtigkeit) in SO_3^{2-}-Form übergeführt; bei 20–23°C mit durchschnittlich 3 ml/min filtriert.

Verschiedene andere Polystyrol-Harze mit eingebauten Hydrochinon/Chinonsystemen[13,14] sowie Ferrocen[12] entwickelten aus Wasserstoffperoxid deutlich Sauerstoff. Besonders stark katalysierte das Fe^{3+}/Fe^{2+}-haltige Tonmineral Nontronit die Peroxidzersetzung.

Stärker konzentrierte Wasserstoffperoxidlösung oder lange Einwirkung auch verdünnterer Lösung greifen jedoch die meisten organischen Redoxite mehr oder weniger stark irreversibel an.

Katalytische Zersetzung am OH^--Anionenaustauscher

Verdünnte Wasserstoffperoxidlösungen zersetzen sich am festen OH^--Anionenaustauscher katalytisch.[9] Dabei erwärmt sich die Lösung mehr oder weniger stark.

Im Gegensatz zur entsprechenden Hydroxidlösung verunreinigt die Festbase die Lösung nicht. Die OH^--Ionen können in salzfreier Lösung das Austauschergerüst nicht verlassen. Daher kann die Reaktion auch in einem sehr großen Lösungsvolumen an einer relativ sehr kleinen, aber hoch konzentrierten Menge OH^--Ionen ortsgebunden ablaufen. Normaler Säulenbetrieb wird allerdings durch die starke Gasentwicklung unmöglich.

Die Anordnungen Abb. 3 und 4 zeigen Möglichkeiten auf, den entwickelten Sauerstoff abzuleiten. Sie erlauben einen angenäherten quasi-Säulenbetrieb mit aufgewirbelter Schicht. Die Hauptmenge Peroxid soll bereits im oberen Säulenteil zersetzt werden. Das untere Drittel bleibt als Reserve zur Entfernung gelegentlich durchbrechender Peroxidspuren verfügbar. Ein solches Vordringen der Peroxidfront in der Säule ist am Ausbleichen der rotbraunen Farbe des OH^--Lewatit M 600 oder, noch empfindlicher, durch beginnende Gasentwicklung zu erkennen.

Als Beispiel bringt Abb. 9 die Durchbruchskurve für 1*M* Wasserstoffperoxidlösung. Der Versuch dauerte vier Wochen, zeitweise war der Durchlauf verlangsamt oder ganz unterbrochen. Die nutzbare Durchbruchskapazität dieser OH^--Anionenaustauschersäule betrug etwa 370,2 mEq H_2O_2/g. Das entspricht formal dem 128-fachen derjenigen des Sulfit-Anionenaustauschers.

Ähnlich dem OH^--Anionenaustauscher wirken auch mit Fe^{2+}/Fe^{3+} und ganz besonders mit MnO_4^-/MnO_2 belegte Ionenaustauscher. Dagegen blieb eine Beladung mit H^+, Na^+ oder Cu^{2+} ohne sichtbare Wirkung. Zum Beispiel fanden sich im Durchlauf einer Säule mit 9 g Lewatit S 100 von aufgegebenen 53,9 mEq Wasserstoffperoxid in der angegebenen Reihenfolge der Beladungen 53,7; 53,8 und 53,3 mEq wieder.

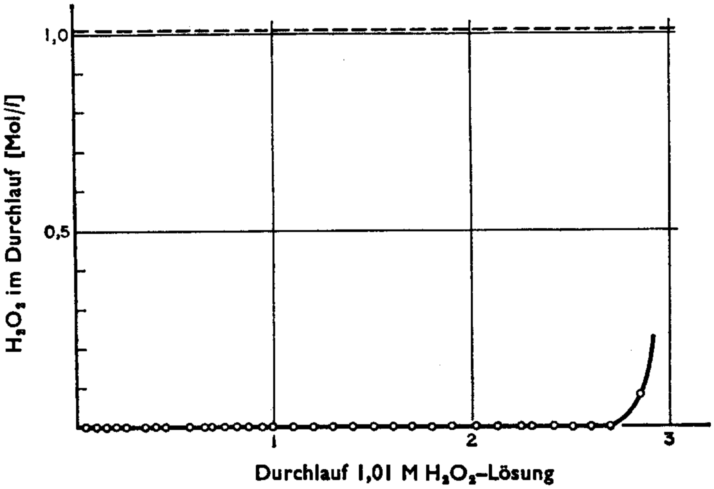

ABB. 9.—Katalytische Zersetzung von 1,01*M* Wasserstoffperoxid an OH^--Lewatit M 600 im quasi-Säulenbetrieb.
20 g Cl^--Lewatit M 600 (0,6–0,75 mm, 22,6% Feuchtigkeit) in OH^--Form übergeführt; bei 20–23°C mit 1 ml/min, jedoch mit Unterbrechungen, filtriert. Säule nach Abb. 4.

DISKUSSION

Vorliegende Arbeit zeigt die Vorteile von einfachen Redox-Ionenaustauschern mit nur irreversibel oxydierbaren Anionen bei der Reduktion ungeladener Moleküle in salzfreier oder salzarmer Lösung. Während Redoxite durch irreversibel Oxydation langsam zerstört werden, ist das Ionenaustrauschergerüst relativ stabil, einfach zugänglich und leicht regenerierbar. Günstig sind Redoxsysteme, welche bei der Oxydation indifferente Anionen wie Sulfat ergeben und bei geringfügiger Elution nicht stören.

Die Entfernung von Wasserstoffperoxid durch Reduktion zu Wasser gelingt besonders rasch am Dithionit-Anionenaustauscher. Auch geringe Sauerstoffspuren werden noch erfaßt. Dithionit hat jedoch den Nachteil eines unübersichtlichen Reaktionsmechanismus, einer Verdoppelung der Anionenladung während der Oxydation und dadurch Elution von Sulfit oder Sulfat. Diese kann bei nur teilweiser Beladung des Anionenaustauschers von diesem selbst, sonst aber durch eine nachgeschaltete Säule mit OH^--Anionenaustauscher entfernt werden. Für andere Zwecke stört die Verunreinigung der Lösung durch Sulfat oder Schwefelsäure jedoch häufig nicht.

Demgegenüber hat der schon von Austerweil[20] zur Entfernung von gelöstem Luftsauerstoff erwähnte Sulfit-Anionenaustauscher den Vorteil eines einfacheren Mechanismus und konstanter Anionenladung. Die Lösung wird nicht verunreinigt. Der Sulfit-Anionenaustauscher ist unter Luftabschluß sehr beständig. Die Grenzen seiner Anwendbarkeit (pH 4,5 bis 7) sind durch die Stabilität von Sulfit einerseits und beginnende Selbstzersetzung des Peroxides andererseits bedingt.

Besondere Bedeutung hat eine halbkontinuierliche und automatische Reduktion des Wasserstoffperoxides am Sulfit-Anionenaustauscher, wenn sie mit einer Vollentsalzung an Ionenaustauschern gekoppelt werden kann. Zum Schutz vor eventuellen Spurenverunreinigungen der behandelten Lösung wird man eine kleine OH^-—und H^+-Ionenaustauschersäule nachschalten. Eine wichtige mögliche Anwendung wäre der einer Radiolyse ausgesetzte Kühlwasserkreislauf entsprechender Atomreaktoren.

Hohe Peroxidkonzentrationen erfordern beim Reduktionsverfahren häufige Regenerationen. Hier erreichte die halbkontinuierliche Zersetzung am OH^--Anionenaustauscher den etwa 130-fachen Umsatz. Die Lösung darf allerdings keine Salzspuren enthalten. Diese tauschen OH^--Ionen aus und blockieren dadurch den Katalysator. Außerdem katalysieren Eisenspuren den oxydativen Angriff des Ionenaustauschergerüstes ungewöhnlich stark.[9]

Die Arbeit wurde im Jahre 1959 ausgeführt. Wir danken für materielle Unterstützung vielmals dem Herrn Bundesminister für wissenschaftliche Forschung, der Deutschen Forschungsgemeinschaft sowie Herrn Dir. Dr. W. Hagge von den Farbenfabriken Bayer in Leverkusen.

Summary—Hydrogen peroxide can be removed semi-continuously from aqueous solution by reduction on an anion-exchange resin in the dithionite or sulphite form, or by catalytic decomposition on a resin in the OH^--form. Simple column arrangements suitable for this purpose providing for exclusion of air, and for quasi-column operation when the resin is vigorously agitated by the evolution of considerable amounts of gas, are described.

Résumé—L'eau oxygénée peut être éliminée de manière semi continue d'une solution aqueuse par réduction sur une résine échangeuse d'anions sous la forme dithionite ou sulfite, ou par décomposition catalytique sur une résine sous forme OH^-. On décrit des dispositifs de colonne simples convenant à cette fin, prévoyant l'exclusion de l'air et l'opération pratique en colonne lorsque la résine est vigoureusement agitée par le dégagement de quantités considérables de gaz.

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SHORT COMMUNICATIONS

Apparatus for the determination of melting points, molecular weights, freezing points and purity, and for the study of melting

(*Received* 10 *June* 1969. *Revised* 4 *May* 1970. *Accepted* 12 *May* 1970)

An apparatus for the rapid precise determination of molecular weights has been developed. It is based on the measurement of melting point lowering, because there are difficulties in obtaining accurate values for freezing points.[1,2] Notice is taken of the conditions which affect precision and arise from processes occurring in the melting system. An equation is deduced for accurate calculation of the melting point, from an estimate of the time at which the melting point occurred, and the co-ordinates of two points in the melting region of the time-temperature record.

EXPERIMENTAL

The vessel was a 10-ml Pyrex glass bulb with two ground-glass necks, the one for filling and emptying having a ground-glass stopper, and the other containing a sealed-in thermistor arranged to have its tip immersed 5 mm into the liquid. The vessel contained 7 g of liquid and five glass balls 6 mm in diameter. The thermistor (FS 23), Standard Telephones and Cables Ltd.) had a resistance of 2000 Ω at 20°, and temperature coefficient 132 Ω/K, and was made one of the ratio arms of a Wheatstone bridge, the out-of-balance current being amplified and recorded on the chart of a recording potentiometer adjusted to give full-scale deflection for the concentration range being used.

The flask was filled with a known weight of solvent and immersed in a freezing-bath for 1 min. It was then placed in an insulated container mounted on the arm of a reciprocating machine and swung uniformly, 90 times a minute, through an arc of 120°.

The temperature-time trace of the pure solvent formed a base line from which subsequent melting-point lowerings could be measured. Some examples are shown in Fig. 1.

Conditions to be observed in design

1. Crystallization of the solvent should be rapid.
2. Residual supercooling in the solid/liquid system or in the temperature measuring device is undesirable.
3. Rapid heat exchange between solid and liquid is necessary so that equilibrium between the two phases can be established quickly.
4. Melting should proceed through a series of equilibrium states, each state, for partially frozen solutions, being in accordance with the freezing point law.
5. The temperature-sensing device must detect small changes accurately. The temperature measured should be that of the solution in equilibrium with frozen solid.
6. At the melting point the concentration of the solution in equilibrium with solid must be constant.
7. The melting point should be relatively indifferent to the rate of melting.
8. A clearly defined melting point is desirable.
9. The apparatus should be simple to use, and the time of measurement short.

DISCUSSION

Crystallization of the organic liquids used, of water and of molten naphthalene and diphenylamine was rapid and clearly defined, largely because of the presence of the glass balls. The melting point was well defined on the recorder trace and by calculation could be measured accurately. The time required to remelt the partially frozen liquid was short, usually about 5 min. The thermistor tip was small and hence the temperature response rapid. Efficiency of mixing was the main factor involved in satisfying the other conditions, and was achieved by means of the glass balls, the uniformity of the mechanical motion and the jerk at the end of each stroke. The uniformity of motion was most important. The efficiency was demonstrated by the smoothness of the trace for pure solvent and by the shape of that for a solution. The shape of the curve follows from the freezing point depression law, which may be expressed as

$$T_L - T_1 = \Delta T_1 = \frac{kn}{w_0 + st_1} \tag{1}$$

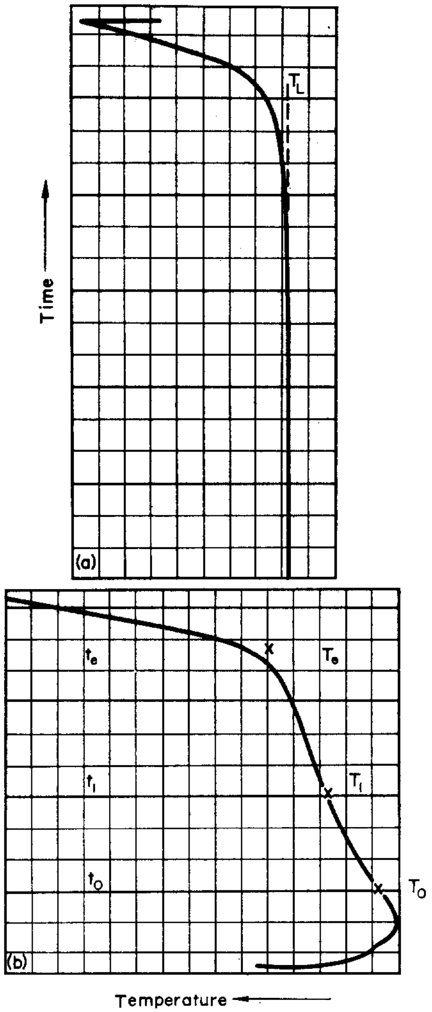

FIG. 1.—Examples of time–temperature curves; (*a*) pure solvent; (*b*) solution.

where k = the cryoscopic constant, n = moles of solute, w_0 = weight of solvent at beginning of melting, T_L = melting point of solvent, s = speed of melting, t_1 = time of melting to temperature T_1.

For any given trace for melting, the only variables are T and t and when plotted against each other they should give a concave curve. The shape of the trace in Fig. 1(*b*) illustrates this. That all such traces were curved confirms the efficiency of mixing.

The rate of heat exchange between the two phases was not only a function of mixing, but also of crystal size and the thermal properties of the two phases. Thus the heat exchange was least for pure solvents where the crystals were large, and greatest for the solvent cyclohexane, the latent heat of which was so low that melting was too rapid for a trace like Fig. 1 to be developed.

Determination of the melting point

The melting point of solvents (T_L) is that portion of the trace which gives a constant temperature over an interval of time. The melting point for solutions can be taken as that temperature where the amount of frozen solid becomes vanishingly small (T_e). At this point,

$$T_L - T_e = \Delta T_e = \frac{kn}{w} \tag{2}$$

where w is the weighed amount of solvent.

The expression used to calculate the melting point is

$$\Delta T_e = \frac{\Delta T_1 \Delta T_0 \alpha}{\Delta T_0(\alpha + 1) - \Delta T_1} \tag{3}$$

where $\Delta T_1 = T_L - T_1$ and $\Delta T_0 = T_L - T_0$ are two temperature differences on the trace, corresponding to times of melting t_1 and t_0, $\alpha = (t_1 - t_0)/(t_e - t_1)$, and where t_e is the time at T_e (see Fig. 1).

From equations (1) and (2) we obtain

$$w_0 + st_1 = \frac{\Delta T_e w}{\Delta T_1}, \tag{4}$$

and as

$$w_0 \Delta T_0 = kn = \Delta T_e w,$$

then

$$\frac{\Delta T_e w}{\Delta T_0} + st_1 = \frac{\Delta T_e w}{\Delta T_1}. \tag{5}$$

Thus,

$$s = \frac{\Delta T_e w}{t_1}\left[\frac{1}{\Delta T_1} - \frac{1}{\Delta T_0}\right] \tag{6}$$

If the rate of melting is the same throughout the melting process, and it is probable that this is so over a small temperature range and relatively short melting times, then the expression above is true whatever the temperature points chosen. Hence,

$$\frac{\Delta T_e w}{t_1 - t_0}\left[\frac{1}{\Delta T_1} - \frac{1}{\Delta T_0}\right] = \frac{\Delta T_e w}{t_e - t_1}\left[\frac{1}{\Delta T_e} - \frac{1}{\Delta T_1}\right] \tag{7}$$

This gives:

$$\left[\frac{1}{\Delta T_1} - \frac{1}{\Delta T_0}\right] = \frac{t_1 - t_0}{t_e - t_1}\left[\frac{1}{\Delta T_e} - \frac{1}{\Delta T_1}\right]$$

or

$$\frac{1}{\Delta T_1} - \frac{1}{\Delta T_0} = \frac{\alpha}{\Delta T_e} - \frac{\alpha}{\Delta T_1}$$

or

$$\frac{(\alpha + 1)}{\Delta T_1} = \frac{1}{\Delta T_0} + \frac{\alpha}{\Delta T_e}$$

whence

$$\Delta T_e = \frac{\Delta T_1 \Delta T_0 \alpha}{\Delta T_0(\alpha + 1) - \Delta T_1}. \tag{8}$$

Estimation of precision

The precision of cryosopic results is usually expressed in terms of temperature as this is the unit of measurement. It was thought that concentration would be a more meaningful term. The cryoscopic constant k estimated from the slope of a plot of melting point depression *vs.* molal concentration m, may be used to estimate the concentration m' corresponding to any given value of ΔT_e,

$$m' = \Delta T_e / k.$$

The differences $(m - m')$ can then be used as a measure of precision.

Results are shown in Table I.

APPLICATIONS

Molecular weights

The precision with which the molecular weights of organic compounds can be measured by the apparatus can be seen from Table I. The mean value of the standard deviations is ±0·002 mole/kg and the experimental value for a substance of molecular weight of 1000 in 1-molal solution would be found to lie between 1004 and 996. If, however, the solution were 0·1 molal, the value would lie between 1040 and 960. It follows that within the bounds of ideality, the more concentrated the solutions the smaller the error. The samples in Table I included solutions up to 1·2 molal.

For a molal solution of a substance of molecular weight 10000, the limits would be 9960 and 10040,

TABLE I.—RESULTS OF MEASUREMENTS AND THEIR PRECISION

Solvent	Solutes	No. of results	Std. devn., *mole/kg*
Water	Sucrose, glucose, urea, catechol, resorcinol, hydroquinone, phenol, aniline, benzylamine	72	±0·0035
Benzene	Naphthalene, α-naphthol, catechol, benzil, fats and oils	65	±0·0016
Dioxan	Naphthalene, benzoic acid, 1,5-, 1,6-, 1,3-, 1,4-, 1,7-, 2,3-, 2,7-dihydroxynaphthalenes, methyl salicylate, nitrobenzene, pyrogallol, catechol, fats and oils	105	±0·0021
Nitrobenzene	Naphthalene, coumarin	20	±0·0015

but it often becomes more difficult to make such a concentrated solution as the molecular weight rises, It would seem unwise to claim that it is possible to extrapolate the readings to high molecular weights. *i.e.*, in excess of 10000, as is sometimes done.

Purity

Taking the mean standard deviation as 0·002 mole/kg and assuming that twice this value is needed for detection, then the minimum amount of impurity that could be detected in organic materials soluble in any of the four solvents suitable, would be 0·0004 mole % if a 1-molal solution were used.

Other uses

It is possible to examine self-associated species in benzene and nitrobenzene[3] and weak complexes in an inert solvent.[4] The number of particles present under certain experimental conditions can be determined and this might be useful in the study of reaction mechanisms.

The nature of the recorder traces enables a study to be made of the last stages of the melting of liquids and dilute solutions. Melting points can be determined and although it is not claimed that T_e is the physical melting point, it is based on theory and reproducible to within ±0·005°.

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Summary—An apparatus for the determination of the melting point of a partially frozen liquid is described. Thermal equilibrium is rapidly attained, largely because of the presence of glass balls in the experimental flask, and the method of agitation. The use of a thermistor and a recording potentiometer allows charting of the temperature changes with time. The melting point can be calculated from points on the trace. The apparatus has been used to study melting point depressions for solutions of hydrocarbons and phenols in benzene, nitrobenzene, water and dioxan.

Zusammenfassung—Ein Gerät zur Bestimmung des Schmelzpunktes einer teilweise gefrorenen Flüssigkeit wird beschrieben. Das thermische Gleichgewicht wird mit Hilfe eines Vorrats von Glaskugeln im Versuchskolben und eines besonderen Rührverfahren rasch erreicht. Ein Thermistor und ein Schreiber ermöglichen es, die zeitliche Änderung der Temperatur zu registrieren. Der Schmelzpunkt kann aus Punkten auf der Registrierspur berechnet werden. Mit dem Gerät sind Schmelzpunktenniedrigungen einiger Lösungen von Kohlenwasserstoffen und Phenolen in Benzol, Nitrobenzol, Wasser und Dioxan untersucht worden.

Résumé—On décrit un appareil pour la détermination du point de fusion d'un liquide partiellement congelé. L'équilibre thermique est rapidement atteint, essentiellement à cause de la présence de billes de verre dans la fiole d'expérimentation et de la méthode d'agitation. L'emploi d'un thermistor et d'un potentiométre enregistreur permet

l'enregistrement des variations de température en fonction du temps. Le point de fusion peut être calculé de points sur le tracé. On a utilisé l'appareil pour étudier les dépressions du point de fusion pour des solutions d'hydrocarbures et de phénols en benzène, nitrobenzene, eau et dioxane.

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A silver electrode in the potentiometric titration of thiols*†

(*Received* 26 *July* 1969. *Revised* 20 *January* 1970. *Accepted* 11 *March* 1970)

THE AMPEROMETRIC method of Benesch *et al.*[1] using silver as the titrant has been used extensively for measuring thiols. Kolthoff and co-workers[2] have made a critical study of the method and discussed the merits of several titrants. We had difficulty in locating the end-point in amperometric titrations, so we tried potentiometry. We have found that simply immersing a piece of silver wire in a solution of a thiol for a short time produces an electrode responsive to thiol concentration. Cecil and McPhee[3] had earlier used a silver–silver sulphide electrode prepared by an involved procedure and the restrictive conditions they reported may have discouraged extensive use of their method.

Since the electrode follows the thiol level, any thiol reagent should be satisfactory as titrant, and the reagent forming the most stable compound should give the sharpest end-point. Mercury(II) salts, monosubstituted organo-mercuric salts and silver nitrate have been used successfully.

The operating procedure was designed to accommodate the slow electrode response, and a simple treatment prior to each titration eliminated the reduction in electrode response that occurred with continued use.

The response of the electrode would be expected to arise from

$$\mathrm{RSH} \rightleftharpoons \mathrm{RS^-} + \mathrm{H^+}; \qquad [\mathrm{RS^-}] = K_1\frac{[\mathrm{RSH}]}{[\mathrm{H^+}]}$$

$$\mathrm{Ag(s)} + \mathrm{RS^-} \rightleftharpoons \mathrm{AgRS(s)} + \mathrm{e}$$

$$E = E^\circ - 0{\cdot}059\log\frac{1}{[\mathrm{RS^-}]}$$

$$= E^{\circ\prime} + 0{\cdot}059\log[\mathrm{RSH}]\ \text{(at constant pH)}$$

The electrode potentials for three different levels of cysteine at pH 7·0, measured with two electrodes (the first a silver wire immersed in the solution until a steady potential was attained, the second deliberately coated with a heavy silver sulphide layer) gave slopes of 0·054 and 0·057 V, confirming the proposed mechanism, though the E° values were different.

EXPERIMENTAL

Preparation of electrode

Coil 0·15 m of 1·27-mm diameter silver wire for several turns round a 4-mm tube. The first time the electrode is used, immerse it briefly in ammonia solution (1 + 3), rinse with demineralized water, immerse it in dilute nitric acid (1 + 3) for 2 min and rinse with demineralized water.

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* This work was supported in part by a USPHS Grant No. 1T1 DE175 and in part by the United States Atomic Energ yCommission, Contract No. W-7401-Eng-49 and has been assigned Report No UR-49-960.

† Thiols are generally referred to as "sulfhydryls" in American and biochemical terminology.

l'enregistrement des variations de température en fonction du temps. Le point de fusion peut être calculé de points sur le tracé. On a utilisé l'appareil pour étudier les dépressions du point de fusion pour des solutions d'hydrocarbures et de phénols en benzène, nitrobenzene, eau et dioxane.

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$$\mathrm{Ag(s)} + \mathrm{RS^-} \rightleftharpoons \mathrm{AgRS(s)} + \mathrm{e}$$

$$\begin{aligned} E &= E^\circ - 0{\cdot}059 \log \frac{1}{[\mathrm{RS^-}]} \\ &= E^{\circ\prime} + 0{\cdot}059 \log\,[\mathrm{RSH}] \text{ (at constant pH)} \end{aligned}$$

The electrode potentials for three different levels of cysteine at pH 7·0, measured with two electrodes (the first a silver wire immersed in the solution until a steady potential was attained, the second deliberately coated with a heavy silver sulphide layer) gave slopes of 0·054 and 0·057 V, confirming the proposed mechanism, though the E° values were different.

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† Thiols are generally referred to as "sulfhydryls" in American and biochemical terminology.

The electrode must be cleaned after each titration; otherwise the potential change at the end-point decreases considerably. Immerse the electrode in ammonia solution (1 + 3) for 1 min (after titration of simple systems; 3–5 min after protein titration) then wash with demineralized water. If the electrode has not been used for a long time, immersion for about an hour is advisable.

Titration assembly

A saturated potassium chloride salt bridge is constructed from borosilicate glass 20 mm in diameter drawn down to a 4-mm tube with a porous piece of carborundum sealed into its end. A silver-silver chloride reference electrode is placed in the salt bridge and the silver wire electrode is placed round the 4-mm tube. A microsyringe readable to 0·1 μl and a multirange millivoltmeter complete the assembly. The burette and potentiometer can be coupled to a recorder for automatic plotting of the titration curve.

Titrants

Mercury(II) chloride, 0·005*M*. Standardized against pure glutathione.

p-*Chloromercuriphenyl sulphonate (PCMPS) solution.* Standardized with glutathione.

Silver nitrate solution. Standardized by adding an excess of standard sodium chloride solution and measuring the excess by an instrumental method.

Titration

Because of the slowness of electrode response, continuous titration is impossible. However, most of the potential change after addition of an increment of titrant occurs within 30 sec, and >90% within 60 sec; no further change occurs after 2 min. A heavily coated sulphide electrode has an even slower response; if the reading at the end of 3 min is used as reference standard, 50–60% of the increase occurs during the first minute, about 30% within the second minute and the rest during the third; longer intervals produce further small changes.

If successive equal additions of titrant are made at equal time intervals, the end-point lies within the increment that gives the greatest potential change. Figure 1 shows two typical titration curves, one for a simple thiol, the other for a complex one.

Only the portion of the titration curve near the end-point need be plotted. The end-point can usually be located within a 2-μl increment, though the electrode will respond to an addition of <1 μl.

Titrations with all three titrants gave curves of the same shape, but with different sizes of potential

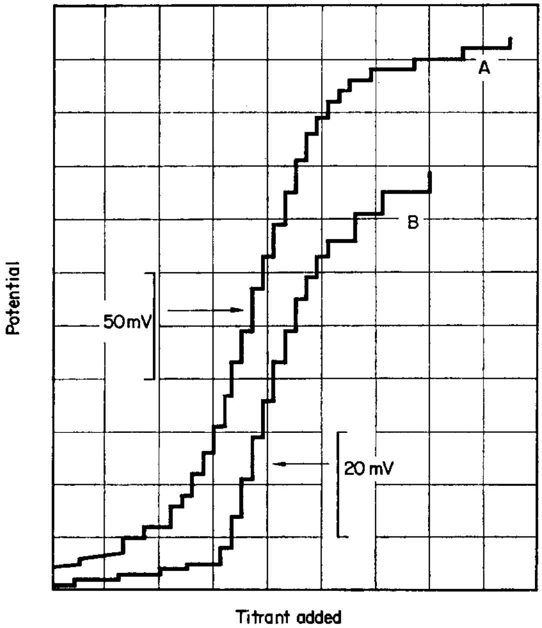

FIG. 1.—Titration curves. A—cysteine; B—albumin.

break, and the conditions for titration differed. Mercury(II) chloride is satisfactory as a titrant at pH 4·5–9·5, PCMPS at pH 7–9·5, and silver nitrate only at pH 9·5 (performance at pH values outside the range 4·5–9·5 was not tested).

Procedure

Place 2 ml of 5% albumin solution and 4 ml of 0·1*M* tris buffer, pH 7·0, in a 10-ml beaker with a small stirring bar. Immerse the electrode just to clear the stirring bar, and place the burette tip just below the surface of the liquid. Add the titrant in increments which decrease as the expected equivalence point is approached. When the potential definitely starts to rise, add increments of exactly 0·002 ml at 2-min intervals.

RESULTS

Titration of cysteine

Although titrations of cysteine solutions gave very sharp end-points at the three pH values studied, only at pH 4·5 were the results consistent when an air atmosphere was used. At pH 7 and 9·5 the results were lower and somewhat erratic until the solutions were freed from oxygen and a nitrogen atmosphere was maintained during titration. Table I shows the results obtained with two different solutions.

TABLE I.—TITRATION OF CYSTEINE WITH MERCURIC CHLORIDE

pH	Titre, *ml* 1	Titre, *ml* 2
4·5	0·1841	0·1940
	0·1800	0·1960
7·0	0·1801	0·1960
	0·1822	0·1901
9·5	0·1820	0·1941
		0·1941
		0·1960

Titration of albumin

Albumin solution kept in a refrigerator for a month showed no change in thiol content, and a nitrogen atmosphere was required only for titration at pH 9. Table II shows the results obtained with different titrants and, for comparison, the results obtained amperometrically.

TABLE II.—TITRATION OF ALBUMIN

Method	Titrant	No. of detns.	SH, *μmole/g*
Potentiometric	$HgCl_2$	21	8·32 ± 0·09
Potentiometric	PCMPS	9	8·65 ± 0·21
Potentiometric	$AgNO_3$	10	8·18 ± 0·09
Amperometric	$HgCl_2$	4	8·26 ± 0·16

Since urea is commonly used to denature proteins, its effect on the titration of albumin was determined. It was necessary to purify reagent grade urea by passing its solution through a mixed-bed ion-exchange resin. When a nitrogen atmosphere was used the same titre was obtained with or without urea present. In an air atmosphere at pH 7, the solution containing urea gave a lower titre.

DISCUSSION

It was thought desirable to carry out titrations near pH 7 in order to maintain conditions as close to physiological ones as possible. Cecil and McPhee[8] found that glutathione could only be titrated in the pH range 1·8–2·2 and cysteine in the range 3·5–7·5 with silver nitrate and their sulphide electrode. In the present work, identical results were obtained with mercury(II) chloride at pH 4·5, 7·0 and 9·5 for simple thiols and albumin provided that a nitrogen atmosphere was maintained.

Mercury(II) chloride is preferred as titrant because it gives the largest potential change at the end-point.

The use of silver as titrant was of special interest. Some doubt has been cast upon the validity of titration with silver in the amperometric methods,[2,4] in which positive errors were attributed to reactions with groups other than thiol. Since the electrode used in the present study responds directly to the thiol level, it is apparent from the results in Table II that silver gives correct results.

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Summary—A silver wire immersed in a thiol solution gives a potential responsive to the thiol concentration, and is a sensitive indicator electrode in the potentiometric titration of thiols with mercury(II) chloride, *p*-chloromercuryphenyl sulphonate, and silver nitrate at pH 4·5–9·5, 7–9·5 and 9·5 respectively. Titrations of simple thiols such as cysteine or a protein such as albumin are equally successful, but the potential break was smaller for the protein. The end-point could be determined within an increment of titrant equal to 5 nmole of thiol. An inert atmosphere is needed for titration at pH $\gg$ 7.

Zusammenfassung—Ein in eine Thiollösung tauchender Silberdraht gibt ein Potential, das ein Maß für die Thiolkonzentration darstellt. Der Draht ist eine empfindliche Indikatorelektrode bei der potentiometrischen Titration von Thiolen mit Quecksilber(II)chlorid, *p*-Chlormercuriphenylsulfonat und Silbernitrat bei pH 4,5–9,5: 7–9,5 bzw. 9,5. Titrationen einfacher Thiole wie Cystein oder eines Proteins wie Albumin sind gleichermaßen möglich; der Potentialsprung war jedoch beim Protein kleiner. Der Endpunkt ließ sich innerhalb einer Zugabe von Titrant feststellen, die 5 nMol Thiol entspricht. Bei Titrationen bei pH $\gg$ 7 benötigt man eine inerte Atmosphäre.

Résumé—Un fil d'argent immergé dans une solution de thiol donne un potentiel sensible à a concentration en thiol, et est une électrode indicatrice sensible dans le titrage potentiométrique des thiols par le chlorure de mercure(II), le *p*-chloromercuriphényl sulfonate et le nitrate d'argent à pH 4,5–9,5, 7–9,5 et 9,5 respectivement. Les titrages de thiols simples tels que la cystéine ou d'une protéine telle que l'albumine sont également couronnés de succés, mais la cassure de potentiel est plus petite pour la protéine. Le point de fin de dosage peut être déterminé avec un incrément d'agent de titrage égal à 5 nmole de thiol. Une atmosphère inerte est nécessaire pour le titrage à pH $\gg$ 7.

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Amperometric complex-formation titration of traces of alkaline earths

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IN A PREVIOUS communication[1] the principles of the amperometric complex-formation titration of metal ions with indication by following the anodic wave of the excess of ligand, have been presented. The work of Campbell and Reilley,[2] who used a dropping mercury electrode, could be extended to a higher sensitivity by using a rotating mercury electrode as the indicator electrode. The criterion for a sharp end-point of a complexometric titration curve appeared to be

$$K'c \geq 2 \times 10^3$$

titration with silver in the amperometric methods,[3,4] in which positive errors were attributed to reactions with groups other than thiol. Since the electrode used in the present study responds directly to the thiol level, it is apparent from the results in Table II that silver gives correct results.

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Summary—A silver wire immersed in a thiol solution gives a potential responsive to the thiol concentration, and is a sensitive indicator electrode in the potentiometric titration of thiols with mercury(II) chloride, *p*-chloromercuryphenyl sulphonate, and silver nitrate at pH 4·5–9·5, 7–9·5 and 9·5 respectively. Titrations of simple thiols such as cysteine or a protein such as albumin are equally successful, but the potential break was smaller for the protein. The end-point could be determined within an increment of titrant equal to 5 nmole of thiol. An inert atmosphere is needed for titration at pH $\gg$ 7.

Zusammenfassung—Ein in eine Thiollösung tauchender Silberdraht gibt ein Potential, das ein Maß für die Thiolkonzentration darstellt. Der Draht ist eine empfindliche Indikatorelektrode bei der potentiometrischen Titration von Thiolen mit Quecksilber(II)chlorid, *p*-Chlormercuriphenylsulfonat und Silbernitrat bei pH 4,5–9,5: 7–9,5 bzw. 9,5. Titrationen einfacher Thiole wie Cystein oder eines Proteins wie Albumin sind gleichermaßen möglich; der Potentialsprung war jedoch beim Protein kleiner. Der Endpunkt ließ sich innerhalb einer Zugabe von Titrant feststellen, die 5 nMol Thiol entspricht. Bei Titrationen bei pH $\gg$ 7 benötigt man eine inerte Atmosphäre.

Résumé—Un fil d'argent immergé dans une solution de thiol donne un potentiel sensible à a concentration en thiol, et est une électrode indicatrice sensible dans le titrage potentiométrique des thiols par le chlorure de mercure(II), le *p*-chloromercuriphényl sulfonate et le nitrate d'argent à pH 4,5–9,5, 7–9,5 et 9,5 respectivement. Les titrages de thiols simples tels que la cystéine ou d'une protéine telle que l'albumine sont également couronnés de succés, mais la cassure de potentiel est plus petite pour la protéine. Le point de fin de dosage peut être déterminé avec un incrément d'agent de titrage égal à 5 nmole de thiol. Une atmosphère inerte est nécessaire pour le titrage à pH $\gg$ 7.

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Amperometric complex-formation titration of traces of alkaline earths

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IN A PREVIOUS communication[1] the principles of the amperometric complex-formation titration of metal ions with indication by following the anodic wave of the excess of ligand, have been presented. The work of Campbell and Reilley,[2] who used a dropping mercury electrode, could be extended to a higher sensitivity by using a rotating mercury electrode as the indicator electrode. The criterion for a sharp end-point of a complexometric titration curve appeared to be

$$K'c \geq 2 \times 10^3$$

where K' is the conditional stability constant of the metal complex involved and c is the original concentration of the metal ion. When errors of 1% or slightly more are tolerable values of $K'c$ of 10^3 or even 10^2 can be used.

In the present paper the determination of the alkaline earth metals with EDTA, EGTA and DTPA as chelating agents* is described. A prediction of the limit of determination can easily be made by means of the sharpness criterion mentioned above. In Table I the conditional stability constants of the various complexes are given for a pH-value of 10. The Table shows that the determination of the alkaline earths should be possible at the $10^{-5}M$-concentration level, when the appropriate chelating agent is used, *i.e.*, any of the three for calcium, EDTA or DTPA for magnesium, DTPA or EGTA for strontium or barium. When errors of about 1% are admissible determinations at the $10^{-6}M$-level should be possible.

TABLE I.—VALUES OF log K'_{MY} AT pH 10

Metal	EDTA	EGTA	DTPA
Ca	10·2	10·9	9·9
Mg	8·2	5·1	8·6
Sr	8·1	8·4	9·0
Ba	7·3	8·3	8·1

As the titration cell is constructed for determinations in a volume of 10 ml the minimum amount of these metals that can be determined should be about 10 nmole, which corresponds to about 0·2–1·4 μg, depending on the metal.

EXPERIMENTAL

Apparatus

The titration cell has a volume of 10 ml. It is connected by means of fritted glass discs on the one side with a saturated calomel electrode and on the other side with a compartment containing an auxiliary tungsten electrode. All three compartments of the titration cell are filled with the same supporting electrolyte solution. The rotating mercury electrode (600 rpm) used as the indicator electrode was described in the previous paper. The Beckmann Electroscan 30 supplied the voltage for the cell and also served for the measurement of the current. Titrations were carried out by adding the titrant solution from a 1-ml syringe microburette.

Selection of the potential

The selection of the potential to be applied to the indicator electrode is very important. The most favourable potential depends on the concentration of the metal ion to be titrated and on the condition of the electrode. The correct selection of the potential can be made by recording polarograms with the indicator electrode of solutions containing the supporting electrolyte solution and small but different amounts of the titrant.

Reagents

Potassium nitrate (10 g) and ammonium nitrate (8 g) were dissolved in 1 litre of distilled water. The pH was adjusted to 10 by addition of potassium hydroxide to give a 0·1*M* buffer solution. A 0·001*M* buffer solution was prepared in a similar way.

Stock solutions of the alkaline-earth metals were prepared from the chemically pure nitrates or sulphates and were standardized complexometrically.

Solutions of EDTA, DTPA, and EGTA were standardized against calcium carbonate.

Procedure

The sample, containing 1–100 μg of the alkaline earth metal, is dissolved in 10 ml of 0·001*M*–0·1*M* buffer solution. The solution is put in the titration cell and titrated with a 10^{-4}–$10^{-2}M$ solution of the appropriate complexing agent; the titration graph is recorded on the Electroscan. In order to avoid too large an *iR*-drop across the cell, the titration is stopped when a 20% excess of the titrant has been added. The end-point is obtained as the point of intersection of the two straight parts of the curve.

* EDTA = ethylenediaminetetra-acetic acid.
EGTA = ethyleneglycol bis(β-aminoethyl ether)-*N*,*N*,*N'*,*N'*-tetra-acetic acid.
DTPA = diethylenetriaminepenta-acetic acid.

RESULTS

In Table II some typical results are given for determinations in the 100-µg range, and in Table III for the 1-µg range.

It can be seen from Table III that $10^{-6}M$ solutions of the alkaline earth metals can be titrated with fair accuracy. The time required for a titration is between 3 and 5 min.

TABLE II.—DETERMINATIONS OF ALKALINE EARTH METALS IN THE 100-µg RANGE AT pH 10

Metal, µg		Error, %	Std. devn., % (no. of detns.)	Titrant
taken	found			
48·7 Mg	47·7	−2	0·5 (4)	EDTA
48·7 Mg	47·8	−2	0·6 (4)	DTPA
59·3 Ca	58·8	−0·8	0·5 (5)	EGTA
79·0 Ca	77·1	−2·2	1·2 (5)	DTPA
128·8 Sr	128·4	−0·3	2·0 (5)	EDTA
128·8 Sr	127·0	−1·4	2·2 (5)	EGTA
128·8 Sr	128·8	—	1·6 (5)	DTPA
269·7 Ba	261·3	−3	5·2 (4)	EGTA
202·4 Ba	201·3	−0·5	3·7 (5)	DTPA

TABLE III.—DETERMINATION OF THE ALKALINE EARTH METALS IN THE 1-µg RANGE AT pH 10

Metal, µg		Error, %	Std. devn., % (5 variates)	Titrant
taken	found			
0·365 Mg	0·371	+1·6	4·1	DTPA
0·365 Mg	0·374	+2·4	2·3	EDTA
0·395 Ca	0·416	+5	3·1	EDTA
0·790 Ca	0·830	+7	2·3	EDTA
1·58 Ca	1·60	+1·2	1·3	EDTA
1·29 Sr	1·29	—	3·5	EGTA
1·29 Sr	1·37	+6	2·0	DTPA
2·02 Ba	2·04	+1	3·2	EGTA
2·02 Ba	2·05	+1·5	5·6	DTPA

Determination of calcium in the presence of magnesium

The investigations have been extended to include the determination of calcium with EGTA in the presence of magnesium. The maximum admissible concentration of magnesium can be found from the sensitivity condition mentioned in the previous paper [equation (19′)]:[1]

$$K'_{Mg}c_{Mg} < (n - 1)$$

where n is the factor by which the sensitivity may be reduced. The determination of $1{\cdot}5 \times 10^{-6}M$ calcium has been carried out in the presence of a 100-fold and a 1000-fold amount of magnesium. A considerable decrease in the slope of the titration curve after the equivalence point and thus a considerable decrease in sensitivity was to be expected in these cases. The experimental results agree reasonably with the predictions, but as the decrease of linearity observed was smaller than predicted,

TABLE IV.—DETERMINATIONS OF CALCIUM WITH EGTA IN THE PRESENCE OF MAGNESIUM

Calcium, µg		Magnesium µg	Error, %	Std. devn., % (no. of detns.)
present	found			
0·596	0·581	37·6	−2·5	5·8 (6)
0·596	0·589	364	−1·2	4·9 (9)

the experiments turned out to be better than expected. An exact agreement could not be expected as the stability constants used in the calculations were determined under conditions other than the actual experimental conditions. The analytical results are given in Table IV.

Although a great number of complexometric titrations of the alkaline earth metals have been described, the amperometric indication of the excess of ligand with a rotating mercury electrode would seem to offer improvements in sensitivity and speed. Only a few minutes are required for each titration.

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Summary—Alkaline earth metals were determined in microgram quantities by complexometric titration with EDTA, EGTA and DTPA. The end-point was detected by following the anodic wave of the chelating agent at the rotating mercury electrode. All the alkaline earths can be titrated at the microgram level with reasonable accuracy, and calcium may be titrated with EGTA in the presence of a 1000-fold excess of magnesium.

Résumé—On a dosé les métaux alcalino-terreux en quantités de l'ordre du microgramme par titrage complexométrique avec EDTA, EGTA et DTPA. Le point de fin de dosage est détecté en suivant la vague anodique de l'agent chélatant sur l'électrode de mercure rotative. Tous les alcalino-terreux peuvent être titrés à l'échelle du microgramme avec une precision raisonnable, et l'on peut titrer le calcium à l'EGTA en la présence d'un excès 1000 fois plus grand de magnésium.

Zusammenfassung—Erdalkalimetalle wurden in Mikrogrammengen durch komplexometrische Titration mit EDTA, EGTA und DTPA bestimmt. Der Endpunkt wurde durch Beobachtung der anodischen Stufe des Chelatbildners an der rotierenden Quecksilberelektrode ermittelt. Alle Erdalkalien lassen sich im Mikrogrammbereich ausreichend genau bestimmen; Calcium kann in Gegenwart eines 1000-fachen Überschusses von Magnesium mit EGTA titriert werden.

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2. R. T. Campbell and C. N. Reilley, *ibid.*, 1962, **9**, 153.

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A microwave-excited emissive detector for gas chromatography
Further studies with sulphur compounds

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This communication describes some improvements to a microwave-excited emissive detector for gas chromatographic detection of some sulphur compounds. The system previously described[1] has been modified by restricting the volume occupied by the discharge, using a catalyst to aid the thermal degradation of the sulphur compounds, using all of the sample eluted from the gas chromatograph, and stabilizing the vacuum in the detector tube.

These modifications have led to an overall improvement in this type of detection technique and have yielded superior detection limits, particularly for those sulphur compounds of relatively low volatility or high thermal stability.

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These modifications have led to an overall improvement in this type of detection technique and have yielded superior detection limits, particularly for those sulphur compounds of relatively low volatility or high thermal stability.

EXPERIMENTAL

Restriction of the discharge

The detector tube used (Fig. 1) was fabricated from 8 mm internal diameter transparent silica tubing with two constrictions, *ca.* 2 mm diameter, such that a bulb *ca.* 30 mm in length was formed. The bulb could be situated almost entirely within the microwave field of either a quarter-wave foreshortened radial line cavity or a quarter-wave Evenson type of cavity, thus maintaining the discharge within the bulb. Under these conditions the plasma was found to be quite stable. Stability was increased further by the use of a large (*ca.* 50 l.) ballast tank in the vacuum line, downstream from the detector, which smoothed out the previously observed fluctuations due to the exhaust action of the vacuum pump.

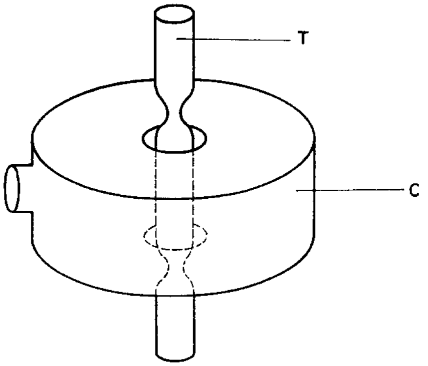

FIG. 1.—Microwave cavity and detector tube.
T—detector tube.
C—quarter-wave foreshortened radial line resonant cavity.

Use of platinum catalyst

A difficulty frequently associated with low-pressure microwave-excited plasmas is the inability to supply sufficient energy to break down relatively stable compounds completely. It was found, however, that a loop of 0·35 mm diameter platinum wire placed in the bulb of the detector tube greatly increased the detection limit of the compounds thiophen, dimethyl sulphoxide and thioglycollic acid. One probable reason for this action is that at the temperature of the discharge the platinum partially vaporizes (substantiated by the presence of platinum atomic emission at 265·9 and 306·6 nm) and aids the fragmentation process. The use of the Evenson quarter-wave cavity also gives increased fragmentation in comparison to the quarter-wave foreshortened radial line cavity.

The physical effects observed with the platinum loop in the bulb of the detector were a concentration of the discharge around the platinum loop, diminution of short-term background noise of the discharge by approximately one half and initiation of the discharge without the use of a "Tesla" vacuum tester at an applied microwave power of 50 W.

Use of total sample

In the present arrangement all of the sample eluted from the column was utilized for microwave detection, by means of the gas chromatographic oven circuit shown in Fig. 2. The outlet from the sample side of the katharometer detector passes back inside the oven and a needle valve is incorporated in the line also within the oven. On the upstream side of this, a T-joint connects the microwave detector and the flow meter into the line. The pipework outside the oven is kept to the minimum consistent with the experimental layout, and is heated to approximately 200° with an electrically heated wire to prevent sample condensation.

Maximum peak height was recorded when the sample was eluted from the gas chromatographic column in the shortest possible time, preferably in less than 90 sec. Long elution times caused the peak to become less well-defined because any tailing or peak broadening in the gas chromatographic system was magnified in the microwave detection unit by the extra pipework involved. However, there must be sufficient resolution of the sample from air and water (which appear as trace impurities) and also from the solvent employed. It was found in our arrangement that a suitable retention time for the sample was between 30 and 80 sec, whilst that of the solvent should exceed this by at least 40 sec.

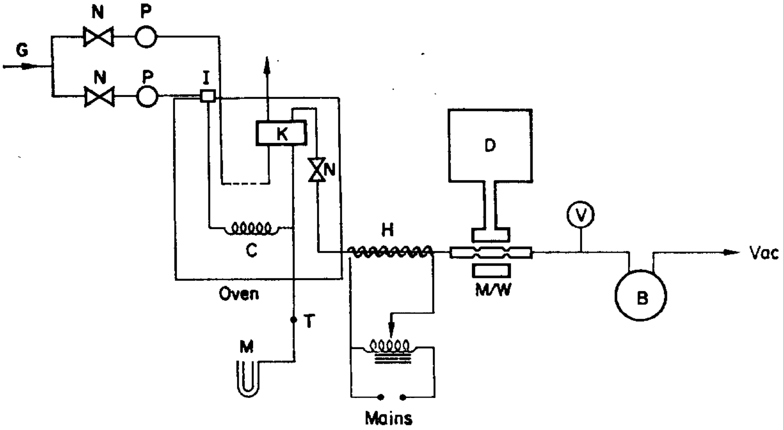

FIG. 2.—Experimental arrangement.

G—carrier gas inlet; *N*—needle valves; *P*—pressure gauges (0–30 psi); *I*—GLC injection block; *K*—katharometer detector; *C*—GLC column; *H*—heating wire (at *ca.* 200°); *D*—detecting and recording system; *M*/*W*—microwave system (see Fig. 1); *V*—vacuum gauge (0–50 mbar); *B*—ballast for vacuum pump; *M*—flow-meter; *T*—on–off tap.

Separation and detection of samples

The general apparatus used in the investigation was the same as that described previously[1] with the exception of the monochromator, which was an Optica CP4 grating instrument.

The carrier gas flow through the column and reference arm of the katharometer detector was first optimized. The tap *T* to the flow-meter was then opened and the needle valve adjusted to register zero flow through the flow-meter. In this way all of the sample eluting from the column passed through the needle valve and was accommodated by the pumping rate of the vacuum pump. Thus, the requisite carrier gas pressure was maintained upstream of the needle valve and maximum vacuum (approximately 4 mbar) downstream. Prior to any determination the tap *T* was closed in order to reduce the "dead" and unswept volumes of the apparatus.

The optimized experimental conditions for the detection of carbon disulphide and thiophen involved the use of a 0·6-m long 6-mm diameter Porapak "P" column, an oven temperature of 200°, benzyl alcohol as solvent and a helium carrier-gas flow-rate of 2 l./hr (producing a pressure of *ca.* 4 mbar in the detector tube). For the detection of dimethyl sulphoxide and thioglycollic acid a 0·6-m, 3-mm diameter Porapak "Q" column was used and a helium carrier-gas flow-rate of 6 l./hr (producing a pressure of *ca.* 8 mbar in the detector tube).

In all instances both the CS bandhead at 257·6 nm and the carbon atomic line at 247·9 nm were monitored, with a photomultiplier voltage of 950 V and monochromator entrance and exit slits of 0·2 mm. Table I shows the relevant retention data obtained under these conditions.

Table II summarizes the detection limits (for a signal to noise ratio of 2) obtained for the sulphur compounds in the quarter-wave foreshortened and quarter-wave Evenson cavities (Electro-Medical

TABLE I.—RETENTION DATA

	Retention time, *sec*	
	Porapak P (helium 2 l./hr)	Porapak Q (helium 6 l./hr)
Gas hold-up time	13	2
Water	17	4
Benzyl alcohol	>150	>150
Carbon disulphide	47	12
Thiophen	85	24
Dimethyl sulphoxide	>150	54
Thioglycollic acid	>150	72

Supplies, Parts Nos. 211L and 214L respectively) with and without the presence of platinum. The detection limits are obtained from the maximum peak height as measured on a chart recorder and refer to a 1-μl sample injection. In this arrangement the detection limit is eventually set by the response time and characteristics of the read-out system. A better method of measurement would be peak integration, probably *via* photon counting, which would not be so dependent on the column characteristics and retention times.

TABLE II.—DETECTION LIMITS FOR SOME SULPHUR COMPOUNDS

Wavelength of measurement, *nm*	Catalyst	Detection limit, *ng* of sulphur* Carbon disulphide 211L†	Carbon disulphide 214L‡	Thiophen 211L†	Thiophen 214L‡	Dimethyl sulphoxide 211L†	Dimethyl sulphoxide 214L‡	Thioglycollic acid 211L†	Thioglycollic acid 214L‡
257·6	None	0·84§		0·67#		30·0		¶	¶
(CS)	Pt	0·15	0·187	0·114	0·071	8·65	4·33	28·7	9·6
247·9	None	1·96						¶	¶
(atomic C)	Pt	0·39	0·15	0·39	0·097	34·6	6·3	¶	¶

* 1-μl injection, measured at maximum peak height, detection limit taken as signal to noise ratio of 2:1.

† Quarter-wave foreshortened radial line cavity.

‡ Quarter-wave cavity (Everson).

§ Previous detection limit 0·2 ng of sulphur.

Previous detection limit 1000 ng of sulphur.

¶ Not detected at 1000 ng of sulphur.

For carbon disulphide, placing platinum in the quarter-wave foreshortened cavity area produces an increase (*ca.* 5-fold) in peak height at both 247·9 and 257·6 nm, but a decrease (by about a quarter) at 257·6 nm for the quarter-wave Evenson cavity; this trend indicates breakdown to atomic species. In all other instances platinum enhances the breakdown (4–5-fold) of the material and the more efficient Evenson quarter-wave resonant cavity yields the most favourable detection limits. Previously[1] thiophen could only be detected at the 1-μg of sulphur level and dimethyl sulphoxide and thioglycollic acid could not even be detected at this level.

CONCLUSIONS

The oven circuit, described above, allows all of the sample eluted from the gas chromatograph to be passed into the gas discharge, which leads to a considerable improvement in the sensitivity achieved by the system. The use of the constricted detector tube restricts the plasma within the bulb of the tube and results in an intense plasma of increased stability which completely fills the entrance slit of the monochromator. Further plasma stability is achieved by using a ballast to smooth out small fluctuations in the pumping rate of the vacuum pump. Lastly, the inclusion of a platinum catalyst in the gas discharge area, and the use of the Evenson type of quarter-wave cavity results in a greater degree of sample degradation.

In summary, for these sulphur compounds of high thermal stability (*i.e.*, thiophen, dimethyl sulphoxide and thioglycollic acid) greatly improved limits of detection may be obtained by using these modifications.

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Summary—Improvements in the design and operation of the microwave excited detector for gas chromatography have led to an increase in the sensitivity and a lowering of detection limits for sulphur compounds.

Zusammenfassung—Verbesserungen in Konstruktion und Betrieb des Mikrowellenantegungsdetektors in der Gaschromatographie führten zu Empfindlichkeitserhöhung und zur Senkung der Nachweisgrenzen für Schwefelverbindungen.

Résumé—Des améliorations dans la conception et le travail du détecteur à excitation microonde pour chromatographie en phase vapeur ont mené à un accroissement dans la sensibilité et un abaissement des limites de détection pour les composés du soufre.

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1. R. M. Dagnall, D. R. Deans, S. J. Pratt and T. S. West, *Talanta*, 1969, **16**, 797.

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Potentiometric determination of lead with DTPA in the presence of large amounts of aluminium

(*Received* 6 *October* 1969. *Accepted* 2 *April* 1970)

Mollenhower[1] has described a direct gravimetric procedure for the determination of lead in glasses by an electrolytic procedure which is very exact. The method proposed here uses diethylenetriaminepenta-acetic acid (DTPA) to determine lead in lead glasses which are high in aluminium and silicon, with ease, speed and accuracy. DTPA forms a relatively weak complex with aluminium,[2] and hence can be used for this titration. Štráfelda[3] has used a silver-EDTA electrode for complexometric titration, and a silver-DTPA electrode was used in the present work.

EXPERIMENTAL

Reagents

DTPA solution, 0·1*M*. Dissolve 39·5 g of DTPA in about a litre of water with addition of sodium hydroxide to adjust the pH to 8·5. Standardize by potentiometric titration with lead nitrate solution. Dilute to 0·05 or 0·01*M* for use in titrations.

Silver nitrate solution, 0·0002*M*

Borate buffer, 0·5*M*. Dissolve 61·83 g of boric acid and 20·0 g of sodium hydroxide in 2 l. of water. The pH should be 9·0–9·5.

Procedure

Weigh 0·5000 g of lead glass or lead silicate into a platinum dish, add hydrofluoric and perchloric acids and when the sample has dissolved completely, or nearly so, heat to dryness. Then add 15 ml of water and 2 ml of concentrated nitric acid. Evaporate to dryness then add 15 ml of water and 2 ml of nitric acid. Boil the solution and add 3–4 drops of 30% hydrogen peroxide. Continue boiling for 15 min to remove excess of peroxide.

Dilute the solution to 100 ml and add 2 g of sodium tartrate. Then, using phenolphthalein as indicator, add sodium hydroxide until the colour changes. Buffer the solution to pH 9 ± 0·1 with the borate buffer, measured by pH-meter as the pH is critical. Add one drop of 0·0002*M* silver nitrate, insert glass and silver electrodes, and titrate the solution with 0·05*M* DTPA until the potential break is reached.

RESULTS

Typical results showed 100·0 ± 0·1% recovery of 9 mg of lead in the presence of 5–50 mg of aluminium. Two glasses, one of composition SiO_2 41·4%; Al_2O_3 17·9% and PbO 40·7% and the

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Potentiometric determination of lead with DTPA in the presence of large amounts of aluminium

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MOLLENHOWER[1] has described a direct gravimetric procedure for the determination of lead in glasses by an electrolytic procedure which is very exact. The method proposed here uses diethylenetriaminepenta-acetic acid (DTPA) to determine lead in lead glasses which are high in aluminium and silicon, with ease, speed and accuracy. DTPA forms a relatively weak complex with aluminium,[2] and hence can be used for this titration. Štráfelda[3] has used a silver-EDTA electrode for complexometric titration, and a silver-DTPA electrode was used in the present work.

EXPERIMENTAL

Reagents

DTPA solution, 0·1*M*. Dissolve 39·5 g of DTPA in about a litre of water with addition of sodium hydroxide to adjust the pH to 8·5. Standardize by potentiometric titration with lead nitrate solution. Dilute to 0·05 or 0·01*M* for use in titrations.

Silver nitrate solution, 0·0002*M*

Borate buffer, 0·5*M*. Dissolve 61·83 g of boric acid and 20·0 g of sodium hydroxide in 2 l. of water. The pH should be 9·0–9·5.

Procedure

Weigh 0·5000 g of lead glass or lead silicate into a platinum dish, add hydrofluoric and perchloric acids and when the sample has dissolved completely, or nearly so, heat to dryness. Then add 15 ml of water and 2 ml of concentrated nitric acid. Evaporate to dryness then add 15 ml of water and 2 ml of nitric acid. Boil the solution and add 3–4 drops of 30% hydrogen peroxide. Continue boiling for 15 min to remove excess of peroxide.

Dilute the solution to 100 ml and add 2 g of sodium tartrate. Then, using phenolphthalein as indicator, add sodium hydroxide until the colour changes. Buffer the solution to pH 9 ± 0·1 with the borate buffer, measured by pH-meter as the pH is critical. Add one drop of 0·0002*M* silver nitrate, insert glass and silver electrodes, and titrate the solution with 0·05*M* DTPA until the potential break is reached.

RESULTS

Typical results showed 100·0 ± 0·1% recovery of 9 mg of lead in the presence of 5–50 mg of aluminium. Two glasses, one of composition SiO_2 41·4%; Al_2O_3 17·9% and PbO 40·7% and the other SiO_2 25·7%; Al_2O_3 20·1%; B_2O_3, 18·6% and PbO 35·6% were analysed, and gave PbO 40·7% and 35·6% respectively.

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Summary—Lead can be titrated accurately in the presence of aluminium with diethylenetriaminepenta-acetic acid, with a silver electrode system for detection of the end-point. The method is very suitable for analysis of lead glasses.

Zusammenfassung—Blei kann in Gegenwart von Aluminium mit Diäthylentriaminpentaessigsäure genau titriert werden; ein Silberelektrodensystem dient zur Endpunktsbestimmung. Die Methode ist zur Analyse von Bleigläsern sehr gut geeignet.

Résumé—On peut titrer le plomb avec précision en la présence d'aluminium au moyen d'acide diéthylènetriaminopentacétique, avec un système d'électrode d'argent pour la détection du point de fin de dosage. La méthode convient très bien à l'analyse de verres au plomb.

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Optimum physical and chemical conditions for the Methylene Blue method of estimating gaseous sulphide in the environment

(*Received* 24 *June* 1969. *Revised* 4 *February* 1970. *Accepted* 29 *April* 1970)

The Methylene Blue method for gaseous sulphide estimation is fairly simple and straightforward, but despite its age[1] has not been very systematically studied, and numerous variants exist.[2–10] Perhaps the only fairly detailed study was made by Gustafsson[2] in 1960.

Besides the absorption peak at about 670 nm, another peak at around 740 nm has been reported.[2–5,11] Hardly anyone has used the latter peak for the sulphide estimation although it has been reported as the more sensitive of the two.[4] We now report an examination of this peak and of the optimum physical and chemical conditions for the determination.

EXPERIMENTAL

Chemical aspects

The various methods in the literature are summarized in Table I. The influence of each reagent was studied in turn.

Cadmium hydroxide suspension. An aqueous suspension of cadmium hydroxide in a bubbler was used to absorb gaseous sulphide, since it has been shown to be an efficient retainer of gaseous sulphide[12] even at comparatively high flow-rates of about 3 l./min. Zinc acetate has been used by others but there is no experimental evidence with regard to its efficiency at higher flow-rates. We have found it unnecessary to wash the cadmium hydroxide free from the sodium chloride (or sulphate) which is formed as a by-product.[6] For normal operation a volume of about 25 ml of suspension containing 200–250 mg of cadmium hydroxide is found to be satisfactory.

Concentration of the dye. Only the sulphuric acid concentration was found to have a significant influence on the optimum amount of *p*-aminodimethylaniline required. We find that the absorbance (for up to 120 μg of sulphide) is maximal and constant at dye concentrations above 0·007% w/v in the final solution, for 1·5*M* sulphuric acid medium. We therefore suggest 4 mg of dye per 50 ml for routine work. If smaller amounts of dye are used as in nos. 2, 4 and 8 of Table I, and the sulphide other SiO_2 25·7%; Al_2O_3 20·1%; B_2O_3, 18·6% and PbO 35·6% were analysed, and gave PbO 40·7% and 35·6% respectively.

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TABLE I.

Method No.	Reference	Final volume, *ml*	Amount of dye used, *mg/50 ml*	Final acidity, *N*	Amount of iron(III), *mg/50 ml*	Acidity of $FeCl_3$, *N*	Remarks
1	3	50	5·0	2·4	5·5	5·0	H_2SO_4 used
2	6	50	2·25	0·22	6·1	0	H_2SO_4 used
3	7	100	7·2	1·0	16·1	0	H_2SO_4 used
4	8, 9	500	1·0	0·2	0·55	0·5	HCl used in the dye solution
5	4	10	12·5	3·6	71·5	2·25	Iron(III) ammonium sulphate and H_2SO_4 used
6	5	250	5·0	0·55	1·2	1·20	HCl used
7	2	100	3·4–6·8	0·6	13·0	0·5	H_2SO_4 and iron(III) ammonium sulphate used
8	10	50–100	1·2–2·5	0·32–0·66	14·7	0	H_2SO_4 used
9	Present work	50	4·0	3·0	10·0	0·5	H_2SO_4 used

concentrations are relatively high, departure from Beer's law is not surprising (*cf.* Johnson and Nishita[13]) although acid concentration also affects adherence to Beer's law.

Sulphuric acid concentration. It is well known that the absorbance of Methylene Blue is pH-dependent, but most studies have been confined to acid concentrations $<0{\cdot}7M$.

We have found that if the acid concentration is not changed between reaction and measurement, only the 675-nm peak is observed for low acidity. With increasing acidity this peak grows and reaches a maximum at a sulphuric acid concentration of about $0{\cdot}4M$. At the same time the 749-nm peak appears and grows in intensity with sulphuric acid concentration up to about $1{\cdot}4M$, at which it becomes constant and about 20% more than the maximum of the 675-nm peak. At higher acidity the 675-nm peak gradually decreases.

The absorbance at 675 nm is dependent on the sulphuric acid concentration both at the time of reaction and at the time of measurement, especially at the lower concentrations. When the reaction and measurement concentrations are both above $1{\cdot}0M$, there is little variation of the absorbance at 675 nm. On the other hand, the absorbance at 749 nm is entirely dependent on the acid concentration at measurement, if the reaction is performed in sulphuric acid $>0{\cdot}7M$. The absorbance at 749 nm also shows dependence on the acid concentration at reaction if this is $<0{\cdot}7M$. There is no appreciable increase in the absorbance at 749 nm if the sulphuric acid concentration at measurement is about $1{\cdot}5M$, and the absorbance is then about 20% higher than the maximum at 675 nm.

We propose that the absorbance at 749 nm or the sum of the intensities at both 675 and 749 nm be used to measure the sulphide concentration (the arithmetic sum of the two remains more steady than the separate values when the acid concentration is varied) and that for both reaction and measurement the sulphuric acid concentration be $\sim 1{\cdot}5M$.

Repetition with hydrochloric in place of sulphuric acid yielded similar results with a slightly different value for the optimum concentration.

Hofmann and Hamm[10] have suggested that the 749-nm peak is due to the interaction of Methylene Blue with a chloroferrate(III) complex, for which an excess of iron(III) is necessary, but our observations show that the 749-nm peak is dependent mainly on the acid concentration.

Beer's law is very closely followed only at higher acid concentrations. If sufficient dye is used, this may account for the deviations reported by earlier investigators, most of whom used low acid concentrations.

We find that too low an iron(III) concentration lowers the absorbance. For <200 μg of sulphide, absorbance is maximal with 8 mg or more of iron(III)/50 ml (if the iron concentration is reduced to 2 mg/50 ml, the absorbance decreases by about 15% at both peaks). The acidity of the iron(III) solution needs only to be the minimum needed to keep the solution clear,[14] whether the chloride or the sulphate is used.

Physical conditions

Temperature. Some workers[2,5,15] have studied the effect of temperature on the absorbance of Methylene Blue, and some have reported that the temperature should be controlled within ±2°.

We find that at normal laboratory temperatures there is hardly any variation in the absorbance with temperature between 10° and 25°. However, when a dye solution containing sulphuric acid is used it is advisable to precool the solutions to around 10° so that on dilution the temperature does not exceed 25°. As discussed later, reaction at 10–15° minimizes gas-phase loss of hydrogen sulphide.

Exposure to light. Some investigators[2,5] have reported that exposure to light adversely affects the absorbance and have recommended shielding from direct light, but have not stated at which point of the procedure the effect occurs.

We find that under normal lighting or in daylight there is no detectable effect on the Methylene Blue during or after the reaction, but that both zinc and cadmium sulphides undergo photodecomposition. This observation is substantiated by the work of Lahman and Prescher.[16] The effect is less on the zinc sulphide, but we prefer to use the cadmium sulphide suspension (200–250 mg of hydroxide in 20–25 ml of water) because of its efficiency for sulphide retention.[11]

The sulphide sampler should be shielded from light during sampling and the sample should be kept in the dark until analysis, especially for sampling of low concentrations of hydrogen sulphide

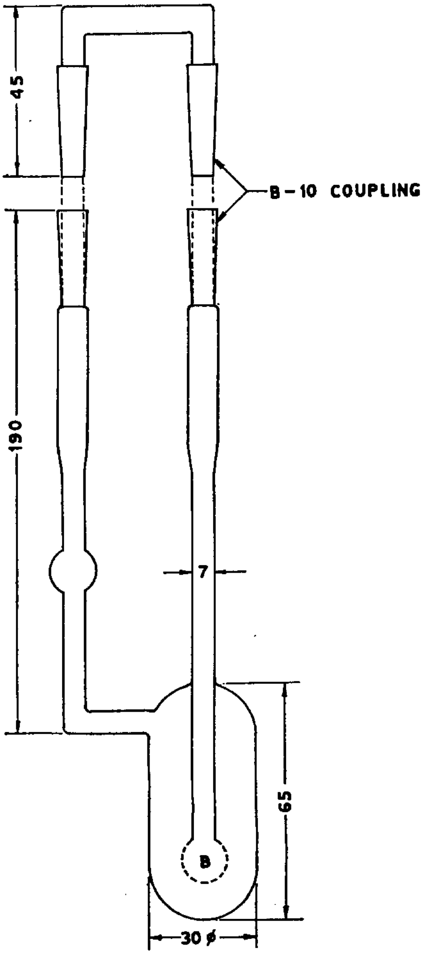

FIG. 1.—Bubbler for hydrogen sulphide sampling.
Dimensions in mm.

over extended periods of time. During and after the reaction, protection from light is not necessary.

Gas-phase losses of sulphide. On addition of the acidic dye solution to the mixture of cadmium hydroxide and sulphide, the hydrogen sulphide evolved immediately reacts with the dye in the presence of iron(III). If, however, the container has an appreciably larger volume than the liquid contents, some of the hydrogen sulphide escapes into the space above the liquid and may not react, thus leading to a negative error.[4,5] This loss can be minimized by performing the reaction in a 50-ml standard flask, but there may be loss of material during transfer from the sampling bubbler. We have therefore developed a special sampling bubbler (Fig. 1), with a total volume of slightly less than 50 ml. The bubbler is shielded from light during sampling and until the reaction is performed in it.

The bubbler is marked at a level corresponding to its capacity minus the volumes of dye and iron(III) solutions to be added (we propose these to be 1 ml of 3% w/v solution of iron(III) chloride [$FeCl_3$ or equivalent amount of $FeNH_4(SO_4)_2$] in 0·5*M* hydrochloric acid and 10 ml of 0·04% w/v solution of *p*-aminodimethylaniline in 7·5*M* sulphuric acid).

About 20 ml of hydroxide suspension are used for sampling and are diluted to the reference mark with distilled water, the dye and the iron solutions are added in quick succession and the bubbler is closed with the link stopper and then shaken briskly. The link is the only gas space.

Capture of hydrogen sulphide is quantitative in this bubbler for concentrations up to 200 $\mu g/m^3$ of air at bubbling rates below 3 l./min. At higher bubbling rates there is a proportionate loss.

Calibration curve

Detailed procedures have been suggested for preparing standard sulphide solutions, and these are often lengthy and need care.[3] It is possible to avoid this problem by determining the average degree of conversion of sulphide into Methylene Blue (by comparing the theoretical amount of the latter with that actually obtained from standards) and then using a standard solution of Methylene Blue and the recovery factor for calibration purposes. Of course, the purity of the Methylene Blue used must be known, especially its degree of hydration, which appears to be variable from source to source of the dyestuff.

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Summary—The sensitivity and reproducibility of the Methylene Blue method for gaseous sulphide estimation have been investigated with respect to physical conditions and the concentrations of the reagents, especially sulphuric acid. A new design of absorber is proposed to minimize gas-phase loss of the sulphide in the final stage of the procedure.

Zusammenfassung—Die Empfindlichkeit und Reproduzierbarkeit der Bestimmung von Sulfid in der Gasphase mit Methylenblau wurden im Hinblick auf die physikalischen Versuchsbedingungen und auf die Konzentration der Reagentien, speziell der Schwefelsäure, untersucht. Ein neukonstruierter Absorber wird vorgeschlagen, um den Verlust von Sulfid in der Gasphase bei der Endstufe des Verfahrens möglichst klein zu halten.

Résumé—On a étudié la sensibilité et la reproductibilité de la méthode au bleu de méthylène pour le dosage du sulfure gazeux par rapport aux conditions physiques et aux concentrations des réactifs, spécialement l'acide sulfurique. Une nouvelle conception de l'absorbeur est proposée pour minimiser la perte en phase gazeuse du sulfure dans le stade final de la technique.

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Determination of platinum, palladium and silver in geological materials and their concentrates by fire assay and emission spectrography

(*Received* 19 *November* 1969. *Accepted* 19 *May* 1970)

PLATINUM, palladium and silver are determined by fire-assay preconcentration and the graphite arc. A measured volume of the assay-bead solution is evaporated to dryness on the surface of two flat-top graphite electrodes and the dry residue excited according to the modified method of Zilberstein.[1]

EXPERIMENTAL

Fire assay

A mixture of 65 g of sodium carbonate, 17 g of potassium carbonate, 17 g of fused borax, 38 g of lead oxide and 13 g of starch is used as flux; 100–150 g of the mixture are placed in a 750-ml fireclay crucible, then 50 or 150 g of sample are added and the contents thoroughly mixed; some flux is added to cover the mixture. The crucible is placed in the muffle of a fire assay furnace preheated to 850–950°, and the temperature is raised to 1000–1100° over a period of 40–50 min. The crucible is then removed and the molten charge is poured into an iron mould and allowed to cool. The slag is carefully chipped and worked away from the lead with a hammer and brush and the lead is tapped into a cube, producing the lead button. The lead of the button is separated from its noble metal content by cupellation.

Typical sample contents were gold from 1 to 3 g/ton and silver from 15 to 20 g/ton. The weights of the beads ranged from 0·5 to 4 mg.

Dissolution of the bead, and spectrographic analysis

The bead is transferred to a 25-ml crucible, 0·8 ml of nitric acid (sp.gr. 1·44) is added and the crucible covered with a watch-glass. The contents are heated slowly and carefully to prevent or to minimise the powdering of the insoluble residue. Palladium and silver are dissolved by the nitric acid and the remaining platinum metals and gold remain undissolved in the form of a black porous mass. The nitric acid solution is transferred quantitatively to another 25-ml crucible and evaporated to a moist residue, which is treated with 5 ml of distilled water and evaporated to moistness again, this water/evaporation step being repeated thrice more. Finally the residue is dissolved with 1 ml of distilled water, from which three aliquot portions of 0·1 ml each are transferred by means of a micropipette to each of two flat-top graphite electrodes previously waterproofed with a 0·5% petroleum ether solution of Apiezon grease "N". The electrodes are dried at 110°, then 0·5 ml of a 1-ppm

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Twelve drops of *aqua regia* are added to the residue to dissolve platinum. The mixture is heated slightly to hasten dissolution. The solution is evaporated to dryness and 4 drops of hydrochloric acid are added and the solution again evaporated to remove the remaining nitric acid. A fourfold evaporation with 5 ml of distilled water is again used. As the concentration of platinum in the samples is very low, the moist residue is mixed with 0·3 ml of distilled water and the entire solution is added to the two electrodes. Consequently only a single result for platinum is obtained. The analytical lines used are given in Table I.

TABLE I.—ANALYTICAL LINES USED IN DETERMINATION OF PLATINUM, PALLADIUM AND SILVER

Element	Analytical line *nm*	Concentration range based on analytical curve, *μg*
Pt	306·471	0·01–0·1
Pd	324·270	0·005–0·15
Ag	328·068	0·00001–0·1

The Mo 317·035 nm lines was used as internal standard throughout.[8]

Apparatus and spectrographic operating conditions

A quartz spectrograph [ISP-28 (USSR)], with a mean reciprocal linear dispersion of approximately 1·6 nm/mm in the working range, was used with a three-lens system. The operating conditions were as follows: slit height 3·2 mm; analytical gap 2 mm; slitwidth 0·020 mm for Pd and Ag and 0·018 mm for Pt; arc generator DB-6 (East Germany) or DG-2 (USSR); current 8 A; microphotometer, Carl Zeiss (Jena) type II, with a slitwidth of 0·015 mm; exposure 30 sec; spectral plates ORWO–WU2; electrodes EKL type T3 (East Germany) and type C3 (USSR).

The concentrations of the elements in the unknown samples are obtained from analytical curves established by plotting the ratio of the intensities of the analytical and internal standard lines minus the background intensities (ordinate) *vs.* log concentration (abscissa).[8] Transmittance measurements are made with a microphotometer.

Preparation of standards

Stock solutions of the elements, 0·1% w/v, are made by dissolving palladium(II) chloride and hexachloroplatinic acid in 0·2*M* hydrochloric acid, and silver nitrate in distilled water. These stock solutions are then diluted with the solvent to give 100, 10, 1, 0·1, 0·01 ppm of palladium and platinum, and 100, 10, 1, 0·1, 0·01, 0·001, 0·0001 ppm of silver. The 1-ppm molybdenum solution is made by appropriate dilution of an ammonium molybdate solution in distilled water.

The standards for determination of each element are made separately by transferring 0·1 ml of each standard solution to each of two flat-top graphite electrodes. After drying, the standards are run by the method described. The concentration of silver in the samples is generally about 100 times that of the palladium. For this reason 0·1 ml of the silver solution (0·1% w/v) is added to the palladium standard electrodes.

RESULTS AND DISCUSSION

The precision of the method is illustrated by the results obtained in 20 replicate determinations. The standard deviations were 10, 4 and 11 ng for 79 ng of platinum, 55 ng of palladium and 81 ng of silver respectively. To illustrate the accuracy of the method, aliquots of palladium and platinum standards were added to 25 and 50 g of copper ore; the material was dried at 110° and analysed according to the method described. The recoveries were 89–92% for 1 μg of platinum and 97–105% for 1 μg of palladium.

Best results with regard to the intensity of the spectral lines were obtained when the acidity of the solutions was maintained at a pH of about 4. At a low pH (0·8) the sensitivity for platinum decreases to 0·1 μg, for palladium to 7 ng, and for silver to 0·5 ng. Excluding the influence of anion content on sensitivity, it was found that when the solutions were at pH 4 there was little or no loss of residue during the arcing process, thus providing good sensitivity.

It was found that a large excess of platinum and palladium does not influence the intensity of the silver line. Hence the method can be used for the determination of silver in platinum or palladium metal. When silver is 100 times greater in concentration than the other two metals. the intensity of the palladium line used is increased, while that of the platinum line is unchanged. When the silver is present in greater excess than this, the sensitivity decreases to 0·1 μg for platinum and 10 ng for palladium and the results are very erratic. This can best be explained in terms of the maximum quantity of dry residue permitted on the surface of the electrodes. Silver enhances the intensity of the molybdenum line and may be used to increase the sensitivity for that element (1 ng) when it is to be determined.

The determination of palladium is not influenced by an excess of platinum and therefore the method can be used for the determination of palladium in platinum metal. When the concentration of palladium is high, the Pd 306·531 nm line interferes with the Pt 306·471 nm line. The platinum 265·945 nm line could then be used, but this has not been investigated experimentally. Gold does not interfere.

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Summary—A method is described for the determination of platinum down to 10 ng, palladium to 5 ng and silver to 10 pg in 50 or 100 g of sample. Fire-assay techniques are used to preconcentrate these metals into a bead which is first treated with nitric acid to dissolve palladium and silver and then with *aqua regia* to dissolve platinum. Both solutions are diluted and adjusted to pH 4, then analysed by optical emission spectrography of the residue from a measured volume evaporated on a pair of flat-top graphite electrodes. This method requires much less sample handling than most published methods for these elements.

Zusammenfassung—Ein Verfahren zur Bestimmung von Platin bis herunter zu 10 ng, Palladium bis 5 ng und Silber bis 10 pg in 50 oder 100 g Probe wird beschrieben. Zur Anreicherung dieser Metalle werden sie in eine Perle geschmolzen; diese wird zuerst mit Salpetersäure behandelt, um Palladium und Silber zu lösen, dann mit Königswasser zur Auflösung von Platin. Beide Lösungen werden verdünnt und auf pH 4 eingestellt; dann wird ein abgemessenes Volumen auf einem Paar flacher Graphitelektroden eingedampft und durch optische Emissionsspektrographie analysiert. Dieses Verfahren erfordert weit weniger Operationen mit der Probe als die meisten bekannten Analysenmethoden für diese Elemente.

Résumé—On décrit une méthode pour la détermination du platine descendant jusqu'à 10 ng, du palladium jusqu'à 5 ng et de l'argent jusqu'à 10 pg dans 50 ou 100 g d'échantillon. Des techniques par voie sèche sont utilisées pour la préconcentration de ces métaux dans une perle qui est d'abord traitée á l'acide nitrique pour dissoudre le palladium et l'argent puis à l'eau régale pour dissoudre le platine. Les deux solutions sont diluées et ajustées à pH 4, puis analysées par spectrographie d'émission optique du résidu d'un volume mesuré évaporé sur une paire d'électrodes en graphite à partie supérieure plane. La méthode nécessite beaucoup moins de manipulation d'échantillon que la plupart des méthodes publiées pour ces éléments.

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Theoretical considerations on the estimation of sample matrix effects in analytical chemistry

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SEVERAL methods in analytical chemistry are used to determine concentration by means of a linear equation of the form

$$R = kC_X + R_{C_X=0} \tag{1}$$

where R is the reading of some instrument, C_X is the concentration of some substance X, k is a proportionality constant (for a given set of conditions), and $R_{C_X=0}$ represents R for a sample identical with that to be analysed except that $C_X = 0$. Thus $R_{C_X=0}$ represents an effect caused by the matrix in which X is to be determined. Examples are photometric determination (where R can be absorbance or emission) and polarography (where R is the current).

The assumption that in equation (1) $R_{C_X=0} = 0$ is usually either stated explicitly, assumed implicitly, or ignored. It can, however, be unjustified and so affect considerably the results obtained through the use of equation (1).

It should be noted that equation (1) states that R is directly proportional to C_X only for a given set of conditions. Thus a change of the concentration C_X effected through a change of the amount of the substance X (m_X) is not equivalent to a change of concentration effected through a change in the volume (V_S) of the pure solvent used—unless the original sample consisted only of the pure solvent and the substance X.

As an example we can consider a volume V_X of some biological fluid, in which m_X represents m moles of calcium. On doubling m_X the term $R - R_{C_X=0}$ will be doubled. However on doubling V by the addition of pure solvent (say water) of volume $V_S = V_X$ the term $R - R_{C_X=0}$ will not necessarily decrease by a factor of 2, as the dilution of the biological fluid can (and generally will) affect the value of both k and $R_{C_X=0}$. Thus the methods based on equation (1) have to take into account the behaviour of both k and $R_{C_X=0}$ on the determination of m_X. The implications of the argument above have already been considered in some detail in a study of the flame photometry of calcium in the presence of strongly interfering substances.[1,2]

It has been shown that k can easily be obtained experimentally. The effect of $R_{C_X=0}$, which is identified with a contribution due to interference, R_I, is more difficult to assess. It has been suggested that some convenient parameter out of the many parameters affecting R could be utilized for the detection and evaluation of R_I. Such utilization of dilution as the changing parameter has been treated theoretically and experimentally,[1,2] but it was shown that dilution is not an ideal parameter for this purpose. In photometry a promising parameter appears to be the wavelength λ. The possible use of this parameter is discussed below.

Let us assume that the instrument (equipped with a monochromator precise within ±0·05 nm)[3] is set initially to the wavelength suitable to the element concerned, *e.g.*, for calcium to 422·7 nm., At this wavelength λ^0 the reading for the unknown mixture will be $R_M{}^0$, and we assume that it is due to the contribution $R_X{}^0$ of the element to be determined, and the contribution $R_I{}^0$ of some interference. On altering λ we shall get a new reading $R_M(\lambda)$, composed similarly:

$$R_M(\lambda) = R_X(\lambda) + R_I(\lambda). \tag{2}$$

At any λ the value R_M is assumed to be directly proportional to the quantity of the substance X, so that at any λ, according to equation (1),

$$k(\lambda) = \left(\frac{\partial R_M(\lambda)}{\partial m_X}\right)_\lambda \tag{3}$$

and

$$R_M(\lambda) = k(\lambda)m_X + R_I(\lambda). \tag{4}$$

To obtain m_X from equation (4) it is necessary to have some information on $R_I(\lambda)$ in addition to the experimentally obtainable $R_M(\lambda)$ and $k(\lambda)$. The simplest assumption is that $R_I = 0$. In such a case $R_M(\lambda)$ plotted against $k(\lambda)$ should give a straight line passing through the origin of the coordinates. A more direct indication, without the necessity of measuring the k's, would be the shape of $R_M(\lambda)$ plotted against λ: with $R_I = 0$ the tails should taper to zero on both sides of λ^0. The next simplest assumption is that R_I is a constant independent of λ. The possibility of the evaluation of m_X in such a simple case is discussed by Herrmann and Alkemade.[4] Following our previous argument, in this case a plot of $R_M(\lambda)$ against $k(\lambda)$ would again yield a straight line, but the intercept would now be not zero but R_I. The plot of $R_M(\lambda)$ against λ would show tails maintaining a constant value on both sides of λ^0. However both $R_I = 0$ and $R_I =$ constant represent only special cases. In general $R_I(\lambda)$ *will* exist, and will *not* be constant. A more reasonable approximation appears to be that $R_I(\lambda)$ can be expressed by a linear function, *e.g.*,

$$R_I(\lambda) = R_I{}^0 + A(\lambda - \lambda^0). \tag{5}$$

Such a situation is described in Fig. 1, assuming a Gaussian line for the element X.

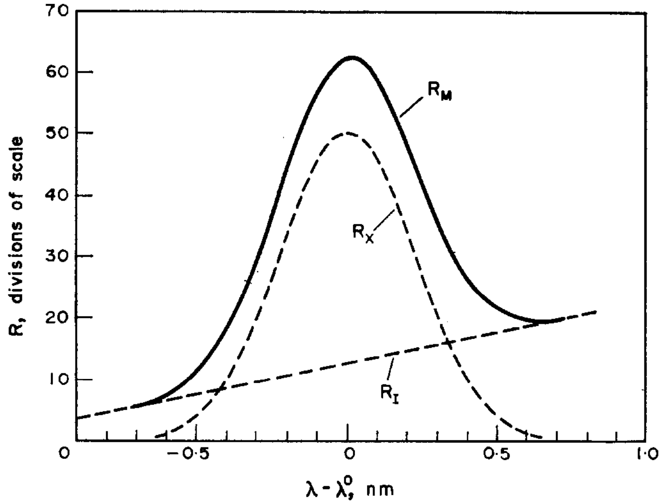

FIG. 1.—R as a function of wavelength, assuming that $R_M = R_X + R_I$ while $R_X = 50 \exp \{-1(\lambda - 422{\cdot}7)^2\}$ and $R_I = 12{\cdot}5 + 10(\lambda - 422{\cdot}7)$.

The numerical values presented in Fig. 1 were obtained from:

$$R_X = 50\, e^{-1(\gamma-422.7)^2} \tag{6}$$

and

$$R_I = 12{\cdot}5 + 10(\lambda - 422{\cdot}7) \tag{7}$$

These values are in line with the $R_X{}^0$ and $R_I{}^0$ obtained previously,[1] and with the spectrum of calcium obtained by Watanabe and Kendall.[5] It is probable that a system of water, lanthanum chloride, calcium chloride and hydrochloric acid follows approximately the behaviour described in Fig. 1.

It can be seen that the experimentally obtained behaviour of $R_M(\lambda)$ can be used to evaluate $R_I(\lambda)$ graphically from the limiting slope of the tails. Introduction of $R_I{}^0$ so obtained into equation (4), with $R_M{}^0$ and k^0 determined experimentally, yields m_X directly. In this case the exact shape of $R_X(\lambda)$ is irrelevant—as long as it approaches zero asymptotically on both sides and not too far from λ^0.

If the linearity of the tails is less obvious, and $R_I(\lambda)$ cannot be deduced directly from the graph, it can still be possible to utilize the experimental values of $R_M(\lambda)$ and $k(\lambda)$ to obtain $R_I{}^0$ and m_X. Theoretically, three experiments should be sufficient to obtain the constants m_X, $R_I{}^0$ and A from equations (4) and (5). In our example, with R_M precise to within ±1%, three measurements at λ's not further than 0·3 nm from λ^0 would already yield m_X with an error of only about 3%. A greater accuracy could be obtained by conducting a larger number of experiments, and determining the constants by least squares. It should be noted that here again the form of R_X need not be Gaussian.

Finally, an approximation can be used to avoid the laborious determination of $k(\lambda)$. If a Gaussian form is assumed for $R_X(\lambda)$, it is easily seen that $k(\lambda)$ must also have a Gaussian form with the same exponent. Thus equation (4) assumes the form:

$$R_M = k^0 e^{-B(\gamma-\gamma^0)^2} m_X + R_I{}^0 + A(\lambda - \lambda^0). \tag{8}$$

Theoretically, five determinations of $R_M(\lambda)$ without any other measurements should suffice to determine the constants k^0, A, B, R_I^0 and m_X. In practice, at least k^0 would be determined experimentally, and a larger number of $R_X(\lambda)$ would be available to obtain reasonable results.

In the last method the function $R_X(\lambda)$ had to be introduced explicitly, to obtain $k(\lambda)$. The assumption that $R_X(\lambda)$ is a Gaussian curve can easily be wrong, as the exact function is determined by many unknown experimental factors. Possibly a Lorentzian shape would be a closer approximation, in which case instead of equation (8) one could use equation (9):

$$R_M = \frac{k^0 m_X}{1 + B(\lambda - \lambda^0)^2} + R_I^0 + A(\lambda - \lambda^0). \qquad (9)$$

Thus an independent study of $R_X(\lambda)$ would be a prerequisite for the use of the last (approximate) method.

The discussion above demonstrates how the method of the changing parameter introduced in reference (1) can be applied to photometry, with λ used as the changing parameter. It can be seen that while the basic principle is the same as that applied in the case of dilution,[1,2] the functions R_M, R_I and k are completely different in the two cases. Similar analyses would have to be carried out in the case of any changing parameter applied to any analytical method based on equation (1). It would be of interest to test experimentally the conclusions reached above—unfortunately commercial atomic absorption flame photometers are unsuitable for such measurements. It would also be of interest to apply the method to other systems employing equation (1).

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Summary—Methods are suggested for evaluating the magnitude of matrix effects on the results of analysis.

Zusammenfassung—Methoden zur Berechnung der Größe des Einflusses der Matrix auf Analysenergebnisse werden vorgeschlagen.

Résumé—On suggère des méthodes pour évaluer la grandeur des influences de gangue sur les résultats d'analyse.

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ANNOTATION

Behaviour of dilute solutions of mercury*

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IN STUDIES on the separation of submicrogram quantities of mercury, many of the steps were followed by using the radioisotope ^{203}Hg. When vials containing the sample were left uncapped, it was noticed that activity was lost.[1] This observation was somewhat surprising in that solutions of ionic mercury are not ordinarily considered to lose appreciable amounts of the element by volatilization at room temperature.

There is ample documentation of the movement of mercury in and out of solutions under a variety of conditions. Magos[2] has shown that rapid isotope exchange occurs when air containing mercury vapour is passed through a ^{203}Hg-labelled mercury(II) acetate solution. Clarkson *et al.*[3,4] have demonstrated the ready movement of mercury from biological systems to air, both *in vitro* and *in vivo*. In one experiment they showed that all the radioactivity in a serum sample appeared in an adjacent mercury pool within a short period of time in a closed Warburg flask. In another they showed that in a serum sample exposed to air or oxygen saturated with mercury vapour there was a continuous uptake of mercury, but in a similar experiment using a 95% nitrogen–5% carbon dioxide atmosphere saturated with mercury vapour there was barely significant uptake, if any. Magos *et al.*[5] reported that micro-organisms normally present in the laboratory and the laboratory water supply were capable of rapidly volatilizing mercury as the metallic vapour from solutions of mercury(II) salts in plasma, broth or urine. They also showed that mercury would volatilize from solutions of mercury(II) chloride after the addition of vitamin C.

In previous reports on the loss of mercury the existence of reducing agents within the system permitted the postulation that reduction to metallic mercury occurred with subsequent volatilization. The present studies were undertaken in order to elucidate the mechanism by which mercury moved from dilute inorganic solutions to which no reducing substances were added.

EXPERIMENTAL

Materials

All solutions were made with reagent grade chemicals and demineralized water. Carrier-free ^{203}Hg was added to the desired quantities of mercury(II) chloride solutions.

Apparatus

For initial studies Warburg flasks were used, but the ease with which separated solutions could mix led to the design of a container, in essence a modified Conway unit, in which the solutions should not accidentally mix and several different solutions could be placed in the same atmosphere to compete for the radioactivity from a single solution. An inverted plastic Petri dish (100 × 20 mm) was fitted into a groove cut into a 10-mm thick "Lucite" sheet. The groove was filled with stop-cock grease. The cups (<40 mm diameter) were made from commercially obtainable polyethylene stoppers.

Procedure

In the Warburg flask, 3 ml of mercury(II) chloride solution in $\sim 0{\cdot}1M$ hydrochloric acid were placed in the main portion, and 1 ml of trapping solution was placed in the side-arm. In some experiments a drop of metallic mercury was covered with the trapping solution, and in others was left uncovered in a separate side-arm. In the special apparatus, equal volumes of original solution and trapping solution were used. The vial containing the trapping solution was placed in a polyethylene bag before insertion into the well of the radioactivity counter.

In the competition experiments and for studying the effect of potassium permanganate on the escape of mercury, the multicup arrangement was used, with 3 ml of trapping solution in each cup, except for metallic mercury which was limited to 2 drops. Experiments were carried out at room temperature with no attempt at accurate temperature control. Gentle mixing was provided by placing the flasks on a gyratory platform shaker.

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RESULTS

In the initial experiments an attempt was made, based on observations already reported in the literature,[4] to determine the conditions under which mercury would move. Accordingly, the atmosphere was varied and metallic mercury was introduced in several ways. The results are summarized in Table I. There was insignificant movement of the isotope except when metallic mercury was in open contact with the atmosphere of the flask. The multicup unit was then used so that several different solutions could be used in competition under various conditions. The results summarized in Table II show that only solutions containing some mercury salts absorb radioactivity. Experiment 3 shows this effect rather strikingly since a potassium nitrate solution without mercury has gained no radioactivity whereas a solution with mercury has gained a sizable fraction of the original activity.

TABLE I.—MOVEMENT OF MERCURY TO VARIOUS TRAPPING SOLUTIONS IN ONE DAY

Activity remaining, *cpm*	Trapping solution	Metallic mercury	Atmosphere	Activity in trap, *cpm*
88100	0·1*M* HCl	none	O_2	0
87600	0·1*M* HCl	none	N_2	0
15	0·1*M* HCl, 0·2*M* KBr	separate	O_2	0
80300	0·1*M* HCl, 0·2*M* KBr	in trap	O_2	434
11	0·1*M* HCl, 0·2*M* KBr	separate	N_2	0
89545	0·1*M* HCl, 0·2*M* KBr	in trap	N_2	62

Original solutions had an activity of 87400 cpm; when metallic mercury was used separated from the trapping solution, all the activity was transferred to the mercury.

TABLE II.—EFFECT OF VARIOUS COMPOUNDS ON MOVEMENT OF RADIOACTIVE MERCURY

Experiment	Dish	Initial composition of liquid in dish	Fraction of original activity, found in dish, %	
1	1	30 μg of Hg + ^{203}Hg	57·7 (1 day)	54·7 (4 days)
	2	10 μg of Hg in HCl + KBr	18·2	22·2
	3	10 μg of Hg in HCl + NH_4Cl	18·0	17·8
	4	10 μg of Hg in NaOH	2·8	1·2
2	1	30 μg of Hg + ^{203}Hg	104 (5 days)	
	2	0 μg of Hg in HCl + KBr	0	
	3	0 μg of Hg in HCl + NH_4Cl	0	
	4	0 μg of Hg in NaOH	0	
3	1	30 μg of Hg + ^{203}Hg	72 (4 days)	
	2	0 μg of Hg + NH_4OH	0	
	3	0 μg of Hg + KNO_3	0	
	4	10 μg of Hg + KNO_3	18	
4	1	30 μg of Hg + ^{203}Hg + $KMnO_4$	100·2 (3 days)	
	2	30 μg of Hg in HCl	0	
	3	10 μg of Hg in HCl + KBr	0	
	4	10 μg of Hg in HCl + KNO_3	0	
5	1	30 μg of Hg + ^{203}Hg + $KMnO_4$	99 (1 day)	
	2	2 drops of mercury	0	
6	1	30 μg of Hg + ^{203}Hg + $KMnO_4$	144 (1 day)	
	2	30 μg of Hg + ^{203}Hg	17·2	
	3	2 drops of mercury	not measured	
7	1	30 μg of Hg + ^{203}Hg + $KmnO_4$	103 (3 days)	
	2	30 μg of Hg + ^{203}Hg	99	

Experiment 1 shows that some differences occur in the ability of various salt solutions to absorb the radioactivity when equal amounts of mercury salts are present. The reasons for this were not pursued.

Table II also summarizes the effects of adding a small quantity of potassium permanganate to the solution initially containing all the radioactivity, or (experiments 6 and 7) to one of the solutions initially containing equal amounts of radioactivity.

The presence of the strongly oxidizing potassium permanganate is shown to prevent movement of radioactivity out of the solution even when liquid mercury is present elsewhere in the system. Other experiments (Table I) had shown that radioactive mercury moved rapidly to a metallic mercury trap. Experiments 6 and 7 (Table II) show that a solution containing permanganate successfully competed with the liquid mercury drops for the radioactivity escaping to a saturated mercury atmosphere from a solution containing no oxidizing agent.

DISCUSSION

The published work on loss of mercury from solutions containing trace quantities has involved either biological solutions or solutions containing a reducing agent. Here it seemed very likely that the mercury escaped as the metallic vapour. However, when movement occurred from inorganic solutions containing no added reducing agents, there was the possibility that a volatile compound of mercury might be involved. The experimental evidence does not support this possibility, and thermodynamic considerations indicate that the mechanism is reduction of mercury(II) to mercury(I) which then disproportionates into mercury(II) and metallic mercury.

Consider the volatilities of mercury and mercury(II) chloride. At 26°, the vapour pressure of mercury is 2·66 μbar,[6] and the solubility in water at 20° is 0·02 μg/ml.[7] The complete reduction of only 1% of a $10^{-5}M$ mercury(II) chloride solution would saturate the solution with mercury, and the gas-phase mercury content would be 23 ng/ml. It is easy to see how a solution containing μg quantities of mercury could exchange its contents rapidly in a process involving metallic mercury.

The vapour pressure of mercury(II) chloride at 26° is 0·1 μbar,[6] which is about 5% that of metallic mercury. However, its partial pressure in a $10^{-5}M$ solution would be only 0·02 pbar, and the gas phase would contain 2×10^{-4} pg/ml. Such small quantities make it unlikely that mercury(II) chloride vapour plays an appreciable role in the movement of the mercury activity out of solution. This conclusion was experimentally verified by showing that increasing the amount of mercury(II) chloride in the initial solution reduced the amount of radioactivity escaping.

The rapid escape of activity from solution when a mercury pool was present and the necessity of having mercury(II) salts in the trapping solution show that an exchange process involving mercury vapour is involved. In order to account for the movement when no mercury vapour is deliberately supplied, we must postulate that a small amount of reducing material is introduced with the various reagents used. A possible mechanism may be proposed, based on the mercury(I) disproportionation equilibrium.[8]

$$\mathrm{Hg_2^{2+} \rightleftharpoons Hg^{2+} + Hg(l)} \quad E = 0{\cdot}065\ \mathrm{V}$$

At equilibrium the ratio $[\mathrm{Hg^{2+}}]/[\mathrm{Hg_2^{2+}}]$ is 6×10^{-3}, so further reduction of $[\mathrm{Hg^{2+}}]$ would permit spontaneous disproportionation and the metallic mercury formed would easily escape from the solution. Such an extensive reduction of the $[\mathrm{Hg^{2+}}]$ levels would not be necessary at room temperature because collisions of molecules could provide about a fifth of the 12 kJ/mole free energy change.

The actual quantities of free mercury(II) and mercury(I) ions in solution are far less than the total amount of mercury(II) salt in solution, as may be determined from the stability constants and solubility products. The solutions used in this study were usually $\sim 0{\cdot}1M$ chloride solutions. The predominant mercury(II) complex is probably $\mathrm{HgCl_4^{2-}}$, and its stability constant[8] is $1{\cdot}2 \times 10^{15}$.

If the mercury(II) in solution is $10^{-5}M$ and the chloride is $0{\cdot}1M$, $[\mathrm{Hg^{2+}}] = 8{\cdot}3 \times 10^{-17}M$. The solubility product of $\mathrm{Hg_2Cl_2}$ is given as $1{\cdot}1 \times 10^{-18}$; in a $0{\cdot}1M$ chloride solution $[\mathrm{Hg_2^{2+}}] = 1{\cdot}1 \times 10^{-16}M$. It may be seen that only a small quantity of mercury(II) need be reduced to give a saturated solution of the mercury(I) ion, which then would remain at a constant level. Furthermore, with smaller quantities of mercuric salts in solution the quantity of mercury(II) ion would decrease whereas that of mercury(I) ion would remain constant. Thus, the disproportionation would be favoured by smaller amounts of the mercury(II) salt in solution. The stability of dilute solutions of mercuric salts thus becomes a question of the quantity of mercury in solution.

The high oxidation potential of the Hg(II)/Hg(I) couple indicates a high probability of reduction by almost any reducing substance. The extreme insolubility of mercury(I) chloride also indicates that a very small quantity of a reducing agent would provide a saturated solution ($1{\cdot}1 \times 10^{-16}M$). The introduction of such low levels of reducing substances through the reagents or even the demineralized water is almost inevitable but difficult to quantitate. However, the postulation is supported by the fact that small amounts of potassium permanganate (Table II) added to solutions containing radioactive mercury effectively prevent the loss of any radioactivity.

A crucial experiment (Table II, No. 6) is that in which equal amounts of mercury(II) salts and of radioactivity are contained in two solutions, but some potassium permanganate has been added to one. A saturated mercury vapour atmosphere is provided by placing 2 drops of liquid mercury in a third dish. Here it is shown that in one day there has been movement out of only one solution, and also substantial increase in activity in the other, which shows that oxidation of the mercury vapour by the permanganate has occurred. A contrasting experiment (No. 7) in which no mercury vapour is provided shows the much slower movement of the radioactivity in the absence of a saturated mercury atmosphere.

CONCLUSIONS

Thermodynamic considerations show that the loss of mercury from a solution which contains the element in the mercury(I) form may occur readily through disproportionation and subsequent loss of metallic mercury. Because of the high oxidation potential of the mercury(II)-mercury(I) system almost any reducing substance can convert some mercury(II) into mercury(I).

Because of the near impossibility of preventing introduction of small amounts of reducing substances by the reagents, the more dilute mercury(II) solutions would be less stable and lose mercury more readily. The only practical method for stabilization would be to add a small excess of an oxidizing substance (such as permanganate) which has a higher oxidation potential than the mercury(II)-mercury(I) system.

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Summary—It is shown that loss of radioactivity from labelled mercury(II) solutions is due to reduction of some mercury(II) by reductants adventitiously introduced, followed by disproportionation of mercury(I) and loss of metallic mercury in the gas phase. The loss can be prevented by addition of a small excess of an oxidant such as permanganate.

Zusammenfassung—Es wird gezeigt, daß der Aktivitätsverlust von markierten Quecksilber(II)-Lösungen auf Reduktion von etwas Quecksilber(II) durch zufällig eingeschleppte Reduktionsmittel beruht. Das Quecksilber(I) disproportioniert dann und metallisches Quecksilber geht in die Gasphase verloren. Der Verlust kann durch Zugabe eines kleinen Überschusses eines Oxidationsmittels wie Permanganat verhindert werden.

Résumé—On montre qu'une perte de radioactivité de solutions de mercure(II) marqué est due à la réduction d'une partie du mercure(II) par des réducteurs introduits accidentellement, suivie par la dismutation du mercure(I) et la perte de mercure métallique dans la phase gazeuse. On peut prévenir la perte par addition d'un petit excès d'un oxydant tel que le permanganate.

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PROFESSOR L. ERDEY

A FEW DAYS after celebrating his sixtieth birthday, Professor Laszlo Erdey died after a heart attack on the 21st of February 1970.

L. Erdey was born on the 12th of February 1910, in the Hungarian town of Szeged. During his grammar school years he won the annual national contest for students in physics. He studied then at the P. Pazmdny (now L. Eötvös) University of Budapest and graduated in 1933 in chemistry, physics and mathematics. Working as a demonstrator and assistant lecturer he obtained his Ph.D. from the same University in 1938. In 1942 he joined the Municipal Chemical and Food Testing Institute of Budapest, and worked also as a part-time lecturer, later as a senior lecturer at the University. In 1949 he was appointed as Head of the Institute of General Chemistry at the Technical University of Budapest, became a full Professor in 1950 and held this post up to his death. He served as Dean of the Faculty of Chemical Engineering at the same University from 1950 to 1953. He was elected as a corresponding member of the Hungarian Academy of Sciences in 1951, and became a full member (Fellow) in 1955. He was a member of several Hungarian and International Chemical Societies. He was a member of the Analytical Committee of the International Union of Pure and Applied Chemistry and served on the Advisory Board of *Talanta* since the journal was started. He was also the Editor-in-Chief of the *Journal of Thermal Analysis* and Regional Editor of the *Journal of Radioanalytical Chemistry*.

He was twice awarded (1951 and 1958) the Kossuth Prize, which is the highest award in Hungary for cultural and professional activities. Among other Hungarian distinctions he was awarded the Golden Degree of the Work Order on his sixtieth birthday by the Hungarian authorities. He was also awarded the Hanus medal of the Czechoslovak Chemical Society.

With his research team in the Institute of General Chemistry at the Technical University of Budapest, which at one time had more than thirty graduate members, L. Erdey did research in almost all branches of analytical chemistry. First he dealt with ascorbinometric titrations, with redox and chemiluminescent indicators, gravimetric analysis and thermal analysis. He later worked also on electroanalytical methods including polarography, organic analysis, spectroscopy, gas chromatography, trace analysis and radiochemical analysis and published more than 500 papers; his textbook on *Quantitative Analysis* and *Volumetric Analysis* (now in their 10th Edition) are widely used by Hungarian-speaking chemists. His main work, *Gravimetric Analysis*, in three volumes, giving both a theoretical treatment of the subject and a critical survey of carefully selected and experimentally tested methods was published in Hungarian, German and English.

His death means a great loss to his friends, younger and older students and co-workers and to analytical chemistry in general.

GYULA SVEHLA

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PROFESSOR LASZLO ERDEY

ONE of the penalties of later middle age is the gradual loss of one's friends. In time one learns to accept the inevitability with philosophy, but when a very special friend departs, particularly when it is unexpected, grief seems to have no bounds; the poignant memories flood in and there is not one road left to escape the torment of the spirit:

"Give sorrow tears,
The grief that does not speak,
Whispers the o'erfraught heart."

But Laci Erdey would not have wanted us to mourn him for long and would rather that we remembered the many good times we all had together. I shall not speak of him as a scientist, nor of his massive contributions to his chosen field, for these are well known and, in any event, have been adequately covered in other obituaries. Instead I will pay tribute to Laci as a friend—the best of friends.

I first met Laci in Lisbon, at the 1956 IUPAC Congress. He was with that other great Hungarian chemist, the late Professor Schulek. At this time I also met, for the first time, R. Přibil and G. Schwarzenbach. All the forementioned, together with H. Flaschka, F. Feigl and C. L. Wilson took supper together. I sat next to Laci and this began our much too short friendship.

He was kind, charming, modest, humorous and highly cultivated. He loved his country beyond measure and took great pride in its achievements. He taught others to think in a like vein and to admire Hungarian contributions to science, medicine art, literature and music. It was always a pleasure to hear him talk on Hungarian wines. Nevertheless, Laci was no chauvinist; he loved Hungary, but in a framework of European culture of which it is part, and like myself felt at home in any country in Europe. Perhaps this represents the most rational way of thinking; to feel part of what one regards as a great unified structure, yet to cherish and maintain the individual character of each of its component parts.

Laci had had to take care of his health for some years after a bad heart attack in Moscow. Yet up to the moment of his death, he felt well and was full of ideas and plans for the future, never thinking that they would never be fulfilled. Perhaps the way of Laci's going is to be envied; though one's deepest sympathy goes out to his wife Anna, who bore the brunt and shock of sudden death.

The time for mourning is now past, let us think of the many and varied pleasures he brought to us. I shall never forget him.

Balatonfured
31 *August* 1970

R. BELCHER

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DEVELOPMENT AND PUBLICATION OF NEW GRAVIMETRIC METHODS OF ANALYSIS

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Summary—A review is made of the factors affecting the accuracy of gravimetric methods, and which need to be investigated in the development of new methods. Recommendations are made for writing up such investigations for publication.

IN THE FIRST paper of this series, Kirkbright[1] laid down a set of requirements for thorough investigation of any proposed new method of spectrophotometric determination and that paper was thought to be timely in view of the large number of reagents being developed for colorimetric analysis and the growing need for some agreement as to the minimum of investigation necessary and on the format for expressing results. Although gravimetric analysis has often been regarded as obsolescent, there are still as many papers published on it[2] as on radiochemical analysis, a field which is rapidly becoming prominent. This is mainly due to the need for elucidation of the theoretical fundamentals of gravimetric analysis (which had developed mainly empirically). Extensive research work is being done on the application of complexing agents to extend the possibilities for specific determination and separation of metal ions, and a certain reviviscence of the field has been brought about by the development of radiochemical analysis, especially activation analysis. Gravimetric methods have not lost their importance in spite of instrumentation and automation. It would be rather difficult to find an instrumental method which did not need the methods of classical chemical analysis to provide the composition of the standards used for calibrating the instrument. The fundamental operation in gravimetric analysis is the quantitative precipitation of the component to be determined, in a form which is free from contaminants and easy to separate from the mother liquor, *i.e.*, easy to filter off and wash. The precipitate must either itself be a stoichiometric compound that is easy to weigh, *i.e.*, involatile, non-hygroscopic, non-efflorescent, and inert to reaction with air, or easily convertible into such a compound by drying or ignition. However simple these requirements may seem, it is rather difficult to keep the error caused by dissolution losses, co- and post-precipitation *etc.* below 0·1 %, which is in most cases required in practice. It is therefore the intention of this paper to lay down a standard set of requirements for development and publication of a gravimetric method, and to discuss the chemical background which makes these requirements necessary.

THE PRECIPITATION PROCESS

Nucleation and crystal growth

The kinetics and thermodynamics of precipitation are important not only in analysis but also in metallurgy, the chemistry of solids and very pure substances, the physics of semiconductors, *etc.* Although considerable effort has been expended on elucidating the fundamentals of the kinetics and thermodynamics of precipitation,[3,4] practically all of it has been devoted to the rather narrow field of precipitation of ionic compounds, although these form by far the minority of the compounds used in analytical practice, and even then, agreement has not finally been reached on such factors as the critical size of a nucleus for crystal growth. From the analyst's point of view, the important features are that contamination by adsorption or occlusion occurs to an extent that is largely governed by the surface area of the precipitate, so it is important to have a small number of crystal particles present, these being of relatively large size. Until the development of precipitation from homogeneous solution (PFHS) the basic rules for production of analytically suitable precipitates had not changed appreciably since von Weimarn.[5]

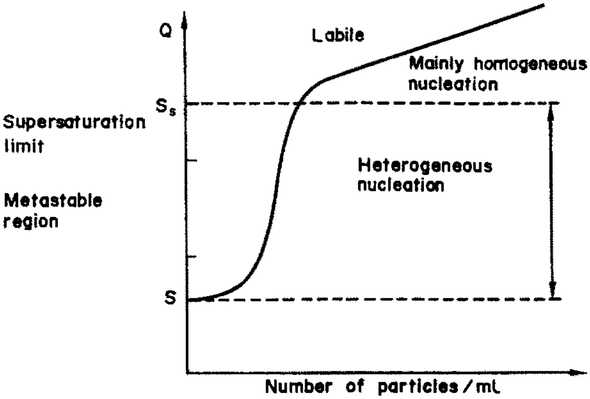

Fig. 1.—Number of particles precipitated, as a function of supersaturation. (Reprinted from *Chem. Anal. Warsaw*, 1968, **13**, 969, by permission.)

It is recognized that the number of precipitated particles and their size distribution are determined by the rate of nucleation and by the rate of growth of the nuclei (which can be defined as the rate of linear growth of a crystal plane). Nucleation occurs in supersaturated solution. The concentration interval between the equilibrium solubility (solubility of large particles) and the critical supersaturation was termed by Ostwald the metastable zone. At the critical supersaturation concentration crystal formation proceeds instantaneously and spontaneously. The metastable zone may greatly differ in width even for precipitates with the same solubility, and great difference may result in the morphology of precipitates, as shown in the case of barium sulphate and silver chloride. Nucleation can be homogeneous (*i.e.*, the nuclei are the same compound as the precipitate) in which case the nuclei are formed by agglomeration and dispersal of the constituents of the precipitate until, as a result of this statistical fluctuation between growth and decrease, a certain critical size is reached, and growth predominates; alternatively nucleation may occur at concentrations lower than the critical supersaturation concentration, and is then called heterogeneous and takes place on foreign surfaces such as those of impurities, vessel walls, or gas bubbles. A plot of number of particles per unit volume, as a function of supersaturation, gives a break-point at the critical supersaturation concentration, and at higher concentrations than this the number of particles produced rapidly increases, with a concomitant decrease in particle size (Fig. 1). A graphical representation gives a clear picture of the nature of nucleation.[6]

Kossel's theory of crystal growth[7] attempted to calculate the energy released when an ion, atom or molecule entered at different points of the lattice. Volmer[8] introduced the concept of a two-dimensional nucleus into Kossel's theory, such an aggregate of atoms or ions being stable on the crystal surface only if bigger than a certain critical size. According to Frank[9] spiral growth proceeds at low supersaturations and a two-dimensional nucleus need not then be formed.

It follows that nucleation must be minimized and growth maximized, if a pure and easily filterable precipitate is to be obtained, and this can be achieved by maintaining a low degree of supersaturation. Several attempts have been made to meet this requirement. Hahn and Otto[10] effected the precipitation from extremely dilute solution, by adding separate solutions of the ion to the precipitated and of the precipitant dropwise to boiling distilled water. The electrolyte concentration is much higher at the end of precipitation than at the beginning. In this way well-formed crystals can be obtained. In contrast, according to Njegovan and Marjanovic[11] precipitation is to be made from cool concentrated solution with a concentrated solution of the precipitant, and the suspension is to be warmed with hot water, during which process recrystallization probably proceeds, but an excessive length of time is required. According to the precision method of Winkler[12] precipitation is best effected from boiling solution with a reagent solution added dropwise. By the use of a known, constant amount of ammonium salt, adsorption can be avoided or reduced. The deviation of the weight of precipitate from the theoretical value can be corrected for. According to the method of Willard and Tang,[13] precipitation from homogeneous solution, the reagent is generated uniformly dispersed throughout the solution of the ion to be precipitated, and so local supersaturation can be avoided. This can be achieved by generating the precipitating reagent *in situ* by a hydrolytic reaction (*e.g.*, hydrolysis of sulphamic acid to produce sulphate), a condensation (*e.g.*, formation of dimethylglyoxime from biacetyl and hydroxylamine), a pH change which itself is brought about by a hydrolytic reaction (*e.g.*, hydrolysis of urea to raise the pH to produce the appropriate 8-hydroxyquinoline species for precipitation of aluminium) *etc*, or the metal ion to be precipitated may be released from a stable complex in the presence of an excess of precipitant (*e.g.*, peroxide oxidation of the bismuth-EDTA complex in the presence of phosphate), or the reaction may be carried out in the presence of an organic solvent (in the case of precipitation with an organic reagent) in sufficient amount to keep the precipitate in solution, followed by slow removal of the solvent by evaporation.

Whatever the method used, it will be affected by such variables as the concentration and temperature of the reagents, of addition or generation or precipitant, length or digestion of the precipitate with the mother liquor, and temperature during filtration. It should be noted that in precipitation from homogeneous solution, in order to avoid unduly prolonged reaction times it is often necessary to take a very large excess (up to 1000%) of the generating reagent, and to quench the reaction by cooling when sufficient precipitant has been produced (a study of kinetic curves will show why).

Solubility of precipitates

Factors affecting the solubility of precipitates can be classified into two groups, according to whether they influence the properties of the solid phase or those of the solution. The precipitate structure, presence of polymorphous modifications and of water of crystallization, particle size distribution, and aging have a remarkable influence on the solubility of precipitates. Of these factors, aging is the most important. By this term is meant those changes which occur in a precipitate on standing in contact with the mother liquor. These changes are discussed in detail in the standard textbooks (*e.g.*, those by Laitinen[14] and by Kolthoff *et al.*[15]) but two of them are of more practical importance than the others. If a species is precipitated in a metastable form and can be transformed into a more stable form with extensive rearrangement of the lattice, then substantial purification will occur in the process (*e.g.*, calcium oxalate dihydrate and trihydrate are metastable with respect to the monohydrate and are converted into it on digestion). Many "hydroxide" precipitates are better described as hydrous oxides, and may undergo slow change in composition on aging. One practical consequence is that hydroxide precipitates left for a considerable length of time may become much more difficult (or even impossible) to redissolve in acid, thus making reprecipitation harder to achieve.

At a certain temperature the mother liquor and precipitate will reach an equilibrium characterized by constancy of the activity product:

$$K_{sp} = a_M{}^m \cdot a_N{}^n$$

where K_{sp} is called the solubility product of the species M_mN_n. The solubility of M_mN_n increases as the activity of its ions in solution decreases (by protonation, hydrolysis, complex formation, oxidation *etc.*). It has been proposed[16] that for direct comparison with stability constants it would be more logical to use an "insolubility product," which would be the inverse of K_{sp}.

Because the object of quantitative analysis is to recover the whole of a particular species, an excess of precipitant must of necessity be used. It follows that the solubility of the precipitate will be decreased by this excess (the common-ion effect), but if the reagent can form charged complexes with the ion of interest, there may be a solubility increase if a very large excess of reagent is used (*e.g.*, silver chloride is soluble in concentrated hydrochloric acid because of formation of $AgCl_2^-$). The wash liquid used may need to contain one of the component species of the precipitate to prevent loss by dissolution in washing, or to contain an electrolyte to prevent peptization of a flocculated colloid, and the salt used must be readily removable from the washed precipitate. Usually an ammonium salt is used, since it will be volatile on suitable heat-treatment of the precipitate. Use of a saturated solution of the precipitate is not to be recommended (positive errors could ensue from precipitation by the common ion excess in the mother liquor still in contact with the precipitate, or if the precipitate is left unduly wet with wash-liquid before ignition or drying, and negative errors if the residual wash-liquid is removed with water).

Factors influencing the properties of the solution can be classified into two groups: those exerting the so-called inert-electrolyte effect because of changes in the ionic strength of the solution, and those causing reactions involving one of the ions of the precipitate, such as hydrolysis of cations, formation of complexes with common or foreign ions, protonation of strongly basic ligands and disproportionation of one of the ions. The extent of all these reactions may markedly depend on the pH, and calculation of their effect is described in the textbooks.[14,15,17]

A particularly insidious influence is exerted by the existence of inert complexes, especially heterobinuclear complexes. The ion to be determined may be initially present in the form of a complex which is thermodynamically unstable relative to the change brought about by addition of precipitant, but kinetically so slow to react that it is effectively stabilized. Worse, it may be present along with a complexing ligand with which it normally forms a labile complex, but which can act as a bridge between it and another ion to form an inert complex, *e.g.*, copper(II)–citrate–chromium(III);[18] the existence of such complexes is often unsuspected. The preliminary history of a solution is often of vital importance, particularly that of the "opening-out" process.

Contamination of precipitates

Contaminations may be classified into two groups: those due to co-precipitation and those caused by post-precipitation. In co-precipitation two types of contamination can be distinguished: adsorption and occlusion. In the case of adsorption, the precipitate particles carry the contaminant on their surface. With colloidal precipitates the coagulated secondary particles may carry in their interior impurities bound by adsorption forces to the primary colloid particles. In occlusion the impurity is inside the primary precipitate particles, whether by mechanical trapping during crystal growth or by formation of solid solutions. The distribution of contaminant in a homogeneous solid solution can be characterized by the Berthelot-Nernst distribution coefficient, D, which describes the thermodynamic equilibrium:[19,20]

$$\frac{[\mathrm{A}]}{[\mathrm{B}]} \text{ in crystal} = D\,\frac{[\mathrm{A}]}{[\mathrm{B}]} \text{ in solution.}$$

A homogeneous distribution is obtained for the crystal as a whole and not only for the surface layer, if there is equilibrium between the solution and crystal.

The heterogeneous distribution of a contaminant can be characterized by the coefficient λ in the Doerner-Hoskins equation[19]

$$\log\left(\frac{[\mathrm{A}]_{\mathrm{initial}}}{[\mathrm{A}]_{\mathrm{final}}}\right) \text{ in solution} = \lambda \log\left(\frac{[\mathrm{B}]_{\mathrm{initial}}}{[\mathrm{B}]_{\mathrm{final}}}\right) \text{ in solution.}$$

According to this the composition of an elementary layer of the precipitate depends on the ratio of the concentrations of the two components in the solution. λ and D differ in that the former is a kinetic constant while the latter is a thermodynamic equilibrium constant.

Very often all forms of contamination are called occlusion, which can cause confusion, since the exact reason for contamination has to be known if it is to be eliminated. Contaminants bound to the precipitate by adsorption are much easier to remove by washing than those occluded.

It is useful to tabulate the ways in which the purity of precipitates can be improved, and this has been done in Table I. It must be stressed, however, that there are many exceptions to these general guiding rules, and that investigation should always be made of the effect of variation of conditions.

Collection and heat-treatment of precipitates

Precipitates that are to be dried at temperatures up to about 250° are invariably collected in borosilicate sintered-glass crucibles. Those which are to be ignited are

TABLE I.—INFLUENCE OF CONDITIONS OF PRECIPITATION ON PURITY

Condition	Form of impurity			
	Mixed crystals	Surface adsorption	Inclusion	Post-precipitation
Dilute solutions	0	+	+	0
Slow precipitation	+	+	+	−
Prolonged digestion	0/+	+*	+	−
High temperature	−	+†	+	0
Agitation	+	+	+	0
Washing	0	++§	0	0
Reprecipitation	0/+	++	++	+
Adjustment of pH	0	0	0	+
Filtration soon after precipitation	0	0	0	++
PFHS	+	++	++	−

* This would have no effect on gelatinous precipitates.

† There are exceptions. Some crystalline precipitates are affected adversely, *e.g.*, $BaSO_4$ and CaC_2O_4, but digestion improves the situation.

§ Gelatinous and curdy precipitates; crystalline precipitates do not reach the required degree of purity by washing alone.

++ Impurity reduced to negligible amounts, though not necessarily by this means alone; other conditions may have to be used in conjunction.

\+ Increased purity, but significant amounts still present.

0 No significant change.

− Decrease in purity.

This table was supplied by Prof. R. Belcher and is based on the one by M. L. Salutsky, in *Treatise on Analytical Chemistry*, I. M. Kolthoff and P. J. Elving eds., Part I, Vol. 1 p. 499, Interscience, New York, 1959.

collected on filter-paper or in crucibles fitted with fritted discs. The latter filters may be made of fused silica or of porcelain. Sometimes use is made of platinum filters fitted with platinum sponge. The use of asbestos (the original Gooch crucible) has largely disappeared. If frits are used, it is essential that the crucibles should be conditioned by repeated heating with solutions of approximately the composition of those with which the crucible is to be used, until the crucible shows no further change in weight on treatment. This is particularly important for work on the micro scale. Because the surface area of the fritted discs is very large, the equilibrium amount of water vapour adsorbed on the surface is also large, and can vary if the humidity changes between weighings. While the effect may not be noticeable on the macro scale (it may amount to one or two hundred micrograms) it is a serious source of error in microanalysis, and microcrucibles should always be used along with a similar crucible as counterpoise. The counterpoise crucible must be given the same heating and cooling treatment as the sample crucibles in order to compensate as far as possible for variation in conditions. Whenever platinum crucibles are used it should be remembered that platinum is appreciably volatile at high temperatures, especially those above 1000°, and an empirically determined correction should be applied for loss, calculated on a temperature and time basis. When silica, glass or porcelain crucibles have been used, the possibility of induced electrostatic charges should not be overlooked,[21] and if necessary a metal crucible can be used to provide a Faraday cage on the balance pan.

The pore-size of the filter must be matched to the particle size of the precipitate. If it is too great there may be loss of material by passage through the filter; if it is too small the filter may clog and filtration be unduly slow.

Once obtained, collected, and washed with a suitable liquid, the precipitate is freed from water by drying or ignition. During this heat-treatment the precipitate may undergo physical or chemical changes which influence its weight and composition.

Winkler[12] has drawn attention to the fact that crystalline precipitates can be dried to constant weight even at room temperature if they are not hygroscopic, do not tend to oxidize, do not react with carbon dioxide present in air and do not decompose in air, though naturally this may take a long time. Sometimes water is removed with alcohol *etc.*

However, the last traces of water cannot always be removed from the precipitate by drying at room temperature. Barium sulphate, for example, may retain water at temperatures up to 600°. Duval[22] systematically studied the thermal behaviour of precipitates by automatically recording the dependence of precipitate weight on temperature. Erdey and Paulik[23,24] have developed the technique further by recording simultaneously the mass loss curve and its derivative, and the differential thermoanalytical curve. These "derivatographic" curves provide useful information concerning the transformations of a precipitate during heat treatment. The optimum drying temperature and the temperature range over which the weight is constant can be determined by the method. However, if static heating conditions are to be used in the analysis and the precipitate is to be weighed in the open air at room temperature, it is essential to check the thermal behaviour of the precipitate under the conditions to be used, and the interaction of the ignition product with wet air at room temperature. For instance, the decomposition temperature of silicomolybdic anhydride has been reported from thermobalance measurements to be about 800°, but on static heating there is loss of molybdenum trioxide at temperatures above 600°; again, calcium oxalate can be converted into the anhydrous form and weighed as such at 200°, but on exposure to laboratory air at room temperature it rapidly reverts to the monohydrate.[25]

The advantages of desiccators have long been shown to be largely illusory,[26,27] except for keeping dust out of crucibles and preventing accidental loss from draughts, sneezes, *etc.* Even if a good desiccant and design of desiccator *can* be found, immediately a dry object is removed into moist air it will begin to adsorb moisture on its surface, so there is no real point in keeping it dry in the first place, unless the material within it is markedly hygroscopic (*e.g.*, dry flour or calcium oxide) but can be sufficiently protected from the atmosphere by a close-fitting lid for there to be no appreciable uptake of water by it during the period needed for weighing. If the final product to be weighed in a gravimetric analyses is hygroscopic the method is inferior. For rapid cooling a block of metal is adequate, and it is essential that the object to be weighed should be at the temperature of the balance.[28]

Thermal methods can also be used to solve analytical problems directly, *e.g.*, strontium, calcium and barium can be determined rapidly without separation, by means of the derivatogram of their oxalates.[29] The method also permits determination of polymorphous modifications when present together, which is rather difficult to do by other methods.[30]

THE APPLICABILITY OF A METHOD

As pointed out long ago by Lundell,[31] an analytical method is not much use in isolation; it must be capable of application to a particular problem. The analysis of a pure solution of a single substance is not usually much of a problem, certainly not in comparison with analysis of a complex mixture. It follows that any new method must be assessed for usefulness, and those species which will affect the results adversely must be delineated, and where possible, means suggested for eliminating their effect. It is also essential that the useful scale of operations should be defined, so that the method is used sensibly. Gravimetric analysis is useful only in certain contexts, and is meaningless in others.

Amount of sample

The sample weight to be taken, and the accuracy of weighing, are both determined by the composition of the material, the overall error that can be tolerated, and the desired speed of analysis. It is obviously faster to filter a small volume of liquid than a large, so scaling down of operations should hasten the analysis. Both weights and volumes must be reduced in similar proportions in order to keep concentrations about the same. The error of weighing a 5-mg precipitate on a microbalance with a standard deviation of 3 μg is about the same as that of weighing a 100-mg precipitate on an ordinary balance with a standard deviation of 0·05 mg, but an attempt to collect 5 mg of precipitate from say 250 ml of mother liquor would be much more likely to produce an erroneous result than would collection of 100 mg from the same volume. At the other end of the scale, an attempt to increase accuracy by collection of 10 g of precipitate would be a self-defeating exercise because of the unwieldy amount of precipitate and the very large volume of liquid to be filtered, coupled with the impossibility of washing the precipitate adequately. The scale of operations is therefore defined at one end by purely manipulative considerations, and at the other by the precision and accuracy sought.

If an overall error of not more than 0·1 % is aimed at, the error of the final weighing must be smaller than this, and in conjunction with the known performance of the balance used will set the magnitude of the weight of precipitate to be collected, and hence the minimum size of sample to be taken. If a correction is to be applied for a reagent blank, due allowance must be made for the uncertainty in determining it.

An important factor in assessing the statistical errors is the conversion factor from weight of product to weight of species sought. The higher the conversion factor, the less significant the statistical weighing error. For example, in determination of copper by electrolytic deposition and weighing, the conversion factor is unity, whereas in determination of silicon as silicomolybdic anhydride, the product weighs about 60 times as much as the amount of silicon in it; a weighing error of 0·1 mg represents an error of 0·1 mg of copper and 16 μg of silicon respectively.

Gravimetric analysis is not at all suitable for trace analysis, and is generally applicable only to major components of a sample, *i.e.*, those present to the extent of at least 1 %, though it can be applied to minor components (0·1–1 %) if an amplification reaction[32] is available or the conversion factor is very favourable or a larger relative error is tolerable.

If carbon is to be determined in a steel by ignition to carbon dioxide in a stream of oxygen, followed by collection and weighing of the product to the nearest 0·1 mg, then if a "factor weight" of sample is taken (*i.e.*, 2·729 g, because CO_2 contains 27·28 % of carbon) 1 mg of CO_2 produced is equivalent to 0·1 % of carbon in the steel. If there is not more than 0·2 % of carbon present there is no point in weighing the sample more accurately than to the nearest 5 mg (2·73 ± 0·005 g) because the maximum error so caused would be <0·001 % of carbon, which is the limiting error imposed by the final weighing operation. On the other hand, if chloride in sodium chloride were to be determined as silver chloride it would be necessary to weigh both sample and product with a relative error of not more than 0·05 % if an overall error of <0·1 % were desired.

Selectivity

The value and applicability of analytical methods, particularly of new gravimetric determinations, depend greatly on selectivity. An analytical reaction (in the case of precipitation) is selective if the reagent reacts only with the ion to be determined, or with few other ions. A reaction is called specific if it is characteristic for one ion only. By selecting suitable conditions, *e.g.*, by adjusting the pH or other factors which affect complex stabilities, selectivity can be increased, and a reaction can be made specific for an ion. Several attempts have been made[22,23] to interpret the specific or selective nature of reactions, but these problems have yet not been finally settled. With knowledge of the stability constants concerned, the degree of specificty of a complex-formation reaction can be calculated.[24]

Two quantities, the recovery factor R and the separation factor ($S_{B/A}$) are used for the quantitative description of the efficiency of a separation. In the separation of ion A from ion B the recovery factor R_A gives the fraction of A recovered in the precipitate at the end. A separation is good if the value of the recovery factor is between 0·999 and 1·000 (or 99·9 and 100·0 %) where Q_A is the quantity of A isolated

$$1 > R_A = \frac{Q_A}{(Q_A)_0} > 0{\cdot}999$$

and $(Q_A)_0$ is the original quantity, and if the accompanying ion is left quantitatively in the original phase. The selectivity of separation can be characterized by the separation factor, $S_{B/A}$:[25]

$$S_{B/A} = \frac{Q_B/Q_A}{(Q_B)_0/(Q_A)_0} = \frac{(Q_A)_0}{(Q_B)_0}\cdot\frac{Q_B}{Q_A} = \frac{R_B}{R_A}$$

In a good separation the amount of B going into the new phase, Q_B, is less than 0·1 % of Q_A, the amount of A in this phase. It is rather difficult to meet these requirements in separations based on precipitation, especially if the amount of B is great compared to that of A. Chromatographic and extraction methods are more effective means for separation.

Assessment of error and precision

The generally accepted values of allowable errors have been given as follows:[33]

Constituent, %	Error, parts per 1000
100	1–3
10	10
1	10–20
0·1	50
0·01–0·0001	100

but these are the errors associated with routine analysis, which usually involves a "go/no-go" type of inspection of material to see whether it fulfils a specification. For research work and particularly for evaluation of a new method, rather higher precision is to be expected.

Some new analytical methods are preferred to older ones because of their simplicity, rapidity or other advantages, but preference should also take heed of the error involved, and this should be given besides the other features.

Errors can be classified into two groups:

Random errors are due to the uncontrollable small changes in experimental conditions and do not depend on the observer or analyst.

Systematic errors are those caused by the imperfections of equipment used and by the limitations of the physico-chemical reaction serving as the basis of determination.

In gravimetric analysis systematic errors arise from imperfections in balances and weights, from solubility of precipitates, co-precipitation *etc.* As a result, the average of replicate analyses deviates from the true value, but since the deviation is usually of well defined direction and size, it can be eliminated by properly calculated corrections. Random errors cannot be eliminated in this way, however. They arise from such factors as variation in performance of a balance on repeated weighing of the same object, random variation of sample composition, small random fluctuations in treatment of individual analyses, *etc.* The distribution of such errors is assumed to be Gaussian, and the standard deviation is calculated to assess the magnitude of the random error. It is easier to compare results for different methods if the relative standard deviation is given. The nature and statistics of errors are discussed in standard texts (*e.g.*, refs. 14 and 34).

It is not enough, however, simply to calculate the error on the basis of the weight of the final product. It may happen that the reagents contain some of the species being determined, or that the precipitate contains foreign species. As pointed out by Berman, Semeniuk and Russell,[35] the usual practice is to take a standard solution of a substance, put it through the recommended procedure, and if the amount found is very close to the amount taken, to call the method satisfactory, whereas what *should* be done is to investigate separately the loss of precipitate to the filtrate, the extent of contamination of the precipitate, the size of the blank, and any other sources of error, to ensure that there has not been a fortuitous compensation of errors. In their work on thorium determination they showed that silica collected by the precipitate just about cancelled out the amount of thorium lost.

The question of blanks and corrections is rather complicated and depends mainly on the scale of working. In microanalysis, for example, it may prove necessary to apply a correction for dust or other particulate matter in the reagents. It is quite easy to accumulate 25 μg or so of foreign matter, and this would constitute an error of $+0{\cdot}1\,\%$ in a precipitate weight of 2·5 mg. Such an error is easily assessed by dissolving the precipitate off the filter (if an organometallic complex is weighed) with an organic solvent, and then drying and reweighing. Purely inorganic precipitates of ignition products can often be dissolved by suitable acids or fusions; silica in them can be determined by the Berzelius method of removal with hydrofluoric and sulphuric acids. Reagent blanks cannot be properly assessed by running a blank determination in the absence of sample. It is also unrealistic to try to assess the blank by direct determination by other means (spectrophotometry, polarography *etc.*) of the amount of determinand present in the reagents. The constituents of the apparatus used may be extracted to a greater or lesser extent during the analytical operations, and the history of the apparatus may affect the amount removed.

The two methods most commonly used for assessing blanks are to apply the method to a standard material of *accurately* known composition and to determine the difference between "taken" and "found," or to apply the method to two different sample weights, one of which is a simple multiple of the other (usually a 2:1 ratio is used) and to compare the value obtained for the smaller sample with that obtained from the difference between the two results. By "accurately" we mean with a precision that will give an experimental error much smaller than the amount of blank sought, and the remarks of Berman *et al.*[35] on "taken" and "found" must be heeded. (It is obvious that if the standard has been analysed by chemical means there already exists a method of adequate precision and accuracy!)

Corrections for solubility of precipitates should be applied only if the solubility has been determined under the conditions used. A simple consideration of the kinetics shows that it is unlikely that wash-water will become saturated with precipitate during normal washing operations. Corrections for the ash of filter paper are usually negligible for all but micro or semi-micro work.

Applications

As pointed out earlier in this paper, a method is not useful unless an application can be found for it. It is the author's duty to find applications and to test the performances of the method under real and simulated conditions, that is with samples that are likely to be met with in practice, or with samples synthesized by mixing known amounts of materials of known purity to provide mixtures of compositions similar to those of "genuine" samples. Attention must be paid to the method of bringing the sample into solution, and its possible chemical effects on the procedure being developed.

PREPARATION OF A PAPER FOR PUBLICATION

Useful guidance on the information necessary in a published paper on an analytical procedure will be found in the articles by Wilson[36,37] and by Chalmers.[38,39] The requirements for adequate development and description of a gravimetric procedure are dealt with at length in the earlier parts of this paper, and are summarized here for convenience and emphasis. The points listed are those that *must* be examined and reported on. Factorial design of the experimentation can save considerable effort and increase the amount of useful information obtained (see *e.g.*, ref. 40.) A useful general survey of gravimetric methods has been given by Beamish and McBryde.[41]

1. *The precipitant.* Solubility, stability of the solid reagent and its solutions, methods of preparation and physical characteristics (m.p. *etc.*) if a new reagent, should all be given.

2. *Method of precipitation.* Details must be given of the permissible chemical composition of the solution before precipitation; the range of absolute amount and concentration of the species to be determined; the pH, temperature and volume of the sample solution before precipitation; the pH, volume, temperature and concentration of the reagent and the rate at which it is to be added (or alternatively details of the method of conducting PFHS); final pH of the solution, time and temperature

of digestion; temperature for filtration; type of filter; volume and number of washes; composition of the wash-liquid; temperature and duration of drying or ignition; special precautions.

3. *Selectivity.* The effect of possible interfering elements and of species likely to be found in sample matrices must be investigated at realistic concentration levels, covering the full range of likely ratios of interfering species to determinand, and preferably with a 100% safety margin (twice the maximum ratio expected in practice). Any masking agents used to improve selectivity should be tested over a wide range of concentration ratios relative to determinand.

4. *Accuracy and precision.* Results of replicate tests and of tests for loss, recovery, contamination *etc.* should be statistically analysed and summarized. If possible statistical tests of comparison with other methods should be made.

5. *Applications.* Procedures suitable for various matrices tested should at least be outlined, or suitable references given to standard procedures. Results for standard samples should be given.

6. *General.* Tolerances on the various procedure parameters should be quoted and the evidence given on which they are based.[36,37] The value of the method should be realistically assessed against the background of other methods, speed, accuracy, cost, selectivity, simplicity, *etc.*

Acknowledgement—We wish to thank Professor R. Belcher and Dr. G. F. Kirkbright for helpful discussion and criticism of the manuscript.

Zusammenfassung—Es wird eine Übersicht über die Faktoren gegeben, die die Genauigkeit gravimetrischer Methoden beeinflussen, und die man bei der Entwicklung neuer Verfahren untersuchen muß. Zur Veröffentlichung solcher Untersuchungen werden Empfehlungen gegeben.

Résumé—On procède à une revue des facteurs affectant l'exactitude de méthodes gravimétriques, et qu'il est besoin d'étudier dans le développement de nouvelles méthodes. On fait des recommandations pour la rédaction de telles études pour publication.

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DETERMINATION OF TRACE CONTAMINANTS IN HYDROGENATION CATALYSTS BY NEUTRON-ACTIVATION ANALYSIS

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Summary—A neutron-activation method has been developed for the determination of the active constituents and contaminants in hydrogenation catalysts. The active constituents of palladium and nickel catalysts (Pd and Ni) and Zn and Co contaminants present in small amount were determined by a direct instrumental method. A NaI(Tl) scintillator and a Ge(Li) semiconductor connected to a multichannel analyser were used for the measurements. A computer was used to evaluate the γ-spectra. Contaminants present in small amount were also determined by means of a radiochemical separation method based on heterogeneous isotopic exchange on mercury(II) sulphide and zinc sulphide precipitates.

THE PROBLEM of the determination of trace contaminants in hydrogenation catalysts arose in connection with caprolactam production. For the hydrogenation of phenol in the gaseous phase, nickel or palladium catalysts are used, on aluminium oxide, graphite or on a mixture of them, as carrier.

Sulphur, selenium, tellurium, phosphorus, arsenic, antimony, bismuth, zinc, mercury, lead and their compounds are catalytic poisons.[1] The activity of the catalyst decreases linearly or exponentially with increasing concentration of the poison, depending on the nature of the bond formed between the active ingredient of the catalyst and poison. Very small amounts of the poison—orders of magnitude smaller than necessary to form a monomolecular layer—may remarkably reduce the activity of the catalyst.[2,3]

It therefore seems reasonable to use an analytical method of very high sensitivity, such as neutron-activation analysis, for determining contaminants which poison hydrogenation catalysts. In the present paper the determination of mercury and zinc will be dealt with. The active ingredients of the catalysts (Pd, Ni) have also been determined, since this is necessary in order to elucidate the mechanism of poisoning.

The nuclear reactions to be taken into account for all components of the system are listed in Table I. The components include the active ingredients, the carrier used to give large surface area (alumina), and the contaminants.

Samples activated with thermal neutrons were evaluated by γ-spectrometry, by direct instrumental measurements with or without radiochemical separation. To separate the radioisotopes of the trace contaminants our method based on heterogeneous isotopic exchange with sulphide precipitates[4,5] has been used.

Table I.—Nuclear data of elements occurring in palladium and nickel catalysts

Stable isotope	Isotope abundance, %	Reaction type	Cross section, *barn*	Radioactive isotope formed	$t_{1/2}$	Energy peak, *MeV*
^{27}Al	100	n, γ	0·21	^{28}Al	2·3 min	0·76; 1·27; 1·77
		n, α	0·0006	^{24}Na	15 hr	1·36; 1·74; 2·25; 2·76
		n, p	0·004	^{27}Mg	9·5 min	0·18; 0·84; 1·01
^{64}Ni	1·08	n, γ	1·52	^{65}Ni	2·6 hr	0·37; 1·12; 1·49
^{58}Ni	67·84	n, p	0·073	^{58}Co	71·3 d	0·51; 0·81; 1·31; 1·66
^{60}Ni	26·16	n, p	0·002	^{60}Co	5·27 y	1·17; 1·33; 2·50
^{196}Hg	0·15	n, γ	420	^{197m}Hg	24 hr	0·13; 0·164
		n, γ	880	^{197}Hg	65 hr	0·077; 0·191
^{198}Hg	10·00	n, γ	0·018	^{199m}Hg	43 min	0·16; 0·37
^{202}Hg	29·8	n, γ	3·8	^{203}Hg	47 d	0·073; 0·279
^{204}Hg	6·8	n, γ	0·43	^{205}Hg	5·1 min	0·203
^{59}Co	37·0	n, γ	16	^{60m}Co	10·5 min	0·06; 1·33
		n, γ	20	^{60}Co	5·27 y	1·17; 1·33
^{64}Zn	48·98	n, γ	0·47	^{65}Zn	245 d	0·51; 1·12
^{68}Zn	18·57	n, γ	0·097	^{69m}Zn	13·9 hr	0·44
			1·0	^{69}Zn	55 min	
^{102}Pd	0·96	n, γ	4·8	^{103}Pd	17 d	0·053; 0·065; 0·298; 0·324; 0·362; 0·498
^{108}Pd	26·7	n, γ	0·26	^{109m}Pd	4·8 min	0·19
		n, γ	10·4	^{109}Pd	13·6 hr	0·022; 0·088; 0·307; 0·42
^{110}Pd	13·5	n, γ	0·05	^{111m}Pd	5·5 hr	0·17
		n, γ	0·21	^{111}Pd	22 min	0·45, 0·62
				^{111}Ag	7·6 d	0·023; 0·247; 0·31; 0·340

EXPERIMENTAL

Apparatus

Gamma spectroscopy. NaI(Tl) scintillators, 35 mm and 60 mm diameter and 75 × 75 mm; measuring heads equipped with photomultiplier. Ge(Li) semiconductor detector, 12·5 ml. Multichannel analysers, 256, 512 and 1024 channel, constructed in the Central Research Institute for Physics of the Hungarian Academy of Sciences (CRIP).

For evaluation of the spectra by computer the data from the analyser were put on punched tape with a Facit printer. The computer (ICT-1905, using Algol language, developed in the CRIP) draws the spectrum on the basis of the data, and determines the amplitude, area, width at half-height, and position of the energy peaks as Gauss curves by simulation, and corrects the data for the background.

Activation. Irradiations were made in the experimental atomic reactor of the CRIP: thermal neutron flux: $3{\cdot}8 \times 10^{13}$ neutrons.cm^{-2}.sec^{-1}; fast neutron flux: $0{\cdot}5 \times 10^{12}$ neutrons.cm^{-2}.sec^{-1} in the channel used. Samples and standards were irradiated for 24 hr under similar conditions.

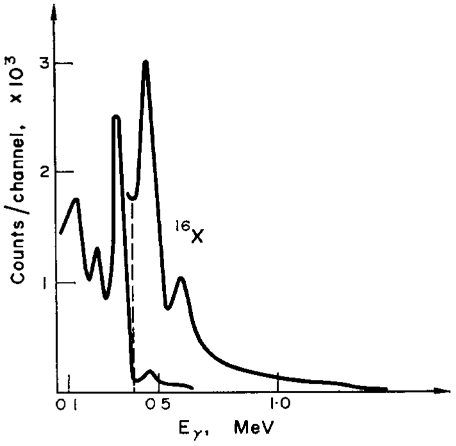

FIG. 1.—γ-Spectrum of palladium standard.

Catalyst samples (5 × 5 mm cylinders of about 150 mg weight) were irradiated sealed in quartz ampoules. Samples were processed after 8–10 days cooling.

Irrespective of the measuring procedure used, catalyst samples were dissolved in 2 ml of nitric acid (1 + 1) in a flask equipped with a reflux condenser, and then diluted to 50 ml with distilled water. Aliquots of the resulting stock solution were used for measurement.

As standards Johnson Matthey's palladium, nickel, cobalt, zinc and mercury compounds of spectral purity were used.

RESULTS AND DISCUSSION

Direct instrumental studies by scintillation detector

Aliquots (1 ml) of the stock solutions of the activated catalyst samples and standards prepared after 10 days cooling were transferred to quartz vessels, evaporated to dryness, and their γ-spectra recorded.

In the γ-spectrum of the palladium standard (Fig. 1) peaks appear at 0·24, 0·34, 0·49 and 0·6 MeV, originating from the radioactive isotopes of palladium and from daughter-isotope ^{111}Ag from ^{111}Pd.

In the γ-spectrum of unused palladium catalyst (Fig. 2) the photopeak of the radioactive isotope ^{65}Zn also appears at 1·12 MeV, as a small amount of zinc was originally present in the catalyst.

In the γ-spectrum of used palladium catalyst appear the photopeaks characteristic of the radioisotopes of zinc and palladium (Fig. 3). On the spectrum obtained with greater amplification (Fig. 4) the 0·279-MeV photopeak of the mercury contaminant

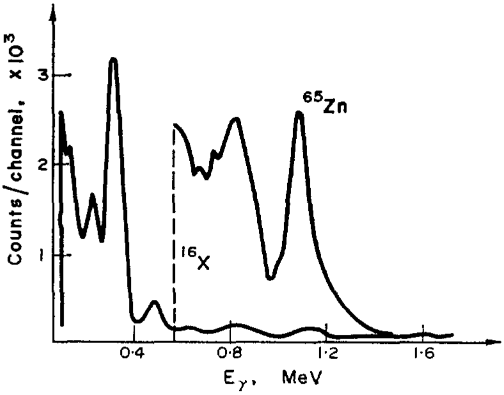

FIG. 2.—γ-Spectrum of unused palladium catalyst.

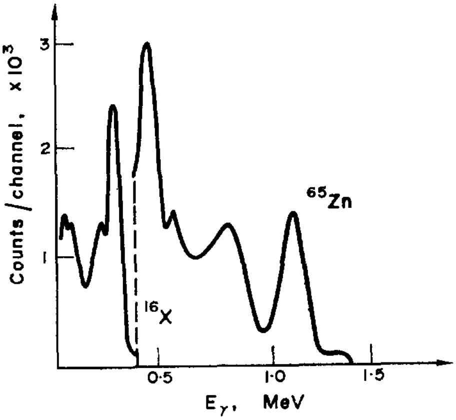

FIG. 3.—γ-Spectrum of used palladium catalyst.

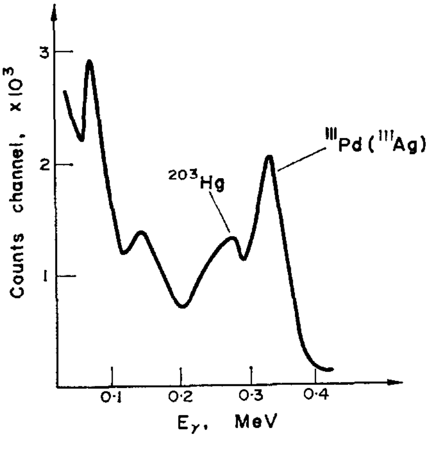

FIG. 4.—γ-Spectrum of used palladium catalyst at higher amplification.

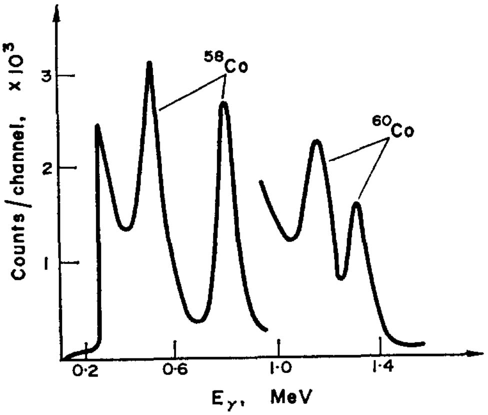

FIG. 5.—γ-Spectrum of unused nickel catalyst.

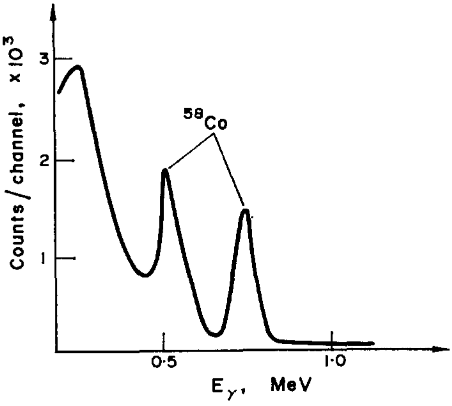

FIG. 6.—γ-Spectrum of nickel standard.

becomes perceptible, but it is not separated from the 0·24-MeV photopeak of palladium.

When scintillation detectors are used, only the palladium active ingredient and zinc contaminant of the catalyst can be determined from the γ-spectra by a direct instrumental method. Before determination of palladium the spectrum of the ^{65}Zn standard was subtracted from the complex spectrum and the 0·34-MeV photopeak of palladium evaluated. In determining palladium and zinc the spectra were evaluated by Covell's method.[6]

In the γ-spectrum of unused nickel catalysts (Fig. 5) the photopeaks of ^{60}Co appeared at 1·17 and 1·33 MeV, and were due to the original cobalt content of the catalyst; in addition there were the 0·51- and 0·81-MeV peaks of radioactive ^{58}Co formed from nickel. In the spectrum of the nickel standard only the 0·51- and 0·81-MeV photopeaks of ^{58}Co appeared (Fig. 6) which indicated that the ^{60}Ni(n, p)^{60}Co nuclear reaction did not proceed to an appreciable extent.

In the γ-spectra of used nickel catalyst obtained with different amplification (Figs. 7 and 8) appeared the peaks of ^{58}Co and ^{60}Co. The photopeak of mercury

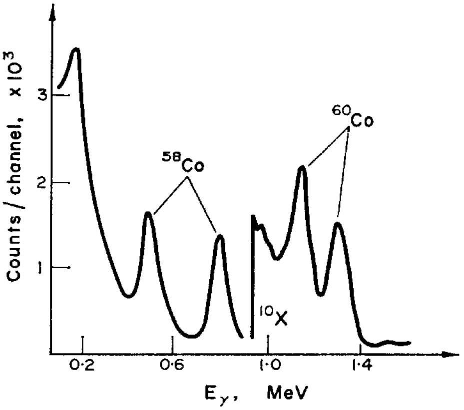

Fig. 7.—γ-Spectrum of used nickel catalyst.

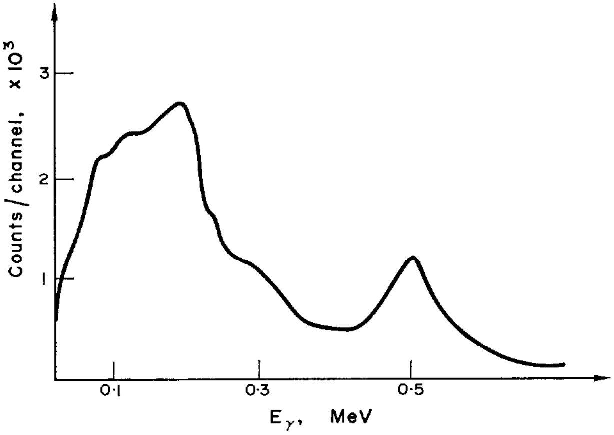

Fig. 8.—γ-Spectrum of used nickel catalyst at higher amplification.

merged in the high-intensity Compton range. On subtraction of the ^{60}Co standard spectrum from the complex spectrum the 1·12-MeV peak of ^{65}Zn appears (Fig. 9), by means of which small amounts of zinc can be determined, although with rather a large error.

Palladium and zinc in palladium catalyst can be determined from the γ-spectra by a direct instrumental method using a scintillation detector.

In the case of nickel catalysts nickel and cobalt can be determined by the method described. The results of the measurements (referred to 150 mg of catalyst, this being the weight of one grain) are presented in Table II.

Direct instrumental measurements with a Ge(Li) semiconductor detector

In the γ-spectrum of the palladium catalyst photopeaks appear at 0·24, 0·31, 0·34 and 1·12 MeV, which are characteristic of the daughter-isotope ^{111}Ag (formed from the radioisotopes of palladium) and of the ^{65}Zn radioisotope. The error of determination by computer-evaluation of the peak areas of the 0·34-MeV peak of

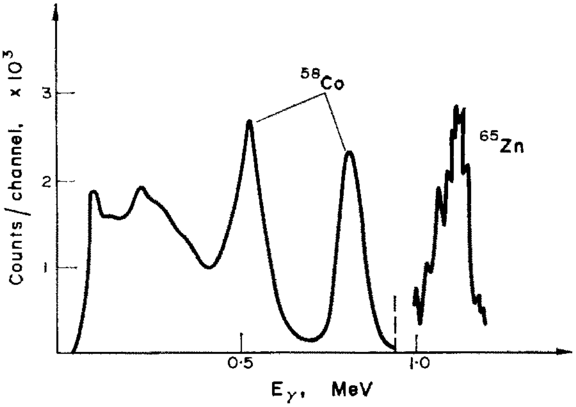

FIG. 9.—γ-Spectrum of used nickel catalyst after subtraction of the γ-spectrum of ^{60}Co standard.

TABLE II.—RESULTS OF STUDIES ON PALLADIUM AND NICKEL CATALYSTS (BY DIRECT INSTRUMENTAL MEASUREMENT)

Palladium catalyst	Measured Zn Average, *mg/grain**	Measured Zn Max. devn. from the mean, %	Measured Pd Average, *mg/grain*	Measured Pd Max. devn. from the mean, %
Unused	0·057	±8·8	0·059	±17
Used	0·061	±8·1	0·060	±20
Nickel catalyst	**Measured Ni Average, *mg/grain***	**Measured Ni Max. devn. from the mean, %**	**Measured Co Average, *mg/grain****	**Measured Co Max. devn. from the mean, %**
Unused	48·9	±1·2	0·015	±7·0
Used	46·9	±1·6	0·014	±5·0

* Mean weight of a grain was 150 mg.

palladium and 1·12-MeV peak of zinc is 5–10%, *i.e.*, these elements can be determined from the γ-spectra.

In the γ-spectrum of used palladium catalyst which contains a small amount of mercury the 0·279-MeV peak of ^{203}Hg radioisotope appeared separately only if a biased preamplifier was used in the measuring equipment. By use of this equipment photopeaks differing by 5 KeV can be resolved. The spectrum of the palladium standard was measured with this equipment after activation (Fig. 10) and after 5 days of cooling (Fig. 11). The figures show that the radioisotopes of palladium transform to ^{111}Ag, because the peaks of the latter appear.

The mercury content of palladium catalyst can be determined without destruction only at concentrations higher than 100 ppm, with an error of ±10–15%.

In the γ-spectra of nickel catalyst taken with a semiconductor detector the 0·51 and 0·81-MeV peaks of ^{58}Co, the 1·17- and 1·33-MeV peaks of ^{60}Co and the 1·12-MeV peak of ^{65}Zn all appeared. In the case of used catalyst contaminated with mercury the 0·279-MeV photopeak of ^{203}Hg appeared in the high-intensity Compton region of these isotopes. Accordingly only the nickel, cobalt and zinc could be determined by evaluation by computer, with an error of ±6–10%.

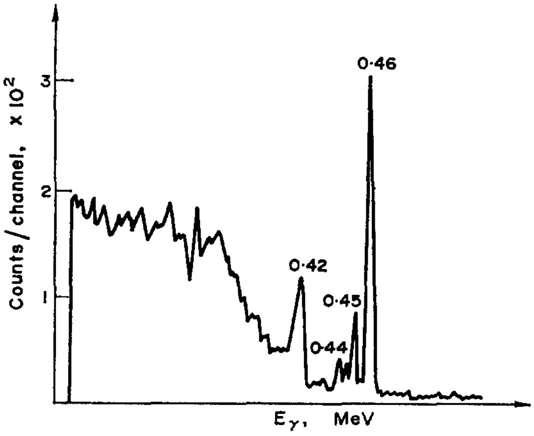

Fig. 10.—γ-Spectrum of an activated palladium standard, made by means of a Ge(Li) semiconductor detector.

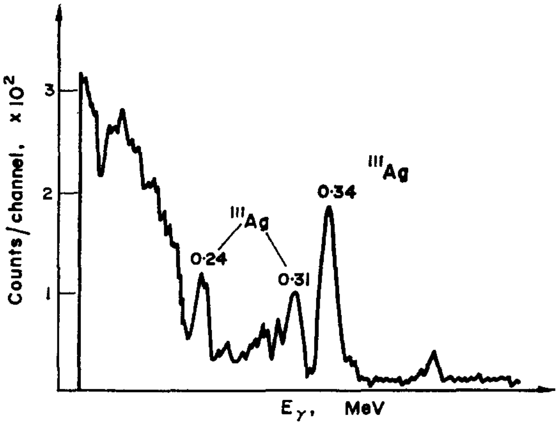

Fig. 11.—γ-Spectrum of palladium standard after 5 days cooling, made by means of a Ge(Li) semiconductor detector.

It can be concluded from the results of direct instrumental studies on catalysts that it is advisable to use a radiochemical separation before determination of trace contaminants, in order to increase sensitivity and accuracy. This is justified, since we wish to determine other trace contaminants for which 8–10 days of cooling are not allowable.

Studies involving radiochemical separation

For the separation of the radioisotopes of trace contaminants the heterogeneous isotopic exchange on metal sulphide precipitates (developed by us[4]) was used. Isotopic exchange was performed on a thin layer (2–3 mm) of the precipitate by a flow technique. The sulphide of an inactive isotope of the ion to be determined was used as the solid phase in each case.

Thus to retain radioactive mercury(II) ions, inactive mercury(II) sulphide was used. Isotopic exchange was carried out in strongly acid solution (1*M* nitric acid), as

TABLE III.—DETERMINATION OF MERCURY AND ZINC IN PALLADIUM AND NICKEL CATALYSTS, AFTER ISOTOPIC EXCHANGE

Sample	Hg		Zn	
	Average, *mg/grain*	Max. devn. from the mean, %	Average, *mg/grain*	Max. devn. from the mean, %
Unused Pd catalyst	—	—	0·061	±4·0
Used Pd catalyst I	0·057	±1·5	0·059	±5·0
II	0·010	±10	0·061	±5·0
III	0·008	±30	0·057	±5·0
Unused Ni catalyst	—	—	0·029	±13
Used Ni catalyst I	0·167	±2	0·030	±13
II	0·137	±3	0·030	±13

the selectivity of separation was found to be highest in this medium. Mercury(II) sulphide precipitate completely retained mercury(II) ions in strongly acid medium, whereas the radioisotopes of zinc, cobalt, palladium, sodium, copper, antimony and arsenic were not retained at all. Radio-zinc ions were separated on zinc sulphide precipitate by isotope exchange. From 0·1*M* nitric acid solution the degree of retention was 99% for radio-zinc, 100% for radio-mercury, 50% for radio-palladium, 7% for cobalt and 0% for sodium. The retention of mercury was to be expected because of the well known precipitate exchange phenomenon.

The retention of palladium and cobalt can be suppressed to 1–2% by adding inactive cobalt or palladium ions to the solution before isotopic exchange.

For the determination of mercury in palladium and nickel catalysts, 1 ml of the stock solution used for the direct instrumental measurements was diluted to 10 ml with 1*M* nitric acid, transferred to a burette and passed at the rate of about 1 ml/min (by dropwise addition and suction) through about 300 mg of mercury(II) sulphide precipitate placed on the filter. The burette was rinsed with about 2 ml of 1*M* nitric acid and this also passed through the precipitate. The γ-spectrum of the mercury (II) sulphide precipitate was recorded with the purpose of evaluation and checking the selectivity of the isotopic exchange.

The mercury present in 1-ml portions of the solutions of mercury standards irradiated under the same conditions as the samples, was retained on mercury(II) sulphide as described above. The products served as a basis for quantitative evaluation of the samples. The isotopic exchange on mercury(II) sulphide is so selective for the components of the samples studied that relative measurements can be made even with an energy-selective scaler.

The zinc content of the catalysts was determined from the filtrate obtained after the isotopic exchange on mercury(II) sulphide. The pH of the filtrate was adjusted to 2, then 10 mg of palladium were added in the case of palladium catalyst and 10 mg of cobalt in the case of nickel catalyst, and the solution was passed through about 300 mg of zinc sulphide at a rate of 0·2–0·3 ml/min by suction. Zinc standard was treated similarly. By the method described the mercury and zinc contents were determined in palladium and nickel catalysts contaminated to different extents. The results of the determinations are presented in Table III. Heterogeneous isotopic exchange, used in the analysis of catalysts, is fast and selective besides having satisfactory accuracy.

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Zusammenfassung—Ein Neutronenaktivierungsverfahren zur Bestimmung der aktiven Bestandteile und der Verunreinigungen in Hydrier-Katalysatoren wurde entwickelt. Die aktiven Bestandteile von Palladium- und Nickelkatalysatoren (Pd und Ni) sowie die in kleinen Mengen anwesenden Verunreinigungen Zn und Co wurden mit einem direkten instrumentellen Verfahren bestimmt. Ein NaJ(Tl)-Szintillator und ein Ge(Li)-Halbleiter wurden in Verbindung mit einem Vielkanalanalysator für die Messungen verwendet. Zur Auswertung der Gammaspektren wurde ein Computer benutzt. In kleinen Mengen anwesende Verunreinigungen wurden auch mit Hilfe eines radiochemischen Abtrennverfahrens bestimmt, das auf heterogenem Isotopenaustausch an Quecksilber(II)sulfid- und Zinksulfid-Niederschlägen beruht.

Résumé—On a élaboré une méthode par activation de neutrons pour la détermination des constituants actifs et des contaminants dans les catalyseurs d'hydrogénation. Les constituants actifs des catalyseurs au palladium et au nickel (Pd et Ni) et les contaminants Zn et Co présents en petites quantités ont été déterminés par une méthode instrumentale directe. Un scintillateur NaI (Tl) et un semi-conducteur Ge (Li) connectés à un analyseur multi-canaux ont été utilisés pour les mesures. On a utilisé une calculatrice pour évaleur les spectres γ. Les contaminants présents en petite quantité ont aussi été déterminés au moyen d'une méthode de séparation radiochimique basée sur l'échange isotopique hétèrogène sur des précipités de sulfure de mercure(II) et de sulfure de zinc.

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APPLICATION OF DISPLACEMENT REACTIONS IN FLAME PHOTOMETRY—I

THE DETERMINATION OF PHOSPHATE BY A FLAME EMISSION METHOD

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Summary—Phosphate ions decrease the flame emission of calcium, but this effect can be partly offset by adding a second metal which partly displaces calcium from the non-excitable species. For the determination of phosphate the sample solution is divided into four equal parts; to each of these, various amounts of calcium and barium ions are added such that the total (molar) concentration of the metals is constant. Plotting the intensity measured at 630 nm *vs.* the calcium content of the solution gives a straight line, the slope of which depends on the concentration of phosphate ions present. The method is suitable for rapid determination of phosphate. Accuracy and precision are within the usual limits characteristic of flame photometric methods.

EMISSION FLAME PHOTOMETRIC methods are frequently applied in chemical laboratories. Their main advantages are simplicity of operation, speed and reasonable precision. The disadvantages, such as chemical and spectral interferences and a certain hazard in manipulation of gases, can easily be overcome by intelligent and careful work. Because the gases used in emission flame photometry offer relatively low energies for excitation, the range of elements which can be determined by flame photometry is rather limited. Though according to the literature,[1] procedures for the determination of more than fifty elements are known, flame photometric determinations are in practice restricted to about ten of these, all metals.

The few methods described for the determination of non-metallic elements fall into two categories. First, some of the non-metals can be determined by measuring the emission of the element or its compounds, *e.g.*, boron can be determined by measuring the emission of the methyl ester of boric acid. On the other hand, some of these elements, mainly in the form of oxo-ions, suppress or enhance the emission of certain metal ions, and this action can, within limits, be proportional to the concentration of the particular ion, so that a quantitative determination can be made. This principle was applied by Dippel, Bricker and Furman[2] for the determination of phosphate by measuring the decrease in emission from calcium. The weakness of this method lies in the fact that the proportionality between the decrease in emission and the concentration of phosphate exists only over a limited concentration range. If the phosphate concentration exceeds a certain value, there is no measurable variation in the calcium emission. Another method suggested more recently for the flame photometric determination of phosphate, by Ratner and Schneider,[3] makes use of the fact that the depressive action does not occur at high flame temperatures. In a first measurement at higher temperature the amount of calcium is measured, this is followed by a measurement of the depressed signal at a lower temperature. From the two results the phosphate content can be determined with an increased accuracy.

Our method makes use of displacement reactions which occur if phosphate, calcium and barium ions are present in one solution. If the phosphate concentration is kept constant, while the relative concentrations of calcium and barium are varied but their total (molar) concentration is kept constant, the measured calcium emission will increase in proportion to the calcium content; the slope of the emission *vs.* concentration (of calcium) curve depends on the phosphate content of the sample.

EXPERIMENTAL

Instruments

Measurements were made both with a simple filter instrument and an instrument with a prism monochromator. The Zeiss Model 3 (Jena) flame photometer was used with the air–acetylene burner. The optimum gas pressures were adjusted according to the manufacturer's recommendation. The calcium interference filter supplied with the instrument was used; this has a maximum transmission at 630 nm with a halfwidth of about 15 nm. The gain was adjusted to obtain a maximum reading of 300 units of the swinging galvanometer (*i.e.*, 30% of full-scale deflection). The Unicam SP 90 combined atomic-absorption and flame-emission spectrophotometer was used in its emission mode. The instrument was equipped with an AEI 10S potentiometer recorder and readings were made using the standard Meker acetylene–air burner. The following parameters were held constant: air flow-rate: 5 l./min, burner height: 20 mm (measured on the scale), slitwidth: 0·1 nm, damping: 4. The acetylene flow-rate was adjusted to give maximum signal in each case, and the gain was adjusted as required.

Reagents

Calcium chloride, 0·5*M*. Prepared by dissolving analytical-grade calcium carbonate in dilute hydrochloric acid.

Barium chloride, 0·5*M*. Prepared from analytical-grade barium chloride dihydrate.

Diammonium hydrogen phosphate, 0·1*M*. Prepared from analytical-grade reagent.

Solutions used for the study of interferences were prepared from the purest available reagents. Metals were added in the form of chlorides; anionic interferences were studied both with the free acids and with their ammonium salts.

Procedure

From 0·5*M* calcium chloride (CA) and 0·5*M* barium chloride (BA) make up four solutions:

Solution *A* 20 parts of CA + 30 parts of BA
Solution *B* 15 parts of CA + 35 parts of BA
Solution *C* 10 parts of CA + 40 parts of BA
Solution *D* 5 parts of CA + 45 parts of BA

These solutions can then be stored indefinitely.

Make up 100 ml of stock solution of the sample to contain 2–8 mmole (200–800 mg) of phosphate, and 20 ml of concentrated hydrochloric acid. In each of four beakers, place 20 ml of the stock solution and 5 ml of one of solutions *A*, *B*, *C* or *D*. Mix the solutions well and measure the flame emission intensities at 630 nm. In a second set of measurements replace the sample solution with 20 ml of water. Plot the emission values *vs.* calcium concentrations (10, 20, 30 and 40 mmole), draw the straight lines and calculate h_0/h_x values as shown in Fig. 4B. Determine the concentration of phosphate in the sample from a calibration curve, obtained in a similar way.

Note. For 0·2–0·8 mmole (20–80 mg) of phosphate use solutions prepared by ten-fold dilution of *A*, *B*, *C* and *D*. By variation of the total concentration of the alkaline earth metals, higher or lower amounts of phosphates can be determined.

DISCUSSION

Under the experimental conditions given, the emission of calcium is strongly depressed in the presence of phosphate, decreasing linearly with increase in the amount of phosphate present until the molar ratio of phosphate to calcium reaches the value 0·67; this corresponds to the formation of tricalcium orthophosphate $Ca_3(PO_4)_2$.[4] If the amount of phosphate relative to calcium is higher than this, the emission becomes almost constant; the signal being only 15–20% of that measured in the absence of phosphate. This type of effect has been widely studied in the past fifteen years, and its explanation has also been attempted.[5-8]

The depressive effect of phosphate on the calcium emission is due to a chemical reaction between calcium and phosphate ions. Since the signal is not completely suppressed, it is obvious that the reaction reaches an equilibrium; there remain free calcium atoms capable of emission. This equilibrium can be shifted by the addition of another metal, which shows similar behaviour to calcium in the presence of phosphate.

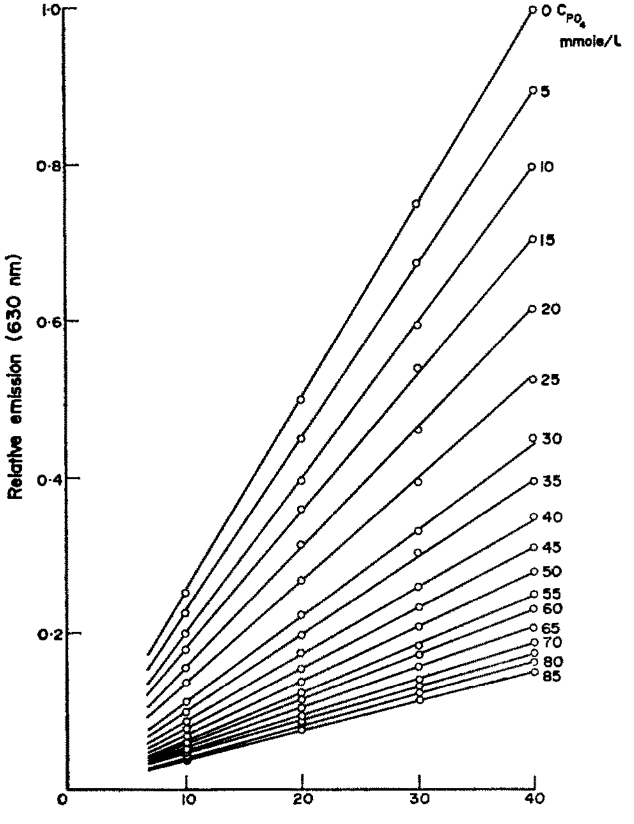


FIG. 1.—Emission for calcium in solutions containing phosphate and barium, such that total metal concentration is always 0·10*M*. Sufficient hydrochloric acid is present to prevent precipitation of the metal phosphates.

The greater the amount of this second metal present, the more calcium will be displaced. If the total metal concentration is kept constant (that is, the metal–phosphate concentration ratio remains unchanged), the signal obtained from the emission of calcium is proportional to the amount of calcium present. This principle can be used for the determination of alkaline earth metals[9] and of lanthanum[10] in the presence of interfering ions.

The slope of the intensity *vs*. calcium concentration plot varies with phosphate concentration; the higher the latter, the smaller the slope of the curve (Fig. 1). The slope depends solely on the concentration of phosphate, and with a suitable calibration curve phosphate concentrations can be determined. The range of phosphate concentration can be narrowed or extended by varying the barium concentration, being extended by using an increased metal ion concentration, and *vice versa*. The set of curves, shown in Fig. 1, behaves like a half-open fan, which can be opened further or closed at will, over a considerable range. Figure 2 shows a set of similar curves with 0·15*M* total alkaline earth metal concentration. The useful range is in this case extended up to 0·07–0·075*M* phosphate. Figure 3 shows narrowing of the range to 0–0·025*M*. As the difference between the slopes of the individual curves becomes larger, the precision of determination increases.

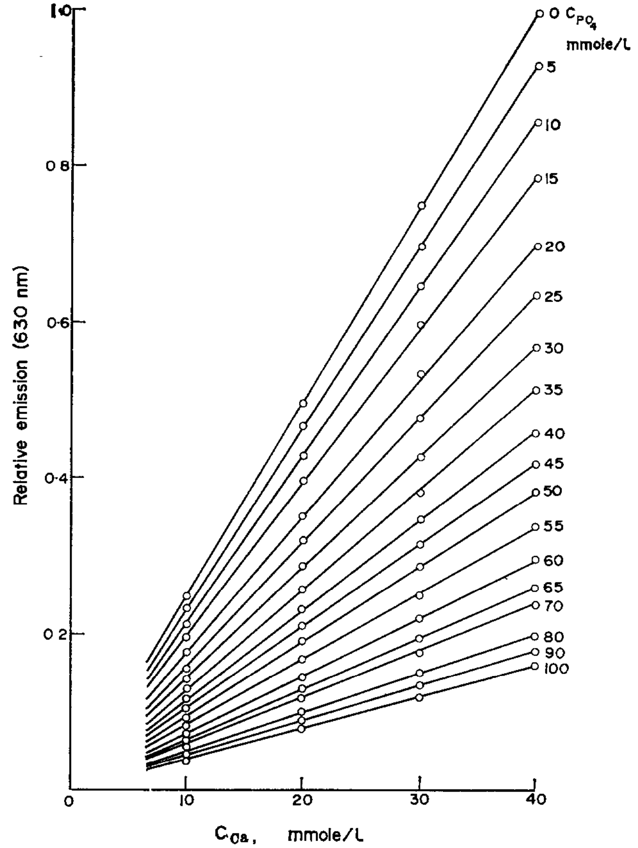


Fig. 2.—As Fig. 1, but total metal concentration = 0·15*M*.

The fact that the extension or contraction of the useful range is achieved by adding more or less barium (but not calcium) to the solution means that the flame photometer is always operated at the same sensitivity, which is an advantage for routine work.

Evaluation of results

Though the set of curves shown in Figs. 1–3 could be used as a chart from which results obtained with unknown samples could be evaluated, it is more practical to use a calibration curve produced from these results. A comprehensive study[11] of the possible variables revealed that the best way to draw the calibration curve was to plot

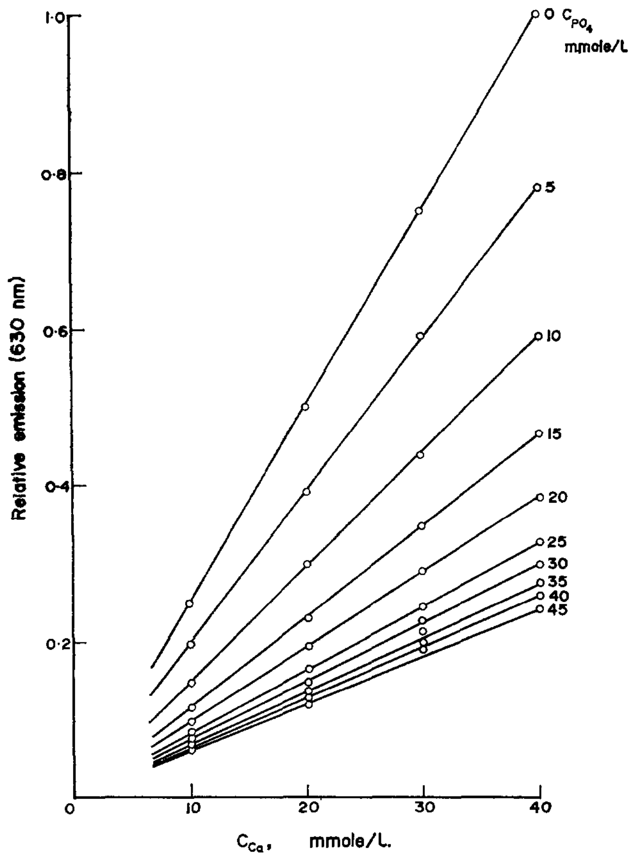
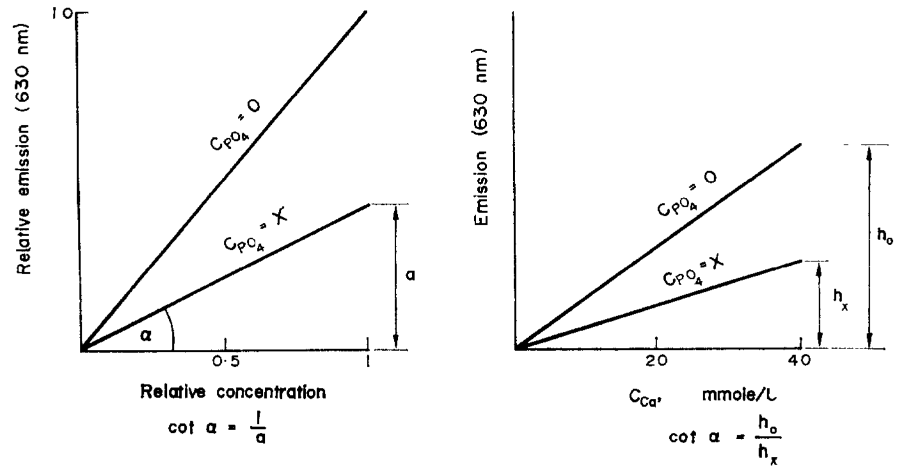


FIG. 3.—As Fig. 1, but total metal concentration = 0·05*M*.

the cotangents of the slope angles of the individual lines as a function of the phosphate concentration. If the relative emissions are plotted (Fig. 4A) the reciprocal value of the height of the line, corresponding to the maximum calcium concentration, gives the required value. If on the other hand, emission readings themselves are plotted against calcium concentration (without calculation of the relative emission values), as shown in Fig. 4B, the two heights, h_0 (which corresponds to the solutions which contain no phosphate) and h_x (the value obtained with the unknown sample) are found, and their ratio then gives the required cotangent. Theoretically it would be sufficient to make two measurements only, that is to use two solutions with equal calcium concentrations, one containing no phosphate at all, the other containing the unknown amount, and to calculate the ratio of their emissions. By using four solutions however, as we suggest, four points on each line (plus the fifth point in the origin) are measured, giving an improved reliability to the results.

Calibration curves, drawn from the graphs given in Figs. 1–3, have a definite S-shape (Fig. 5). Mathematically these can be expressed as

$$y = y_0\left[1 + \exp -\left\{\frac{4b}{y_0}\cdot(C - C_1)\right\}\right]^{-1} + g$$



(A) (B)

FIG. 4.—Measurement of the slope of the curves.

where c is the phosphate concentration, y is the variable (cot α) plotted on the calibration curve and y_0, b, C_1 and g are constants. For the middle curve, which corresponds to 0·1M total metal concentration, these constants are $y_0 = 6{\cdot}25$; $C_1 = 50$; $b = 0{\cdot}075$ and $g = 0{\cdot}5$. Details of the mathematical analysis of this curve are described elsewhere;[11] they are of little interest for the practical analytical chemist.

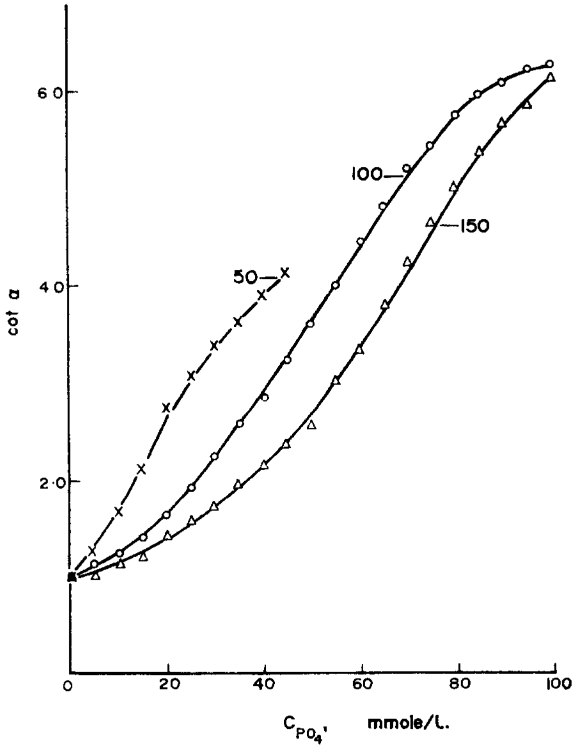


FIG. 5.—Calibration curves for the determination of phosphate at total metal concentrations of 0·05, 0·10 and 0·15M.

The middle parts of the curves are nearly straight lines, and have similar slopes for the different total alkaline earth concentrations; thus the sensitivity of these determinations remains the same for all concentration ranges examined in this study.

Experiments were made with solutions containing 0–0·01*M* phosphate when the total alkaline earth metal concentrations used were 5, 10 and 15 m*M*. The experimental conditions were the same as given above, but the gain of the instruments had to be readjusted appropriately. Results under such circumstances are also satisfactory. With 0–1 m*M* phosphate and 0·5, 1 and 1·5 m*M* total alkaline earth metal, the results are not sufficiently reproducible, mainly because of limitations in the sensitivity of the radiation detector.

Results, accuracy and precision

A typical set of results, obtained with 100 and 10 m*M* total alkaline earth metal concentration, is shown in Table I. The coefficients of variations, obtained by measuring the same samples on 12 different working days (that is, after switching on the flame photometer, and readjusting the parameters), are shown in the last column. As can be seen, these decrease slightly with increase of phosphate concentration. An explanation of this, based on the application of the law of propagation of errors, has been attempted.[11]

TABLE I

Concentration of phosphate, m*M*	Found	Error %	Coefficient of variation %
(a) Total metal concentration: 100 m*M*			
25·0	25·5	+2·2	±4·1
30·0	30·8	+2·6	±3·7
35·0	35·6	+1·7	±3·5
40·0	40·8	+2·0	±3·2
45·0	45·1	+0·3	±3·0
50·0	50·6	+1·2	±2·9
55·0	56·4	+2·8	±2·8
60·0	60·8	+1·3	±2·7
65·0	65·8	+1·2	±2·6
70·0	71·2	+1·7	±2·5
75·0	75·9	+1·4	±2·3
80·0	81·4	+1·8	±2·3
(b) Total metal concentration: 10 m*M*			
3·0	3·15	+5	—
4·0	4·06	+1·5	—
5·0	5·15	+3	±4·4
6·0	6·08	+1·4	—
7·0	7·12	+1·7	—
8·0	8·10	+1·3	—

These results indicate that the method can be applied for a rapid determination of phosphate. The total time required, excluding the switching-on and warming up time of the instrument is less than 10 min, and even this is mainly used for dissolution and preparation of solutions. The method was applied for the rapid assay of fertilizers based on ammonium phosphate.

Effect of foreign ions

Small amounts (not exceeding a 1:1 molar ratio) of antimony, copper, magnesium, manganese, nickel, potassium, sodium and acetate do not cause errors > ±5% in the final result. Ammonium ions, antimony and chloride can be tolerated in amounts 10 times that of the phosphate. Sodium can also be tolerated in 10-fold amounts (relative to phosphate) if an instrument with a monochromator is used with a fairly narrow slitwidth. Medium interference (*e.g.*, an error below 10%) was found in the presence of zinc and mercury in amounts equimolar with the phosphate, and with 10-fold amounts of manganese, potassium and sodium (with a filter instrument). Large errors were caused by the presence of equimolar or 10-fold amounts (relative to phosphate) of aluminium, chromium, cobalt, iron, strontium, tin and nitrate. A 10-fold amount of copper, magnesium, nickel or acetate causes large errors. Cobalt and iron cause negative errors, but all other ions cause positive ones.

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Zusammenfassung—Phosphationen vermindern die Flammenemission von Calcium, aber dieser Effekt kann zum Teil aufgehoben werden, wenn man ein zweites Metall zusetzt, das Calcium zum Teil aus der nicht anregbaren Spezies verdrängt. Zur Bestimmung von Phosphat wird die Probenlösung in vier gleiche Teile geteilt; zu jedem Teil werden verschiedene Mengen Calcium und Bariumionen gegeben, in der Weise, daß die (molare) Gesamtkonzentration der Metalle konstant ist. Trägt man die bei 630 nm gemessene Intensität gegen den Calciumgehalt der Probe auf, so erhält man eine Gerade, deren Steigung von der Phosphationenkonzentration abhängt. Die Methode eignet sich zur raschen Phosphatbestimmung. Genauigkeit und Richtigkeit liegen im üblichen Rahmen flammenphotometrischer Methoden.

Résumé—Les ions phosphate abaissent l'émission de flamme du calcium, mais cette influence peut être partiellement compensée par l'addition d'un second métal qui déplace partiellement le calcium de l'espèce non excitable. Pour le dosage du phosphate, la solution échantillon est divisée en quatre parties égales; à chacune de celles-ci, on ajoute des quantités diverses d'ions calcium et baryum, de sorte que la concentration totale (molaire) des métaux soit constante. Le tracé de l'intensité mesurée à 630 nm par rapport à la teneur en calcium de la solution donne une ligne droite dont la pente dépend de la concentration des ions phosphate présents. La précision et la justesse sont situées dans les limites habituelles caractéristiques des méthodes de photométrie de flamme.

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DETERMINATION OF THE OPTIMUM RESULTANT EFFECT OF FACTORS INFLUENCING HETP-VALUES

THE FOLLOWING OF PARALLEL DIFFUSION AND MASS-TRANSFER PROCESSES

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Summary—One of the most important problems of analytical gas chromatography, both in theory and in practice, is the following of parallel diffusion and mass-transfer processes, with the primary aim of determining the optimum resultant effect of factors influencing the HETP-value. Starting from the work of Costa Neto and collaborators, it is shown that the approximate equation developed by these authors can be deduced from the theory of gas chromatography. Subsequently, by means of the new approximation, the effect of individual factors is determined, and processes proceeding simultaneously are followed.

GAS CHROMATOGRAPHY belongs to the group of multistep operations carried out with continuous contact between two phases, and for want of an exact explicit solution differential equations are used to describe them. These equations cannot in practice be utilized for following the processes occurring, or for the examination of the factors affecting them, though in theory they presumably may describe the processes correctly. This is why the gas chromatographic process is studied and described with the aid of approximative methods which are much simpler, though less exact, than are differential equations.

Among these methods the two best known are the so-called plate theory of Glueckauf[1] and the kinetic or rate theory linked with the name of van Deemter.[2]

Since practical experience has shown that the deviation of the results exceeds the range of experimental errors in the investigation both of the factors influencing the HETP values and of the simultaneous diffusion and mass-transfer processes, the need arose for a new and closer approximation, comprising also van Deemter's equation.

After critical evaluation of pertinent literature, it was thought that the equation published by Costa Neto and co-workers[3] is suitable for this purpose:

$$\mathrm{HETP} = A + \frac{B}{u} + Cu + \frac{D}{u^2} + Eu^2 \tag{1}$$

where HETP is the column length (mm) equivalent to one theoretical plate, and A, B, C, D and E are constants which at constant temperature and under unchanged gas chromatographic conditions are dependent only on the nature of the substance investigated, and u is the linear carrier-gas flow-rate (mm/sec). (It should be mentioned here that in our present work we do not wish to take part in the dispute that has flared up again recently concerning the definition, interpretation, *etc*, of the theoretical plate number or of the HETP value.)

THEORY

Let us write, according to Glueckauf, the theoretical plate number of a substance in a given gas-chromatographic system:

$$n = 16\left(\frac{t_R}{w}\right)^2 \tag{2}$$

where n is the number of theoretical plates of the substance, t_R is the retention time of the substance, w is the width of the chromatographic peak of the substance (in the same units as t_R). On the basis of the theoretical plate number and the column length, the column length corresponding to one theoretical plate, the so-called HETP-value,[4] is obtained, since

$$\text{HETP} = L/n \tag{3}$$

where L is the column length (mm).

Equation (1) can be deduced with the aid of equation (3) from equation (2), by using the following relationships, proved already in one of our earlier works:[5]

$$t_N = m_1/u \tag{4}$$

and

$$w = m_2 \,.\, \zeta + b \tag{5}$$

where t_N is the net retention time (sec), m_1 is the slope of the linear equation (4) (mm), m_2 is the slope of the linear relationship (5) (mm), and b is the intercept with the ordinate (sec).

ζ is the linear rate coefficient (sec/mm) and is given by

$$\zeta = \frac{(u + F)}{u^2}, \tag{6}$$

where F is a constant depending on the gas-chromatographic system and on the nature of the substance (mm/sec).

Equation (2) can be written in the following form from consideration of equations (4) and (5):

$$n = 16\left(\frac{m_1/u}{m_2\zeta + b}\right)^2. \tag{7}$$

The substitution of (7) into (3) results in

$$\text{HETP} = \frac{L}{16}\left(\frac{m_2\zeta + b}{m_1/u}\right)^2. \tag{8}$$

On substitution of (6) into (8), and transformation, the following expression is obtained:

$$\text{HETP} = \frac{L}{16}\left(\frac{bu}{m_1} + \frac{m_2}{m_1} + \frac{m_2F}{m_1u}\right)^2. \tag{9}$$

Expansion gives

$$\text{HETP} = \frac{L}{16}\left[\left(\frac{b}{m_1}\right)^2 u^2 + 2\left(\frac{b}{m_1}\right)\left(\frac{m_2}{m_1}\right)u + \left(\frac{m_2}{m_1}\right)^2 + 2\left(\frac{b}{m_1}\right)\left(\frac{m_2F}{m_1}\right) + \right.$$
$$\left. + 2\left(\frac{m_2}{m_1}\right)\left(\frac{m_2F}{m_1}\right)\Big/ u + \left(\frac{m_2F}{m_1}\right)^2\Big/ u^2\right]. \tag{10}$$

On introduction of the identities

$$A = \frac{L}{16}\left[\left(\frac{m_2}{m_1}\right)^2 + 2\left(\frac{b}{m_1}\right)\left(\frac{m_2F}{m_1}\right)\right] \tag{11}$$

$$B = \frac{L}{8}\left(\frac{m_2}{m^1}\right)\left(\frac{m_2F}{m_1}\right) \tag{12}$$

$$C = \frac{L}{8}\left(\frac{b}{m_1}\right)\left(\frac{m_2}{m_1}\right) \tag{13}$$

$$D = \frac{L}{16}\left(\frac{m_2F}{m_1}\right)^2 \tag{14}$$

$$E = \frac{L}{16}\left(\frac{b}{m_1}\right)^2 \tag{15}$$

equation (10) becomes

$$\mathrm{HETP} = A + \frac{B}{u} + Cu + \frac{D}{u^2} + Eu^2 \tag{16}$$

which is identical with equation (1), so it can be considered as proved that equation (1) can be deduced from the theory of gas chromatography.

In comparison with the well known equation of van Deemter, (1) and (16) contain two further constants (D and E). In our opinion, it is due to these two constants that this equation gives a better approximation for description of the gas chromatographic process, which of necessity involves a whole series of complicated interactions and simultaneous processes. Although the interpretation of these two constants is not yet fully clear, it is already certain that the constant D, the dimension of which is acceleration of volumetric gas-flow, (mm^3/sec^2) permits a better following of the diffusion processes.

The case is similar with the constant E, the dimension of which is reciprocal linear acceleration (sec^2/mm). This latter constant makes possible the better description of mass-transfer processes. Though the investigation and interpretation of both these constants necessitates further experimental work, it promises theoretical results of considerable importance.

On the basis of equation (16), the upper and lower limits of the applicability of the gas-chromatographic process in terms of the carrier gas flow-rate can be more easily interpreted. At high linear gas flow-rates, the value of Eu^2 becomes very large, and makes separation impossible. On the other hand, at very low linear velocities, when u is smaller than 0·001 mm/sec, the term D/u^2 becomes very large and prevents practical work.

HETP$_{\min}$ is obtained by the differentiation of (16):

$$(\mathrm{HETP})' = -\frac{B}{u^2} + C - 2\frac{D}{u^3} + 2Eu = \frac{2Eu^4 + Cu^3 - Bu - 2D}{u^3}\,. \tag{17}$$

Since (HETP)$'$ = 0 at the minimum, the numerator of the equation must be zero, *i.e.*,

$$2Eu^4 + Cu^3 - Bu - 2D = 0. \tag{18}$$

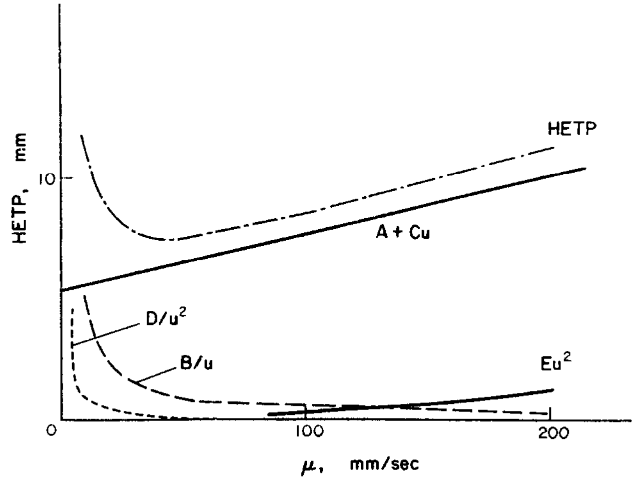

Fig. 1.—The function corresponding to equation (16) for a general case, apportioned to the several constants.

The solution of this fourth-degree equation gives the carrier gas flow-rate corresponding to $\mathrm{HETP}_{\mathrm{min}}$.

The general shape of the function corresponding to equation (16) is shown in Fig. 1, for a particular set of constants.

Table I.—Values for n-butane in a spiral copper column 3·0 m long, 4·0 mm in diameter, packed with 12·5% w/w of silicone oil DC-550 on 60/80 mesh Chromosorb W support, at 40·0 ± 0·1°C, in nitrogen as carrier gas

u *mm/sec*	*A* *mm*	*B/u*, *mm*	*Cu*, *mm*	D/u^2, *mm*	Eu^2, *mm*	HETP *mm*
10	0·69	1·40	0·16	1·21	0·02	3·48
20	0·69	0·70	0·33	0·30	0·07	2·08
30	0·69	0·47	0·49	0·13	0·15	1·93
40	0·69	0·35	0·66	0·08	0·26	2·03
50	0·69	0·28	0·82	0·05	0·41	2 24
60	0·69	0·23	0·98	0·03	0·59	2·52
70	0·69	0·20	1·15	0·02	0·80	2·85
80	0·69	0·18	1·31	0·02	1·04	3·23
90	0·69	0·16	1·47	0·015	1·32	3·65
100	0·69	0·14	1·64	0·012	1·63	4·10
110	0·69	0·13	1·80	0·010	1·97	4·59
120	0·69	0·12	1·97	0·008	2·34	5·12
130	0·69	0·11	2·13	0·007	2·75	5·68
140	0 69	0·10	2 29	0·006	3·19	6·27
150	0·69	0·09	2 46	0 005	3·66	6·90
160	0·69	0 09	2·62	0 005	4·16	7·56
170	0·69	0·08	2 78	0·004	4·69	8·25
180	0·69	0·08	2·95	0 004	5·27	8·98
190	0·69	0·07	3·11	0·003	5·87	9·74
200	0·69	0 07	3·28	0·003	6·50	10·54

EXPERIMENTAL

Carlo Erba Fractovap Model C, D and GD gas chromatographs were used with classical packed gas-chromatographic columns. The most important gas-chromatographic parameters are listed in connection with the examples given.

Table I shows the applicability of equation (16) to the results obtained for n-butane. The new

TABLE II.—CONSTANTS OBTAINED WITH n-HEPTANE UNDER THE EXPERIMENTAL CONDITIONS SUMMARIZED IN TABLE III

u, *mm/sec*	HETP-value, *mm*	
	nitrogen as carrier	argon as carrier
10	1·04	0·97
20	0·52	0·47
30	0·41	0·35
40	0·39	0·32
50	0·42	0·32
60	0·45	0·33
70	0·51	0·34
80	0·57	0·38
90	0·64	0·42
100	0·72	0·46
110	0·83	0·51
120	0·92	0·56
130	1·04	0·62
140	1·15	0·67
150	1·28	0·74
160	1·42	0·81
170	1·57	0·88
180	1·72	0·96
190	1·89	1·03
200	2·04	1·13
250	3·02	1·63
500	10·9	5·6
750	23·8	12·1
1200	41·6	21·1

TABLE III.—GAS-CHROMATOGRAPHIC PARAMETERS USED IN THE STUDY OF THE GAS-CHROMATOGRAPHIC BEHAVIOUR OF MEMBERS OF HOMOLOGOUS SERIES

Gas chromatograph: Carlo Erba Fractovap Model D
Detector: FID
Sensitivity: 16 × 100
Sample: 0·3 μl of model mixture introduced by means of a Hamilton syringe
Column: spiral aluminium tube, 2·40 m long, 2·0 mm in diameter
Column packing: 10 % w/w of SE-30 on 60/80 mesh Chromosorb W
Carrier gas: nitrogen at an inlet pressure of 100–300 kN/cm^2
Auxiliary gases:
    hydrogen, inlet pressure 14·2 kN/m^2
    oxygen, inlet pressure 14·9 kN/m^2
Column temperature: 100 ± 0·1°C
Evaporator temperature: 210·0 ± 1·0°C
Recorder: Speedomax G; 2·5 mV final amplitude, 1·0 sec response
Chart speed: 50·8 mm/min

approximation, equation (16), also makes it possible to study the factors affecting separation. As an example of our investigations in this respect, the effect of the nature of the carrier gas on the HETP-value is shown in Table II.

Equation (16) has also been used for study of the gas-chromatographic behaviour of members of a homologous series in terms of HETP-values; n-hexane, n-heptane and n-octane were used as model substances. Gas-chromatographic parameters used in the experimental series are summarized in Table III, and the constants obtained are in Table IV.

The constants determined made possible the comparative investigation and the following of the

TABLE IV.—CONSTANTS OBTAINED FOR n-HYDROCARBONS UNDER EXPERIMENTAL CONDITIONS SPECIFIED IN TABLE III, FOR HETP MEASURED IN mm

Substance	*A*	*B*	*C*	*D*	*E*
n-C_6	2·99	20·52	0·1145	43·86	1·365 × 10^{-3}
n-C_7	1·08	6·91	0·0530	13·76	0·811 × 10^{-3}
n-C_8	0·35	2·52	0·0210	6·56	0·470 × 10^{-3}

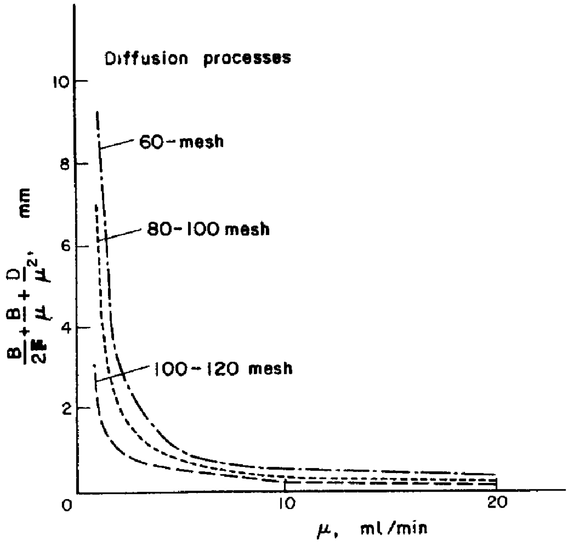

FIG. 2.—Course of the diffusion processes in the case of n-octane with supports of various grain size.

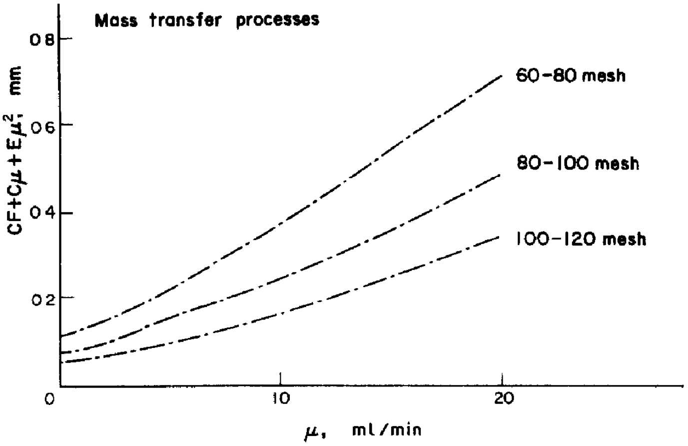

FIG. 3.—Curves characteristic of mass-transfer processes in the case of n-octane.

simultaneous diffusion and mass-transfer processes. Figure 2 shows the course of the diffusion processes, while Fig. 3 illustrates the curves characteristic of the mass-transport processes. Finally, the changes in HETP-value caused by column temperature are presented in Fig. 4.

DISCUSSION

The practical application of the equation discussed in the paper often meets difficulties, although the equation is theoretically correct. There are two reasons for

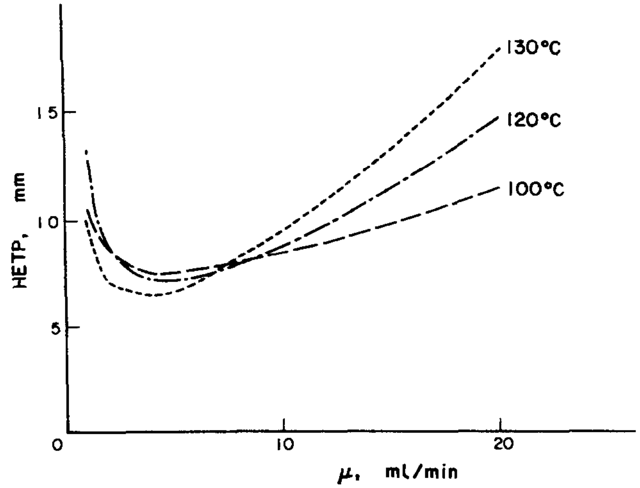

FIG. 4.—The effect of column-temperature on the HETP-value in the case of n-octane.

this. The first is that the conversion of volumetric carrier-gas flow-rate into linear flow-rate poses certain difficulties. The second is the fact that the determination of the constants is reliable only when calculated from the weighted arithmetic mean values of an adequate number of parallel measurements. According to our experience, when the determination of the volumetric carrier-gas flow-rate is made from the average of 11 parallel measurements, the factor necessary for the conversion into linear flow-rate is determined experimentally and then calculated, and the retention data are measured electronically (electronic timer), then very reliable data suitable for a variety of theoretical and practical investigations are obtained, which are worth the time and trouble spent for their determination. The few examples presented are intended rather for demonstration purposes and not to prove the applicability of the new approximation. Its merits will be verified by researchers using it.

Acknowledgement—We thank the firm Carlo Erba (Milan, Italy) for support materials and columns.

Zusammenfassung—Eines der wichtigsten Probleme der analytischen Gaschromatographie in Theorie und Praxis ist die Verfolgung paralleler Diffusions- und Massentransportprozesse, wobei primär der optimale Effekt der verschiedenen Faktoren erzielt werden soll, die den HETP-Wert bestimmen. Ausgehend von den Arbeiten von Costa Neto und Mitarbeitern wird gezeigt, daß man die von diesen Autoren aufgestellte Näherungsgleichung aus der Theorie der Gaschromatographie ableiten kann. In der Folge werden mit Hilfe der neuen Näherung die Einflüsse individueller Faktoren ermittelt und gleichzeitig ablaufende Prozesse verfolgt.

Résumé—L'un des problèmes les plus importants de la chromatographie en phase gazeuse analytique, tant en théorie qu'en pratique, est de suivre les processus parallèles de diffusion et de transfert de masse, avec le but primordial de déterminer l'influence résultante optimale de facteurs influant sur la valeur HETP. Partant du travail de Costa Neto et collaborateurs, on montre que l'équation approchée développée par ces auteurs peut être déduite de la théorie de la chromatographie en phase gazeuse. Par suite, au moyen de la nouvelle approximation, l'influence de facteurs individuels est déterminée, et les processus se développant simultanément sont suivis.

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RETENTION OF RADIONUCLIDES ON METAL SULPHIDE PRECIPITATES

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Summary—The retention of various radionuclides on metal sulphide precipitates has been studied. The sulphide precipitates quantitatively retained the common radionuclides. The condition for 100% retention in a thin layer is small particle size (a few μm) in the precipitate. This can be ensured by pulverization of the dried precipitate of metal sulphide. $^{203}Hg^{2+}$ is retained by mercury sulphide and $^{65}Zn^{2+}$ by zinc sulphide by isotopic exchange. The retention of foreign radioactive ions can be reduced or even eliminated by counter-carrier technique in cases where the retention is not due to chemical reaction, precipitate exchange. The isotopic exchange with mercury(II) sulphide and zinc sulphide enables mercury and zinc ions to be separated rapidly and determined in the presence of a number of interfering ions.

In connection with the determination of metal contaminants, especially of zinc and mercury in hydrogenation catalysts by destructive activation analysis, there arose the idea of a systematic study of the possibilities of the separation and determination of traces of metal ions by heterogeneous isotopic exchange, or, speaking more cautiously, by retention on metal sulphide precipitates.

Heterogeneous isotopic exchange with precipitates has only recently been extensively used for quantitative separation or determination in the course of activation analysis. The isotopic exchange of solid silver sulphide with its ions in solution has been studied by Peschanski[1] by means of ^{110}Ag and ^{35}S. The isotopic exchange between radio-silver and silver halides was first recommended for quantitative determination by Langer.[2] Sunderman and Meinke[3] allowed a solution containing radioactive silver ions to react with silver chloride precipitated on a platinum wire. Rai, Nethaway and Wahl[4] have thoroughly studied the conditions under which $^{140}Ba^{2+}$, $^{90}Sr^{2+}$ and $^{113}Sn^{4+}$ are quantitatively retained from aqueous solutions on barium sulphate, strontium carbonate, and tin(IV) or tin(II) sulphide precipitates respectively by (according to their assumption) isotopic exchange. Hamaguchi, Onuma, Watanabe and Kuroda[5] utilized the exchange reaction of strontium between the sulphate precipitate and salt solution for separating carrier-free ^{90}Sr and ^{90}Y. Qureshi, Shahid and Hasany[6] used isotopic exchange with strontium sulphate or oxalate for the radiochemical separation of ^{90}Sr from aqueous solution. Qureshi and Shabbir[7] applied isotopic exchange with antimony trioxide to the radiochemical separation of antimony. In the course of the determination of tin in nickel Csajka[8] adsorbed the radioactive ^{125m}Sn isotope on tin dioxide precipitate after dissolving the activated sample. Girardi, Pietra and Sabbioni[9] studied the retention of different radioactive ions on twelve precipitates of ionic character, mainly on oxides and phosphates, and on ion-exchange resins, with special regard to the radiochemical possibilities of separation.

We have used the reaction

$$ZnS + {}^{*}Zn^{2+} \rightleftharpoons {}^{*}ZnS + Zn^{2+}$$

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as model reaction for the investigation of the isotopic exchange of sulphide precipitates. The asterisk denotes radio-zinc.

EXPERIMENTAL

Isotopic exchange or retention was studied by flow technique, which permitted rapid work, and, as the inactive precipitate was in contact with only a small amount of active solution in unit time, the technique ensured a higher ratio of inactive to active material than that existing if the solution had been shaken with the precipitate until equilibration. Filter paper was placed on the perforated glass plate of the glass funnel shown in Fig. 1 and a known amount of the precipitate placed on the filter paper. The necessary washing liquid and active solutions were poured on the precipitate, and the required rate of filtration was adjusted by suction. The degree of retention can be calculated from the original activity of the active solution poured on, and that of the filtrate (counts n_0 and n respectively). The exchange yield is given by

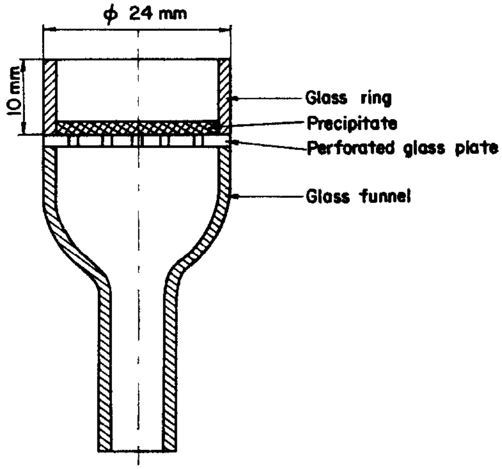

FIG. 1.—Filter for isotopic exchange.

$$Q = \frac{100(n_0 - n)}{n_0}\ \%.$$

For determination of metal traces the activity of the precipitates is measured after the exchange and related to that of a standard. A retention of 99–100% has to be ensured on 350–400 mg of precipitate, since this constitutes a layer thickness small enough not to cause an error due to self-absorption.

In the experiments 10 ml of the active solution at the required pH were passed through the suitably pretreated precipitate by suction, followed by 5 ml of nitric acid solution at the same pH as the active solution. The filtrate was diluted to 20 ml in a volumetric flask. The activity n of n 10-ml aliquot was measured; n_0 was measured at the same dilution. For the activity measurements a measuring head equipped with a hollow NaI(Tl) scintillator and an NK-108 energy-selective scaler produced by the Gamma Works (Hungary) were used, counting the total number of impulses under the corresponding photopeaks, in the differential mode. In this position the signal to noise ratio was so favourable that the counts measured for the filtrate exceeded the background even in the case of 99% retention. Gamma-spectra were recorded on an NTA-256 channel analyser constructed in the Hungarian Academy of Sciences Central Research Institute for Physics.

RESULTS

Isotopic exchange on zinc sulphide: effect of the structure of the precipitate on the exchange yield

The isotopic exchange was made with crystalline and amorphous zinc sulphide.

Preparation of crystalline zinc sulphide. $ZnSO_4 \cdot 7H_2O$ (18 g) and $(NH_4)_2SO_4$ (5 g)

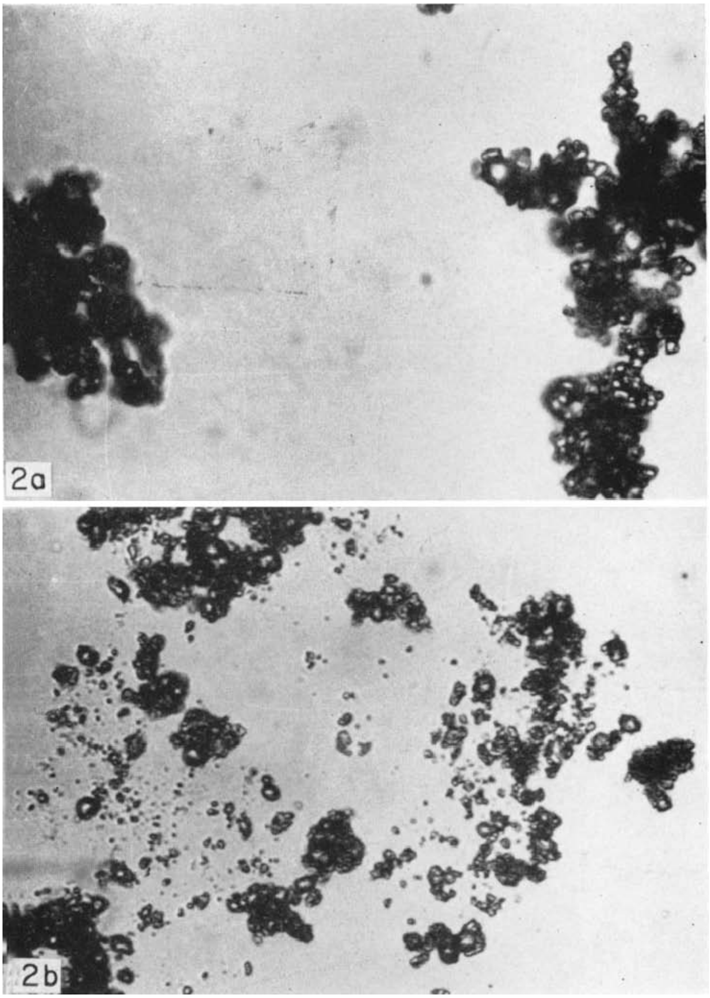

FIG. 2.—Photomicrograph of crystalline zinc sulphide precipitates.
Apparatus: Zeiss NF research microscope M-990. (*a*) $Q = 40{\cdot}8\%$; (*b*) the same precipitate after 10 min powdering, $Q \sim 100\%$.

were dissolved in 200 ml of 0·01 M sulphuric acid and the solution was heated to 60° and maintained at this temperature for 2·5 hr during which time gaseous hydrogen sulphide was passed through it with stirring. Then heating was stopped and gas passed for a further 0·5 hr. The slurry was stored for four days in a stoppered flask, then filtered on a porosity 4 sintered-glass filter, and the precipitate washed first with 0·01 M sulphuric acid saturated with hydrogen sulphide, then with carbon disulphide and benzene to dissolve any sulphur possibly precipitated, then dried at 110° for 1 hr. The washing with carbon disulphide and benzene can be omitted, as, according to our experiments, sulphur precipitated on silica carrier does not bind active zinc ions.

Preparation of amorphous zinc sulphide. $ZnSO_4 \cdot 7H_2O$ (8 g) was dissolved in 100 ml of water. The solution was heated to 60° and 100 ml of freshly prepared ammonium sulphide solution were added with stirring. The precipitate was filtered off after two days' sedimentation, washed with distilled water and dried at 80° for 1 hr.

Solutions containing radioactive zinc. For isotopic exchange, practically carrier-free $^{65}Zn^{2+}$ solutions were prepared from a $^{65}ZnCl_2$ solution with 7 mCi/ml specific activity, by dilution with 0·01 M nitric acid in such a way that the activity of the solutions was 480 and 790 cpm/ml.

Zinc sulphide precipitates were in each case treated with inactive zinc sulphate solution. Ten ml of 1 M zinc sulphate were passed through the precipitate on the filter. We wished to ensure the retention of active zinc ions by isotopic exchange instead of adsorption on the surface. According to preliminary experiments made with equal portions of crystalline zinc sulphide precipitate taken from the same lot, the values of Q agree within 1 % in the case of equal flow-rates (0·5 ml/min), whereas if the precipitates are taken from different lots, Q varies between 95 and 100 %. The deviations were even greater (40–100 %) if the period of passage of gas and temperature of precipitation were varied.

To elucidate the reasons for the great differences in exchange yield the crystalline structure and morphology of some zinc sulphide precipitates were studied. The X-ray diffraction patterns of precipitates exhibiting different exchange properties were similar, *i.e.*, there was no difference in their crystalline structure. Experimental lattice constants agreed well with literature values taken from A.S.T.M. cards (see Table I). Zinc sulphide crystallizes in the dihexagonal bipyramidal class of the hexagonal system, and so do the precipitates prepared by us. On the other hand, microscopic studies have shown that thin layers of the precipitates have an exchange yield equal to or higher than 99 % only if they consist mainly of particles a few μm in size. Precipitates with poor exchange ability were found to consist of larger agglomerates of the small primary particles. The necessary particle size can be produced by powdering the precipitate in an agate mortar for about 10 min, *e.g.*, see Fig. 2, in which the microscopic image of a poorly exchanging precipitate (*a*) and of one with good exchange properties (*b*) are shown; (*b*) was obtained from (*a*) by powdering. The exchange yield of crystalline zinc sulphide therefore can be made independent of the conditions of precipitation, by subsequent powdering.

The exchange yields of amorphous zinc sulphide precipitates taken from different lots are the same, reaching 100 % in the case of 400–420 mg of precipitate at a flow-rate of 0·5 ml/min. According to microscopic examination, amorphous zinc sulphide precipitates mainly consist of particles some μm in size, and the particle size distribution is more uniform than that of the crystalline modification. The amorphous

TABLE I.—X-RAY DIFFRACTION DATA FOR CRYSTALLINE ZINC SULPHIDE PRECIPITATES

d, nm experimental	*d, nm* literature
0·311	0·312
0·189	0·190
0·162	0·163
—	0·331

Apparatus: Mikrometa 2, X-ray tube: Cu, $\lambda = 0{\cdot}15405$ mm; filter: Ni; diameter of chamber: 57·4 mm; $V = 40$ kV; $i = 20$ mA; exposure time: 2 hr; development temperature: 18°, development time 5 min.

precipitate is, however, very difficult to filter off and the loss of precipitate during isotopic exchange is greater owing to the higher solubility.

By treatment of the active zinc precipitate with 10–20 ml of 2*M* inactive zinc sulphate that is 0·01*M* in nitric acid, part of the active nuclei can be transferred to the solution, which in our opinion supports the assumption that an isotopic exchange takes place on the zinc sulphide precipitate. By the flow technique, a maximum of 53% redissolution could be reached, whereas by the batch technique the redissolution was 55% of this, after 5 hr of shaking. Unfortunately, redissolution of active zinc ions can not be utilized for increasing the selectivity of analysis.

Isotopic exchange with zinc sulphide: effect of experimental conditions on the exchange yield

The effect of the pH, specific activity and flow-rate of the active solution on the exchange yield was studied.

According to the experiments the isotopic exchange can be performed with solutions 0·01*M* or maximally 0·1*M* in nitric acid (see Table II). The precipitate is capable of exchange at even higher acid concentrations—the specific activity of the precipitates is the same at varying acid concentrations—but owing to the high degree of dissolution precipitate particles containing active nuclei may also be dissolved. For studying the effect of pH nitric acid was selected, since the hydrogenation catalysts studied readily dissolve in it, and therefore nitric acid is present during separation by isotopic exchange following dissolution of the samples.

TABLE II.—EFFECT OF ACID CONCENTRATION ON THE ISOTOPIC EXCHANGE WITH ZINC SULPHIDE

Acid concentration, *M*	*Q*%	Weight loss, %	Specific activity of precipitate, *cpm/g*
0·01	100	4·6	5300
0·10	94·6	8·3	5390
1·00	66·3	25·6	5710
2·00	50·9	30·4	4050

As the zinc content of the samples is usually unknown before analysis, it was important to study the relationship between the weight of precipitate required to give

100% exchange yield, and the specific activity and flow-rate of the solution of zinc ions. As reflected by the results in Table III, when the specific activity of the solution increases to 1·7 times that of the original value, the weight of precipitate has also to be increased by a factor of at least 1·7.

A flow-rate of 0·5 ml/min was found to be the optimum for 100% exchange yield with 400 mg of precipitate; doubling the flow-rate reduces the efficiency of isotopic exchange.

Retention of different metal ions on sulphide precipitates

Besides the isotopic exchange of ^{65}Zn the retention of ^{203}Hg, ^{64}Cu, ^{76}As, ^{122}Sb, ^{24}Na, ^{58}Co and ^{103}Pd on sulphide precipitates was studied (see Table IV). The specific activity of the practically carrier-free solutions was about 500 cpm/ml. The sulphides were precipitated with hydrogen sulphide from solutions containing hydrochloric acid.[10]

TABLE III.—EFFECT OF THE SPECIFIC ACTIVITY ON THE ISOTOPIC EXCHANGE WITH ZINC SULPHIDE

Specific activity of solution, *cpm/ml*	Weight of precipitate, *mg*	*Q*%,	Time of passage of solution, *min*
480	380	100	35
790	380	64·3	35
790	380	65·2	90
790	660	100	35

TABLE IV.—RETENTION OF RADIONUCLIDES ON SULPHIDE PRECIPITATES

Precipitate	Concentration of HNO$_3$, *M*	Retention of active ions, %							
		Hg^{2+}	Zn^{2+}	Cu^{2+}	Sb^{3+}	As^{3+}	Pd^{2+}	Co^{2+}	Na^{+}
HgS	1·0	100	—	—	—	—	—	—	—
ZnS	0·01	100*	100				50	7	—
CuS	1·0			100					—
Sb$_2$S$_3$	1·0 HCl				100				—
As$_2$S$_3$	1·0					100			—

* By precipitate exchange.

As shown by the results in the table, sulphide precipitates practically completely retain their own cations. With mercury(II) sulphide the existence of isotopic exchange could be proved experimentally in the same way as for zinc sulphide.

The radionuclides listed in Table IV do not interfere with the determination of mercury(II) ions by isotopic exchange with mercury(II) sulphide. In the γ-spectrum of the precipitate (see Fig. 3) only the photopeak of ^{203}Hg appears.

Zinc sulphide binds mercury(II) ions by a chemical reaction—precipitate exchange:

$$ZnS\downarrow + Hg^{2+} = HgS\downarrow + Zn^{2+}$$

If no precipitate exchange takes place, the interfering effect of foreign radionuclides can be reduced by counter-carrier technique, *i.e.*, by dilution with the inactive isotope. In this way the interference from ^{103}Pd and ^{58}Co in the determination of zinc can be eliminated, or reduced. The peak of ^{58}Co in the γ-spectrum of the zinc sulphide

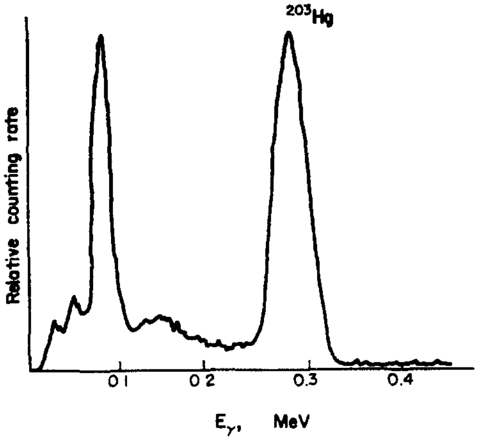

Fig. 3.—Gamma-spectrum of HgS precipitate after isotopic exchange. The original solution contained ^{203}Hg, ^{65}Zn, ^{64}Cu, ^{76}As, ^{122}Sb, ^{58}Co, ^{109}Pd and ^{24}Na.

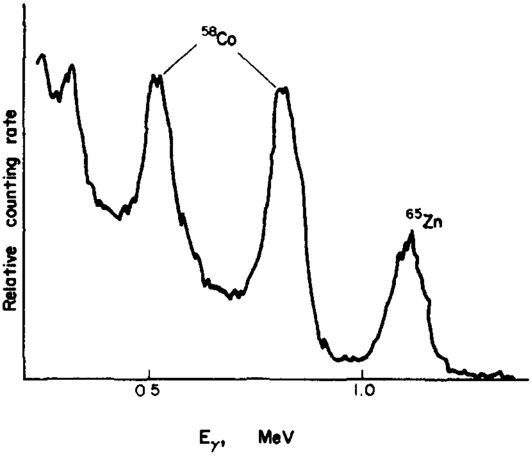

Fig. 4.—Gamma-spectrum of ZnS precipitate after isotopic exchange. The original solution contained ^{65}Zn, ^{109}Pd, ^{58}Co and ^{24}Na.

precipitate taken after isotopic exchange (see Fig. 4) does not disturb the evaluation of the photopeak of ^{65}Zn.

In the case of catalysts on aluminium oxide support ^{24}Na is formed in great amount during activation, owing to the reaction ^{27}Al (n, α) ^{24}Na; however, ^{24}Na is not retained on sulphide precipitates. Thus the method described ensured complete separation from ^{24}Na.[11]

Acknowledgements—We thank the late Professor László Erdey for enabling the work to be done, Senior Lecturer S. Gál for the X-ray diffraction work and Research Fellow L. Pólos for preparing the photomicrographs.

Zusammenfassung—Die Retention verschiedener Radionuklide an Metallsulfidniederschlägen wurde untersucht. Die Sulfidniederschläge hielten die eingenen Radionuklide quantitativ fest. Bedingung für 100% Retention in einer dünnen Schicht ist eine kleine Teilchengröße (einige μm) im Niederschlag. Das läßt sich durch Pulverisieren des getrockneten Metallsulfidniederschlags erhalten.

$^{203}Hg^{2+}$ wird an Quecksilbersulfid und $^{65}Zn^{2+}$ an Zinksulfid durch Isotopenaustausch festgehalten. Die Retention fremder radioaktiver Ionen kann mit Hilfe von inaktiven Isotop verringert oder gar ausgeschlossen werden; in Fällen, wo die Retention nicht auf chemischer Reaktion Niederschlaganstansch bericht. Der Isotopenaustausch mit Quecksilber(II) sulfid und Zinksulfid ermöglicht die rasche Trennung und die Bestimmung von Quecksilber- und Zinkionen in Gegenwart einer Anzahl störender Ionen.

Résumé—On a étudié la rétention de divers radionucléides sur des précipités de sulfures métalliques. Les précipités de sulfures retiennent quantitativement les radionucléides communs. La condition pour une rétention de 100 % dans une couche mince est une petite dimension de particule (quelques μm) dans le précipité. Ceci peut être assuré par pulvérisation du précipité séché du sulfure métallique. $^{203}Hg^{2+}$ est retenu par le sulfure de mercure et $^{65}Zn^{2+}$ par le sulfure de zinc par échange isotopique. On peut réduire ou même éliminer la rétention d'ions radioactifs étrangers par une technique à contre-support dans les cas où la rétention n'est pas due à une réaction chimique, échange de précipité. L'échange isotopique avec le sulfure de mercure (II) et le sulfure de zinc rend possible la séparation rapide des ions mercure et zinc et leur détermination en la présence d'un certain nombre d'ions gênants.

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STUDIES ON THE MELTS OF ALKALI METAL ACETATES

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Summary—The density, viscosity, and electrical conductivity of alkali metal acetates were measured over the temperature interval between melting and decomposition. The apparent activation energies of the equivalent conductivities and viscosities were calculated. It has been concluded from the results that alkali metal acetates, similarly to alkali metal benzenesulphonates studied earlier, exhibit properties quite unlike those of alkali metal halides. In the dependence of equivalent conductivity on the nature of the cation, the anomalous behaviour of lithium salts appears to be due to association prevailing in the melt phase.

PREVIOUSLY, the changes in properties of alkali metal acetates with increasing temperature have mainly been studied with special regard to phase equilibria, changes in crystalline modification and mechanism of decomposition reactions.[1–6] Relatively few data are available in connection with the temperature interval between melting and decomposition,[7–10] although the investigation of the properties of the molten state is of interest from both a theoretical and a practical point of view.

After studying melts of alkali metal benzenesulphonates[11] we started studies on molten alkali metal acetates in order to compare the behaviour of the two types of compound, and to obtain data characteristic of alkali metal acetate melts.

EXPERIMENTAL

Lithium, sodium, potassium, rubidium and caesium acetates used in the experiments were either commercial products or made by ourselves. The compounds were purified by multiple recrystallization from alcohol–dioxan mixture, and dried to remove water of crystallization. The purity of the products was checked by elemental analysis and melting point measurement. The temperature ranges in which they formed stable melts were determined with a DTA instrument at a low heating rate (1°/min) and by a Paulik-Paulik-Erdey derivatograph (MOM, Hungary). To characterize the molten state, the density, electrical conductivity and viscosity were measured as a function of the temperature. The methods have been described earlier.[11]

RESULTS AND DISCUSSION

The results of DTA and derivatographic measurements are presented in Table I. The data show that all five compounds studied have stable melts, over a relatively wide temperature range depending on the cation, in which no weight or enthalpy change takes place; thus their transport phenomena can be studied easily. The temperature interval between melting and decomposition increases with increasing atomic number of the cation. The data obtained by the two methods do not coincide perfectly, which is due partly to the dynamic nature of the measurements and partly to inaccuracies. This fact, however, did not affect our further experiments, since the

TABLE I

Acetate	Data obtained by DTA, °C			Data obtained by derivatograph, °C						Theoretical change in weight, %
				from the DTA curve			from the DTG curve		from the TG curve	
	Melting point	Decomposition		Melting point	Decomposition		Decomposition		change in weight, %	
		starting	max.		starting	max.	starting	max.		
Li	280	320	425	275	at m.p.	417	320	375	44·0	44·0
Na	332	380	488	340	375	470	350	475	31·5	35·2
K	302	390	477	285	420	485	375	485	28·5	29·6
Rb	241	380	474	228	380	485	340	480	22·0	20·1
Cs	197	380	449	179	325	473	340	476	15·0	15·1

measurements were started below the melting point, and the temperature was raised to the decomposition temperature at a rate of 0·5°/min. The chemical changes proceeding at the decomposition temperature and accompanied by the formation of gaseous product were sensitively indicated by the measuring method used. Heating was stopped at this temperature.

The density of the salt melts as a function of the temperature is shown in Fig. 1. These data were necessary for the conversion of specific conductivities into equivalent conductivities.

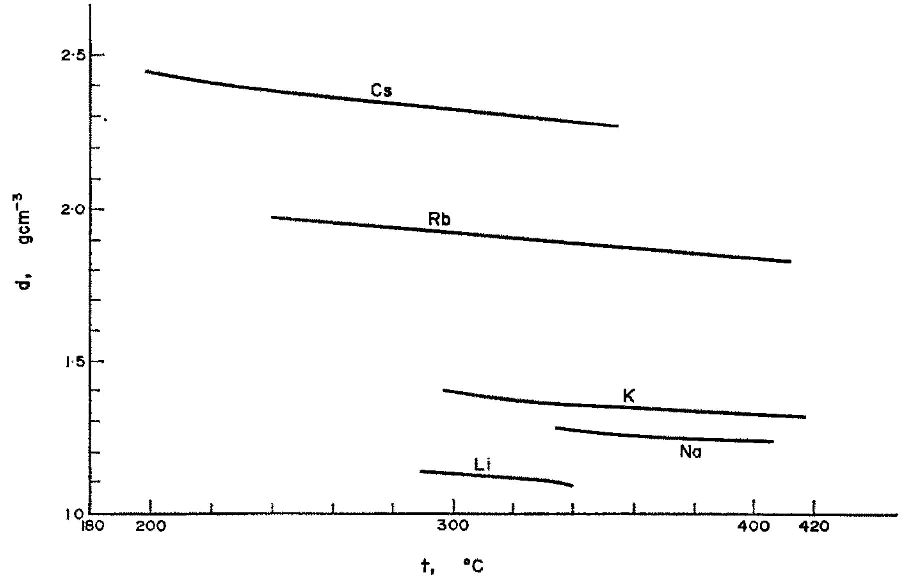

FIG. 1.—Temperature dependence of the density of alkali metal acetates.

The temperature dependence of the equivalent conductivity of the salt melts studied is presented in Fig. 2. The impedance of the measuring cell containing platinum electrodes is only little affected (within the limits of error) by the capacitance of the

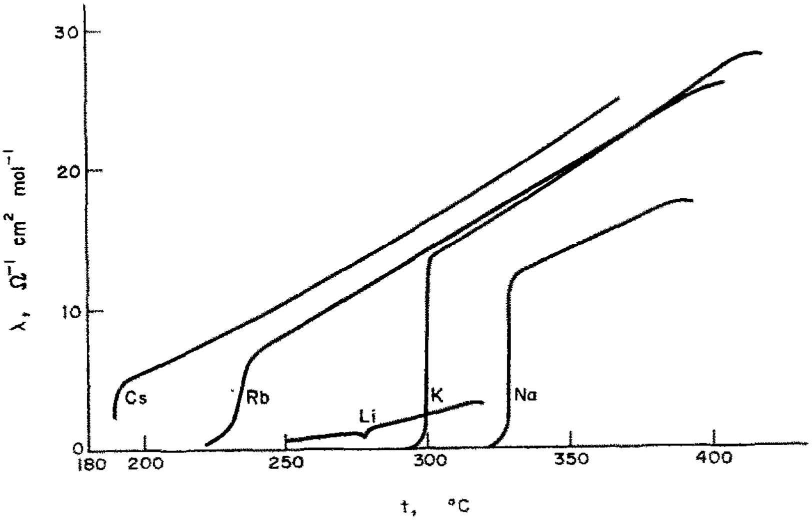

FIG. 2.—Temperature dependence of the equivalent electrical conductivity of alkali metal acetates.

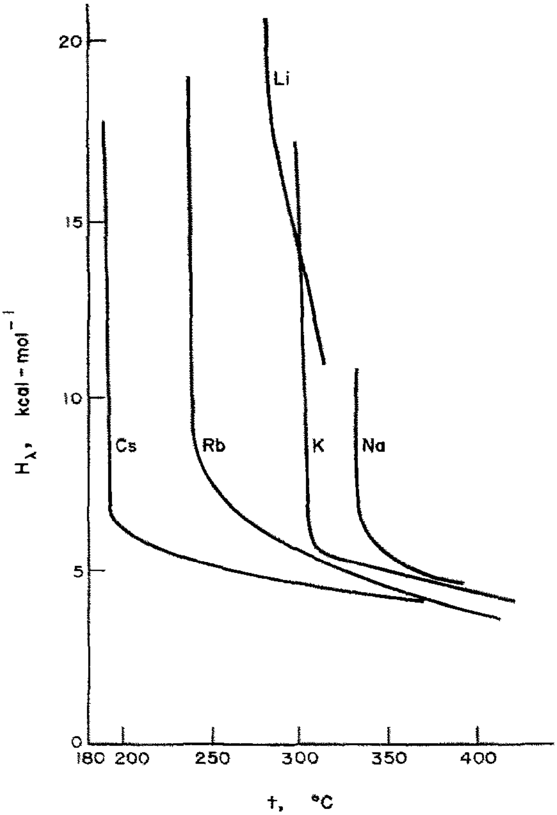

FIG. 3.—Temperature dependence of the apparent activation energy of conductivity of alkali metal acetates.

electrodes, according to our experience and the literature data,[12,13] and therefore a constant-frequency 1-kHz measuring bridge can be used.

The apparent activation energy of conductivity was determined from the Arrhenius equation, from the slope of a plot of the logarithm of the conductivity *vs.* $1/T$. It can be concluded from the measurements and figures that none of the melts studied behaves ideally. The remarkable change of the activation energy with temperature is indicative of complex interactions (Fig. 3). The change of the equivalent conductivity of the salts with the nature of the cation seems unusual when compared with similar data measured for alkali metal halides. The equivalent conductivity of alkali metal halides near their melting point was found to decrease with increasing diameter of the cation for a series of salts of the same halide ion. The case is similar with the different halides, of one cation, the conductivity decreasing with increasing diameter of the anion.[14] With alkali metal acetates, as indicated by the data in Table II, quite different tendencies were observed. The equivalent conductivities measured in the vicinity of the melting point increased with the atomic number of the cation up to potassium, then decreased again. The conductivities measured near the decomposition temperature showed a similar change with the atomic number with the difference that the equivalent conductivities of the potassium, rubidium and caesium salts were practically identical. At a medium temperature the tendencies are intermediary between those at the melting and decomposition temperatures.

The trends were found to be similar in the case of alkali metal benzenesulphonates.[11] The very low equivalent conductivity of the lithium salt, and also the relatively low conductivity of the sodium salt is presumably due to the existence of the dimeric structure above the melting point, owing to polarization by the cations. In other words, the cation–anion bond has a remarkably covalent nature even in the molten phase. The equivalent conductivities of the salts studied not only depend on the diameter of the cation but are also influenced by the associated structure prevailing in the molten phase. The nature of the bond, however, also depends on the anion.

TABLE II

Acetate	Equivalent conductivity, Ω^{-1} . *cm*^{2} . *mole*$^{-1}$		
	at melting point, T_{melting}	at decomposition temperature, T_{decomp}	at medium temperature, T_{m}
Li	1·4	3·2	2·3
Na	12·0	16·5	14·3
K	13·4	24·6	18·8
Rb	6·6	23·0	15·1
Cs	4·9	24·6	14·6

$$T_{\text{m}} = \frac{T_{\text{decomp}} + T_{\text{melting}}}{2}$$

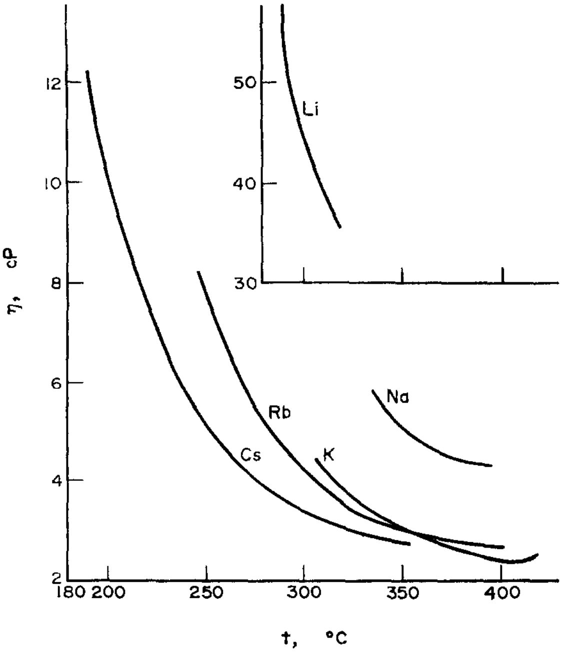

FIG. 4.—Temperature dependence of the viscosity of alkali metal acetates.

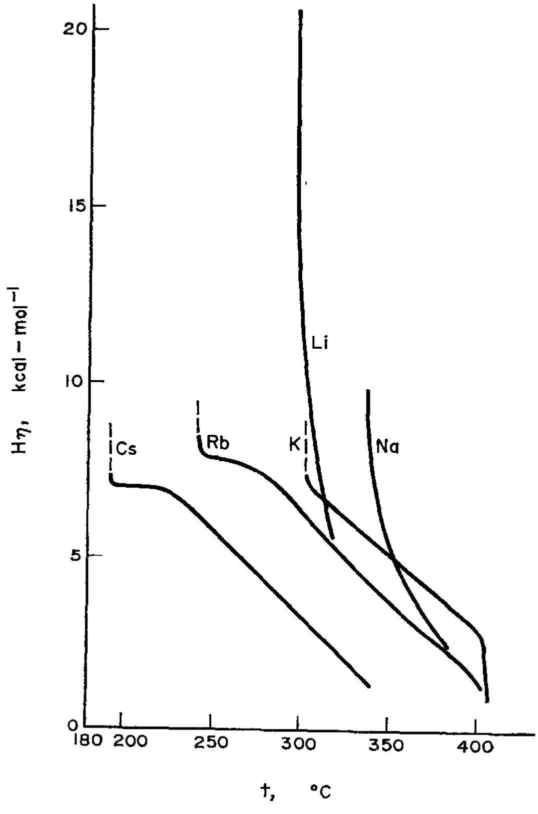

FIG. 5.—Temperature dependence of the apparent activation energy of viscosity of alkali metal acetates.

This statement is supported by the experimental fact (see Fig. 2) that the conductivity of solid lithium acetate does not change much on melting, whereas the conductivities of the other alkali metal acetates change more or less sharply at the melting point. Furthermore, the very high apparent activation energy of the conductivity of the lithium salt in comparison to those of other alkali metal acetates also indicates the high degree of order of the melt of lithium acetate.

The tendencies observed in the change of the viscosities of the melts are in good agreement with the conductivities and the conclusions drawn from them. The temperature dependence of the viscosities of the melts of alkali metal acetates is shown in Fig. 4. The extremely high viscosity of the lithium acetate melt as compared to that of the other acetates studied, and also the high apparent activation energy of viscosity as determined on the basis of the Arrhenius equation is also evidence of the high degree of order of the melt. The temperature dependence of the activation energies of viscosity is shown in Fig. 5. The structure of melts in the ideal case can be characterized by the Walden formula[15] as follows:

$$\eta^n = \text{constant}$$

The condition for ideal behaviour is the constancy of n.

There was found no temperature interval over which this relationship was valid for the data measured by us. The investigation of the molten state of organic salts will be extended to other model compounds in future in order to find further relationships between the properties of the salt and the nature of the constituent ions.

Résumé—On a mesuré les densité, viscosité et conductivité électrique d'acétates de métaux alcalins dans l'intervalle de température compris entre la fusion et la décomposition. On a calculé les énergies d'activation apparentes des conductivités équivalentes et des viscosités. On a conclu, des résultats, que les acétates de métaux alcalins, comme les benzènesulfonates de métaux alcalins étudiés antérieurement, présentent des propriétés tout à fait différentes de celles des halogénures de métaux alcalins. Dans la dépendance de la conductivité équivalente par rapport à la nature du cation, le comportement anormal des sels de lithium paraît dû à une association prévalant dans la phase fondue.

Zusammenfassung—Dichte, Viskosität und elektrische Leit fähigkeit von Alkalimetallacetaten wurden im Temperaturbereich zwischen Schmelzen und Zersetzung gemessen. Die scheinbaren Aktivierungsenergien der Äquivalentleitfähigkeit und der Viskosität wurden berechnet. Es wurde der Schluß gezogen, daß die Acetate der Alkalimetalle, ähnlich wie die früher untersuchten Benzolsulfonate, ganz andere Eigenschaften haben als die Halogenide. Bei der Abhängigkeit der Äquivalentleitfähigkeit vom Kation scheint das anomale Verhalten der Lithiumsalze davon zu rühren, daß in der geschmolzenen Phase überwiegend Assoziate vorliegen.

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SPECTROCHEMICAL ANALYSIS OF HARD METALS BY A ROTATING DISC TECHNIQUE

EFFECT OF IMPREGNATION AND COMPLEXING AGENTS

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Summary—A spectrographic method has been developed for the simultaneous determination of the constituents W, Co, Ti, Ta and Nb and contaminants Fe, Ni, Cr, Mn, Mg and Ca in hard metals. The samples were dissolved in hydrofluoric acid and nitric acid and the solutions stabilized with citric acid. Graphite discs were waterproofed in order to ensure control of the introduction of solution into the source. For the five types of hard metal samples studied no inter-element effect was observed. Titanium has also been determined by means of a double-beam optical spectrometer.

OF THE STANDARD methods for the analysis of hard metals only two will be cited here, in which ion-exchange columns are used for the separation of ions.[1,2] These methods are rather time-consuming, and of low accuracy (2–4% error). Furthermore, they do not permit the quantitative separation of tantalum and niobium.

X-Ray fluorescence methods are commonly used for the simultaneous determination of the constituents of hard metals, by the direct method,[3] powder technique[4] and solution technique.[5] Complex inter-element effects occur during X-ray fluorescence analysis and standards covering a limited concentration range are needed for each type of method.

The inhomogeneity of hard metals is an obstacle to their direct spectrochemical analysis, so solution techniques are required for quantitative analysis. The technique recommended for the spectrographic determination of refractory transition metals was suitable for our work[6] but had not yet been used in the analysis of hard metals.

EXPERIMENTAL

The hard metals analysed represented ten different categories which could be classified into five groups with certain exceptions. The constituents and their concentration ranges are given in Table I.

TABLE I.—HARD METAL TYPES STUDIED

	Constituent %				
Type	WC	TiC	TaC	Co	NbC
I	60–65	25–30	—	3–6	—
II	65–75	13–18	0–5	6–8	0–0·5
III	70–80	5–10	0–4	6–10	0–0·4
IV	80–90	—	0–3	4–7	0–0·3
V	75–85	—	—	18–22	—

Preparation of sample solutions

The basic materials (metal carbide and cobalt powder mixtures), used for making hard metal tips, were freed from paraffin with benzene in a Soxhlet extractor. Tips were broken up by chipping. From the samples so treated, 200 mg were dissolved in a platinum crucible with 10 ml of concentrated hydrofluoric acid, with dropwise addition of nitric acid. It is necessary to remove or neutralize excess of acid after dissolution, in order to prevent corrosion of the instruments used. In the X-ray fluorescence method cited,[5] boric acid was used to complex hydrogen fluoride. In the present case, however, it seemed better to remove free acid because of its possible thermal decomposition during excitation. Evaporation with sulphuric acid[6] could not be used, as tungstic acid was precipitated. Therefore hydrogen fluoride was removed by adding 25 ml of citric acid solution (200 mg/ml) and evaporating to low bulk on a steam-bath. The residue was diluted with water and the evaporation repeated, this step being carried out twice. The final residue was diluted with 10 ml of copper sulphate solution (50 mg of Cu/ml) and then with water to 25 ml in a volumetric flask, and finally transferred to a plastic storage vessel. It has been reported[7] that copper(II) can form a complex with hydrogen fluoride, so any of the latter possibly retained in solution might be masked in this way. In addition, the copper served as internal standard and spectrochemical buffer.[8]

Solutions prepared as described contained 8 mg of sample, 20 mg of copper and 200 mg of citric acid per ml. The solutions remained unchanged for two days if the titanium content was >10% and for longer periods if it was less. For studying the effect of citric acid on the excitation, solutions containing 100 mg of citric acid per ml were also prepared.

Preparation of standard solutions

Stock solutions were prepared from metals of spectroscopic purity as described for sample preparation. Standard solutions were prepared from the stock solutions by mixing. According to the classification in Table I, five types of reference standards were prepared. Contaminants were added in the form of their solutions in nitric acid (in hydrochloric acid in the case of chromium).

Choice of the electrical parameters of excitation

High-voltage spark excitation was used,[6] and the solution consumption was 0.07 ml/min (averaged over 6 min). In the case of spectrometric determinations low-voltage spark excitation was used with a similar consumption of solution.

Pretreatment of graphite discs

In the residue methods the graphite supporting electrode is water-proofed. The differences in the size and structure of the electrodes and in chromatographic phenomena are less important in the case of the rotating disc technique than with the residue methods.

These effects, however, cannot be neglected.[9] The pretreatment reduces these effects, but also reduces the amount of solution carried into the spark gap. This unfavourable effect can be eliminated by the use of an impregnating agent which decomposes on the surface of the disc during excitation allowing the disc to become absorbent again. The absorption of solution may be controlled by the spark discharge, and a thin layer of solution is formed.[10,11] The impregnating solution used (cellulose nitrate in acetone) has been described previously.[12] Graphite discs were immersed in this solution (a 1:4 solution of "Zapon" lacquer on acetone). The impregnated discs were placed on a glass sheet and dried by means of an infrared lamp.

The effects of the variation in the concentration of citric acid and the impregnation of the discs are demonstrated by the excitation–time studies presented in Fig. 1, where log intensity is plotted *vs.* time for alloy type II. The intensity of the lines decreases with increasing citric acid concentration for both impregnated and non-impregnated discs. Impregnation increases the line intensity in the case of low citric acid concentrations and reduces it at high citric acid concentrations. The thickness of the solution layer is presumably reduced both by increase in citric acid concentration and by impregnation of the discs. In the course of the present work these effects were utilized. Analyses were made under conditions corresponding to curves *B*. These curves are similar in shape, which indicates the absence of selective evaporation. The discs that had not been impregnated previously were rotated in the solution for 90 sec before excitation was started, during which time saturation equilibrium could be established. With impregnated discs this operation is unimportant. Impregnation provides protection against corrosion and contamination of the shaft.

Experimental conditions

In the case of the rotating disc equipment a carbon shaft[13,14] and a plexi-glass solution container were used. The shaft of the motor was connected to the carbon shaft by a flexible steel drive. On the closed electrode stands a 6-mm diameter hole was made in an appropriate position for the flexible shaft. The graphite disc was 10 mm in diameter, and 3.2 mm thick and rotated at 10 rpm: 1 ml of solution was used. The penetration depth of the disc was 2 mm.

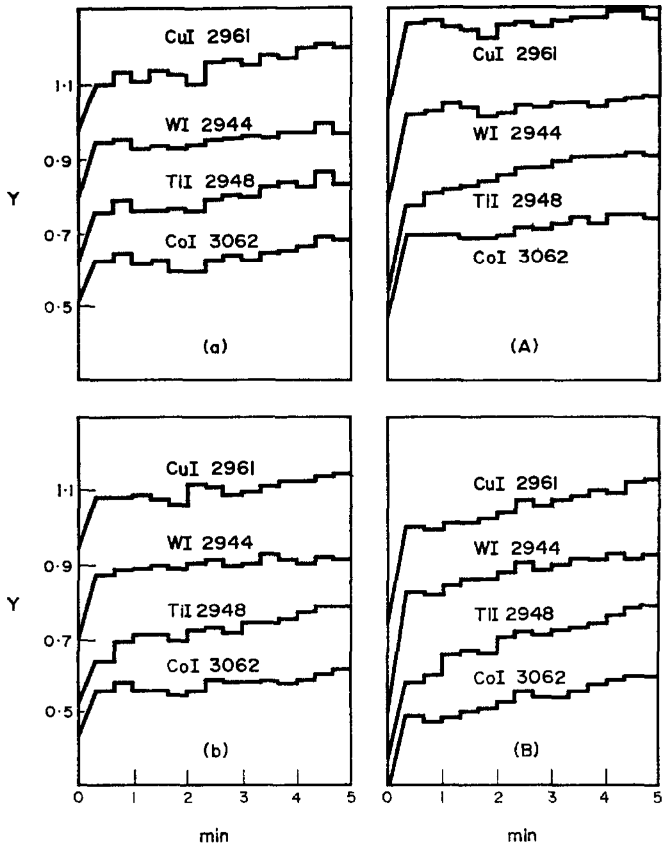

FIG. 1.—Log intensity (Y) *vs.* time.
(*a*) 100 mg of citric acid/ml; without impregnation
(*A*) 100 mg of citric acid/ml; with impregnated disc
(*b*) 200 mg of citric acid/ml; without impregnation
(*B*) 200 mg of citric acid/ml; with impregnated disc.

Spectrographic method

Source. RFT, HFO-1 high-voltage spark generator, 15 kV peak-voltage, 6 nF capacitance, 0·08 mH added self-inductance, 3-mm spark gap, 6·15-mm diameter hemispherical-end graphite counter-electrode; 30-sec presparking, 120-sec exposure.

Spectrograph. Hilger and Watts, Type E 478, quartz optics. Wavelength range 249–360 nm. Slitwidth 0·02 mm. To ensure maximum illumination of the slit the source was placed at the focus (for ultraviolet light) of a quartz lens (Hilger and Watts, F 1509).[15] (Distance of the source from the slit 0·38 m, distance of the lens from the source 56 mm.) With this method of illumination the exposure time necessary to obtain the same line blackening was about 1/7 that with internal focusing. However, this method was unsuitable for spectrograms made by using a step wedge for calibration, so in this case internal focusing was used.

Photographic conditions. Gevaert, Scientia 34 B 50 emulsion, Kodak D 19 developer (4 min, 20°), mechanical agitation during development.

Evaluation of results. A Radelkisz Spectator analogue computer,[16] using the general P-transformation according to Kaiser, was employed. Background correction was applied only for the analytical lines of constituents and impurities.

Spectrometric method

Source. GEU-1 (USSR) low-voltage arc and spark generator with electronic control, 220 V, 10 μF, no added self-inductance, 0·8 A (effective). Spark gap 2 mm; presparking and exposure time 60 sec.

Spectrometer. FESZ-1 (USSR) double-beam spectrometer (visible range, photocell detectors, polychromatic reference light, measurement of integral intensity ratios). Entrance slit 0·04 mm; exit slit 0·06 mm; analytical line Ti I 498·2 nm (adjusted by hand). The intensity of the reference light was reduced by a filter with 17% transmission.

RESULTS

Shape of the analytical curves

The spectrographic analytical curves for all constituents and contaminants were linear and reference standards of all five types gave the same analytical curve. The analytical line pairs used and the corresponding concentration ranges are presented in Table II. Analytical curves were plotted as intensity ratio vs. concentration.

Table II.—Data characteristic of the evaluation and analytical performance

Analytical line, *nm*	Concentration range %	Coeff. of variation* %	Detection limit, c_d, %
Ti I 498·175†	2–26†	2·2† (15)	—
Ti II 283·216	5–26	3·4 (15)	—
Ti II 316·177	0·5–5	3·2 (3)	—
Ti II 323·452	0·08–0·5	6·2 (0·2)	0·038
W I 294·738	50–85	2·9 (70)	—
Co I 306·182	4–25	3·2 (10)	—
Ta 301·254	1–6	5·4 (4)	0·37
Nb II 295·088	0·2–0·6	5·7 (0·4)	0·084
Fe II 259·957	0·03–0·5	4·3 (0·1)	0·015
Ni I 305·082	0·09–0·3	6·7 (0·2)	0·044
Cr II 284·325	0·02–0·2	7·4 (0·1)	0·013
Mn I 279·482	0·02–0·2	6·5 (0·1)	0·083
Mg II 279·553	0·004–0·02	6·3 (0·01)	0·0023
Ca II 317·933	0·04–0·2	5·6 (0·1)	0·017

* The figure in brackets is the concentration of the element used for determination of the coefficient of variation.

† Data for spectrometric method. All other data refer to the spectrographic method in which the CuI 303·610-nm reference line was used for the determination of all constituents and contaminants.

Precision and sensitivity

To study the precision of the method 20 parallel measurements were made and the coefficient of variation was calculated by means of the usual relationship;[17] the results are also given in Table II.

To characterize sensitivity we wished to calculate the detection limit according to Kaiser's criterion,[18] but its interpretation and application are not consistent in the literature.[19–21] We tried to keep to Kaiser's criterion, however, by using the relationship

$$c_d = \left(\frac{3\sigma_{BU}}{a}\right)^{1/b}$$

where c_d is the limit of detection, a and b are the constants of Lomakin and Scheibe's analytical function, and σ_{BU} the standard deviation of the "relative blank intensity" (blank intensity at the wavelength of the analytical line divided by the intensity of the reference line). The average relative blank intensity and the corresponding standard deviation were determined from 20 spectrograms from a solution of type V (free of contaminants). The constant *a* is the slope of the analytical curve, and in the cases studied *b* was equal to unity. The c_d values are given in Table II.

DISCUSSION

The greatest advantage of the method lies in its relative freedom from inter-element effects, which presumably is related to the linear nature of all the analytical curves. These properties can be accounted for by the non-selective evaporation of the constituents during excitation. This is partly due to the formation of a thin solution layer and partly to the similar volatilities of the fluorides of the constituents.

Zusammenfassung—Ein spektrographisches Verfahren zur gleichzeitigen Bestimmung der Hauptbestandteile W, Co, Ti, Ta und Nb und der Verunreinigungen Fe, Ni, Cr, Mn, Mg und Ca in Hartmetallen wurde entwickelt. Die Proben wurden in Flußsäure und Salpetersäure gelöst und die Lösungen mit Zitronensäure stabilisiert. Die Graphitscheiben wurden wasserabstoßend gemacht, um das Einbringen der Lösung in die Lichtquelle zu regeln. Bei den fünf untersuchten Typen von Hartmetallproben wurden keine gegenseitigen Störungen der Elemente beobachtet. Titan wurde auch mit Hilfe eines optischen Zweistrahl-Spektrometers bestimmt.

Résumé—On a développé une méthode spectrographique pour la détermination simultanée des constituants W, Co, Ti, Ta et Nb et des contaminants Fe, Ni, Cr, Mn, Mg et Ca dans les métaux durs. On dissout les échantillons en acide fluorhydrique et acide nitrique et stabilise les solutions avec l'acide citrique. Des disques de graphite ont été rendus étanches à l'eau afin d'assurer le contrôle de l'introduction de la solution dans la source. Pour les cinq types d'échantillons de métaux durs étudiés, on n'a pas observé d'influence inter-éléments. On a aussi dosé le titane au moyen d'un spectromètre optique à double faisceau.

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SHORT COMMUNICATIONS

Selektive Bestimmung in verdünnter Lösung befindlicher Säuren von verschiedener Stärke durch oszillometrische Titration

(*Eingegangen am* 19. *Mai. Angenommen am* 3. *Juni* 1970)

IN DER LITERATUR der letzten Jahren sind für die Bestimmung nebeneinander anwesender Säuren von verschiedener Stärke Titrationen in nichtwäßriger Lösungen angegeben.[1–6] Bei diesen Methoden wird die Selektivität durch Auswahl eines geeigneten Lösungsmittels erreicht.

Nach dem von uns ausgearbeiteten Verfahren ist eine Möglichkeit gegeben durch Auswahl einer Maßlösung von geeigneter Basenstärke, Säuren von verschiedener Stärke in wäßriger Lösung nebeneinander zu bestimmen. Die Titration beruht auf folgender Reaktion:

$$\mathrm{HA} + \mathrm{B} \overset{K}{\rightleftharpoons} \mathrm{A} + \mathrm{BH}$$

$$K = \frac{K_\mathrm{B}}{K_\mathrm{A}} > 10^{1,3}$$

wo K_B und K_A die Protonierungskonstanten der Basen B und A sind.

Ist die Protonierungskonstante der Base B ungefähr 20-mal größer als diejenige der Base A, so verläuft die Reaktion praktisch quantitativ.

Titriert man zwei verschiedene starke Säuren, wo

$$K_{\mathrm{A(I)}} > K_{\mathrm{A(II)}}$$

so verwendet man eine Base B, die eine Protonierungskonstante

$$K_{\mathrm{A(I)}} > K_\mathrm{B} > K_{\mathrm{A(II)}}$$

hat.

In diesem Falle ist die Säure HA(II) mit der Base B selektiv titrierbar. Im Gegensatz zur potentiometrischen Titration ist die oszillometrische Titration für die Bestimmung des Endpunktes auch in denen Fällen geeignet, wo das Verhältnis

$$\frac{K_\mathrm{B}}{K_{\mathrm{A(II)}}}$$

kaum größer als 20 ist. Auf Grund dieses Prinzips haben wir die Titration einiger Säuren durchgeführt. (Siehe Tabelle 1).

EXPERIMENTELLER TEIL

Stammlösungen. Lösungen (0,1*M*) von Trichloressigsäure, Monochloressigsäure, Ameisensäure, Oxalsäure, Maleinsäure. Die Lösungen wurden durch Einwaage bereitet, ihr Titer wurde durch potentiometrische Titration mit einer Natriumhydroxid Maßlösung ermittelt.

Maßlösungen. Molare Lösungen von Kaliumdihydrogenphosphat, Natriumacetat, Natriumformiat und 0,5*M* Lösung von Natriumfluorid. Der Fluoridgehalt der Natriumfluoridlösung wurde nach Erdey[7] als PbClF gravimetrisch bestimmt; der Titer der übrigen Maßlösungen wurde nach Ionenaustausch an einem Kationenaustauscher in H^+-Form mit Natriumhydroxid Maßlösung potentiometrisch bestimmt.

Für die Herstellung der Lösungen wurden in jedem Falle Reagenzien von *p.a.* Qualität verwendet.

Apparate und Instrument

Oszillotitrator, Typ OK 302 der Firma Radelkis; Meßfrequenz *ca.* 140 MHz.
pH-Meter, Typ OP 204 der Firma Radelkis.
Acryl-Bürette, Typ XT 5220 "XLON".

Titration

Eine Portion von 1 bis 10 ml der entsprechenden Säure wurde in einer Meßzelle auf 100 ml verdünnt, daß die Lösung die obere Elektrode erreiche. Nach dem Einschalten und nach entsprechender Einstellung des Apparats wurde der Lösung in 0,05 bis 0,1 ml Portionen, aus einer Mikrobürette—im Falle der Natriumfluoridlösung aus der Acryl-Bürette—die entsprechende Maßlösung

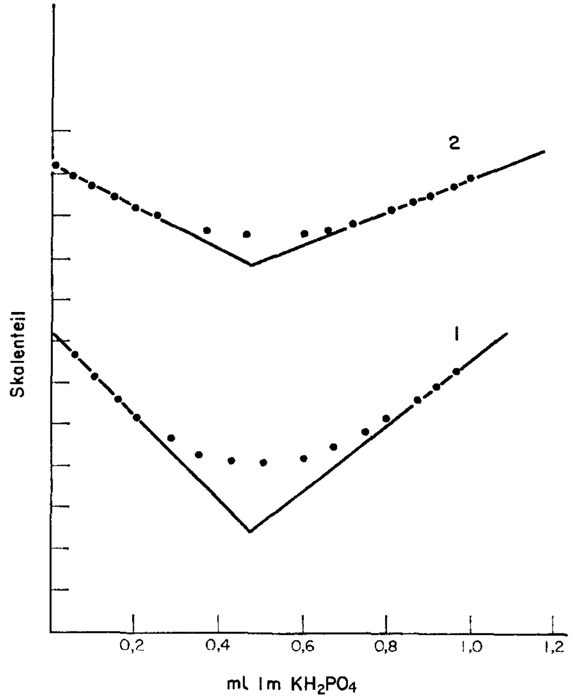

Abb. 1.—1. Titration von 10 ml 0,1*M* Trichloressigsäure in 100 ml Volumen mit 1*M* Kaliumdihydrogenphosphat.

2. Titration von 10 ml 0,1*M* Trichloressigsäure in 100 ml Volumen mit 1*M* Kaliumdihydrogenphosphat in Gegenwart von 10 ml 0,1*M* Monochloressigsäure.

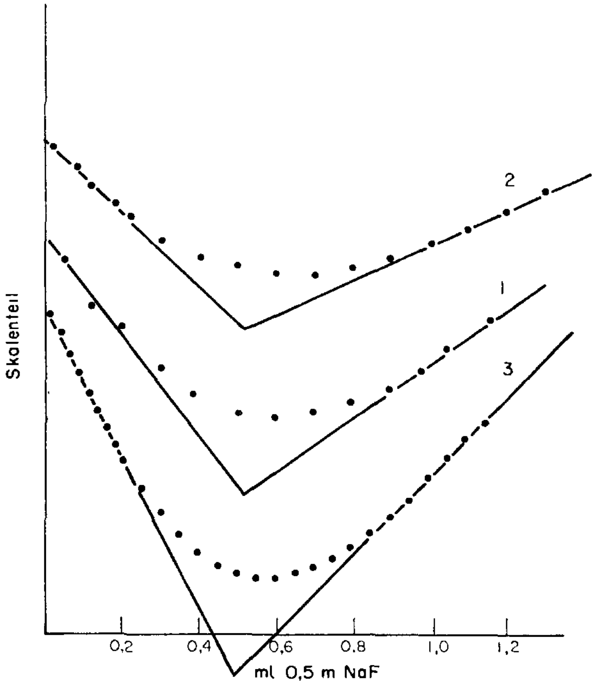

Abb. 2.—1. Titration von 2,5 ml 0,1*M* Oxalsäure in 100 ml Volumen mit 0,5*M* Natriumfluorid.

2. Titration von 2,5 ml 0,1*M* Oxalsäure in 100 ml Volumen mit 0,5*M* Natriumfluorid in Gegenwart von 2,5 ml 0,1*M* Essigsäure

3. Titration von 5,0 ml 0,1*M* Maleinsäure in 100 ml Volumen mit 0,5*M* Natriumfluorid.

zugefügt. Nach dem Erreichen des Äquivalenzpunktes wurde ein etwa 50 bis 100%-iger Überschuß an Maßlösung zugefügt. Der Äquivalenzpunkt wurde graphisch ermittelt.

ERGEBNISSE UND DISKUSSION

Die Analysenergebnisse sind in Tabelle I zusammengestellt.

TABELLE I.—TITRATIONSERGEBNISSE

Bestimmte Säure	$\log K_{A(II)}$	0,1M Lösung, ml genomm.	0,1M Lösung, ml gefund	Begleitsäure, 0,1M	$\log K_{A(I)}$	Volumen, *ml*	Abweichung, %
Titrationen mit Kaliumdihydrogenphosphat Maßlösung, $\log K_B = 2{,}12$							
CCl_3COOH	0,89	10,00	9,90	$CH_2Cl\ COOH$	2,86	10,00	−1,0
CCl_3COOH	0,89	10,00	9,96	—		—	−0,4
Titrationen mit Natriumfluorid Maßlösung, $\log K_B = 3{,}45$							
$CH_2ClCOOH$	2,86	2,00	1,98	—		—	−1,0
$CH_2ClCOOH$	2,86	2,00	1,96	CH_3COOH	4,76	2,00	−2,0
$(COOH_2)$	1,19	2,50	2,52	$COOH{\cdot}COONa$	4,21	2,50	+0,8
$(COOH_2)$	1,19	2,50	2,52	$COOH{\cdot}COONa$	4,21	2,50	+0,8
				CH_3COOH	4,76	2,00	
$C_2H_2(COOH)_2$ Maleinsäure	2,00	5,00	5,00	$C_2H_2COOH{\cdot}COONa$	6,26	5,00	±0,0
Titrationen mit Natriumacetat Maßlösung, $\log K_B = 4{,}76$							
$HCOOH$	3,75	1,00	0,99	—		—	−1,0
CCl_3COOH	0,89	2,00					
$CH_2ClCOOH$	2,86	2,00	4,04	—		—	+1,0

Da der Unterschied zwischen den Protonierungskonstanten der titrierten und titrierenden Systeme nicht allzu beträchtlich ist, wird sich die Leitfähigkeit in der Umgebung des Äquivalenzpunktes kaum oder gar nicht ändern. Dieser Abschnitt ist desto größer, je näher die Protonierungskonstante der Basen-Maßlösung zur Protonierungskonstante der konjugierten Base der titrierten Säure liegt. In diesem Falle kann man die zur Bestimmung des Äquivalenzpunktes notwendigen Kurven nur dann mit Sicherheit konstruieren, wenn wenigstens etwa 50 bis 100% Überschuß an Maßlösung verwendet wird.

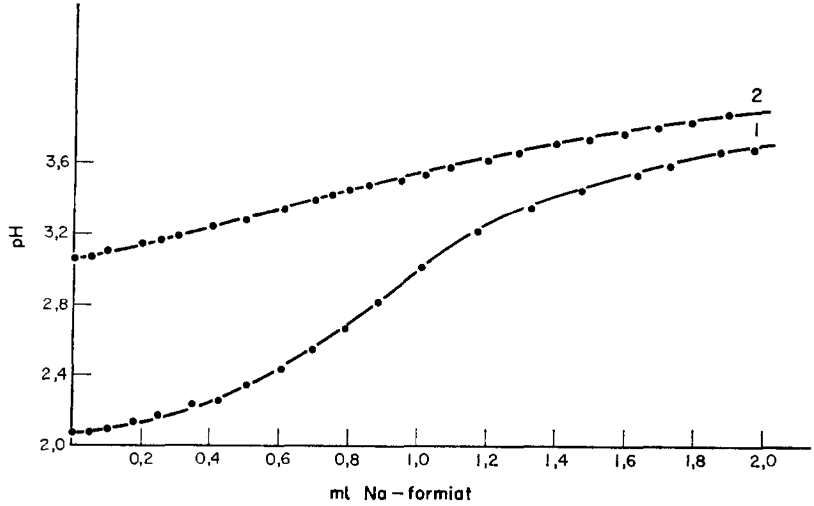

ABB. 3.—1. Potentiometrische Titration von 10 ml 0,1M Trichloressigsäure in 100 ml Volumen mit 1M Natriumformiat.
2. Potentiometrische Titration von 1 ml 0,1M Trichloressigsäure in 100 ml Volumen mit 0,1M Natriumformiat.

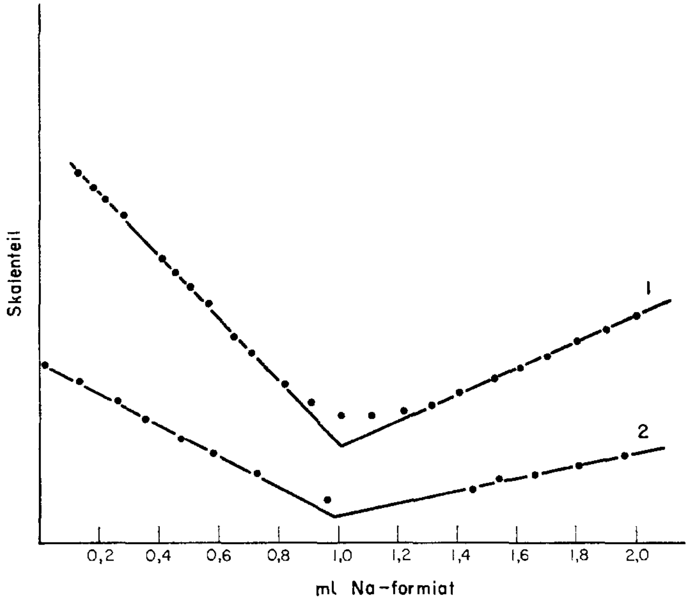

ABB. 4.—1. Oszillometrische Titration von 10 ml 0,1*M* Trichloressigsäure in 100 ml Volumen mit 1*M* Natriumformiat.
2. Oszillometrische Titration von 1 ml 0,1*M* Trichloressigsäure in 100 ml Volumen mit 0,1*M* Natriumformiat.

Es war festzustellen, daß die anwesende Begleitsäure einer 2 bis 10 fachen Menge der zu bestimmenden Säure keine störende Wirkung verursacht, aber die Kurve wird weniger steil sein (Abb. 1, Kurve 1 und 2; Abb. 2, Kurve 1 und 2). Versuche wurden auch mit 100 facher Menge der Begleitsäure durchgeführt. Ein ml 0,1*M* Trichloressigsäure wurde in Gegenwart von 100 ml 0,1*M* Essigsäure titriert, die 20% Mehrverbrauch an Maßlösung verursachte. Ist die Begleitsäure schwächer als Essigsäure, so ist der Fehler selbstverständlich geringer.

Abbildung 2 zeigt die Titrationskurven zweiwertiger Säuren. Oxalsäure und Maleinsäure sind mit Natriumfluorid Maßlösung als einwertige Säuren titrierbar. Auch auf diese Säuren bezieht sich die Feststellung über die zwei einwertigen Säuren verschiedener Stärke.

Vergleichende Titrationen mit der Trichloressigsäurelösung wurden auch potentiometrisch durchgeführt. Abbildung 3 zeigt die potentiometrischen Titrationskurven. Als Maßlösung wurde Natriumformiat verwendet. Dieselben Titrationen mit oszillometrischer Endpunktanzeige sind in Abb. 4 dargestellt. Die Kurven 1 zeigen die Titrationsergebnisse der $10^{-2}M$ Trichloressigsäurelösung, die Kurven 2 sind Ergebnisse mit der $10^{-3}M$ Lösung. Wir benutzten sowohl 1*M* als auch 0,1*M* Natriumformiat Maßlösungen. Aus den Abbildungen ist es ersichtlich, daß die potentiometrischen Kurven auch in $10^{-2}M$ Konzentration schwer auswertbar sind, hingegen die Kurven der oszillometrischen Titrationen sind in beiden Fällen gut auszuwerten.

Zusammenfassend kann festgestellt werden, daß im Falle richtiger Auswahl der Titrierbase, die Titrationen der Säuren von verschiedener Stärke durch oszillometrische Endpunktindikation selektiv durchzuführen sind.

$$\text{Im Falle } \frac{K_{A(I)}}{K_{A(II)}} > 10^2, \quad \text{und} \quad \frac{K_B}{K_{A(II)}} > 10^{1,3}$$

im Konzentrationsbereich von 10^{-2}–$10^{-3}M$ beträgt der relative Fehler ±1,0%.

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Zusammenfassung—Zur selektiven Titration einer Säure in einem Säuregemisch aus zwei verschieden starken Säuren verwendet man eine solche Basederen Protonierungskonstante zwisschen denen der beiden konjugierten Basen liegt ($K_{A(I)} > K_B > K_{A(II)}$). Im Falle $K_{A(I)}/K_{(II)A} > 10^2$ und $K_B/K_{A(II)} > 10^{1,3}$, im Konzentrationsbereich 10^{-2}–$10^{-3}M$, beträgt der relative Fehler für die oscillometrische Titration ±1%.

Summary—The stronger of a pair of weak acids may be selectively titrated in aqueous solution when the conjugate base of a third acid of intermediate strength is used as titrant. Titrations of 10^{-2}–$10^{-3}M$ solutions can be followed by high-frequency oscillometric measurements with an error of about 1%, when the strengths of the two acids differ by a factor of 10^{2} or more, and of the acid and titrant by $10^{1.3}$ or more.

Résumé—On peut titrer sélectivement en solution aqueuse le plus fort d'une paire d'acides faibles lorsque la base conjuguée d'un troisième acide de force intermédiaire est utilisée comme agent de titrage. On peut suivre les titrages de solutions 10^{-2}–$10^{-3}M$ par mesures oscillométriques de haute fréquence avec une erreur d'environ 1%, lorsque les forces des deux acides diffèrent d'un facteur de 10^{2} ou plus, et celles de l'acide et de l'agent de titrage de $10^{1.3}$ ou plus.

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Investigation of alkali metal and ammonium tetraphenylborates by infrared spectrophotometry

(*Received* 19 *May* 1970; *Accepted* 4 *June* 1970)

SODIUM and lithium tetraphenylborates are good precipitating agents used for the gravimetric determination of potassium, rubidium, caesium, and ammonium, and some other metal ions and organic bases containing oxygen and nitrogen,[1–9] according to the equation

$$[B(C_6H_5)_4]^- + X^+ = X[B(C_6H_5)_4]$$

In most cases sodium tetraphenylborate is used as reagent, this being more stable than the lithium salt. Precipitation with tetraphenylborate is widely used in analytical practice since it can be made selective by choosing the experimental conditions appropriately, so that some constituents can be determined in the presence of others relatively simply. Heavy alkali metal and ammonium ions all precipitate together when the reagent is added and they can be separated only by a long procedure.[8] As the determination of these ions in the presence of one another is often necessary, the development of methods for doing this may be of interest.

Ammonium and alkali metal ions can be precipitated with tetraphenylborate in neutral, weakly acidic (acidified with mineral acids or acetic acid) and weakly alkaline solution. Of the procedures described in the literature[2,3,8,10–12] the one given by Kohler[2] was used in the present work. Precipitation was effected at room temperature from solutions $0{\cdot}1M$ in hydrochloric acid, under which conditions Mg, Ca, Al, Fe(III), Co(II), Ni, Mn, Cu(II), SO_4^{2-} and PO_4^{3-} ions did not interfere. In these circumstances sodium tetraphenylborate is a selective and very good precipitant of alkali metal and ammonium ions. In solutions that are $0{\cdot}1M$ in mineral acid the precipitate formed consists of coarse crystals which settle quickly. The precipitate is easy to filter off on a porosity-4 sintered-glass filter. As wash-liquid a saturated solution of the precipitate was used.

Summary—The stronger of a pair of weak acids may be selectively titrated in aqueous solution when the conjugate base of a third acid of intermediate strength is used as titrant. Titrations of 10^{-2}–$10^{-3}M$ solutions can be followed by high-frequency oscillometric measurements with an error of about 1%, when the strengths of the two acids differ by a factor of 10^{2} or more, and of the acid and titrant by $10^{1,3}$ or more.

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Ammonium and alkali metal ions can be precipitated with tetraphenylborate in neutral, weakly acidic (acidified with mineral acids or acetic acid) and weakly alkaline solution. Of the procedures described in the literature[2,3,8,10-12] the one given by Kohler[2] was used in the present work. Precipitation was effected at room temperature from solutions $0{\cdot}1M$ in hydrochloric acid, under which conditions Mg, Ca, Al, Fe(III), Co(II), Ni, Mn, Cu(II), SO_4^{2-} and PO_4^{3-} ions did not interfere. In these circumstances sodium tetraphenylborate is a selective and very good precipitant of alkali metal and ammonium ions. In solutions that are $0{\cdot}1M$ in mineral acid the precipitate formed consists of coarse crystals which settle quickly. The precipitate is easy to filter off on a porosity-4 sintered-glass filter. As wash-liquid a saturated solution of the precipitate was used.

The infrared spectra of alkali metal and ammonium tetraphenylborate precipitates were taken (in KBr pellets) with a Zeiss UR 10 infrared spectrophotometer from 400 to 4000 cm^{-1}. The spectra are presented in Fig. 1. The bands in the spectra were assigned, and the identity and purity of the precipitates checked by comparing the spectra with those found in the literature.[13-15] The spectra of the alkali metal tetraphenylborates are practically identical. The effect of the different electronegativities of the ions is very small, as is shown by the slightly different positions and intensity ratios of the corresponding bands. The spectrum of ammonium tetraphenylborate contains more bands than those of the alkali metal tetraphenylborates, since it contains the N—H bands from the ammonium ion. The wave-numbers of these bands are characteristic of ammonium tetraphenylborate, so ammonium ions can be determined in the presence of alkali metal ions without separation, by means of infrared spectrophotometry on the basis of these bands.

The bands in the infrared spectra can be assigned as follows.

Aromatic C—H stretching vibrations appear between 2970 and 3080 cm^{-1}, the number of which is equal to the number of hydrogen atoms attached to the ring (five bands). Between 1980 and 1880 cm^{-1} appear the overtones and combination bands of the out-of-plane C—H deformation and C—C deformation vibrations, which are rather weak and not very characteristic.

Aromatic C—C stretching vibrations occur between 1593 and 1400 cm^{-1}, whereas the in-plane deformation vibrations of aromatic C—H groups lie between 1250 and 950 cm^{-1}.

The very strong and sharp bands between 900 and 700 cm^{-1} are the out-of-plane C—H deformation vibrations of five neighbouring hydrogen atoms.

In the spectrum of ammonium tetraphenylborate the stretching and bending vibrations of the NH_4^+ group appear at 3223 and 1405 cm^{-1}. These bands can not be found in the spectra of the alkali metal tetraphenylborates. The intensities of these bands depend only on the amount of ammonium tetraphenylborate, under fixed experimental conditions. It is favourable to use the band at 1405 cm^{-1} for determining ammonium ions, as the results obtained by measuring at 3223 cm^{-1} are less accurate owing to the presence of a small but uncontrollable amount of adsorbed water, as O—H stretching vibrations also appear in this region.

First the possibilities of the determination of ammonium ions in two-component systems were studied. Two-component calibration mixtures were prepared containing ammonium ions and potassium, rubidium or caesium ions, and then two-component precipitates were prepared from the mixtures. From each precipitate KBr pellets were pressed (3 mg of precipitate/1 g of KBr) and the infrared spectra run at a low recording speed (50 cm^{-1}/min) from 1270 to 1500 cm^{-1}; 3 parallel precipitations were made from each mixture and 3 spectra taken of each precipitate. The absorbance for the band at 1405 cm^{-1} was calculated by the base-line technique. The relationship between the absorbance and concentration of ammonium tetraphenylborate was calculated by the method of least squares. The equations of the calibration lines and data concerning the reliability of calculation are presented in Table I.

TABLE I.—DATA FOR CALIBRATION CURVES FOR THE DETERMINATION OF AMMONIUM TETRAPHENYLBORATE

	Equation of the calibration curves	S	S_a	S_b
In the presence of K^+	$A = 0{\cdot}027 + 0{\cdot}0083C$	±0·006	±0·002	±0·0001
In the presence of Rb^+	$A = 0{\cdot}041 + 0{\cdot}0081C$	±0·010	±0·003	±0·0002
In the presence of Cs^+	$A = 0{\cdot}027 + 0{\cdot}0083C$	±0·007	±0·001	±0·0001
In the presence of K^+, Rb^+, Cs^+	$A = 0{\cdot}013 + 0{\cdot}0083C$	±0·012	±0·002	±0·0001

C = concentration of NH_4BPh_4 in wt%.
S = standard deviation of the points of the line.
S_a and S_b = standard deviations of the slope and intercept respectively.

Next the possibility of determining ammonium ions in the presence of all the alkali ions without separation was studied. In order to prepare the calibration series, 0·1M stock solutions were used in amounts which ensured identical ratios of the alkali metal tetraphenylborates in the precipitates prepared from them. The calibration curve was prepared in a way similar to that used for two-component systems (see Table I).

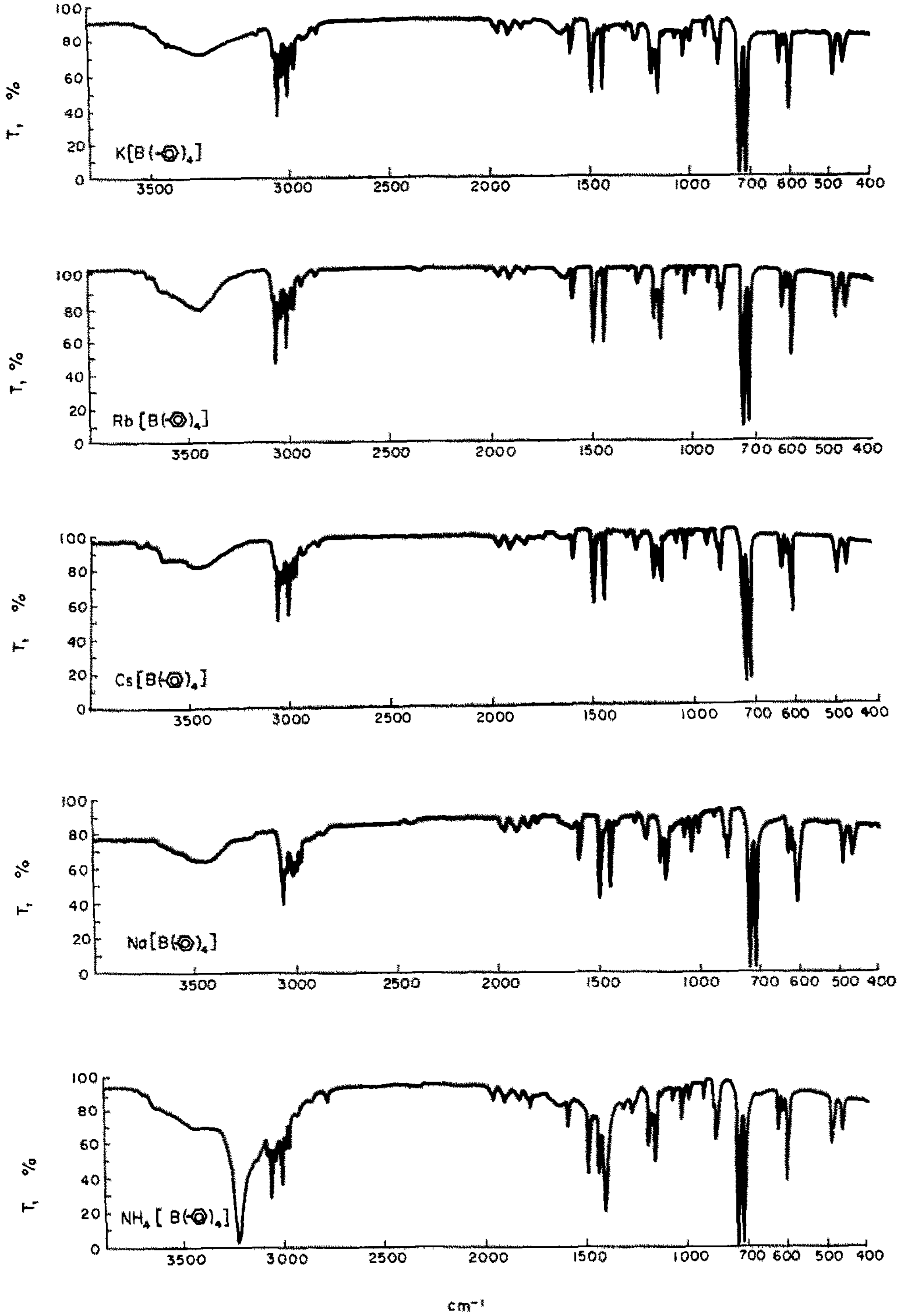

FIG. 1.—Spectra of the tetraphenylborates of (*a*) K^+, (*b*) Rb^+, (*c*) Cs^+, (*d*) Na^+, (*e*) NH_4^+.

TABLE II

In the presence of K^+			In the presence of Rb^+		
NH_4BPh_4, *wt%*	Standard deviation, *wt%*	Error, %	NH_4BPh_4, *wt%*	Standard deviation, *wt%*	Error, %
23·9	1·6	−1·4	21·7	0·9	+1·5
32·0	0·4	+2·2	29·4	1·0	+2·5
48·5	1·9	+1·4	45·5	1·5	−1·8
65·3	1·1	+0·5	62·5	1·4	−1·7
73·8	1·1	−1·5	71·4	0·3	−1·6
In the presence of Cs^+			In the presence of K^+, Rb^+, Cs^+		
NH_4BPh_4, *wt%*	Standard deviation, *wt%*	Error, %	NH_4BPh_4, *wt%*	Standard deviation, *wt%*	Error, %
19·9	4·1	+1·0	10·0	2·4	−3·0
27·1	1·1	+2·8	25·0	1·9	−1·2
42·7	1·2	+0·9	40·0	1·7	+1·8
59·9	1·5	−1·8	57·1	1·0	+1·5
69·1	0·8	+1·1	72·7	0·9	−2·8
			84·2	0·5	−1·7

Finally measurements were made with solutions of known composition in order to estimate the error and standard deviation of the method. The results of these measurements are given in Table II.

As shown by the calibration lines, standard deviations and errors, ammonium ions can be determined in the presence of alkali metal ions without preliminary separation, by means of infrared spectrophotometry. The accuracy of the results approaches that of the results obtained by gravimetric analysis involving separation. The method is especially suited to the determination of micro amounts and to routine analyses, owing to its rapidity and simplicity.

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Summary—The infrared spectra of alkali metal and ammonium tetraphenylborates have been studied and an infrared spectrophotometric method developed for the determination of ammonium ions in the form of the tetraphenylborate. The N–H deformation vibration band appearing at 1405 cm^{-1} in the spectrum of ammonium tetraphenylborate has been utilized for quantitative evaluation; the tetraphenylborates of the alkali metals do not exhibit absorption at this frequency. Thus ammonium ions can be determined as the tetraphenylborate in the presence of alkali metal ions without preliminary separation.

Zusammenfassung—Die Infrarotspektren der Alkali- und Ammoniumtetraphenyloborate wurden untersucht und ein infrarotspektrophotometrisches Verfahren zur Bestimmung von Ammoniumionen in Form ihres Tetraphenyloborats entwickelt. Zur quantitativen Auswertung wurde die N-H-Deformationsschwingungsbande verwendet, die im Spektrum von Ammoniumtetraphenyloborat bei 1405 cm^{-1} erscheint; die Alkali-Tetraphenyloborate absorbieren bei dieser Wellenzahl nicht. So können Ammoniumionen in Gegenwart von Alkalimetallionen ohne Abtrennung als Tetraphenyloborat bestimmt werden.

Résumé—On a étudié les spectres infra-rouges des tétraphénylborates de métaux alcalins et d'ammonium, et l'on a élaboré une méthode spectrophotométrique infra-rouge pour le dosage d'ions ammonium sous forme de tétraphénylborate. On a utilisé la bande de vibration de déformation N-H apparaissant à 1405 cm^{-1} dans le spectre du tétraphénylborate d'ammonium pour l'évaluation quantitative; les tétraphénylborates des métaux alcalins ne présentent pas d'absorption à cette fréquence. Ainsi les ions ammonium peuvent être déterminés à l'état de tétraphénylborate en la présence d'ions des métaux alcalins sans séparation préalable.

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Use of complex displacement reactions in photometric analysis

(*Received* 19 *May* 1970. *Accepted* 2 *June* 1970)

THE USE of complex displacement reactions in photometric determinations is advantageous if no suitable photometric reagent is available for the direct determination of a metal ion, or where metal ions of similar behaviour are separated chromatographically and the eluate is monitored photometrically by means of the same colour reaction.

The principle of the method, if trace amounts of a metal ion M are to be determined, can be given as follows. Let us consider the case where two chelate-forming agents are used, the one as masking agent and the other as photometric reagent, both forming 1:1 complexes with metal ions.

To the sample solution containing the metal ion M is added excess of a reagent solution containing a stable stoichiometric complex BL and a photometric reagent Y. If the equilibrium conditions are favourable, M replaces B in the complex and the liberated B—the amount of which is equivalent to that of the ion M originally present—forms a coloured compound with Y, which can be estimated photometrically. The reactions are:

$$M + BL \rightleftharpoons ML + B \tag{1}$$

$$B + Y \rightleftharpoons BY \tag{2}$$

Charges are omitted for simplicity.

To obtain a complete (>99%) displacement reaction between M and BL, the equilibrium constant of reaction (1) must be greater than 100.

$$K_1 = \frac{K_{ML}'}{K_{BL}'} > 10^2. \tag{3}$$

Résumé—On a étudié les spectres infra-rouges des tétraphénylborates de métaux alcalins et d'ammonium, et l'on a élaboré une méthode spectrophotométrique infra-rouge pour le dosage d'ions ammonium sous forme de tétraphénylborate. On a utilisé la bande de vibration de déformation N-H apparaissant à 1405 cm^{-1} dans le spectre du tétraphénylborate d'ammonium pour l'évaluation quantitative; les tétraphénylborates des métaux alcalins ne présentent pas d'absorption à cette fréquence. Ainsi les ions ammonium peuvent être déterminés à l'état de tétraphénylborate en la présence d'ions des métaux alcalins sans séparation préalable.

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Charges are omitted for simplicity.

To obtain a complete (>99%) displacement reaction between M and BL, the equilibrium constant of reaction (1) must be greater than 100.

$$K_1 = \frac{K_{ML}'}{K_{BL}'} > 10^2. \qquad (3)$$

K_{ML}' and K_{BL}' are the conditional stability constants of the complexes ML and BL respectively. The conditional stability constants defined and used by Ringbom[1] can be expressed with the side reaction coefficients:

$$K_{ML}' = \frac{K_{ML}}{\alpha_M \cdot \alpha_L} \tag{4}$$

$$K_{BL}' = \frac{K_{BL}}{\alpha_B \cdot \alpha_L}\,. \tag{5}$$

where α_M, α_B and α_L are the side-reaction coefficients for the ions M, B and ligand L respectively. K_{ML} and K_{BL} are the thermodynamic stability constants. By substitution we have:

$$K_1 = \frac{K_{ML} \cdot \alpha_B}{K_{BL} \cdot \alpha_M} > 10^2. \tag{6}$$

In presence of the photometric reagent the main side-reaction of B is presumably reaction (2). Thus

$$\alpha_B \sim \alpha_{B(Y)} = 1 + [Y]K_{BY} \tag{7}$$

Since $[Y]K_{BY} \gg 1$, the first term on the right-hand side can be omitted.

In most cases the photometric reagent is a weak organic acid, and the protonation of the ligand Y must also be considered, by means of the side-reaction function $\alpha_{Y(H)}$:

$$\alpha_{B(Y)} \sim [Y']\frac{K_{BY}}{\alpha_{Y(H)}} \tag{8}$$

where

$$\alpha_{(Y)H} = 1 + [H^+]k_1 + [H^+]^2k_1k_2 + \cdots \tag{9}$$

and k_1, k_2 *etc* are the protonation constants of the ligand Y. By use of equation (8), requirement (6) can be modified:

$$K_1 = \frac{K_{ML} \cdot K_{BY}}{K_{BL} \cdot \alpha_M \cdot \alpha_{Y(H)}}\,[Y'] > 10^2. \tag{10}$$

The second important requirement is that the displacement reaction between BL and Y

$$BL + Y \rightleftharpoons BY + L \tag{11}$$

should not take place to any appreciable extent (*i.e.*, <1%). Thus the equilibrium constant for this reaction, K_2, must be < 0·01:

$$K_2 = \frac{K_{BY}'}{K_{BL}'} < 10^{-2} \tag{12}$$

or

$$K_2 = \frac{K_{BY} \cdot \alpha_{L(H)}}{K_{BL} \cdot \alpha_{Y(H)}} < 10^{-2}. \tag{13}$$

There is also a third requirement which must be fulfilled for the quantitative photometric determination to be made, namely the completeness of reaction (2), the formation of the coloured complex, *i.e.*,

$$\frac{[BY]}{[B']} = K_{BY}'[Y'] > 10^2. \tag{14}$$

On comparing requirement (10) with requirement (14) it can be concluded that a photometric determination based on a complex displacement reaction can be realized if the two metal ions chosen form with the masking agent L complexes of nearly the same strength, but only one of them (B) reacts with the photometric reagent ($\alpha_{M(Y)} \sim 1$).

By using the deduced requirements (10), (13) and (14) the most favourable conditions for photometric determinations can be found by calculation.

Example

The indirect photometric determination of erbium(III) can be made in a $10^{-1}M$ ammonium lactate buffer solution of pH 4 by using the copper(II)-ethylenediamine tetra-acetate (CuEDTA) complex of stoichiometric composition and 1-(2-pyridylazo)-2-naphthol (PAN) as indicator.

Log $K_{\mathrm{CuEDTA}} = 18\cdot8$; log $K_{\mathrm{ErEDTA}} = 18\cdot98$;[2] log $K_{\mathrm{CuPAN}} = 16\cdot0$;[3] the formation constants of the erbium(III) lactate complexes are log $\beta_1 = 2\cdot77$, log $\beta_2 = 5\cdot11$, log $\beta_3 = 6\cdot70$;[4] those of the copper(II) lactate complexes are log $\beta_1 = 3\cdot02$; log $\beta_2 = 4\cdot84$;[5] the protonation constant of lactate is log $k = 3\cdot76$, those of PAN are log $k_1 = 12\cdot2$; log $k_2 = 1\cdot9$.[3]

In the calculations requirements (10), (13) and (14) must be considered. In a solution at pH 4

$$\alpha_{\mathrm{lac(H)}} = 1 + 10^{-4} . 10^{3\cdot76} = 10^{0\cdot2}$$

$$\alpha_{\mathrm{Er(lac)}} = 1 + 10^{-1\cdot2} . 10^{2\cdot77} + 10^{-2\cdot4} . 10^{5\cdot11} + 10^{-3\cdot6} . 10^{6\cdot7} = 10^{3\cdot25}$$

$$\alpha_{\mathrm{PAN(H)}} = 1 + 10^{-4} . 10^{12\cdot2} + 10^{-8} . 10^{14\cdot1} = 10^{8\cdot2}$$

According to requirement (10):

$$\log K_{\mathrm{ErEDTA}} + \log K_{\mathrm{CuPAN}} + \log [\mathrm{PAN'}] - \log K_{\mathrm{CuEDTA}} - \log \alpha_{\mathrm{Er(lac)}} - \log \alpha_{\mathrm{PAN(H)}} > 2$$

$$18\cdot98 + 16\cdot0 + \log [\mathrm{PAN'}] - 18\cdot8 - 3\cdot25 - 82 > 2 \quad \log [\mathrm{PAN'}] > -2\cdot73$$

The concentration of the PAN reagent must be at least $2 \times 10^{-3}M$.

The other two requirements can also be fulfilled by using $2 \times 10^{-3}M$ reagent concentration.

$$\alpha_{\mathrm{Cu(lac)}} = 1 + 10^{-1\cdot2} . 10^{3\cdot02} + 10^{-2\cdot4} . 10^{4\cdot84} = 10^{2\cdot53}$$

$$\log K_{\mathrm{CuPAN}} = 16 - 2\cdot53 - 8\cdot2 = 5\cdot27$$

$$\log \alpha_{\mathrm{EDTA(H)}} = 8\cdot2 \text{ (at pH 4)}$$ [1]

Requirement (13):

$$\log K_{\mathrm{CuEDTA}} + \log \alpha_{\mathrm{PAN(H)}} - \log K_{\mathrm{CuPAN}} - \log \alpha_{\mathrm{EDTA(H)}} > 2$$

$$18\cdot8 + 8\cdot2 - 16 - 8\cdot6 = 2\cdot4 > 2$$

and requirement (14):

$$\log K_{\mathrm{CuPAN}} + \log [\mathrm{PAN'}] > 2$$

$$5\cdot27 - 2\cdot7 = 2\cdot57 > 2.$$

The photometric determination can be realized by using the conditions given. This has also been proved by measurements.[6]

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J. INCZÉDY

Summary—The theoretical requirements for the quantitative photometric determination of trace amounts of metal ions by use of complex displacement reactions are discussed and a calculation method using conditional equilibrium constants and side-reaction functions defined and used by Ringbom is recommended. As an example, the requirements in the determination of erbium(III) by using copper(II)–EDTA complex and PAN indicator in ammonium lactate buffer solutions are calculated.

Zusammenfassung—Die theoretischen Anforderungen an die quantitative photometrische Bestimmung von Spuren von Metallionen mit Hilfe von Komplexverdrängungsreaktionen werden diskutiert und ein Berechnungsverfahren empfohlen, das die Gleichgewichtskonstanten unter den betreffenden Bedingungen und Nebenreaktionsfunktionen verwendet. Als Beispiel werden die Anforderungen an die Bestimmung von Erbium(III) mit dem Kupfer(II)-EDTA-Komplex und PAN als Indikator in Ammoniumlactat-Pufferlösungen berechnet.

Résumé—On discute des exigences théoriques pour la détermination photométrique quantitative de traces d'ions métalliques par réactions de déplacement de complexe et l'on recommande une méthode de calcul utilisant les constantes d'équilibre conditionnelles et les fonctions de réaction secondaire. A titre d'exemple, on calcule les exigences de la détermination de l'erbium (III) en utilisant le complexe cuivre (II)-EDTA et l'indicateur PAN en solutions tampons de lactate d'ammonium.

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Application of direct thermometric analysis in iodometry

(*Received* 28 *May* 1970. *Accepted* 5 *June* 1970)

IODOMETRIC determinations are most often made indirectly, owing to the difficulties of end-point detection. Systems with a standard redox potential more positive than that of the iodine–iodide couple are allowed to react with excess of iodide and the resulting iodine is titrated with standard sodium thiosulphate solution. Similarly, systems with a redox potential less positive than that of the iodine–iodide system are preferably determined by oxidation with excess of iodine and back-titration with sodium thiosulphate.

In the last decade thermometric titration has been used for several redox reactions.[1] Determinations were made in the usual way and order; *e.g.*, copper(II) was determined by adding excess of potassium iodide and titrating with sodium thiosulphate, the temperature change due to the heat of reaction being measured and used to evaluate the amount of copper.[2] The large heat of dilution of sodium thiosulphate, however, renders the determination rather inaccurate.

According to our considerations, two ways present themselves for the more accurate and simple performance of iodometric thermometric determinations.

1. Application of a solution of iodide ions as the titrant.
2. Compensation of the heat of dilution of sodium thiosulphate solution[3] by use of an exothermic process which does not affect the main reaction.

The determination of chlorine in chlorine water was chosen as a model in which no side-reactions had to be considered. Direct determination was used for measurement,[3] *i.e.*, equal amounts of the reagent were added to solutions of equal heat capacities, and the temperature changes were found to be proportional to the concentration of the component to be determined. The amount of reagent added must, of course, be in excess of that required in the reaction.

EXPERIMENTAL

Reagents

Saturated chlorine water. The chlorine content was frequently checked by iodometric titration.[4]

Potassium iodide solution, 20% *w/v* (*about* 1·6*M*).

Acidified potassium iodide solution. Potassium iodide solution (20%, 90 ml) and concentrated hydrochloric acid (10 ml).

Sodium thiosulphate solution, 1*N*.

Sodium thiosulphate solution containing glycerine. Sodium thiosulphate solution (1*N*, 65 ml) + glycerine ($d_4^{20} = 1{\cdot}231$; 35 ml).

Apparatus

Directhermom produced by MOM (Hungarian Optical Works).

Procedure

Preparation of the calibration graph. By pipette, 1, 2, 5, 10, 20 ml of chlorine water were transferred to the plastic vessel of the Directhermom and diluted to 200 ml with distilled water. A magnetic stirrer was placed in the vessel and the latter put into the equipment. Next a 2-ml immersion pipette was filled with 20% potassium iodide solution, and mounted on the measuring head. The pipette

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To prepare an accurate calibration curve the amount of chlorine present at the time of reaction had to be determined—owing to the volatility of chlorine—by measuring the liberated iodine equivalent to the chlorine present in the chlorine water. For this purpose the plastic vessels were removed from the equipment and their iodine contents titrated with dilute sodium thiosulphate solution (1 ml of which was equivalent to about 1 mg of chlorine—*i.e.*, ~0·03*N*) in presence of starch indicator. The scale reading was plotted as a function of mg of chlorine present in 200 ml of sample solution, and gave a linear graph.

The immersion pipette system of the Directhermom allows several determinations to be made successively on the same sample. In the present case both the direct and indirect determinations of chlorine can be made, *i.e.*, after addition of potassium iodide the iodine formed can also be determined on the basis of its reaction with sodium thiosulphate. For the thermometric determination of the liberated iodine 1*N* sodium thiosulphate was used in 2-ml immersion pipettes. The reagent was first added to the blank solution, which already contained 2 ml of potassium iodide acidified with hydrochloric acid. Under these conditions a scale reading of −60 was obtained at sensitivity 1, owing to the endothermic nature of the dilution of sodium thiosulphate. Starting from the well known fact that the dilution of glycerine with water is an exothermic process, a glycerine to thiosulphate solution ratio could be found experimentally, at which no heat effect was observed on adding the mixture to the blank, *i.e.*, the heat of dilution was compensated. The composition of this thermoneutral mixture was 65 ml of 1*N* sodium thiosulphate + 35 ml of glycerine. The calibration line passed through the origin and was linear when this thermoneutral mixture was used.

Another series of measurements was made, for determination of chlorine in chlorine water, as follows. One immersion pipette contained potassium iodide acidified with hydrochloric acid, and another thiosulphate solution containing glycerine. After addition of potassium iodide to the test

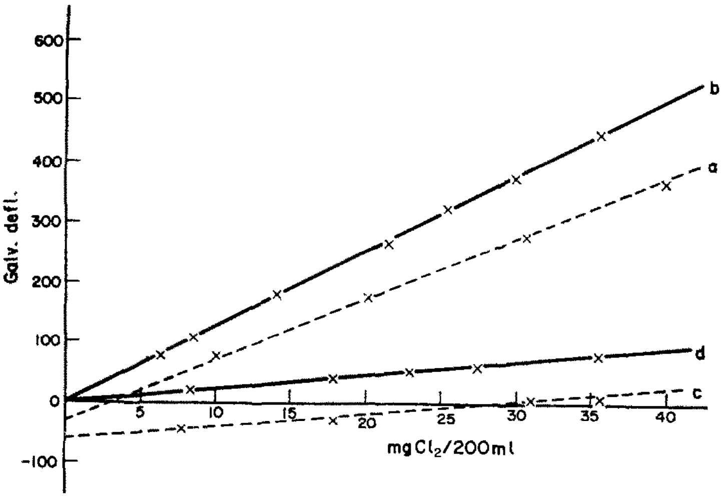

Fig. 1.—Determination of the chlorine content of chlorine water.
a Reagent 20% potassium iodide solution.
b Reagent thermoneutral potassium iodide solution.
c Reagent sodium thiosulphate solution.
d Reagent thermoneutral sodium thiosulphate solution.

solution the galvanometer deflection was read and the galvanometer was set to zero again. Next the thiosulphate solution was added and the temperature change read. The scale reading was equal to the difference in the values given by the two reactions.

Because the slope of the calibration curve is much higher for the iodide–chlorine reaction than for the reaction of iodine with thiosulphate (Fig. 1), the direct determination with iodide is much the more advantageous.

Determination of active chlorine in bleaching powder

As an application of the method described, the active chlorine in commercial bleaching powder was determined.

Procedure. Transfer a 0·1–0·2 g sample of bleaching powder to the plastic vessel of the Directhermom in which 200 ml of distilled water have been placed previously. Fill the immersion pipette with about 2 ml of thermoneutral potassium iodide solution. After stirring for 3 min, add 3 drops of 10% hydrochloric acid to neutralize the solution, switch on the galvanometer and set it to zero. Then add the thermoneutral potassium iodide solution and wait about 100 sec for the galvanometer to reach maximum deflection. Use the chlorine water calibration graph.

Results. For comparison purposes, the results obtained by the thermometric method described are given in Table I, along with those of the conventional iodometric method. The reason why the results of thermometric determinations are lower than those of the conventional iodometric method lies in the non-instantaneous nature of the reaction; as the temperature of the reaction volume becomes higher than that of the surroundings, owing to the exothermic reaction, the cooling effect of the environment which leads the galvanometer deflection being smaller than it should be. The reaction used for the calibration curve is faster, and this difference in rate accounts for the error. The error could be eliminated if the calibration curve were prepared by titrating the iodine liberated by different weights of bleaching powder and plotting galvanometer deflection *vs.* amount of chlorine equivalent to the iodine liberated.

TABLE I.—THE CHLORINE CONTENT OF BLEACHING POWDER

By iodometric titration, %	By Directhermom method, %
30·9	30·4 ± 0·1
30·0	29·5 ± 0·1
28·3	27·8 ± 0·1
26·8	26·3 ± 0·1
25·2	24·8 ± 0·1

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Summary—Elementary chlorine was determined by a thermometric method using potassium iodide as reagent. The temperature rise corresponding to the heat of reaction was proportional to the chlorine content. Iodine formed in the reaction was also determined with sodium thiosulphate. The heat of the chlorine-iodide reaction is about five times that of the iodine–thiosulphate reaction. Direct determination with potassium iodide is simpler and more rapid than the indirect one.

Zusammenfassung—Elementares Chlor wurde thermometrisch mit Kaliumjodid als Reagens bestimmt. Der der Reaktionswärme entsprechende Temperaturanstieg war zur Chlorkonzentration proportional. Das bei der Reaktion freigewordene Jod wurde auch mit Natriumthiosulfat bestimmt. Die Wärmetönung der Reaktion Chlor-Jodid ist etwa fünfmal so groß wie die der Reaktion Jod-Thiosulfat. Die direkte Bestimmung mit Kalium-jodid ist einfacher und geht schneller als die indirekte.

Résumé—On a déterminé le chlore élémentaire par une méthode thermométrique en utilisant l'iodure de potassium comme réactif. L'élévation de température correspondant à la chaleur de réaction est proportionnelle à la teneur en chlorure. L'iode formé dans la réaction a aussi été dosé par le thiosulfate de sodium. La chaleur de la réaction chlore–iodure est environ cinq fois celle de la réaction iode–thiosulfate. Le dosage direct par l'iodure de potassium est plus simple et plus rapide que le dosage indirect.

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Determination of nickel and copper by precipitation from homogeneous solution as their salicylaldimine complexes

(*Received* 28 *May* 1970. *Accepted* 11 *June* 1970)

SALICYLALDIMINE was first used for the determination of metal ions by Duke.[1] The procedure recommended by him resulted in a voluminous, gel-like precipitate which was difficult to handle. The composition and thermal behaviour of the precipitate were studied by Pariaud and Labeille[2] and by Marin and Duval.[3] The precipitate was found to have a metal to ligand ratio of about 1:2, but the composition was not reproducible and Duval[3] did not recommend the procedure as an analytical method.

The purpose of the present work has been to produce a crystalline precipitate of well-defined composition by precipitation from homogeneous solution. The reagent was prepared in the solution by the reaction of salicylaldehyde and ammonia, the latter being formed in the solution slowly. The composition and thermal behaviour of the precipitate were studied as well as the pH dependence of its solubility.

EXPERIMENTAL

Reagents

Copper(II) and nickel sulphate solutions. Prepared from analytical grade reagents by accurate weighing. The copper solution was standardized gravimetrically by precipitation of copper(I) thiocyanate and by electrogravimetry, and the nickel solution by the dimethylglyoxime method and by electrogravimetry.

Ammonium carbonate solution, 20% *w/v*. Prepared from the analytical grade reagent.

Urea solution, 20% *w/v*. Prepared from the analytical grade reagent.

Salicylaldehyde solution, 4% *in alcohol.*

Procedure

Two methods have been developed. As salicylaldimine reacts instantaneously with metal ions, the rate of precipitation is controlled in both cases by the rate of formation of the reagent. The two methods differ in the way that the ammonia needed is liberated.

In one method ammonia was produced by hydrolysing a hot (95°) aqueous solution of urea. The ammonia produced reacted with the salicylaldehyde, and the product with the metal ion present.

In the second method solutions of salicylaldehyde and ammonium carbonate were added to the solution of the metal ion to be determined. The solution of ammonium carbonate contains free ammonia in an amount depending on the pH. This free ammonia reacts with the salicylaldehyde. The rate of precipitation can be controlled by adjusting the pH to a suitable value.

Résumé—On a déterminé le chlore élémentaire par une méthode thermométrique en utilisant l'iodure de potassium comme réactif. L'élévation de température correspondant à la chaleur de réaction est proportionnelle à la teneur en chlorure. L'iode formé dans la réaction a aussi été dosé par le thiosulfate de sodium. La chaleur de la réaction chlore–iodure est environ cinq fois celle de la réaction iode–thiosulfate. Le dosage direct par l'iodure de potassium est plus simple et plus rapide que le dosage indirect.

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Method A. To the solution containing 2–10 mg of nickel or copper in a 400-ml beaker add 10 ml of 4% alcoholic salicylaldehyde solution and 50 ml of 20% aqueous urea solution. Then dilute to 200–300 ml, and warm the solution on a steam-bath for 2–3 hr, during which time a nice crystalline precipitate is formed. Collect the precipitate on a sintered-glass filter, porosity 3, in the cold and wash it with cold water. Dry the precipitate at 110° for 2 hr.

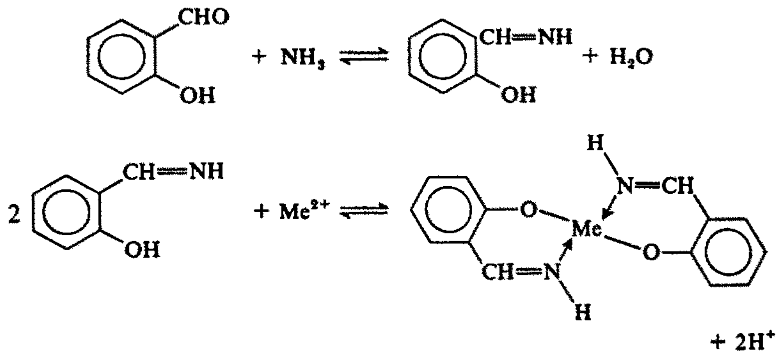
Method B. To the solution containing 2–90 mg of nickel or copper in a 400-ml beaker add 10 ml of 4% alcoholic salicylaldehyde solution and 10 ml of 20% aqueous ammonium carbonate solution. In some minutes a crystalline precipitate forms. Wait for 1–2 hr and then collect the precipitate on a porosity-3 sintered-glass filter and wash it with distilled water.

RESULTS

The organic matter in the filtrates was decomposed with a mixture of hydrogen peroxide and sulphuric acid, then the solution was evaporated to dryness, the residue dissolved in water, and traces of nickel or copper were determined spectrophotometrically. The amount of nickel or copper in the filtrates was found to be smaller than 0.05 mg.

The processes taking place in the course of the determination are accompanied by consumption of ammonia and liberation of acid, so it seemed to be of importance to study the pH-dependence of the solubility of the precipitate. The following reactions take place in the solution:

$$NH_4^+ + H_2O \rightleftharpoons NH_3 + H_3O^+$$



As shown by the equations, two protons are liberated in the reaction of salicylaldimine with the metal ion. The liberated acid must be neutralized in order to carry the reaction to completion. If a constant pH is to be maintained during the reaction (as the rate of reaction is controlled by the pH) the solution must have rather a high buffer capacity. Ammoniacal buffers have highest capacity at pH 9.2. The required buffer capacity could be ensured by increasing the concentrations of both ammonia and ammonium salt.

According to our experiments, to precipitate amounts of nickel or copper smaller than 100 mg at least 2 g of ammonium carbonate are necessary. If the amount of the ammonium salt is smaller the metal salicylaldehyde complex also precipitates.

The pH-dependence of the solubility of the precipitates was studied. Portions (0·5 g) of the dried nickel or copper complex were weighed and transferred to a double-walled vessel and 100 ml of water were added. The temperature of the solution was adjusted to 25·0 ± 1° by means of a VEB U-8 ultrathermostat, the suspension was agitated by a magnetic stirrer, and after 2 hr aliquots were withdrawn at 30-min intervals. The change in the absorbance of the solution was measured spectrophotometrically. When the concentration of the solution did not change further—after about 4–5 hr of agitation—a 50-ml aliquot of the solution was evaporated to dryness and the residue decomposed with a mixture of hydrogen peroxide and sulphuric acid. In the solution so obtained, copper was determined photometrically at 436 nm with sodium diethyldithiocarbamate and nickel at 450 nm with dimethylglyoxime. As shown in Fig. 1, the copper salicylaldimine complex has minimum solubility at pH 8–11 and the solubility of the nickel salicylaldimine complex is lowest in the pH range 8·5–10·5. In the methods described the pH was between 8 and 9.

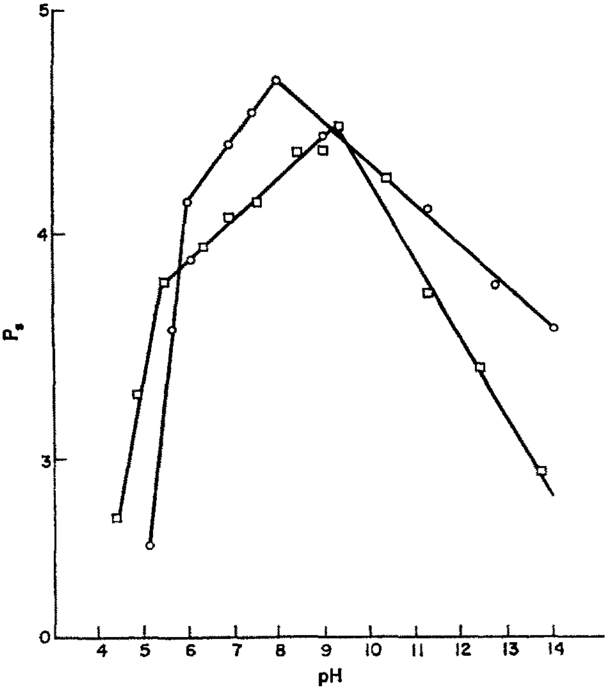


FIG. 1.—Dependence of solubility exponent (p_s) on pH: □ copper complex; ○ nickel complex.

TABLE I

Cu taken, *mg*	Coefficient of variation, %	
	Conventional method	PFHS method
5·86	1·0	0·3
11·72	0·4	0·2
29·32	0·2	0·1
58·60	0·1	0·03

TABLE II

Ni taken, *mg*	Coefficient of variation, %	
	Conventional method	PFHS method
7·81	1·3	0·5
15·62	0·5	0·3
39·05	0·1	0·1
78·10	0·1	0·05

The accuracy of the precipitation from homogeneous medium as compared to that of the conventional method can be judged on the basis of Table I for copper and Table II for nickel. The coefficient of variation was determined from 6 parallel measurements for different sample weights.

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Summary—A method has been developed for the gravimetric determination of copper and nickel as their salicylaldimine complexes, by precipitation from homogeneous solution. The complexes are crystalline precipitates which are very easy to filter off and wash. The accuracy of the determinations is higher than that of the conventional precipitation method.

Zusammenfassung—Ein Verfahren zur gravimetrischen Bestimmung von Kupfer und Nickel durch Fällung aus homogener Lösung als Komplexe mit Salicylaldimin wurde entwickelt. Die Komplexe sind kristalline Niederschläge, die sehr leicht zu filtrieren und auszuwaschen sind. Die Genauigkeit der Bestimmungen ist größer als bei der herkömmlichen Fällungsmethode.

Résumé—On a élaboré une méthode pour le dosage gravimétrique du cuivre et du nickel sous forme de leurs complexes salicylaldimine, par précipitation à partir d'une solution homogène. Les complexes sont des précipités cristallisés qui sont très aisés à filtrer et laver. La précision des dosages est supérieure à celle obtenue par la méthode de précipitation ordinaire.

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Application of chemiluminescent indicators in EDTA titrations

(*Received* 16 *June* 1970. *Accepted* 22 *June* 1970)

TWO CHEMILUMINESCENT indicators have so far been used for end-point detection in chelatometric titrations: luminol and lucigenine.[1-3] Both emit intense chemiluminescent light in alkaline medium, in the presence of oxidizing agents (*e.g.*, hydrogen peroxide). The emission reaction is catalysed by heavy metal ions. The mechanism of chemiluminescence is, however, different for the two indicators.

THEORETICAL

In the chemiluminescence of luminol (3-aminophthalic hydrazide), hydroxyl or oxygen free radicals play an important role.[1,4-6] These free radicals are produced during the decomposition of hydrogen peroxide in alkaline medium in the presence of catalysts, *e.g.*, heavy metal ions. From the luminol molecule, which is capable of emission, an unstable peroxide is formed in the presence of free radicals, and is transformed into inactive aminophthalic acid with emission of light. If the heavy metal ions necessary to induce emission are bound by a suitable complexing agent, luminol will not emit light. Luminol can be used as a chelatometric indicator.

In the emission from lucigenine (*N*,*N*′-dimethyldiacridylium nitrate) perhydroxyl ions play an important part. Perhydroxyl ions are formed during the decomposition of hydrogen peroxide in alkaline medium.[7] In the presence of perhydroxyl ions but the absence of catalysts, lucigenine molecules emit a steady green light; under similar conditions, but in the presence of catalyst ions, a more intense, irreversible emission can be observed for a shorter period of time. This is due to the fast decomposition of perhydroxyl ions in the presence of catalysts. If the heavy metal ions acting as catalyst are bound in the form of complexes the decomposition of perhydroxyl ion can be prohibited and the emission of the indicator stabilized.

Accordingly, if heavy metal ions are titrated with EDTA, the end-point of the titration is indicated by the disappearance of the light of luminol or by the appearance of the steady chemiluminescence of lucigenine. When, in turn, EDTA solution is titrated with, *e.g.*, copper(II), the first excess of titrant is indicated by the appearance of the chemiluminescent light of luminol, or by the disappearance of the luminescence from lumigenine.

Summary—A method has been developed for the gravimetric determination of copper and nickel as their salicylaldimine complexes, by precipitation from homogeneous solution. The complexes are crystalline precipitates which are very easy to filter off and wash. The accuracy of the determinations is higher than that of the conventional precipitation method.

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TABLE I

Metal taken, μmole	Added 0·01*M* EDTA, *ml*	Luminol				Lucigenine			
		0·01*M* $CuSO_4$ used, *ml*	Metal found, μmole	Error, %	Relative std. devn., %	0·01*M* $CuSO_4$ used, *ml*	Metal found, μmole	Error, %	Relative std. devn., %
Cd^{2+} 48·1	10·00	5·15	48·5	+0·8	0·1	5·19	48·1	0·0	0·1
96·2	20·00	10·42	95·8	−0·4		10·48	95·2	−1·0	
192·4	50·00	30·83	191·7	−0·4		31·20	188·0	−2·3	
Zn^{2+} 51·3	10·00	4·75	52·5	+2·4	0·6	4·93	50·7	−1·2	0·1
102·5	20·00	9·52	104·8	+2·3		9·78	102·2	−0·3	
205·1	50·00	29·09	209·1	+2·0		29·40	206·0	+1·0	
Ni^{2+} 49·3	10·00	5·00	50·0	+1·4	0·2	5·13	48·7	−1·2	0·1
98·7	20·00	10·22	97·8	−0·8		10·26	97·4	−1·2	
197·3	50·00	30·54	194·6	−1·4		30·43	195·4	−1·0	

On the basis of this observation a chelatometric method has been developed by Erdey and Buzás[1] for the direct determination of copper(II) and indirect determination of lead and mercury(II). In the present paper the direct chelatometric determination of cadmium, zinc and nickel will be dealt with.

EXPERIMENTAL

Reagents

Copper(II) sulphate solution, 0·01*M*. Dissolve 2·5 g of $CuSO_4.5H_2O$ in 200 ml of distilled water, add 1 ml of 10% sulphuric acid, dilute to 1 litre and standardize electrogravimetrically.[3]

EDTA solution, 0·01*M*.

Test solutions, 0·01*M*. Solutions of cadmium, zinc and nickel were prepared and standardized gravimetrically.[3]

Luminol solution, 0·01%. Warm (on a steam-bath) 0·1 g of luminol in 500 ml of water containing 5 ml of 1*M* sodium hydroxide until completely dissolved, then dilute to 1 litre.

Lucigenine solution, 0·5%. Dissolve 0·5 g of lucigenine in 100 ml of water with mild warming, then filter the solution. Both indicator solutions can be stored indefinitely without decomposition.

All the reagents used were of analytical purity. Demineralized distilled water was used to prepare standard and reagent solutions.

Procedure

Add excess of 0·01*M* EDTA to an ~0·01*M* solution of the metal ion to be determined. Make the solution alkaline with 20 ml of 4*M* ammonia solution in the case of cadmium and nickel, and with 5 ml of 0·1*M* sodium hydroxide in that of zinc. Then heat the solutions to 90°, add 3 ml of luminol or 1 ml of lucigenine solution and 1 ml of 3% hydrogen peroxide solution and titrate with 0·01*M* copper(II) sulphate in a dark room.

In the presence of luminol the end-point is indicated by the appearance of an intense bluish chemiluminescence, whereas in the presence of lucigenine the green chemiluminescence of the solution suddenly ceases.

Data concerning the reproducibility and standard deviation of the method are presented in Table I. The results for titrations are averages of three parallel measurements and the relative standard deviation was calculated on the basis of six parallel titrations.

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Summary—The chemiluminescent indicators lucigenine and luminol are readily applicable to end-point detection in the EDTA titration of cadmium, zinc and nickel ions. Back-titration with copper(II) gives reproducible results. The end-point is indicated by the disappearance of the green chemiluminescence of lucigenine, or by the appearance of the bluish luminescence of luminol.

Zusammenfassung—Die Chemilumineszenzindikatoren Lucigenin und Luminol lassen sich gut zur Endpunktsbestimmung bei der EDTA-Titration von Cadmium, Zink und Nickel verwenden. Rücktitration mit Kupfer(II) gibt reproduzierbare Ergebnisse. Der Endpunkt wird durch das Verschwinden der grünen Chemilumineszenz von Lucigenin oder durch das Auftreten der bläulichen Lumineszenz von Luminol angezeigt.

Résumé—Les indicateurs chimioluminescents lucigénine et luminol sont aisément applicables à la détection du point de fin dosage dans le titrage à l'EDTA des ions cadmium, zinc et nickel. Le titrage en retour avec le cuivre(II) donne des résultats reproductibles. Le point de fin de dosage est indiqué par la disparition de la chimioluminescence verte de la lucigénine, ou par l'apparition de la luminescence bleuâtre du luminol.

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Combined derivatographic and thermo-gas-titrimetric examination of the thermal decomposition of copper tetra-ammine sulphate monohydrate

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THERMOANALYTICAL methods in general do not furnish unambiguous information on the course of decomposition processes if the thermal decomposition reaction is a complex one and more or less overlapping reactions occur with the release of two or more gaseous decomposition products, as happens in the decomposition of copper tetra-ammine sulphate monohydrate during which water and ammonia escape in the temperature range between 20 and 400°. In such cases even complex thermoanalytical methods, *e.g.*, derivatography[1,2] where the thermogravimetric (TG), derivative thermogravimetric (DTG), differential thermal analysis (DTA) and temperature change (T) curves of a single sample are simultaneously recorded, do not yield an exact picture of the gas-evolution processes. Although TG and DTG curves make it possible to evaluate the whole weight-change quantitatively, they cannot furnish separate information on the partly overlapping processes such as the escape of water and ammonia.

For investigation of such problems we developed our combined derivatographic and thermo-gas-titrimetric method.[3,4] In Fig. 1 the automatically operating combined device is shown schematically. On the basis of an earlier principle[1,2] the device records the TG, DTG, DTA and T curves. By means of inert carrier gas streaming over the sample the evolving gaseous decomposition products (*e.g.*, ammonia and water) are quantitatively transported into an aqueous absorbing solution, the pH of which changes and so alters the potential difference between the glass and calomel electrodes dipping into the solution, whereupon an amplifier coupled to the electrodes sets an automatic burette in operation. The burette feeds titrant to the absorbing solution until the original value of the potential difference between the electrodes has been restored. The slide contact of a potentiometer moves along with the piston of the burette, and the galvanometer coupled to the potentiometer records the thermo-gas-titrimetric (TGT) curve. The derivative device, moving along with the axis of the burette, works on the principle of the derivatograph, and permits recording of the derivative of thermo-gas-titrimetric curve (DTGT)

The thermal decomposition of copper tetra-ammine sulphate monohydrate has already been studied by several investigators. On the basis of dilatometric and thermogravimetric measurements Rencker,[5] and Rencker and Vallet[6] concluded that it gradually decomposes between 125 and 400° with splitting off of ammonia and water. The residue is copper sulphate. Anous[7] found essentially the same. Flóra,[8,9] on the basis of derivatographic measurements, reached similar conclusions but also made suggestions concerning the splitting-off process of water and ammonia.

EXPERIMENTAL

The copper tetra-ammine sulphate monohydrate was prepared according to Berzelius,[10] by adding ethanol to a concentrated ammoniacal solution of copper sulphate, filtering off, washing first with ammoniacal ethanol, then with ethanol and last with diethyl ether. The precipitate was dissolved, the solution made alkaline in a distillation apparatus, and the ammonia collected and titrated.

In the course of the thermal analysis the ammonia released was absorbed in hydrochloric acid absorbing solution at pH 3·6. The automatic titrator maintained this pH during the whole process by addition of hydrochloric acid. After a test was completed, the ammonia contents of the absorbing solution were checked by distillation from alkaline solution and titration.

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Combined derivatographic and thermo-gas-titrimetric examination of the thermal decomposition of copper tetra-ammine sulphate monohydrate

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THERMOANALYTICAL methods in general do not furnish unambiguous information on the course of decomposition processes if the thermal decomposition reaction is a complex one and more or less overlapping reactions occur with the release of two or more gaseous decomposition products, as happens in the decomposition of copper tetra-ammine sulphate monohydrate during which water and ammonia escape in the temperature range between 20 and 400°. In such cases even complex thermoanalytical methods, *e.g.*, derivatography[1,2] where the thermogravimetric (TG), derivative thermogravimetric (DTG), differential thermal analysis (DTA) and temperature change (T) curves of a single sample are simultaneously recorded, do not yield an exact picture of the gas-evolution processes. Although TG and DTG curves make it possible to evaluate the whole weight-change quantitatively, they cannot furnish separate information on the partly overlapping processes such as the escape of water and ammonia.

For investigation of such problems we developed our combined derivatographic and thermo-gas-titrimetric method.[3,4] In Fig. 1 the automatically operating combined device is shown schematically. On the basis of an earlier principle[1,2] the device records the TG, DTG, DTA and T curves. By means of inert carrier gas streaming over the sample the evolving gaseous decomposition products (*e.g.*, ammonia and water) are quantitatively transported into an aqueous absorbing solution, the pH of which changes and so alters the potential difference between the glass and calomel electrodes dipping into the solution, whereupon an amplifier coupled to the electrodes sets an automatic burette in operation. The burette feeds titrant to the absorbing solution until the original value of the potential difference between the electrodes has been restored. The slide contact of a potentiometer moves along with the piston of the burette, and the galvanometer coupled to the potentiometer records the thermo-gas-titrimetric (TGT) curve. The derivative device, moving along with the axis of the burette, works on the principle of the derivatograph, and permits recording of the derivative of thermo-gas-titrimetric curve (DTGT)

The thermal decomposition of copper tetra-ammine sulphate monohydrate has already been studied by several investigators. On the basis of dilatometric and thermogravimetric measurements Rencker,[5] and Rencker and Vallet[6] concluded that it gradually decomposes between 125 and 400° with splitting off of ammonia and water. The residue is copper sulphate. Anous[7] found essentially the same. Flóra,[8,9] on the basis of derivatographic measurements, reached similar conclusions but also made suggestions concerning the splitting-off process of water and ammonia.

EXPERIMENTAL

The copper tetra-ammine sulphate monohydrate was prepared according to Berzelius,[10] by adding ethanol to a concentrated ammoniacal solution of copper sulphate, filtering off, washing first with ammoniacal ethanol, then with ethanol and last with diethyl ether. The precipitate was dissolved, the solution made alkaline in a distillation apparatus, and the ammonia collected and titrated.

In the course of the thermal analysis the ammonia released was absorbed in hydrochloric acid absorbing solution at pH 3·6. The automatic titrator maintained this pH during the whole process by addition of hydrochloric acid. After a test was completed, the ammonia contents of the absorbing solution were checked by distillation from alkaline solution and titration.

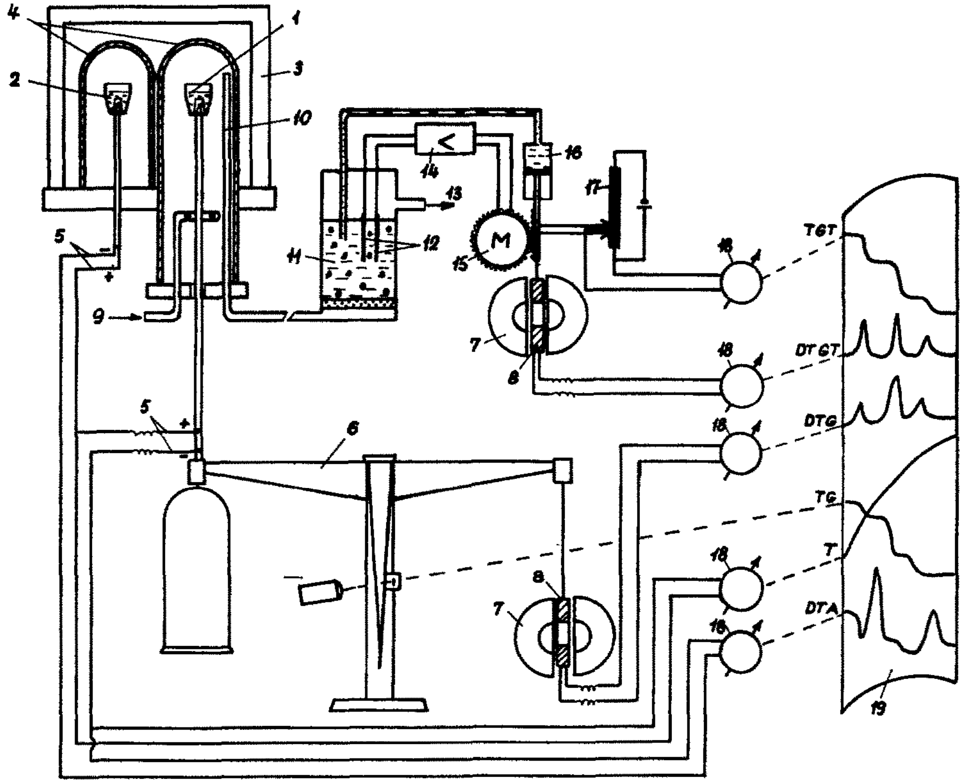

FIG. 1.—Schematic diagram of the combined derivatographic and thermo-gas-titrimetric device.

1—Sample, 2—inert substance, 3—furnace, 4—quartz bulbs, 5—thermocouples, 6—balance, 7—permanent magnet, 8—coil, 9—inlet of inert gas, 10—gas outlet, 11—absorber, 12—electrodes, 13—exhaust, 14—amplifier, 16—motor of the automatic burette, 17—automatic burette, 17—potentiometer, 18—galvanometers, 19—photo-paper.

Because during the thermal decomposition a small amount of sulphur trioxide might have been released and absorbed in the absorbing solution, thus affecting the titration, sulphate was determined in the residual solution from the ammonia distillation.

The sample weighed about 130 mg and was heated at a rate of 10°/min. The carrier gas was nitrogen, freed from oxygen by a catalytic reaction, and dried over phosphorus pentoxide. A platinum crucible 16 mm in height and 14 mm in diameter was used.

DISCUSSION

The DTA curve showed that only endothermic reactions occurred, and was in accordance with the DTG curve, showing that apart from processes connected with weight change, no other transformations (*e.g.*, recrystallization) occurred in the sample.

The TG curve shows decomposition processes taking place in three steps. The magnitude of the first step corresponds to a weight loss caused by the joint release of one mole of water and two moles of ammonia, all quantities, here and later, being related to one mole of compound. The second step indicates the release of a further mole of ammonia. The third step shows a greater loss of weight than that corresponding to the last mole of ammonia. There must therefore be loss of some other decomposition product, in the temperature region 300–360°.

The first step of the TGT curve indicates the release of two moles of ammonia, the second one the splitting off of one mole. The third step of the titration curve is smaller than would correspond to the release of one mole of ammonia. Assuming that the sample had the correct stoichiometry, and that all the ammonia was released, there are two possible explanations for this apparent discrepancy. Some acidic decomposition product could be released during the third step and neutralize part of the ammonia, or part of the ammonia released could be thermally decomposed and so not titrated.

The DTGT curve shows the change in the rate of consumption of titrant. On comparing the DTGT curve with the DTA and DTG curves, deviations can be noticed. The DTA and DTG curves indicate by their double peak that between 90 and 210° two decomposition products, water and ammonia, were released. The DTGT curve shows in the same temperature range only a single peak which means that this curve represents the rate of splitting off of one component, ammonia.

The TGT and TG curves represent the release of ammonia and ammonia + water respectively, if formation of other gaseous decomposition products is excluded. It is worth noting that—from among the many possibilities—there is only one way in which the two curves can be brought into agreement without contradiction of the other experimental results, as is shown in Fig. 2. That is, we suppose that in the second period of thermal decomposition only ammonia was released and accordingly the TGT and TG curves were fully in accordance. On the basis of the two curves—by difference calculations—the curve representing the release of water can be constructed (see dotted line in Fig. 2).

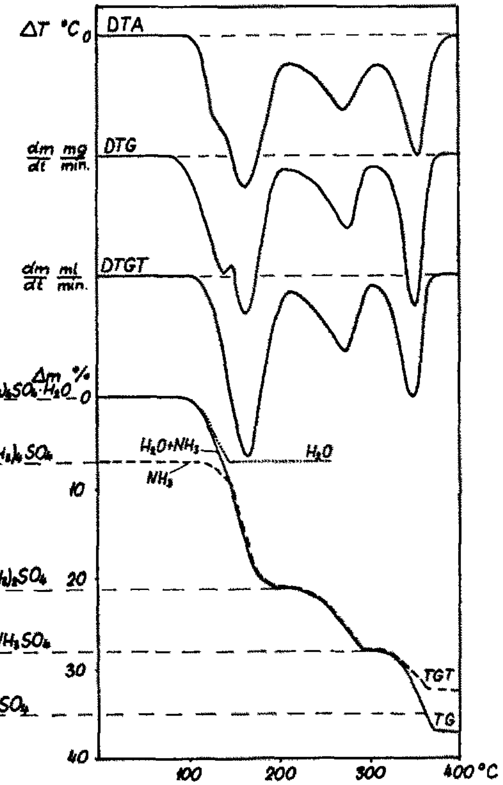

FIG. 2.—Thermogram of the combined derivatographic and thermo-gas-titrimetric examination of copper tetra-ammine sulphate monohydrate.

Examination of the thermal decomposition of copper tetra-ammine sulphate monohydrate under the experimental conditions described above can lead to the following conclusions.

During the first decomposition stage, between 90 and 200°, one mole of water and two of ammonia are released. According to the curves in Fig. 2 decomposition starts with the release of water and only after loss of part of the water does ammonia begin to split off. The two processes overlap to such a degree that the relative amounts of the two decomposition products cannot be determined solely from the TG and DTG curves.

The magnitude of the second decomposition step corresponds to the release of one mole of ammonia. During the third decomposition stage ammonia and a small quantity of sulphur trioxide are released, which is why the third step of the TG curve is bigger, while that of the titration curve is smaller, than is theoretically required. This also explains the 1 % difference in the results in columns 3 and 4 of Table I.

According to the amount of sulphate recovered from the absorbing solution, the titration curve should give only an ammonia content 1·1 % less than the theoretical, but the difference according to columns 2 and 3 of Table I is 2·3 %. Consequently the titration curve gives lower results than the theoretical for loss of 1 mole of ammonia because not only is part of the ammonia neutralized by the sulphur trioxide released, but part of the ammonia also decomposes. The ammonia decomposition starts under the given circumstances only at temperatures above 320°, as proved by the deviation of the TG and TGT curves over this temperature. The amount of ammonia decomposed (difference between columns 2 and 4 of Table I) is 1·3 % relative to the sample weight, or 4·6 % of the total ammonia, or about 20 % of the ammonia released in the last step. These results are essentially in agreement with those obtained by Wendlandt and Southern[11] by a different method.

TABLE I.—TITRIMETRIC RESULTS OF AMMONIA DETERMINATION IN COPPER TETRA-AMMINE SULPHATE MONOHYDRATE AT DIFFERENT STAGES IN THE EXAMINATION

	Ammonia content, %				
	1	2	3	4	5
	27·72	27·4	25·3	26·1	1·1
		27·4	25·0	26·2	1·1
		29·6	25·2	26·4	1·0
Mean		27·5	25·2	26·2	1·1

1. Theoretical ammonia content.
2. Ammonia content of the sample determined by titration.
3. By continuous titration during thermal examination.
4. Results obtained after distillation and titration of the ammonia contents of the absorption solution after completion of the thermal examination.
5. Ammonia equivalent to sulphur trioxide liberated (which yielded 9·7, 10·1 and 8·7 mg of $BaSO_4$ in the respective determinations).

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Summary—The thermal decomposition of copper tetra-ammine sulphate monohydrate has been investigated by a combined derivatographic and thermo-gas-titrimetric method. It has been found that decomposition starts with splitting off of the water of crystallization and only after part of this water has departed does stepwise release of ammonia begin. First two moles, then one and finally again one mole of ammonia (per mole of compound) are released. It has been established that a small amount of sulphur trioxide splits off during the last decomposition step, and that about 20 % of the last ammonia to be released is thermally decomposed.

Zusammenfassung—Die thermische Zersetzung von Kupfertetrammin-sulfat-Monohydrat wurde mit Hilfe eines kombinierten derivatographischen und thermo-gastitrimetrischen Verfahrens untersucht. Es zeigte sich, daß die Zersetzung mit dem Abspalten des Kristallwassers beginnt; erst wenn Teil dieses Wassers ausgetreten ist, beginnt die stufenweise Freisetzung von Ammoniak. Zuerst werden zwei Mol, dann eines und zuletzt nochmals ein Mol Ammoniak (pro Mol Ausgangsverbindung) frei. Es wurde nachgewiesen, daß während des letzten Zerfallsschrittes eine kleine Menge Schwefeltrioxid abgespalten wird und daß etwa 20% des letzten freiwerdenden Mols Ammoniak thermisch zersetzt werden.

Résumé—On a étudié la décomposition thermique du sulfate de cuivre tétrammine monohydraté par une méthode combinée dérivatographique et thermo-gaz-titrimétrique. On a trouvé que la décomposition commence avec le départ de l'eau de cristallisation et le dégagement graduel d'ammoniac ne commence qu'après que soit partie une fraction de cette eau. D'abord deux moles, puis une et finalement de nouveau une mole d'ammoniac (par mole de composé) sont libérées. On a établi qu'une petite quantité d'anhydride sulfurique s'élimine durant le dernier stade de décomposition et qu'environ 20% de l'ammoniac libéré en dernier est thermiquement décomposé.

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G. SVEHLA

Also, they would like to record their sincere thanks for the help given by

R. E. WAINERDI

who retires from the Advisory Board.

Dr. G. SVEHLA, Reader in Analytical Chemistry, Queen's University, Belfast, was born in Hungary in 1929. He graduated from the Technical University of Budapest in 1951 and took his Ph.D. in 1959. After working at the Technical University of Budapest and spending one year as Research Fellow in Aberdeen, Scotland, he joined Queen's University in 1966. He is a Fellow of the Royal Institute of Chemistry and recently became co-editor of Wilson and Wilson's *Comprehensive Analytical Chemistry*. His publications are on ascorbinometric titrations, catalytic analysis, flame photometry and on problems of error calculation. With his research team in the Department of Analytical Chemistry at Queen's University, Dr. Svehla works on the application of Landolt reactions in analytical chemistry, radiofrequency titrations in non-aqueous media, the use of displacement reactions in flame photometry and on polarography.

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Mr. H. J. Francis, Jr. (U.S.A. Regional Editor) presents a specially bound 1968 volume of *Talanta* to Prof. H. Flaschka (on left), whose papers with Dr. J. Garrett on "Substoichiometric Masking" (1968, **15**, 589, 595) were adjudged the best-written, stylistically, of the year. The presentation was made in Pennsylvania on 22nd November 1969.

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THE INTERNATIONAL UNION OF PURE AND APPLIED CHEMISTRY

Paris, France, 8–10 July 1970

Topics: Solvation, Electroanalytical Methods in Non-Aqueous Solvents, Electrochemical Investigation of Ionic Equilibria (acid–base, redox, complexation, *etc*), Organic Electrode Reactions.

Note: Studies encompassing these subjects in fused salts will be included in the coverage.

The number of participants is restricted to 200: registration fee; $30.

For further information apply to the Executive Chairman, Dr. J. Badoz-Lambling, Laboratoire de Chimie Analytique, ESPCI 10 rue Vauquelin, PARIS 5, France.

INTERNATIONAL SOLVENT EXTRACTION CONFERENCE 1971

This Conference will be held under the auspices of The Society of Chemical Industry, Koninklijk Instituut van Ingenieurs, The Institution of Chemical Engineers, and Koniklijk Nederlandse Chemische Vereniging, in The Hague, Holland, 19–23 April 1971. Offers of papers must be made by 28 February 1970. Further information may be obtained from ISEC '71, 14 Belgrave Square, London, S.W.1.

Talanta, 1970, Vol. 17, pp. i to ii. Pergamon Press. Printed in Northern Ireland

PAPERS RECEIVED

Determination of fluoride in oxides by means of the fluoride ionactivity electrode: M. A. Peters and D. M. Ladd. (22 *June* 1970)

Chelatbildende Austauscherharze XI. Abtrennung des Be(II) vom Al(III) am Chelatustauscher auf der Basis von *o*-(2-Hydroxy-phenylazo)benzosäure: E. Blasius, K.-P. Janzen and W. Fallot-Burghardt. (17 *July* 1970)

Polarographische Be(III)-Bestimmung mit *o*-(2-Hydroxy-5-methyl-phenylazo)benzosäure: E. Blasius. K.-P. Janzen and W Fallot-Burghardt. (17 *July* 1970)

Rapid polarographic method for the microdetermination of organically-bound phosphorus: S. W. Bishara and M. E. Attia. (22 *July* 1970)

Cation-exchange behaviour of several elements in formic acid solutions: Mohsin Qureshi and Waqif Husain. (22 *July* 1970)

Spectrophotometric studies on the complexes of vanadium(V) with some *N*-arylhydroxamic acids: J. P. Shukla and S. G. Tandon. (23 *July* 1970)

A borax fusion technique for quantitative X-ray fluorescence analysis: J. H. H. G. van Willigen, H. Kruidhof and E. A. M. F. Dahmen. (23 *July* 1970)

Zur Elementaranalyse des Schwefels im Nanogramm-Bereich: Adolf Grünert and Günther Tölg (23 *July* 1970)

Spectrophotometric determination of cadmium in nuclear-grade Zircaloy-2 after selective extraction with a liquid anion-exchanger: G. Ghersini and S. Mariottini. (30 *July* 1970)

Photometric complex-formation titration of submicromolar amounts of metal—II: J. Kragten. (30 *July* 1970)

Determination of nanogram amounts of nickel by flameless atomic-absorption spectroscopy: S. Dipierro and G. Tessari. (5 *August* 1970)

Purification and characterizing properties of the analytical reagent quinizarin-2-sulphonic acid and its sodium salt: J. A. Thomson and G. F. Atkinson. (7 *August* 1970)

Spectrophotometric investigations of lanthanon(III) complexes with oximidobenzotetronic acid: G. S. Manku, A. N. Bhat and B. D. Jain. (7 *August* 1970)

Potentiometric titration of cerium and manganese at room temperature—I. Determination of formal redox potential of Mn^{7+}/Mn^{3+}, Ce^{4+}/Ce^{3+} and Mn^{3+}/Mn^{2+} in condensed phosphoric acid: P. P. Naidu and G. G. Rao. (14 *August* 1970)

Potentiometric titration of cerium and manganese at room temperature—II. Analysis of steels, alloys ores, rocks and minerals: P. P. Naidu and G. G. Rao. (14 *August* 1970)

Detection and identification of cannabis constituents by luminescence spectrophotometry: A. Bowd, P. Byrom, J. B. Hudson and J. H. Turnbull. (14 *August* 1970)

Potentiometric titrations with a mercury–mercury sulphide electrode: T. R. Williams, S. Piekarski and C. Manning. (14 *August* 1970)

Uranium(VI) complexes of oxine and its derivatives: A. Corsini, J. Abraham and M. Thompson. (14 *August* 1970)

Spectrophotometric determination of lanthanum, thorium and iron(III) with chromotropic acid azo dyes of the pyridine series: A. K. Majumdar, and A. B. Chatterjee. (21 *August* 1970)

Synergistic effects in the solvent extraction of zinc with salicylaldoxime: A. P. Rao and S. P. Dubey (21 *August* 1970)

Determination of chloride by displacement of hydrogen cyanide from mercuric cyanide: M. K. Bhatty and P. C. Uden. (21 *August* 1970)

Analytical application of the urease method for determination of biuret: P. Bozadziev, E. Balabanova and L. Ilcheva. (25 *August* 1970)

The effect of orthophosphate on the gravimetric determination of pyrophosphate: P. Bozadziev, M. Georgieva and L. Ilcheva. (25 *August* 1970)

Resin beads as indicators in precipitation titrations: Mohsin Qureshi, Saidul Zafar qureshi and Nighat Zehra. (25 *August* 1970)

Spectrophotometric determination of germanium with Cathechol Violet and cetyltrimethylammonium bromide: C. L. Leong. (25 *August* 1970)

Talanta, 1970, Vol. 17, pp. i to ii. Pergamon Press. Printed in Northern Ireland

PAPERS RECEIVED

Design of olfactory detection reactions based on isocyanide formation: E. J. POZIOMEK. (11 *June* 1970)

Massenspektrometrische Untersuchungen zur Elementaranalyse organischer Verbindungen—I. Einlasssystem zur Analyse von Gasgemischen in grossen Temperatur- und Druckbereichen: W. WALISCH and O. JAENICKE. (12 *June* 1970)

Massenspektrometrische Untersuchungen zur Elementaranalyse organischer Verbindungen—II. Bestimmung von Verbrennungsprodukten in Trägergasstrom durch Peakintegration: OTTAKAR JAENICKE and W. WALISCH. (12 *June* 1970)

Spectrophotometric determination of ruthenium with 3,4-diaminobenzoic acid: G. H. AYRES and J. A. ARNO. (22 *June* 1970)

The determination of zinc in copper by atomic-fluorescence flame spectroscopy: P. D. WARR. (22 *June* 1970)

Fluorimetric determination of aluminium and lead: D. R. HAWORTH and E. A. LAMSARGES. (22 *June* 1970)

Determination of noble metals by neutron-activation analysis: R. GIJBELS. (22 *June* 1970).

Extraction with long-chain amines—IV. Separation and colorimetric determination of gold: JIŘÍ ADAM and RUDOLF PŘIBIL. (23 *June* 1970)

The possibilities for separation and simultaneous determination of *N*-unsubstituted- and *N*-substituted nitroimidazoles and criteria for distinguishing between them: D. DUMANOVIĆ and S. PERKUČIN. (23 *June* 1970)

Determination of dimetridazole in reaction mixtures: D. DUMANOVIĆ and S. PERKUČIN. (23 *June* 1970)

Infrared determination of barium, strontium, sodium, and potassium sulphates by the pellet technique: DAVID E. CHASAN and GEORGE NORWITZ. (26 *June* 1970)

Anion-exchange separations of metal ions in thiocyanate media: JAMES S. FRITZ and EDWARD E. KAMINSKI. (29 *June* 1970)

Chromatographic separation and colorimetric determination of gold: J. S. FRITZ and W. G. MILLEN. (9 *July* 1970)

Spectrophotometric determination of EDTA: S. N. BHATTACHARYYA and K. P. KUNDU. (14 *July* 1970).

Gas chromatography of metal chelates with carrier gas containing ligand vapour: TAITIRO FUJINAGA, TOORU KUWAMOTO and SHIGEO MURAI. (14 *July* 1970)

Professor L. Erdey: GYULA SVEHLA. (15 *July* 1970)

Application of displacement reactions in flame photometry—I. Determination of phosphate by a flame emission method: E. SZEBENY, P. J. SLEVIN, G. SVEHLA and L. ERDEY. (15 *July* 1970)

Application of displacement reactions in flame photometry—II. Flame-photometric determination of alkaline earth metals in the presence of interfering anions: P. J. SLEVIN, E. GYÖRY-SZEBENYI and G. SVEHLA. (15 *July* 1970)

Identification of some polyatomic inorganic anions as their diphenyliodonium salts by infrared spectroscopy, and interpretation of the spectra: A. J. BOWD, D. THORBURN BURNS and R. GRZESKOWIAK. (20 *July* 1970)

Talanta, 1970, Vol. 17, pp. i to ii. Pergamon Press. Printed in Northern Ireland

PUBLICATIONS RECEIVED

Microanalysis by the Ring Oven Technique: HERBERT WEISZ. 2nd Ed. Pergamon, Oxford, 1970. Pp. ix + 170. 60s. $8.00.

The success of the ring oven and of the first edition of this monograph is evidenced by the number of publications that have appeared since 1961 on applications of the technique. Users of the method will welcome having all the applications brought together.

Chemical Methods of Rock Analysis: PAUL G. JEFFERY. Pergamon, Oxford, 1970. Pp. xv + 509.

As a practical guide to the chemical analysis of rocks, this book represents the fruits of many years experience by a well known worker in the field. Methods are given for the determination of over 50 elements, and there are useful chapters on sample preparation and decomposition, statistics, and various schemes of analysis. The work seems likely to become a standard text for rock analysts for many years to come.

The Destruction of Organic Matter: T. T. GORSUCH. Pergamon, Oxford, 1970. Pp. viii + 152.

This little book gives a most useful compilation of information on the fate of various elements during destruction of organic matter by various means, particular attention being paid to the losses that may occur if an injudicious choice of conditions is made. The author is well known for his pioneering work in this field, during his tenure of the first Society for Analytical Chemistry research fellowship. As he points out, all too often little or no attention is paid to these matters, and they are glossed over-or not mentioned at all in many papers on trace analysis. This book will help to redress the balance and remove the excuse of ignorance.

Communications in Soil Science and Plant Analysis: J. BENTON JONES, JR., editor. Dekker, New York, 1970. $20.00 per annum (6 issues).

A new journal intended to give rapid publication of papers on soil science and crop production.

British Ceramic Abstracts: British Ceramic Research Association, Stoke on Trent, 1970. £10 per annum (6 issues); £2 per single issue.

A new abstracts journal dealing with all aspects of ceramics from raw materials to finished products.

Teoría y Práctica de la Cromatografía en Fase Gaseosa: L. GASCÓ. Publicaciones Cientificas de la Junta de Energia Nuclear, Madrid, 1970. Pp. XXIV + 549. 715 Pesetas.

For those who read Spanish, this is a useful exposition of the theory and practice of gas chromatography, with documentation up to 1969. The main emphasis is perhaps on theory and instrumentation, but there is fair coverage of applications to industrial, organic, inorganic and physical chemistry. Thanks to the habit of taking over scientific terminology from one language to another, the text is fairly readily interpreted even by someone who does not speak Spanish.

Quantitative Analytical Chemistry: Vol. I Introduction to Principles, Vol. II Short Introduction to Practice: H. A. FLASCHKA, A. J. BARNARD, JR. and P. E. STURROCK, Barnes & Noble, New York, 1969. Vol. I pp. xiii + 594, 52s. Vol. II pp. ix + 290, 27s.

The authors' aims are to present the fundamentals of the subject so that students of limited background can gain a good grounding in quantitative analytical chemistry. Classical and instrumental methods are dealt with. Small basic points, often skipped over in more advanced texts are dealt with clearly and simply. Worked or illustrative examples appear on nearly every page. In the practical directions the student is told what the procedure is all about, how to follow the procedure and then how to deduce what went wrong. Some may find it a bit pedantic but few, if honest, will not find some long-puzzling point explained, and the students for whom it is intended will offer thanks to the authors for their clarity.

Analytical Chemistry in Space: edited RICHARD E. WAINERDI. Pergamon, Oxford, 1970. Pp. vii + 277 £7.

One of the most exciting future projects for scientific research is the analysis of extraterrestrial material. The results of such analyses will provide new insights into problems connected with the origin of the solar system. This book describes progress in this fascinating new extension of analytical chemistry. Since many of the operations may be carried out by remote control in space or on other planets there is a concentration on instrumental techniques. The results of determinations using these techniques must be transmitted to earth by radio signals. Examples of these techniques which are described in the various chapters include mass spectrometry, neutron activation and neutron scattering. In addition to such descriptions, however, the book contains a considerable amount of material of cosmochemical interest with details of the structure and atmospheres of planets. This book will be of interest not only for the analytical chemist but also to students interested in astronomy and astro-physics. There is an excellent foreword by Sir Bernard Lovell.

Periodate Oxidation of Diol and Other Functional Groups. Analytical and Structural Applications: GLENN DRYHURST. Pergamon, Oxford, 1970. Pp. xii + 191. 70s. $9.50.

This book is a comprehensive review of one of the most valuable reactions encountered in carbohydrate chemistry, namely periodate oxidation. The material includes an account of preparative and analytical procedures and outlines the application of the method to structural chemistry. There are also details of anomalous periodate oxidations and of the use of the reaction in preparative organic chemistry. There is an extensive bibliography and the book will be of value to both analytical chemists and those involved in the study and practice of carbohydrate chemistry.

LOUIS GORDON MEMORIAL AWARD

THE Editorial Board and the Publisher of TALANTA have great pleasure in announcing that the Louis Gordon Memorial Award for 1969, for the best-written paper published that year in TALANTA, has been made to Dr. S. J. Lyle and Mr. V. C. Nair, of the University of Kent, for their paper on "Reversed-Phase Partition Chromatographic Separations with 2-Ethylhexyl Dihydrogen Phosphate and Di-2-Ethylhexyl Hydrogen Phosphate", *Talanta*, 1969, **16,** 813.

Talanta, 1970, Vol. 17, pp. i to ii. Pergamon Press. Printed in Northern Ireland

PAPERS RECEIVED

Separation and determination of mixtures containing *p*-aminosalicylic acid and *m*-aminophenol: Martin I. Blake and James Hunt. (13 *January* 1970)

Etude polarographique et physicochimique de *N*-oxydes—II. Mécanisme de réduction et phénomènes d'hydration des acétyl et benzoyl pyridines *N*-oxydes: E. Laviron, R. Gavasso and M. Pay. (19 *January* 1970)

Anwendung der Röntgenfluoreszenz zur Bestimmung der Konzentration der Elemente Phosphor bis Uran in Lösung: B. Magyar. (12 *February* 1970)

Absorptiometric determination of sulphide ion: S. A. Rahim and T. S. West. (23 *February* 1970)

Oxidation state of selenium dissolved in pure sulphuric acid: Yasuaki Shimoishi. (23 *February* 1970)

Chromic thiocyanate complexes in chemical analysis—V. Gravimetric, conductometric and potentiometric determination of Ag(I) by Reinecke salt analogues: I. Gănescu, Al. Popescu and Cs. Verhelyi. (23 *February* 1970)

Studies on the extraction and determination of metal salts with methyl isobutyl ketone—XIII. Extraction of thorium and uranium: Norio Ichinose. (24 *February* 1970)

Studies on the extraction and determination of metal salts with methyl isobutyl ketone—XIV. Extraction of gold: Norio Ichinose. (24 *February* 1970)

Column chromatographic separation of gallium, indium and thallium: J. S. Fritz, R. T. Frazee and G. L. Latwesen. (25 *February* 1970)

Spectrophotometric aspects of *m*-mercaptoacetamidophenol: Estimation of copper, ruthenium, rhodium, palladium, iridium and cobalt: S. N. Kakkar, H. Sarwan Singh and Narinder Singh Poonia. (27 *February* 1970)

Gravimetric aspects of *m*-mercaptoacetamidophenol: Estimation of ruthenium, rhodium, iridium and cobalt: S. N. Kakkar, H. Sarwan Singh and Narinder Singh Poonia. (27 *February* 1970)

Manual and automated determination of traces of phosphorus by substoichiometric isotope dilution: Adolf Zeman, Juraj Leško, Jiří Prejza, Niels Groth-Andersen and Jaromír Růžička. (2 *March* 1970)

Researches on the formation of ferrocyanide—I. Cu(II) and Zn(II) ferrocyanides: Athos Bellomo. (2 *March* 1970)

Researches on the formation of ferrocyanides—II. Ag(I) and Pb(II) ferrocyanides: Athos Bellomo. (2 *March* 1970)

Properties and analytical applications of the heteropolymolybdates of phosphorus, arsenic, silicon and germanium—I. Spectrophotometric examination of the heteropoly acids: A. Halász and E. Pungor. (3 *March* 1970)

Properties and analytical applications of the heteropolymolybdates of phosphorus, arsenic, silicon and germanium—II. Modifications of the heteropoly acids: A. Halász and E. Pungor. (3 *March* 1970)

Properties and analytical applications of the heteropolymolybdates of phosphorus, arsenic, silicon and germanium—III. Examination of two- and three-component systems without separation: A. Halász and E. Pungor. (3 *March* 1970)

Properties and analytical applications of the heteropolymolybdates of phosphorus, arsenic, silicon and germanium—IV. Microdetermination of phosphorus and silicon by measurement of the molybdenum content of the heteropoly acids: A. Halász, K. Polyák and E. Pungor. (3 *March* 1970)

Spectrophotometric determination of traces of antimony: Věra Stará. (3 *March* 1970)

Spectrophotometric determination of niobium by ferron: G. C. Shivahare and M. K. Mathur. (4 *March* 1970)

Precipitation of some acidinide element complex ions with hexammine cobalt(III). Determination of thorium: Kaoru Ueno and Michio Hoshi. (4 *March* 1970)

Interferences in atomic-absorption spectrometry combined with extraction: Masaaki Yanagisawa, Hitoshi Kihara, Masami Suzuki and Tsugio Tekauchi. (5 *March* 1970)

Use of $LiBO_2$ flux for K–Ar dating: Joan C. Engels and C. O. Ingamells. (9 *March* 1970)

Silver complexes with chelating compounds—III. Studies on pentaethylenehexamine chelates: Knut Henning Schrøder. (11 *March* 1970)

Silver complexes with chelating compounds—IV. Studies on tetraethylenepentamine chelates: Knut Henning Schrøder. (11 *March* 1970)

Molecular emission characteristics of various metal fluorides in a low-temperature hydrogen diffusion-flame: R. M. Dagnall, B. Fleet, T. H. Risby and D. R. Deans. (11 *March* 1970)

Recent development in substoichiometric analysis: Jiří Starý and Jaromír Růžička. (11 *March* 1970)

Spectrotitration of ethane-1-hydroxy-1,1-diphosphonic acid with thorium-diaminocyclohexanetetra-acetate: S. J. Liggett and R. A. Libby. (13 *March* 1970)

Quantitative analysis in pharmacy and pharmaceutical chemistry by nuclear magnetic resonance spectroscopy: D. M. Rackham. (16 *March* 1970)

Atomic fluorescence characteristics and analytical determination of manganese in an air–acetylene flame: L. Ebdon, G. F. Kirkbright and T. S. West. (16 *March* 1970)

Changing parameters in analytical chemistry: Adam Shatkay. (19 *March* 1970)

Fully automatic apparatus for stripping voltammetry. Application to the determination of triphenyltin compounds: M. D. Booth, M. J. D. Brand and B. Fleet. (19 *March* 1970)

A microwave excited emissive detector for gas chromatography. Further studies with sulphur compounds: R. M. Dagnall, S. J. Pratt, T. S. West and D. R. Deans. (19 *March* 1970)

Talanta, 1970, Vol. 17, pp. i to ii. Pergamon Press. Printed in Northern Ireland

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Chelating properties of α-oximinocarboxamides—I. α-Oximinophenyl–acetamide isomers: Dominick A. Coviello and Hamed M. El-Fatatry. (8 *August* 1969)

Chelating properties of α-oximinocarboxyamides—II. Syn-α-oximinophenylacetamide:copper(II) complexes: Hamed M. El-Fatatry, Cecilio E. Gracias and Dominick A. Coviello. (8 *August* 1969)

Chelating properties of α-oximinocarboxyamides—III. Effect of structural features on the chelating tendencies of syn-α-oximinocarboxyamides: Dominick A. Coviello and Hamed M. El-Fatatry. (8 *August* 1969)

Volumetric determination of mercury(II) with thioacetamide: Barbara Coulter and David G. Bush. (10 *November* 1969)

Analytical applications of mixed ligand extraction equilibria. Nickel–dithizone–phenanthroline complex: Ben S. Freiser and Henry Freiser. (4 *December* 1969)

Fällung des Wismuts als Bis(triphenylselenonium)-pentachlorobismutat(III): Max Ziegler and Luder Ziegler. (12 *December* 1969)

Untersuchungen an Reagenzien für Niob und Tantal—VI. Spektrophotometrische Bestimmung von Niob(V) und Tantal(V) mit Dibromgallussäure: Gerhard Ackerman and Siegfried Koch. (15 *December* 1969)

Die Schnellanalyse des Flußspats durch destillative Abtrennung und alkalimetrische Bestimmung seines Fluorgehaltes: Ottmar Steinhauser and Paul Von Fargstein. (15 *December* 1969)

Versatile instrument for direct of differential a.c. resistance or conductance measurements of solutions: Eugene D. Olsen and Robert J. Martin. (22 *December* 1969)

Potentiometrische Kieselsäurebestimmung unter Verwendung einer Titanelektrode: G. Ackermann (23 *December* 1969)

Ein reversibler Indikator in der Bromatometrie. Die Bestimmung des As(III) und Sb(III): J.Bognár. (29 *December* 1969)

Extraction of radiozinc, radioiron and radiomanganese from acidic alcohol and acetone solutions: A Alian. (29 *December* 1969)

Macroreticular chelating ion-exchangers: R. F. Hirsch, E. Gancher and F. R. Russo. (29 *December* 1969)

Determination of Reinecke Salt by oxidation with Chloramine-T: P. N. K. Nambisan and C. G. R. Nair. (29 *December* 1969)

An analytical study of the vanadium(IV)–chromium(VI) reaction: K. Sriraman. (30 *December* 1969)

Influence of pH in fluorescence and phosphorescence spectrometric analysis: S. G. Schulman and J. D. Winefordner. (31 *December* 1969)

Extraction of tungsten with 8-hydroxyquinoline and some of its derivatives: Hady Ewadh, N. P. Rudenko, V. I. Kuznetsov and L. S. Gudym. (31 *December* 1969)

Enthalpimetric determination of fluoride: Carl E. Johansson. (7 *January* 1970)

Niederschlagsbildung—I. Korngrösseverteilung in einem Schnellmischapparat erhaltenen Bariumsulfatniederschläge: Candin Liteanu and Harald Lingner. (7 *January* 1970)

Niederschlagsbildung—II. Einfluß einiger Faktoren auf die Korngrösseverteilung bei Bariumsulfatniederschlägen: C. Liteanu and Harald Lingner. (7 *January* 1970)

Thermochromatographie sur papier—XIII. Considérations sur l'efficacité de la séparation en chromatographie à gradient de température: C. Liteanu and S. Gocan. (7 *January* 1970)

Étude sur les electrodes-membranes polymère + plastifiant—II. L'utilisation de l'électrode-membrane PVC et tricrésylphosphate dans le titrage potentiométrique du HCl par NaOH: C. Liteanu and Elena Hopîrtean. (7 *January* 1970)

L'utilisation des membranes pour l'indication du point d'equivalence—VI. La membrane de papier-parchemin imprégnée de $BaSO_4$ pour des titrages acido-basiques en mileau nonaqueux: C. Liteanu and Maria Miscu. (7 *January* 1970)

8-Amino-7-hydroxy-4-methylcoumarin as a chelating reagent for uranyl(II): D. K. Rastogi, A. K. Srivastava, P. C. Jain and B. R. Agarwal. (9 *January* 1970)

Determination of stability constant of complexes from ultrasonic velocity measurements: Shobhay Laxmi and Som Prakash Srivastava. (9 *January* 1970)

Complex formation with triethylenetetraminehexa-acetic acid—III. Silver chelates: Knut Henning Schrøder. (12 *January* 1970)

Silver complexes with chelating compounds—II. Studies on tetraethylenepentamine and pentaethylenehexamine. Ligand protonations: Knut Henning Schrøder. (12 *January* 1970)

Silver complexes with chelating compounds—V. *Trans*-1,2-diaminocyclohexane-*N*,*N*,*N'*,*N'*-tetra-acetic acid chelates: Knut Henning Schrøder. (12 *January* 1970)

Coulometric determination of Ce(III) in alkaline solutions with electrogenerated octacyanomolybdate(V) ion: R. Cordova-Orellana and F. Lucena-Conde. (14 *January* 1970)

Solvent extraction of 12-molybdophosphoric acid with dibutylsulphoxide: M. N. Sastri and S. V. J. Swamy. (14 *January* 1970)

Submicro determination of aluminium, bismuth or copper in organometallic compounds: R. Belcher, Barbara Crossland and T. S. F. W. Fennell. (14 *January* 1970)

Extraction with long-chain amines—II. Colorimetric determination of iron with a sulphonated derivative of ethylenediamine-*N*,*N'*-bis(*o*-hydroxyphenylacetic acid): Rudolf Přibil and Jiří Adam. (19 *January* 1970)

3,5,7,4'-Tetrahydroxyflavone (kaempferol) as a chromogenic reagent for gallium and indium: B. S. Garg and R. P. Singh. (19 *January* 1970)

Separation and gravimetric estimation of uranium(VI) with pyridine-2-aldoxime and 6-methylpyridine-2-aldoxime: Narayan Kumar, G. S. Manku, A. N. Bhat and B. D. Jain. (20 *January* 1970)

Complex compounds of bismuth(III) with nitrilotriacetic acid: B. P. Karadakov and D. I. Venkova. (22 *January* 1970)

Reaktionsstufen—Coulometrie—I. Theoretische Prinzipien: Peter Gründler and Heinz Holzapfel. (22 *January* 1970)

Reaktionsstufen—Coulometrie—II. Analytische Untersuchung von Stoffgemischen: Peter Gründler and Heinz Holzapfel. (22 *January* 1970)

Talanta, 1970, Vol. 17, pp. i–iii. Pergamon Press. Printed in Northern Ireland

PUBLICATIONS RECEIVED

Instrumental Analysis Manual: GEORGE G. GUILBAUT and LARRY G. HARRIS. Dekker, New York, 1970. Pp. 444, $7.75.

Printed in offset litho, this book is described as a preliminary edition, to be followed after a year of use and revision by a final version. Some 49 experiments, each described in sufficient detail to ensure success in the hands of students, fall under the six main headings Optical methods, Electronics, Electrochemical methods, Separation methods, Radiochemistry and Miscellaneous. Useful up-to-date references are given and the inclusion of such experiments as those on atomic fluorescence, enzyme kinetics and ion-selective electrodes will make this volume interesting and instructive reading for tutors as well as for students. The discussion points raised after each descriptive section provide a good test of the student's understanding of the work.

Solvent Extraction of Metals: A. K. DE, S. M. KOPKAR and R. A. CHALMERS. Van Nostrand Reinhold, London, 1970. Pp. 259, $6.00.

This very broad field has been efficiently surveyed and the results presented in a concise and readable form, tabulated according to the extracting ligand. The first chapter (40 pages) introduces the field of solvent extraction chemistry. The theory of extraction equilibria is covered briefly and attention is given to more recent developments such as synergism, liquid ion-exchangers (*e.g.*, alkyl amines) and liquid cation-exchangers (*e.g.*, alkyl phosphoric acids). Each succeeding chapter contains a useful discussion on the reagent, its uses and chemistry, the relevant tables of detailed information and an extensive list of references. This is likely to prove a very valuable handbook, and a copy should be in every laboratory concerned with separation chemistry.

Advances in Chromatography, Vol. 9: eds. T. CALVIN GIDDINGS and ROY A. KELLER. Dekker, New York, 1970. Pp. xiv + 358. £8. 18. $18.75.

In introducing this volume the editors rightly lay stress on the importance of dealing with the problems of separating mixtures of totally unknown nature, rather than, as is normally the case in publications on chromatography, dealing with the purification of compounds of predetermined nature. Future volumes will be of greatly enhanced value if the scope is so widened. This remark in no way disparages the present very useful addition to the series of volumes on *Advances in Chromatography* which deals with reversed-phase extraction chromatography in inorganic chemistry, the determination of the optimum conditions to effect a separation by gas chromatography, advances in the technology of lightly loaded glass-bead columns, radiochemical separations and analyses by gas chromatography and analysis of volatile flavour components of foods.

Allied Spectroscopy Reviews, Vol. 3: ed. EDWARD J. BRAME, JR. Dekker, New York, 1970. Pp. xii + 346. £8.7. $17.50.

This latest addition to the series of books on applied spectroscopy is a miscellany of surveys on physical techniques in analytical chemistry. Some have a very restricted scope, as for example the study of the structure of nucleic acids by infrared spectroscopy; others have a more general appeal, as for example the description of the combination of the techniques of gas chromatography and mass spectrometry. Electronic spectra are discussed under the headings of recent advances in emission spectroscopy and the spectra of radical ions. A less familiar topic is a review of the applications of X-ray spectroscopy to clinical analysis.

Complexones: N. M. DYATLOVA, V. YA. TYOMKINA and I. D. KOLPAKOVA, ed. R. P. LASTOVSKY, Khimiya, Moscow, 1970. Pp. 417.

This monograph deals with an important class of organic compounds broadly applied in chemical analysis, chemical engineering and other branches of science and technology, *i.e.*, with complexones. In the first part of the book the fundamental laws of complex formation are described and methods of investigation considered, as well as the main thermodynamic functions characteristic of equilibrium in aqueous solutions, and the kinetics of complex formation.

The second part, the largest, deals with the properties of both well-known and new complexones, and the dependence of complex-forming properties on the structures of these compounds is demonstrated. Carboxyalkyl amines are described, and the influence of the introduction of additional iminoacetic groups and of steric factors on the stability of complexes is explored. Attention is paid to complexones containing hetero-atoms, such as oxygen, nitrogen or sulphur, in their aliphatic or cyclic radicals, which considerably modify the properties of ligands. New complexones with hydroxy- and alkylphosphonic-groups have been extensively studied. Conclusions are reached concerning their specific behaviour and the mechanism of complex formation. Both coloured and fluorescent complexones are described. Special attention is paid to polycomplexones, that is to polymeric ion-exchanges containing carboxyalkyl groups. Polycomplexones have been successfully applied in chemical analysis and chemical engineering.

The third part of the monograph is a review of methods for the synthesis of complexones and their solid metal complexes. The application of complexones in different branches of science and technology is described in the fourth part.

The application of complexones as titrants and masking agents in chemical analysis, for the separation of rare earths, for cleaning of instrument surfaces in heat-power engineering, for preventing chlorosis of plants in agriculture—all these applications of complexones are reviewed in the book. In the appendix the reader will find valuable information on dissociation constants of a large number of complexones and the stability constants of their complexes with a number of cations.

Atomic Absorption Spectroscopy: R. J. Reynolds, K. Aldous and K. C. Thompson. Griffin, London, 1970. Pp. 201. £4.50.

The authors are clearly AAS enthusiasts and try hard to convince the reader that this is *the* method. But why compare it with visual colorimetry to show its superiority? Why emphasize the simplicity of the technique when the problems of matrix effects and non-linear calibration curves (which are adequately discussed) often necessitate special precautions? The "excellent reproducibility" referred to does not seem to be born out by many of the recorder tracings illustrating the text. The inclusion of a wealth of practical details—the tricks of the trade that make the methods succeed—probably justifies the authors' claim that this book is for the operator, to save him time and trouble. A substantial chapter contains useful information for the determinations of the individual elements, similar to the (free) data sheets of some manufacturers. Short but interesting sections discuss Instrumentation, Further Techniques, and Theory.

Undergraduate Instrumental Analysis: James W. Robinson. Marcel Dekker, New York, 1970. Pp. 379. £5.50. $11.50.

The title is somewhat misleading—the book is written as an introduction for students, to many of the modern instrumental methods of analysis, and ought to remain on the graduate's bookshelf for further consultation. It is biased towards spectroscopic methods, and rather more to their use by the organic chemist. The tendency to become a critical catalogue of techniques and machines is partly balanced by a good introduction dealing with errors and sampling. Further chapters cover Spectroscopy, NMR, IR, UV, AAS, Spectrophotometry, Flame photometry, Emission Spectrography, X-ray spectroscopy, Chromatography, Thermal methods, Mass spectrometry, and Electrochemistry, the last-mentioned being disproportionately brief and hardly matching the standard of the rest of the book. The clear explanations will make this text easily readable also by trainee technicians, at whom it is aimed, besides students.

Activation Analysis: Miloslav Rakovic. Iliffe, London, 1970. Pp. 339. £6.00.

This is a useful guide to the method. All aspects of the theory and practice are dealt with briefly in the first two-thirds of the book. The last third is taken up with a summary of methods for elements, usefully grouped according to type of sample e.g. iron, water, plastics *etc.* Several important topics are treated too briefly and the references only go to 1964, with a few in 1965. Then, it was a very good book, but by now it has dated appreciably.

The Application of X-Ray Fluorescence in Ceramic Analysis: Results of some Co-operative Studies on Aluminosilicates and Magnesites: R. P. Eardley and G. J. Oliver. British Ceramic Research Association, Stoke-on-Trent, 1970. Special Publication No. 69. Pp. 51. £1.50.

Analytical Chemistry of Zirconium and Hafnium: ANIL K. MUKHERJI. Pergamon, Oxford, 1970. Pp. xiii + 281. £4.50. $12.00.

A comprehensive account of the literature up to 1967 on the analytical chemistry of these two elements, both by classical and by instrumental methods. The sections on the means of separating the two will be of interest to inorganic as well as analytical chemists. As is usual in this series, the details of procedures add to the general value of the work.

Analytical Chemistry of Nickel: CLYDE L. LEWIS and WELLAND L. OTT. Pergamon, Oxford, 1970. Pp. ix + 233. £5.50. $14.85.

A companion volume to an earlier one entitled "Analysis of Nickel" which dealt with determination of other elements in nickel metal, this book deals with the determination of nickel in various matrices, and gives a thorough survey of the classical and instrumental methods available. There is also a most useful general survey of the chemistry of nickel.

Volume 17, 1970

January–June, Nos. 1–6

SUBJECT INDEX

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Talanta, 1970, Vol. 17, p. ii. Pergamon Press. Printed in Northern Ireland

NOTICE

FOURTEENTH CONFERENCE ON ANALYTICAL CHEMISTRY IN NUCLEAR TECHNOLOGY

Mountain View Hotel and Motor Lodge, Gatlinburg, Tennessee 37738, U.S.A.
13–15 October 1970

THE FOURTEENTH Conference on Analytical Chemistry in Nuclear Technology will be held in Gatlinburg, Tennessee, 13–15 October 1970, under the sponsorship of the Analytical Chemistry Division, Oak Ridge National Laboratory.

Papers up to 25 minutes in length, that describe original, unpublished work related to the following topics are solicited by the Program Committee.

1. Applications of Digital Computers in Analytical Chemistry.
2. New Sensors and Detectors for use in Studies Related to Environmental Pollution.
3. Problems Associated with the Purity of Reagents for use in Chemical Analysis.
4. Sample Preparation and Dissolution—Vital Steps in Chemical Analysis.
5. Papers on Topics of General Interest Related to Analytical Chemistry in Nuclear Technology.

Those who wish to make contributions should submit an abstract of 200–500 words not later than 20 June 1970. The title, name of the author, an estimate of the time that will be required for the presentation, and in case of multiple authorship, an indication of the name of the speaker should accompany the abstract.

Abstracts of papers and inquiries concerning the conference including request for programmes, should be directed to the Oak Ridge National Laboratory, P.O. Box X, Oak Ridge, Tennessee 37830, Attention: L. J. Brady, Chairman.

The registration fee, except for full-time students, is $10.00 per person. A registration fee of $5.00 will be required for attendance of one day or any part thereof.

Reservation for lodging should be made by direct communication with The Mountain View Hotel and Motor Lodge, Gatlinburg, Tennessee 37738, U.S.A.

TRADE MARKS

Our attention has been drawn to the trade mark status of the word "Nimonic", a trade mark of Henry Wiggin & Co. Ltd, referring to their nickel–chromium high-temperature alloys. The term should not be used as a generic term for such alloys (see *Talanta*, 1969, **16**, 438).

Authors are asked to be particularly careful to indicate when trade marks are being used, by putting them in inverted commas and giving them a capital initial letter.

Talanta, 1970, Vol. 17, p. iii. Pergamon Press. Printed in Northern Ireland

NOTICES

SOCIETY FOR APPLIED SPECTROSCOPY

The 10th National Meeting of the Society for Applied Spectroscopy (also the XXII Mid-America Symposium on Spectroscopy) will be held at Stouffer's Riverfront Inn in St. Louis, Missouri, 18–22 October 1971. Original papers are invited for general sessions on spectroscopy (including X-ray, emission, atomic absorption, flame emission, atomic fluorescence, absorption, electron, resonance, mass and nuclear) and gas chromatography. Papers are also invited for symposia on use of computers and new frontiers in spectroscopy, literature and data retrieval, and spectroscopy in environmental control, biomedicine, space and oceanography.

Titles and abstracts (on 215 × 280 mm paper and within an area of 150 × 250 mm) should be sent to Dr. E. F. Kaelble, Monsanto Company, Inorganic Research Department, 800 North Lindbergh Blvd., St. Louis, Missouri 63166, U.S.A., by 15 April 1971.

Talanta, 1970. Vol. 17, pp. iii. Pergamon Press. Printed in Northern Ireland

PAPERS RECEIVED

Kinetic studies of xenon trioxide as an oxidant—I. Determination of alcohols: R. H. Krueger, S. Vas and B. Jaselskis. (27 *April* 1970)

Determination of platinum and palladium in geological materials by neutron-activation analysis after fire-assay preconcentration: J. J. Rowe and F. O. Simon. (12 *May* 1970)

Combined derivatographic and thermo-gas-titrimetric examination of the thermal decomposition of copper tetra-ammine sulphate monohydrate: J. Paulik and F. Paulik. (28 *May* 1970)

Application of direct thermometric analysis in iodometry: P. Marik-Korda and L. Erdey. (28 *May* 1970)

Determination of nickel and copper by precipitation from homogeneous solution in the form of their complexes with salicyladimine: L. Erdey and L. Pólos. (28 *May* 1970)

Colorimetric determination of pyrogallol and 2,6-dimethoxyphenol with diphenylpicrylhydrazyl: George H. Schenk and Nancy K. Sweiczowski. (1 *June* 1970)

Contributions to the basic problems of complexometry—XXIV. Determination of aluminium in the presence of very large amounts of manganese: Rudolf Přibil and Vladimír Veselý. (2 *June* 1970)

Extractive spectrophotometric determination of micro and sub-micro amounts of fluoride: J. P. S. Haarsma and J. Agterdenbos. (2 *June* 1970)

The equilibrium constant for extraction of mercury(II)-*o*-*o*′-dimethyldithizone into toluene: J. Agterdenbos, B. A. H. G. Jütte and R. A. van der Welle. (2 *June* 1970)

Retention of radionuclides on metal sulphide precipitates: O. Gimesi, É. Bányai, M. Csajka and A. Szabadkázy. (4 *June* 1970)

Electrochemical behaviour of isopropanol at platinum electrodes: A. Rehioui and O. Johansson. (5 *June* 1970)

Improved conditions for conductometric titrations of weak bases in acetic acid: Vilim J. Vajgand and Tibor J. Pastor. (9 *June* 1970)

Cerimetric determination of dithionate: V. R. Nair and C. G. R. Nair. (10 *June* 1970)

Cerimetric determination of polythionates: V. R. Nair and C. G. R. Nair. (10 *June* 1970)

Quantitative analysis of phospholipids: S. C. Rastogi, K. C. Srivastava and R. D. Tiwari. (11 *June* 1970)

Design of olefactory detection reactions based on isocyanide formation: E. J. Poziomek. (11 *June* 1970)

Extraction of protactinium by amines from sulphuric acid solutions: M. A. Awwal and D. J. Carswell. (15 *June* 1970)

The error in absorption measurements, caused by the use of non-monochromatic light: J. Agterdenbos and J. Vink. (15 *June* 1970)

An induction furnace for the determination of cadmium in solutions and zinc-base metals by atomic-absorption spectroscopy: J. B. Headridge and David Risson Smith. (15 *June* 1970)

Microdetermination of naturally occurring kaempferol: platinic chloride as oxidizing agent in alkaline medium: S. A. I. Rizvi and O. C. Saxena. (16 *June* 1970)

Application of chemiluminescent indicators in chelatometry: L. Erdey, O. Weber and I. Buzás. (16 *June* 1970)

Determination of the trace contaminants in hydrogenation catalysts by neutron-activation analysis: L. Erdey, E. Szabó, O. Gimesi and M. Casjka. (16 *June* 1970)

Studies on the melts of alkali metal acetates: Z. Halmos, T. Meisel, K. Seybold and L. Erdey. (16 *June* 1970)

Determination of the optimum resultant effect of factors influencing HETP-values. The following up of parallel diffusion and mass-transfer processes: J. Takács, L. Mázor, M. Kucsera-Pápay and T. Kozma. (16 *June* 1970)

Differential thermal analysis of transitions in finely-divided solids suspended in liquid media: D. A Blackadder and T. L. Roberts. (16 *June* 1970)

A contribution to the use of chelating agents in anodic stripping voltammetry: Ludmila Zieglerová, Karel Štulík and Jan Doležal. (16 *June* 1970)

Talanta, 1970. Vol. 17, p. iii. Pergamon Press. Printed in Northern Ireland

PUBLICATIONS RECEIVED

Dissociation Constants of Inorganic Acids and Bases in Aqueous Solution: D. D. PERRIN. Butterworths, London, 1969. Pp. 103. 44s.

This is the third volume of a series prepared at the request of the Commission on Electrochemical Data of IUPAC (and is therefore published as part of *Pure and Applied Chemistry*, 1969, Vol. 20). Over 200 compounds (including hydrolysable metal ions) are listed with as much information as is necessary to appreciate the usefulness of the data. The literature has been covered up to 1967. The author points out that this collection aims to cover only pK_a and pK_b values. and the reader is referred to *Stability Constants* (Sillén and Martell) for other equilibrium constants Not only research workers in inorganic and physical chemistry, but also teachers of the latter in search of data for problems will find this a valuable and useful handbook.

Gas Chromatography: L. SZEPESY (English trans. ed. E. D. MORGAN). Iliffe, London, 1970. Pp. 8 + 384. 100s.

This is a further addition to the substantial number of texts dealing with gas chromatography. This example has a very complete introductory section outlining the theory of the technique and this is followed by an exhaustive description of the apparatus construction. There are sections describing the qualitative and quantitative applications of gas chromatography to analytical chemistry and an excellent account of the use of the method in process control. Some more unusual applications detailed here include those of elemental analysis and the determination of surface area. This is a text which can be recommended to third year undergraduates, research workers and the analytical chemist in industry.

Practical Manual of Gas Chromatography: ed. JEAN TRANCHANT. Elsevier, London, 1969. Pp. XIX + 387.

This is the English translation of the second French Edition of the manual. It collects together a body of factual material concerned with the purely empirical aspects of gas chromatography. There are chapters dealing with both qualitative and quantitative analysis with the gas chromatograph and a section describing other applications of the technique. There are over eight hundred references to the literature and the text is profusely illustrated.

Enzymatic Methods of Analysis: GEORGE G. GUILBAULT. Pergamon Press, Oxford, 1970. Pp. xv + 347. 75s.

This book introduces the reader to the subject of enzymes and the methods used for following the kinetics of enzyme reactions. Then follow chapters dealing with the determination of Enzymes, Substrates, Activators and Coenzymes, and Inhibitors. The last two chapters discuss the Immobilized Enzyme (which has simplified the production and marketing of enzymes) and the use of Automation in Enzymic Analysis. This is a field of rapidly growing interest to analysts, particularly since equipment designed for following the kinetics of reactions automatically is commercially available, and this book should provide a useful and readable guide for anyone interested in trace analysis. Printed by offset-litho, it is not as lengthy as its 347 pages would suggest, but the literature coverage up to 1968 is good.

Talanta, 1970, Vol. 17, p. iii. Pergamon Press. Printed in Northern Ireland

PUBLICATIONS RECEIVED

Acids and Bases—Their Quantitative Behaviour: R. P. BELL, 2nd Ed. Methuen, London, and Barnes & Noble, New York, 1969. Pp. 111. £1·30.

The first edition of this book appeared in 1952, since which time the use of several new techniques has increased our knowledge of some aspects of the field, and created a considerable amount of renewed interest. This second edition is as brief and readable as its predecessor, but contains useful additions on the rates of very fast reactions such as proton exchange, and the uses of hydrogen isotopes for helping in the elucidation of some acid–base reactions. Other chapters cover the nature of acids and bases, acid–base equilibria in water, acids and bases in non-aqueous solvents, interionic attraction in acid–base equilibria, acid–base strength and molecular structure, and alternative uses of the terms acid and base. This book should have a very wide readership, and ought to be read by all final-year students of chemistry.

Advances in Chromatography, Vol. 8: Ed. J. CALVIN GIDDINGS and ROY A. KELLER, Marcel Dekker, New York, 1969. Pp. xvi + 400. 198s.

This invaluable series continues to compress the vast literature in a highly heterogeneous field into a readable volume. The topics are diverse. They include chapters on the principles of gel filtration, the thermodynamics of liquid–liquid chromatography, the selection of optimum solvents for countercurrent distribution, the separation of chloroplast pigments and a series of sections on gas chromatography relating to the performance of various types of columns, flow programming, analysis of vehicular exhaust emissions, and the study of reaction kinetics. The articles are up to date and the standard of book production high.

Characterisation and Analysis of Polymers by Gas Chromatography, Vol. 3: MALCOLM P. STEVENS, Marcel Dekker, New York and London, 1969. Pp. xii + 198. 122s.

This book is the third volume in a series devoted to Techniques and Methods of Polymer Evaluation; the earlier two were concerned with thermal analysis. Particular emphasis is placed in the current volume on applications of gas–liquid chromatography to the identification of volatile components either in polymers as such or in chemically or thermally degraded polymers. Useful assistance is given in applying pyrolysis to the identification of polymers by "fingerprint" type comparisons with known polymers. Topics covered include—the analysis of volatile materials in polymers, the characterisation of polymers by thermal and chemical degradation, and the study of monomeric purity. The bibliography is comprehensive and up to date.

Talanta, 1970, Vol. 17, p. iii. Pergamon Press. Printed in Northern Ireland

PAPERS RECEIVED

Two new spectrophotometric reagents for copper: LAWRENCE STOOKEY. (10 *November* 1969)

Extraction of vanadium(V)–*N*-benzoyl-*N*-phenylhydroxylamine complexes from sulphuric acid media containing chloride or fluoride ions: ELSIE M. DONALDSON. (17 *November* 1969)

Complexation of nickel by *o*-(2-thiazoylazo)-4-chlorophenol: F. KAI and H. IZUMI. (19 *November* 1969)

Studies on nucleation from solution of some analytically important metal chelates: J. A. VELAZQUEZ and O. E. HILEMAN, JR. (20 *November* 1969)

Determination of vanadium in refractory metals, steel, cast iron, alloys and silicates by extraction of its NBPHA complex from sulphuric-hydrofluoric acid media: ELSIE M. DONALDSON. (21 *November* 1969)

On the extraction of acids and neptunium from aqueous alcohol and acetone solutions: A. ALIAN, R SHABANA and A. HAGGAG. (26 *November* 1969)

Arsenazo III and its analogues—VII. The colour reactions of rare earths with a new reagent—carboxinitrazo: S. B. SAVVIN and T. V. PETROVA. (28 *November* 1969)

Colour changes of chemical indicators—III. Colour specification and its accuracy: STANISLAV KOTRLÝ and KAREL VYTŘAS. (3 *December* 1969)

Determination of some methylcarbamate insecticides by a.c. polarography and cyclic voltammetry: M. D. BOOTH and B. FLEET. (3 *December* 1969)

Determination of carbon monoxide in metal carbonyl complexes—II. Development of a volumetric finish: A. D. CAMPBELL and P. E. NELSON. (4 *December* 1969)

Relative sensitivity of rare earth elements in spark-source mass spectrometry: ELEN ROALDSET. (8 *December* 1969)

Direct titrimetric microdetermination of thallium(I), indium and gallium—I. Microdetermination of indium–thallium(I) and indium–gallium without separation: O. C. SAXENA. (9 *December* 1969)

Extractions with long-chain amines—I. Extraction of some metal Xylenol Orange complexes into methyltrioctylammonium chloride (Aliquat 336-S): RUDOLF PŘIBIL and VLADIMÍR VESELÝ. (9 *December* 1969)

Mass spectrometric analysis of carbon monoxide–nitrogen mixtures: J. R. MAJER. (12 *December* 1969)

Organic solvent effect on phosphomolybdic acid and its analytical application: TAITIRO FUJINAGA, MUTSUO KOYAMA and TOSHITAKA HORI. (12 *December* 1969)

Dosage protomètrique des hydrogènes mobiles a l'aide de l'amidure de sodium: MARCEL MIOCQUE, JEAN-MICHEL VIERFOND and ANNICK REYNET. (12 *December* 1969)

Indirect determination of fluorides by the EDTA titration of samarium: H. F. COMBS and E. L. GROVE. (17 *December* 1969)

Hydrocarbures et pollution atmosphérique: DENISE HALOT. (18 *December* 1969)

PROFESSOR L. ERDEY

This month marks the 60th birthday of Professor L. Erdey, Head of the Institute of General and Analytical Chemistry, Technical University of Budapest, and Member of the Hungarian Academy of Sciences. He was born in 1910 in Szeged, studied at the University of Budapest, and graduated in 1932. He obtained his Ph.D. in 1939. He became Professor and Head of his present Institute in 1949. From what was then a small Institute he has built a large teaching and research establishment, with at one time 36 members of staff. With this team he did research on several topics. First he dealt with ascorbinometric titrations, using Variamine Blue indicator. An extensive work on chemiluminescent indicators and titrations was followed by thermoanalytical investigations, works in emission spectroscopy, flame photometry, radiofrequency titrations, catalytic analysis, polarography and related electrochemical techniques, radiochemical and microanalytical methods. He published several hundred papers, and also textbooks on Qualitative and Quantitative Analysis. His main work *Gravimetric Analysis* has been published in Hungarian, English and German. During these creative years he served also as Dean of the Faculty of Chemical Engineering and as Honorary Secretary to the Chemical Sciences Division of the Hungarian Academy. He won the Kossuth prize (the highest award in Hungary for cultural activities) twice. He is the Editor-in-Chief of *Journal of Thermal Analysis* and is on the Editorial Board of several Hungarian Journals of Chemistry. Since its establishment he has served on the advisory board of *Talanta.*

His colleagues, pupils and friends wish him many happy returns and every success in the forthcoming years.

Gyula Svehla

Talanta, 1970, Vol. 17, p. iii. Pergamon Press. Printed in Northern Ireland

PAPERS RECEIVED

2,1,3-Naphtho(2,3-c)-selenadiazole as a reagent for the determination of macro to sub-micro quantities of palladium: Herbert K. Y. Lau and Peter F. Lott. (23 *October* 1969)

Determination of Co, Cu, Fe, Ga, W and Zn in rocks by neutron-activation and anion exchange–separation: O. Johansen and E. Steinnes. (27 *October* 1969)

Theory of titration curves—VII. The properties of derivative titration curves for strong acid–strong base and other isovalent ion-combination titrations: Thelma Meites and Louis Meites. (27 *October* 1969)

Spectrophotometric determination of niobium by 8-hydrozyquinoline-5-sulphonic acid: G. C. Shivahare and M. K. Mathur. (28 *October* 1969)

Spectrophotometric determination of nickel(II) with phosphomolybdic acid: R. L. Heller and J. C. Guyon. (28 *October* 1969)

Contributions to the analytical chemistry of osmium and ruthenium—IX. The dimercapto derivatives of asymmetric triazine as colour reagents for osmium: Gr. Popa, C. Lazăr and C. Cristescu. (3 *November* 1969)

Studies on a new 2,2′-bipyridyl hexathiocyanato chromate(III): M. L. Anand. (3 *November* 1969)

Molar absorptivity and stability of some complex compounds of the form BA_n: I. Paralescu. (3 *November* 1969)

Studies on extraction into nitrobenzene—II. On the mechanism of the extraction of phosphomolybdic acid and traces of caesium: J. Rais and P. Selucký. (5 *November* 1969)

Sulphoxides as solvating reagents for the separation of metal ions: David C. Kennedy and J. S. Fritz. (7 *November* 1969)

Extraction chromatography of uranium with dioctylsulphoxide: J. S. Fritz and David C. Kennedy. (7 *November* 1969)

Spectrophotometric determination of ruthenium(III) and iridium(IV) and spectral characteristics of other noble metal complexes with 8-hydroxyquinoline *N*-oxide: R. D. Gupta, G. S. Manku, A. N. Bhat and B. D. Jain. (10 *November* 1969)

Rapid ion-exchange determination of caesium-137 in natural waters with inorganic exchange materials supported on silica gel—II. Ammonium phosphomolybdate-silica gel: Kikuo Terada, Kiyoshi Sawada and Toshiyasu Kiba. (11 *November* 1969)

Composition of the thorium(IV)–8-hydroxyquinoline adduct: A. Corsini and J. Abraham. (11 *November* 1969)

Kinetochromic spectrophotometry—III. Determination of fluoride *via* catalysis of the zirconium–Methylthymol Blue reaction: R. V. Hems, G. F. Kirkbright and T. S. West. (12 *November* 1969)

Alizarin Red S as metallochromic indicator: Rajinder Pal Singh. (17 *November* 1969)

Determination of platinum, palladium and silver in geological materials and their concentrates by fire assay and emission spectrography: E. G. Koleva and S. H. Arpadjian. (19 *November* 1969)

Talanta, 1970, Vol. 17, pp. iii to iv. Pergamon Press. Printed in Northern Ireland

PUBLICATIONS RECEIVED

The Determination of Carboxylic Functional Groups: R. D. TIWARI and J. P. SHARMA, Pergamon, Oxford, 1970. Pp. vii + 132. 60s, $8.00.

One of the most commonly encountered problems in the analysis of natural products is the determination of carboxylic acid functional groups. This monograph reviews the very large number of methods which have been devised for the solution of this problem. In addition to the many chemical procedures which have been reported in the literature there is an account of the application of physical methods to the determination of acidic groups. Derivatives of carboxylic acids such as acid chlorides, anhydrides, amides and esters may also be determined by many of these techniques and chapters are devoted to descriptions of the appropriate analytical methods. There is also a section dealing with the much more difficult problem of binary and multicomponent mixtures.

The Determination of Organic Peroxides: R. M. JOHNSON and I. W. SIDDIQI, Pergamon Press, Oxford, 1970. Pp. ix + 119. 50s, $6.75.

The ever increasing industrial use of organic peroxides and hydroperoxides as initiators in polymerization processes makes the publication of a review of methods for their analysis particularly welcome at the present time. Because of their reactive nature, peroxides are comparatively simple to detect and there are a large number of methods which rely upon this fact. The book devotes chapters to the more familiar chemical methods based on the release of iodine and the oxidation of iron (II) but the more recent work on chromatographic procedures is also included. There are sections dealing with other physical techniques such as spectrophotometry, polarography and gas chromatography. A particularly useful feature of the book is a chapter on the selection of the most appropriate method for any particular peroxide mixture.

Ion Exchange in Analytical Chemistry: WILLIAM RIEMAN III and HAROLD F. WALTON, Pergamon, Oxford, 1970. Pp. xiii + 295. 130s, $17.50.

The object of this volume in the well known Pergamon Monographs in Analytical Chemistry series is to give a broad survey of all aspects of ion-exchange methods, covering preparation, structure, properties, and applications of all kinds of exchangers, and giving a useful account of the basic theory in a form calculated to be of most use to the analyst. From simple demineralization to use of ion-exchange membranes and studies on complex ions, there is something for everyone in this book.

Activation Analysis: A Bibliography: Part I, Addendum 1—Issued December 1969; Part 2, Revision 1—Issued December 1969; edited G. J. LUTZ, R. J. BORENI, R. S. MADDOCK and W. W. MEINKE *NBS Technical Note* 467. U.S. Department of Commerce, Washington D.C., 1970 Pp. 264. $8.50 per set, sold in sets only.

Errors, Measurement and Results in Chemical Analysis: K. ECKSCHLAGER, Van Nostrand-Reinhold, London, 1969. Pp. 155, 60s.

This book should be close to the hand of all analytical chemists. It discusses the sources of error inherent in the most common methods and gives an account of the statistical procedures necessary for the evaluation of experimental results. The statistical methods are described in a down to earth way and are illustrated by exemplary treatments of analytical results. Methods for handling small numbers of results are given their due as are rapid graphical methods. Parts are uneven, e.g., errors in colorimetry due to stray light are not mentioned and the tiro who wished to compute a simple regression curve would be advised to consult one of the more formal works listed in the bibliography. Despite its blemishes, the range of coverage and its practical approach make it a most valuable book.

Chemistry of Complex Equilibria: M. T. BECK, Van Nostrand-Reinhold, London, 1970. Pp. 285, 90s.

The author provides an extensive and realistic review of complex equilibria. The methods available for the determination of equilibrium constants are outlined and critically evaluated. He considers that the formation of mononuclear complexes with one ligand only is abnormal and consequently he gives a welcome emphasis to polynuclear complexes, protonation of chelates and mixed ligand complexes. He also discussed the factors which determine the value of the stability constant of a metal complex. The text contains many graphs and experimental data taken from original papers, which are used to exemplify an approach to a particular problem and there are over 1000 references. Workers in the field will find it very useful and it will be of value to those who wish to widen their background, since the style is clear and the coverage good.

DR. RUDOLF PŘIBIL

DR. RUDOLF PŘIBIL, who is the senior research chemist of the Polarographic Institute of the Czechoslovak Academy of Sciences, attains his 60th birthday this year. Dr. Přibil was born on 23 July 1910, in Prague. He studied chemistry, mathematics and physics at Charles University in Prague, his interest being concentrated mostly on analytical chemistry. He received the degree of Doctor of Natural Sciences in 1933. He continued to work under Prof. O. Tomíček as an assistant in the Institute of Analytical Chemistry in the Faculty of Natural Sciences at Charles University until the second World War. When the University was closed by the Germans, Dr. Přibil worked in a chemical factory in Rybitví as a research analyst. After the war Dr. Přibil turned his attention to the rebuilding of the Institute of Analytical Chemistry at Charles University.

In 1946 he made his "habilitation" in the field of analytical chemistry and continued as the assistant of Prof. O. Tomíček. In 1948–1950 Dr. Přibil was head of the Institute of Inorganic and Forensic Chemistry in the Faculty of Natural Sciences at Charles University. At the same time he continued teaching in the Institute of Analytical Chemistry. In 1950 he left the University to act as head of the Division of Analytical Chemistry in the Institute for Pharmacy and Biochemistry, where he worked until 1955. From 1955 Dr. Přibil worked in the Czechoslovak Academy of Sciences as a research worker and in 1958 became head of the Laboratory of Analytical Chemistry.

Influenced by his teacher Prof. O. Tomíček, Rudolf Přibil began his research activity in the field of potentiometry. After World War II he turned his interest to the application of complex-forming substances in analytical chemistry. In the series of papers written by G. Schwarzenbach and describing the properties of some polyaminopolycarboxylic acids he recognized the role which these compounds may play in analytical methods. In 1947 he started a systematic study devoted to the application of EDTA in gravimetry, colorimetry, polarography, and solvent extraction. Since 1953 he has studied chelometric titration with EDTA and classical chelometric indicators. He was mostly interested in the problem of increasing the selectivity of chelometric titrations, and successfully applied the masking properties of triethanolamine, fluoride and various thio-compounds, in EDTA titrations.

In 1956 Přibil published his first paper devoted to a new type of metallochromic indicator—on Xylenol Orange. These indicators of phthalein and sulphophthalein type were (and still are) very suitable for EDTA titrations and are now manufactured all over the world. Přibil's paper influenced the other analysts to begin research work in this field and thus EDTA titrations became a new branch of modern volumetric analysis.

In the sixties Přibil studied mostly the chelometric determination of rare earths, zirconium *etc*, and on the basis of his experience in chelometry developed a series of methods for the analysis of various industrial materials. Recently he has studied the possibility of the application of metallochromic indicators in spectrophotometry and in extraction colorimetry.

Dr. Přibil has published about 250 papers and 15 monographs. He was awarded the State Prize for chemistry in 1953 and in 1958 received the academic degree of

Doctor of Science. He has been a Regional Editor of *Talanta* since its inception in 1958. As a lecturer or visiting professor he has visited many research institutions and universities in Europe, America and Asia. Due to his personal charm and social activity he has thus found a lot of friends throughout the world. All his friends, students and co-workers wish him much health and personal success.

Long life to our Rudla!

M. KOPANICA

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PAPERS RECEIVED

Möglichkeiten und Grenzen bei der Verwendung von Filterpapier als Träger bei der röntgenspektrometrischen Analyse: G. Ackermann, R.-K. Koch, H. Ehrhardt und G. Sanner. (20 *August* 1970)

Cation-exchange separation of uranium in dimethylsulphoxide medium: Gilbert E. Janauer, J. Korkisch and S. A. Hubbard. (21 *August* 1970)

La réaction des nitrilotriacétates métalliques avec la cycloleucine: J. Israeli, J. R. Cayouette and R. Volpe. (10 *September* 1970)

Sensitivity and detectability for manganese(II) determination in solution by kinetic methods of analysis: Horacio A. Mottola and Carl R. Harrison. (21 *September* 1970)

Determination of rare earths in selected rare-earth matrices by spark-source mass spectrometry: D. A. Griffith, R. J. Conzemius and H. J. Svec. (21 *September* 1970)

The "Haltafall" program—some corrections and comments on recent experience: Björn Warnqvist and Nils Ingri. (29 *September* 1970)

Traitement mathématique des resultats du dosage titrimétrique: N. A. Chernova, P. P. Melnicov, L. N. Komissatova and V. I. Spytzin. (2 *October* 1970)

Determination of silver in ores and metallurgical concentrates by a combination of fire-assay preconcentration (using tin as collector) and atomic-absorption spectrophotometry: P. E. Moloughney and J. A. Graham. (5 *October* 1970)

A general computer approach for calculating rate constants from near-equilibrium kinetic studies: V. S. Sharma and D. L. Leussing. (15 *October* 1970)

Extraction with long-chain amines—V. Colorimetric determination of cobalt with nitroso-R salt: Jiří Adam and Rudolf Přibil. (21 *October* 1970)

Potentiometric studies on ternary complex formation. Cu(II), Ni(II), Zn(II) or Cd(II)-iminodiacetic acid-amino acid: Ghanshyam Sharma and J. P. Tandon. (21 *October* 1970)

Oxalato complexes of tervalent thallium: Titrimetric determination of thallium(III): S. R. Sagi and K. V. Ramana. (26 *October* 1970)

Chromatographic separation of vanadium, tungsten and molybdenum with a liquid anion-exchanger: James S. Fritz and Joseph J. Topping. (29 *October* 1970)

Studies on potassium chlorate as a primary oxidimetric reagent: C. Radhakrishna Murty and G. Gopal Rao. (30 *October* 1970)

Thermometric titrimetry: Determination of nickel and selenium by direct injection enthalpimetry, with a thermometric titrator of simple design: A. E. Beezer and A. K. Slawinski. (5 *November* 1970)

Determination of hydrogen in sodium by an amalgamation method: Masao Takahashi. (6 *November* 1970)

A titrimetric method for the rapid determination of carbon in steel with an aqueous titrant: J. M. Ottaway, D. W. Whymark, B. Metters and B. G. Cooksey. (9 *November* 1970)

A new conductivity method for studying reaction kinetics: R. S. Roy and M. M. Misra. (12 *November* 1970)

Study of the oxidation state of plutonium in solution by a flow-coulometric method: Sorin Kihara, Tadashi Yamamoto, Kenji Motojima and Taitiro Fujinaga. (12 *November* 1970)

Determination of plutonium by two-step flow coulometry: Sorin Kihara, Tadashi Yamamoto, Kenji Motojima and Taitiro Fujinaga. (12 *November* 1970)

Iodobenzene dichloride as a new oxidimetric titrant in non-aqueous media: P. N. Krishnan Nambisan and C. G. Ramachandran Nair. (16 *November* 1970)

Talanta, 1970, Vol. 17, p. iv. Pergamon Press. Printed in Northern Ireland

ERRATUM

In the paper by A. Townshend and A. Vaughan, *Talanta*, 1970, **17**, 289, in Table III, the amounts of zinc taken and found should be in *ng*, not *μg*.

Talanta, 1970, Vol. 17, pp. iv to v. Pergamon Press. Printed in Northern Ireland

PUBLICATIONS RECEIVED

XXIst International Congress of Pure and Applied Chemistry, Prague, 1967. Congress Lectures Butterworths, London, 1969. pp. 273. £5.00.

Three fields of chemistry received special attention at this Congress: Automation in Analytical chemistry, Toxicological chemistry, and Chemistry of nucleic acid components. The topics covered in the second section are of considerable interest to a very wide group of readers, including the many analytical chemists whose job it is to detect and determine traces of toxic compounds. The lectures are entitled Dangers de l'ère chimique, The fate of foreign compounds in man and animals, Exposure tests in industrial toxicology, Diagnosis of poisoning by products in the home, and Analysis of biological material in industrial toxicology.

The first section includes lectures on more familiar topics with a general discussion of Analytical chemistry and automation, and more specific papers on Automation of analytical processes (in steel works), Controlled-potential electrolysis and the rates of homogeneous reactions, Automation in functional group analysis, and Automation in the elucidation of the structure of organic compounds. The contents of the book also appear in *Pure and Applied Chemistry*, 1969, Vol. **18**.

Solute-solvent interactions: Eds. J. F. Coetzee and Calvin D. Ritchie, Dekker, New York and London, 1969. pp. 653. $29.50.

The rapidly increasing interest in the nature of solutions and the thorough physicochemical study of their properties in connection with other branches of chemistry such as acid-base work, non-aqueous solutions, and reaction kinetics has prompted the publication of this book. The interest among analytical chemists in this field is obviously growing, too, and many will find a perusal of some of the chapters of this book worthwhile and stimulating. The first two chapters, on Heats and entropies of ionization (a critical survey of published data for Brönsted acids in aqueous solution) and Medium effects and pH in non-aqueous solvents (dealing with the theory and problems of pH scales and pH measurement) serve as an introduction to the subsequent six chapters on Acidity functions, Interactions in dipolar aprotic solvents, The selective solvation of ions in mixed solvents, Solvent isotope effect on thermodynamics of non-reacting solutes, Solvent isotope effects for equilibrium and reactions, and Organoalkali compounds in ethers. This is a useful up-to-date reference book for the research worker.

Introduction to the Chemical Analysis of Plastics: A. Krause and A. Lange, Iliffe, London, 1969. Pp. x + 225. 60s.

This is essentially a laboratory handbook on the identification of plastics, plasticizers and fillers by simple chemical and physical tests. No theory is given and methods such as spectrophotometry, polarography and gas chromatography are intentionally omitted. A wide range of materials is covered and the volume, which keeps within the limits stated, should be of value for identification and in the preparation of more complex methods of analysis.

Pharmaceutical Chemistry, Vol. 2: Ed. L. G. Chatten. Pp. xiv + 773 Dekker, New York and London, 1969. Pp. xiv + 773. £14; $29.50.

This comprehensive book is the second of two volumes and deals with the theory and application of instrumental techniques in pharmaceutical analysis. Although directed mainly at the senior undergraduate and postgraduate student of pharmacy, it should serve as a valuable reference work for the practising pharmaceutical chemist himself. This volume contains chapters on the following topics: ultraviolet, visible and infrared spectrophotometry, Raman spectroscopy, fluorimetry, mass spectrometry, nuclear magnetic resonance, gas chromatography, polarography, atomic-absorption, X-ray and radiochemical methods, turbidimetry and nephelometry, optical crystallography, refractometry, polarimetry, potentiometric and amperometric titrations, current flow methods, coulometric methods and chronopotentiometry. Most chapters provide a comprehensive list and some chapters include questions, problems and practical experiments to demonstrate certain applications. Each monograph is clearly written and well illustrated, containing many photographs and diagrams of modern analytical instruments.

A Programmed Introduction to Gas-Liquid Chromatography: J. B. Pattison. Heydon, London, 1969. Pp. xv + 303. 45s.

This book contains a great deal of very familiar data presented in a rather unusual form. The approach is that of an elementary textbook on physical chemistry dealing with the vapour-liquid equilibria. There is a fair amount of practical detail, some rather trivial in character and a series of questions and answers. The book is suitable for sixth-form students and first-year degree courses.

Liquids and Liquid Mixtures, 2nd Ed.: J. S. ROWLINSON. Butterworths, London, 1969, pp. xv + 371. £6 10s.

This is a revised second edition of a definitive work by the world authority on the subject. The scope of the book is largely unchanged, but all tables have been recalculated. The material includes the thermodynamic treatment of vapour-liquid equilibria for pure liquids and an interpretation of the phenomena associated with mixing in terms of inter-molecular forces. The book provides an excellent basis for an advanced course for graduate students.

Outline of Industrial Organic Chemistry: ALFRED RIECHE. Butterworths, London, 1968. Pp. xix + 572. 98s.

This is a translation of the 3rd edition (1964) of "Grundiss der technischen organischen Chemie" originally based on lectures by the author at Jena University. The coverage is very wide and the text is supplemented by numerous tables of technical and economic data. The chemistry of coal, oil and natural gas, hydrocarbons and derivatives occupies one half of the book, the second half being divided in approximately equal parts between carbohydrates, fermentation chemistry, and fats and soaps (100 pp) synthetic organic chemistry and plastics (85 pp) and pharmaceuticals, dyestuffs and explosives (90 pp). This is both a useful reference work and an interesting history of the organic chemical industry.

Electrochemistry at Solid Electrodes: RALPH N. ADAMS. Dekker, New York, 1969. Pp. 402. $18.75.

The aim of this book is to discuss the use and application of solid electrodes, the approach being essentially that of the experimentalist. The first half covers the theoretical considerations, and the second has chapters on Investigation of electrode processes, Fabrication of electrode systems, and Applications to organic compounds. The large amount of valuable practical information in the second part reflects the author's wide experience in this field. The book is aimed at graduates and research students, particularly those in the field of organic electrochemistry.

Lipid Chromatographic Analysis, Vol. 2: Ed. GUIDO V. MARINETTI. Dekker, New York, 1969. Pp. xii + 596. $27.50.

The various authors have produced a compilation of established and new techniques of value in the chromatographic analysis of steroids, sterols, bile acids, alcohols, prostaglandins, vitamins A and D, tocopherols and other compounds. One of the main advantages of the book is that minor, but important, manipulative and other practical points are explained. There is considerable and valuable critical appraisement of the various methods, and literature up to 1966 is well covered in addition to a few references to more recent literature. The literary style is uneven. There are numerous laboratory colloquialisms and several misprints. The book will serve as a valuable concise handbook on the subject.

Molten Salts: Ed. GLEB MAMANTOV. Dekker, New York, 1969. Pp. xvi + 611. $16.75; £6.

This collection of essays on the chemistry of molten salts gives a useful picture of current research and thinking in this field of chemistry, and may prove fruitful in catalysing analytical thought on the application of molten salt systems to analysis.

SUMMARIES FOR CARD INDEXES

Use of tetracyanoplatinate(II) for the luminescent detection of metal ions: B. C. Capelin and G. Ingram, *Talanta*, 1970, **17**, 187. (Department of Chemistry and Geology, Portsmouth Polytechnic, Portsmouth, Hampshire, England.)

Summary—The tetracyanoplatinate(II) (TCP) ion forms insoluble fluorescent compounds with many metal ions. This property has not hitherto been exploited for analytical use. The soluble sodium TCP salt has been applied as a reagent for metal ion detection. Fluorescent precipitates useful for detection of the metal ions were obtained with Y(III), Zr(IV), Ag(I), Zn(II), Cd(II), Hg(I), Hg(II), Al(III), Pb(II), La(III) and Th(IV). Limits of detection ranged from 5 to 200 ppm. With ammonium acetate as a masking agent, selective detection of 10 ppm of silver was achieved in the presence of the other metal ions. As little as 20 ppm of zirconium can be detected in the presence of hafnium, which yields a non-fluorescent precipitate.

L'automatisation en analyse par activation neutronique et ses applications à la production industrielle: J. Perdijon, *Talanta*, 1970, **17**, 197. (Centre d'Études Nucléaires de Grenoble, Rue des Martyrs, 38-Grenoble, France.)

Summary—Reasons are given for the applications of activation analysis being generally confined to laboratory use. Conditions are given for application of analytical methods to industrial process control, in particular for automatic determination of oxygen in steels.

A study of some matrix effects in the determination of beryllium by atomic-absorption spectroscopy in the nitrous oxide–acetylene flame: B. Fleet, K. V. Liberty and T. S. West, *Talanta*, 1970, **17**, 203. (Chemistry Department, Imperial College, London, S.W. 7.)

Summary—A study has been made of a number of interferences observed in the trace determination of beryllium by atomic-absorption in the nitrous oxide–acetylene flame. The major negative interference caused by the presence of excess of aluminium salts may be overcome by the use of 8-hydroxyquinoline. Magnesium and silicon also depress the Be signal but most other metals cause enhancement. In most instances the enhancements may be made uniform by the addition of potassium ions to the sample solution.

ИСПОЛЬЗОВАНИЕ ТЕТРАЦИАНОПЛАТИНАТА(II) ДЛЯ ОБНАРУЖЕНИЯ ИОНОВ МЕТАЛЛОВ МЕТОДОМ ЛЮМИНЕСЦЕНЦИИ:

B. C. Capelin and G. Ingram, *Talanta*, 1970, **17**, 187.

Резюме—Тетрацианоплатинат(II) ион (ТЦП) образует нерастворимые флуоресцирующие соединения с рядом ионов металлов. Этой характеристикой до сих пор не пользовались для аналитических целей. Растворимую натриевую соль ТЦП применили в качестве реагента для обнаружения ионов металлов. Флуресцирующие осадки, используемые для обнаружения ионов металлов получены с У(III), Zr(IV), Ag(I), Zn(II), Cd(II), Hg(I), Hg(II), Al(III), Pb(II), La(III) и Th(IV). Чувствительность составляла 5 до 200 мг/л. С использованием ацетата аммония в качестве маскирующего агента получено селективное опредение 10 мг/л серебра в присутствии других ионов металлов. Определено до 20 мг/л циркония в присутствии гафния, который образует нефлуоресцирующий осадок.

АВТОМАТИЗАЦИЯ НЕЙТРОННОАКТИВАЦИОННОГО АНАЛИЗА И ЕГО ПРИМЕНЕНИЕ В ПРОМЫШЛЕННОМ ПРОИЗВОДСТВЕ:

J. Perdijon, *Talanta*, 1970, **17**, 197

Резюме—Обсуждено применение активационного анализа, который в правиле использован только в лаборатории. Даны условия для применения аналитических методов в рагулировании промышленных процессов, в частности в автоматическом определении кислорода в сталях.

ИЗУЧЕНИЕ НЕКОТОРЫХ МАТРИЧНЫХ ЭФФЕКТОВ В ОПРЕДЕЛЕНИИ БЕРИЛЛИЯ МЕТОДОМ АТОМНО-АБСОРБЦИОННОЙ СПЕКТРОСКОПИИ В ПЛАМЕНИ ЗАКИСИ АЗОТА И АЦЕТИЛЕНА:

B. Fleet, K. V. Liberty and T. S. West, *Talanta*, 1970, **17**, 203.

Резюме—Изучен ряд мешающих эффектов обнаруженных в определении следов бериллия методом атомно-абсорбционной спектроскопии в пламени закиси азота и ацетилена. Главное мешающее действие, вызвано присутствием избытка солей алюминия можно избечь использованием 8-оксихинолина. Магний и кремний также снижают сигналь бериллия но большинство других металлов повышают этот сигналь. В большинстве случаев добавление к раствору ионов калия выравнивает эти повышения.

Determination of microgram amounts of metals by chronometric analysis: A. Pall, G. Svehla and L. Erdey, *Talanta*, 1970, **17**, 211. (Institute for General and Analytical Chemistry of the Technical University, Budapest, Hungary.)

Summary—The reaction between peroxidisulphate and iodide, modified by the addition of thiosulphate to show the Landolt effect, has been used for the determination of copper and iron in the range 1–100 μg/ml, based on the catalytic effect of these ions. The procedure is rapid and simple, and the errors are less than 10%. The interference from iron in the determination of copper may be overcome by the addition of a masking reagent such as fluoride.

Verwendung mäßig dissoziierter Komplexe bei spektralphotometrischen Bestimmungen—II. Reaktionen von Arsenazo III mit Uranyl und Thorium(IV): J. Borák, Z. Slovák und J. Fischer, *Talanta*, 1970, **17**, 215. (Institut für reine Chemikalien, Lachema Brno, Tschechoslowakei.)

Summary—The reaction of uranyl ion with Arsenazo III in acid solution gives rise to the formation of two complexes of the type ML, the proportions of these two being dependent on the acidity. The molar absorptivities of the complexes at 565 nm are $5{\cdot}3 \times 10^3$ and $8{\cdot}8 \times 10^3$ l.mole^{-1}.mm^{-1}. The formation constants have been determined, and the apparent variation in the sensitivity of the reaction is explained. In acid solution thorium forms complexes with Arsenazo III of the types M_2L, ML (two), and ML_2, the last of which is analytically useful, although partially dissociated. It predominates in strongly acid solution containing a large excess of reagent, and has a molar absorptivity at 658 nm of $12{\cdot}8 \times 10^3$ l.mole^{-1}.mm^{-1}.

2,4-Bis(4-nitrobenzazo)resorcinol-6-sulphonic acid as a new acid-base indicator: J. Jeník and F. Renger, *Talanta*, 1970, **17**, 231. (Department of Analytical Chemistry, College of Chemical Technology, Pardubice, Slov. povstání 565, Czechoslovakia.)

Summary—2,4-Bis(4-nitrobenzazo)resorcinol-6-sulphonic acid is suggested as a new visual acid-base indicator, which because of its colour sharpness and other qualities is useful in titrations of weak acids. There are two colour transitions, one from yellow to red at pH 6·8–8·2, the other from red to blue-violet at 10·5–13·0. The corresponding dissociation constants are pK_1 7·64, and pK_2 11·64.

ОПРЕДЕЛЕНИЕ МИКРОГРАММОВЫХ КОЛИЧЕСТВ МЕТАЛЛОВ МЕТОДОМ ХРОНОМЕТРИЧЕСКОГО АНАЛИЗА:

A. PALL, G. SVEHLA and L. ERDEY, *Talanta*, 1970, **17**, 211.

Резюме—Реакция пероксидисульфата с иодидом, изменена добавлением тиосульфата для получения эффекта Ландольта, применена в определении меди и железа в пределах 1–100 мкг/мл на основе каталитического действия этих ионов. Метод является быстрым и несложным, а ошибки меньше чем 10%. Влияние железа в определении меди избегнуто добавлением маскирующего агента, на пример фторидиона.

ПРИМЕНЕНИЕ УМЕРЕННО ДИССОЦИИРОВАННЫХ КОМПЛЕКСОВ В АНАЛИЗЕ СПЕКТРОФОТОМЕТРИЧЕСКИМ МЕТОДОМ—II. РЕАКЦИИ АРСЕНАЗО III С УРАНИЛОМ И ТОРИЕМ(IV):

J. BORÁK, Z. SLOVÁK and J. FISCHER, *Talanta*, 1970, **17**, 215.

Резюме—В реакции уранилиона с арсеназо III в кислом растворе образуются два комплекса типа ML, отношение которых зависит от кислотности раствора. Дифференциальные молярные светопоглощения комплексов при 565 нм равны 5,3 × 10^3 и 8,8 × 10^3 л.моль$^{-1}$.мм$^{-1}$. Определены константы образования и разъяснено видимое колебание чувствительности реакции. В кислом растворе торий образует комплексы с арсеназо III типа M_2L, ML (два) и ML_2; последным можно пользоваться в анализе хотя он частично диссоциирован. Этот комплекс преобладает в сильнокислом растворе в присутствии большего избытка реагента, его дифференциальное молярное светопоглощение равно, при 658 нм, 12,8 × 10^3 л.моль$^{-1}$.мм$^{-1}$.

2,4-БИС(4-НИТРОБЕНЗАЗО)РЕЗОРЦИНОЛ-6-СУЛЬФОНОВАЯ КИСЛОТА В КАЧЕСТВЕ НОВОГО КИСЛОТНО-ЩЕЛОЧНОГО ИНДИКАТОРА:

J. JENÍK and F. RENGER, *Talanta*, 1970, **17**, 231.

Резюме — 2,4-Бис(4-нитробензазо)резорцинол-6-сульфоновая кислота предложена в качестве нового визуального кислотно—щелочного индикатора, который является полезным в титровании слабых кислот вследствие его острой перемены цвета и других характеристик. Имеются две перемены цвета, одна из желтого в красный при pH 6,8–8,2, другий—из красного в сине-фиолетовый при 10,5–13,0. Соответствующие константы диссоциации равны pK_1 7,64 и pK_2 11,64.

Silver(III) as an oxidative titrant. Determination of some sugars, carboxylic acids and inorganic ions: P. K. Jaiswal and K. L. Yadava, *Talanta*, 1970, **17**, 236. (Chemical Laboratories, University of Allahabad, Allahabad, India.)

Summary—Silver(III) has been stabilized as its tellurato complex and used for the oxidation of sugars, organic acids, ferrocyanide, sulphide, peroxide and thiosulphate, the excess of oxidant being measured by reducing it with an excess of arsenite and then titrating the surplus arsenite with iodine.

The volumetric determination of nitrite with chloramine T: J. Agterdenbos, *Talanta*, 1970, **17**, 238. (Laboratory of Analytical Chemistry, State University, Utrecht, The Netherlands.)

Summary—Nitrite may be determined by oxidation with chloramine T, reaction of the excess of chloramine T with excess KI, and titration of I_2 formed, with thiosulphate. The reproducibility and some interferences are discussed.

Exchange reactions of ternary ion-association complexes directly in the organic phase: R. W. Burke, *Talanta*, 1970, **17**, 240. (Institute for Materials Research, National Bureau of Standards, Washington, D.C., U.S.A. 20234.)

Summary—The analytical implications of exchanging a highly coloured or fluorescent group R for a non-coloured or non-fluorescent one directly in the organic phase are discussed for ternary ion-association complexes of the type $[ML_n^-]R^+$. Several examples are given to illustrate the approach.

СЕРЕБРО(III) В КАЧЕСТВЕ ОКИСЛИТЕЛЬНОГО ТИТРОВАННОГО РАСТВОРА. ОПРЕДЕЛЕНИЕ НЕКОТОРЫХ САХАРОВ, КАРБОНОВЫХ КИСЛОТ И НЕОРГАНИЧЕСКИХ ИОНОВ:

P. K. JAISWAL and K. L. YADAVA, *Talanta*, 1970, **17**, 236.

Резюме—Серебро(III) стабилизировано в форме его теллурато-комплекса и использовано для окисления сахаров, органиче ских кислот, ферроцианида, сульфида, перекиси и тиосульфата. Избыток окислительного реагента определяли его восстановлением с избытком арсенита и оттитровыванием избыточного арсенита с иодом.

ТИТРИМЕТРИЧЕСКОЕ ОПРЕДЕЛЕНИЕ НИТРИТА ХЛОРАМИНОМ Т:

J. AGTERDENBOS, *Talanta*, 1970, **17**, 238.

Резюме—Нитрит определяли окислением с хлорамином Т, реагированием избытка хлорамина Т с избытком KI и титрованием образующегося I_2 с тиосульфатом. Обсуждены воспроизводимость результатов и некоторые мешающие действия.

РЕАКЦИИ ОБМЕНА ТРОЙНИХ ИОНОАССОЦИАЦИОННЫХ КОМПЛЕКСОВ НЕПОСРЕДСТВЕННО В ОРГАНИЧЕСКОЙ ФАЗЕ:

R. W. BURKE, *Talanta*, 1970, **17**, 240.

Резюме—Рассмотрено аналитическое значение замены сильноокрашенной флуоресцирующей группы R за неокрашенную или нефлуоресцирующую группу непосредственно в органической фазе для случая тройних ионоассоциационных комплексов типа $[ML_x^-]R^+$. Приведено число примеров для объяснения вопроса.

The structure of primary nickel dithizonate: Michael Laing and P. A. Alsop, *Talanta*, 1970, **17**, 242. (Department of Chemistry, University of Natal, Durban, and Department of Chemistry, University College of Rhodesia, Salisbury.)

Summary—Primary nickel dithizonate is found to be isostructural with the palladium and platinum complexes, and the nickel dithizonate molecule is shown to contain nickel in an approximately square planar configuration bonded to the organic ligand through both sulphur and nitrogen atoms.

Determination of dicyclohexylamine in sodium cyclamate: J. W. Erskine and A. F. Williams, *Talanta*, 1970, **17**, 244. (Research and Development Department, I.C.I., Nobel Division, Stevenston, Ayrshire.)

Summary—Dicyclohexylamine is determined in sodium cyclamate at levels of concentration down to the order of 1 ppm by measurement of the yellow colour of the chloroform extract of its Bromophenol Blue complex.

Coulometrische Titration von Hypochloriten und Chloraten: Peter Gründler and Heinz Holzapfel, *Talanta*, 1970, **17**, 246. (Sektion Chemie, Karl-Marx-Universität, Liebigstrasse 18, 701 Leipzig, D.D.R.)

Summary—Hypochlorite was determined by direct coulometric titration with iron(II) in an acetate buffered solution. Chlorate was titrated with titanium(III) in $2M$ hydrochloric acid. Amperometric indication with one and two electrodes, respectively, was used. Mixtures of hypochlorites and chlorates, *e.g.*, in industrial electrolytes, may be analysed.

КРИСТАЛЛИЧЕСКАЯ СТРУКТУРА ПЕРВИЧНОГО ДИТИЗОНАТА НИКЕЛЯ:

MICHAEL LAING and P. A. ALSPO, *Talanta*, 1970, 17, 242.

Резюме—Первичный дитизонат никеля является изоструктурным с комплексами палладия и платины, а никель в молекуле дитизоната никеля присутствует в приблизительно квадратической планарной конфигурации связанной с органическим лигандом через атомы серы и азота.

ОПРЕДЕЛЕНИЕ ДИЦИКЛОГЕКСИЛАМИНА В ЦИКЛАМАТЕ НАТРИЯ:

J. W. ERSKINE and A. F. WILLIAMS, *Talanta*, 1970, 17, 244.

Резюме—Дициклогексиламин определен в цикламате натрия до концентраций величины I части на Миллион измерением желтого цвета хлороформового экстракта его комплекса с бромофеноловым голубым.

КУЛОНОМЕТРИЧЕСКОЕ ТИТРОВАНИЕ ГИПОХЛОРИТОВ И ХЛОРАТОВ:

PETER GRÜNDLER and HEINZ HOLZAPFEL, *Talanta*, 1970, 17, 246.

Резюме—Гипохлорит определяли непосредственным кулонометрическим титрованием с железом(II) в растворе, буферированном ацетатным буфером. Хлорат титровали с титаном(III) в $2M$ соляной кислоте. Исплоьзовано амперометрическое индицирование с одним или двумя электродами, соответственно. Метод позволяет анализировать смеси гипохлоритов и хлоратов, на пример промышленные электролиты.

SUMMARIES FOR CARD INDEXES

Komplexe der Anthranil-*N*,*N*-diessigsäure mit Metallen in der Oxydationsstufe +4—I. Zirkonium und Hafnium: C. Drăgalescu, Septimia Policec and T. Simonescu, *Talanta*, 1970, **17**, 557. (Academia Republicii Socialiste Romania, Baza de Cercetări Stiintifice, Timişoara, Blv. Mihai Viteazul 24, Romania.)

Summary—Spectrophotometric studies have shown that zirconium and hafnium form complexes with anthranil-*N*,*N*-diacetic acid (ANDA) in aqueous solution, with the compositions Me:ANDA 1:1 and 1:2. The conditional stepwise formation constants at pH 1 were found to be $k_1 = 20 \pm 5$ and $k_2 = 1{\cdot}42 \times 10^6$ for zirconium, and $k_1 = 10 \pm 5$ and $k_2 = 1{\cdot}22 \times 10^5$ for hafnium.

Gleichzeitige spektrophotometrische Bestimmung des Zirkoniums und Hafniums: Septimia Policec, T. Simonescu und C. Drăgulescu, *Talanta*, 1970, **17**, 567. (Academia R.S.R., Baza de Cercetări Stiinţifice, Timişoara, Mihai Viteazul 24, Romania.)

Summary—Zirconium may be determined in the presence of hafnium by ultraviolet spectrophotometry at the isosbestic wavelengths of 218·2, 243·3 or 298·5 nm, with anthranil-*N*,*N*,-diacetic acid in dilute acid solution. Hafnium may be determined in the presence of zirconium from measurements at 216·5, 242·5 or 297 nm. Concentrations in the range 2–36 μg/ml (Zr) and 3–70 μg/ml (Hf) may be determined, and in admixture, from 2·5 to 80% of Zr in Hf, and *vice versa*, with an error of 3–4%.

Analysis by phase titration of three-component systems containing two mutually immiscible components: S. K. Suri, *Talanta*, 1970, **17**, 577. (Chemistry Department, Indian Institute of Technology, New Delhi-29, India.)

Summary—A method, based on phase titration, for the analysis of ternary mixtures containing two mutually immiscible or partially miscible components is described. It can also be used for the determination of tie-lines. The method is illustrated by its application to the system consisting of benzene, cyclohexane and nitromethane.

КОМПЛЕКСЫ АНТРАНИЛ-*N*,*N*-ДИУКСУСНОЙ КИСЛОТЫ С МЕТАЛЛАМИ В СТЕПЕНИ ОКИСЛЕНИЯ +4—I. ЦИРКОНИЙ И ГАФНИЙ:

C. Drăgulescu, Septimia Policec and T. Simonescu, *Talanta*, 1970, **17**, 557.

Резюме—Спектрофотометрические изучения показали что цироконий и гафний образуют комплексы с антранил-*N*,*N*-диуксусной кислотой (АНДК) в водном растворе, состава Ме:АНДК = 1:1 и 1:2. Обусловленные ступенчатые константы образования при pH 1 равны $\kappa_1 = 20 \pm 5$ и $\kappa_2 = 1{,}42 \times 10^5$ для циркония, и $\kappa_1 = 10 \pm 5$ и $\kappa_2 = 1{,}22 \times 10^5$ для гафния.

ОДНОВРЕМЕННОЕ ОПРЕДЕЛЕНИЕ ЦИРКОНИЯ И ГАФНИЯ СПЕКТРОФОТОМЕТРИЧЕСКИМ МЕТОДОМ:

Septimia Policec, T. Simonescu and D. Drăgulescu, *Talanta*, 1970, **17**, 567.

Резюме—Цирконий определен в присутствии гафния методом ултрафиолетовой спектрофотометрии при изоабестических длинах волн 218,2, 243,5 или 298,5 нм, с антранил-*N*,*N*-диуксусной кислотой в разбавленных растворах кислот. Гафний определяют в присутствии циркония измерением светопоглощения при 216,5, 242,5 или 297 нм. Метод позволяет определять 2–36 мкг/мл Zr и 3–70 мкг/мл Hf, а всмеси—2,5–80 % Zr в Hf и обратно, с ошибкой равной 3–4 %.

АНАЛИЗ МЕТОДОМ ФАЗОВОЙ ТИТРАЦИИ ТРЕХКОМПОНЕНТНЫХ СИСТЕМ СОДЕРЖАЩИХ ДВА НЕРАСТВОРИМЫХ ОДИН В ДРУГОМУ КОМПОНЕНТА:

S. K. Suri, *Talanta*, 1970, **17**, 577.

Резюме—Описан метод, основан на фазовой титрации, для анализа тройных смесей содержащих два нерастворимых или частично растворимых один в другому компонента. Метод применим в определении связывающих линий. Метод иллютсрирован его применением в системе бензол-циклогексан-нитрометан.

Determination of vanadium in refractory metals, steel, cast iron, alloys and silicates by extraction of an NBPHA complex from a sulphuric–hydrofluoric acid medium: Elsie M. Donaldson, *Talanta*, 1970, **17**, 583. (Mineral Sciences Division, Mines Branch, Department of Energy, Mines and Resources, Ottawa, Canada.)

Summary—A method for determining up to 0·15% of vanadium in high-purity niobium and tantalum metals, cast iron, steel, non-ferrous alloys and silicates is described. The proposed method is based on the extraction of a red vanadium(V)–*N*-benzoyl-*N*-phenylhydroxylamine complex into chloroform from a sulphuric–hydrofluoric acid medium containing excess of ammonium persulphate as oxidant. The molar absorptivity of the complex is 428 $l.mole^{-1}.mm^{-1}$ at 475 nm, the wavelength of maximum absorption. Interference from chromium(VI) and cerium(IV) is eliminated by reduction with iron(II). Common ions, including large amounts of titanium, zirconium, molybdenum and tungsten, do not interfere.

Relative sensitivity of rare earth elements in spark-source mass spectrometry: Elen Roaldset, *Talanta*, 1970, **17**, 593. (Institutt for Geologi, University of Oslo, Oslo, Norway.)

Summary—A method for calculating the relative sensitivity factors for the rare earth elements in geological material is outlined. A close correlation is found between the relative sensitivity factors calculated and isotopic mass and the first ionization potential for the elements. The points are grouped in the vicinity of a regression line, which may be used to determine the relative sensitivity factors for all the rare earth elements.

Indirect determination of fluorides by the EDTA titration of samarium: H. F. Combs and E. L. Grove, *Talanta*, 1970, **17**, 599. (IIT Research Institute, Chicago, Illinois 60616, U.S.A.)

Summary—Fluorides are determined by the back-titration of excess of samarium with EDTA to the canary yellow end-point of Methylthymol Blue. The fluoride is precipitated and digested in a solution buffered at pH 2·5–3·0 with monochloroacetate buffer. After digestion, the pH is adjusted to 5·6–5·8 with pyridine and the excess of samarium is back-titrated in the presence of the precipitate, for samples with small quantities of fluoride. The procedure was used to analyse simple fluorides, fluoroborates and some other fluoro-complexes.

ОПРЕДЕЛЕНИЕ ВАНАДИЯ В ОГНЕУПОРНЫХ МЕТАЛЛАХ, СТАЛИ, ЧУГУНЕ, СПЛАВАХ И СИЛИКАТАХ ИЗВЛЕЧЕНИЕМ В ФОРМЕ КОМПЛЕКСА С НБФГА ИЗ СЕРНО-ФТОРИСТОВОДОРОДНОКИСЛЫХ СРЕД:

Elsie M. Donaldson, *Talanta*, 1970, **17**, 583.

Резюме—Описан метод определения до 0,15% ванадия в высокочистотном металлическом ниобие и тантале, в чугуне, стали, цветных сплавах и силикатах. Метод основан на извлечении красного комплекса ванадия (V) с *N*-бензоил-*N*-фенилгидроксиламином (НБФмА) хлороформом из раствора серной и фтористоводородной кислоты, содержащего избыток персульфата аммония в качестве окислителя. Молярное светопоглощение комплекса равно 428 л.моль$^{-1}$.мм$^{-1}$ при 475 нм, т.е. при длины волн максимума светопоглощения. Влияние хрома(VI) и церия(IV) исключено восстановлением с железом(II). Обыкновенные ионы, включая большие количества титана, циркония, молибдена и вольфрама не мешают определению.

ОТНОСИТЕЛЬНАЯ ЧУВСТВИТЕЛЬНОСТЬ РЕДКОЗЕМЕЛЬНЫХ ЭЛЕМЕНТОВ В МАСС-СПЕКТРОМЕТРИИ С ИСКРОВЫМ ИСТОЧНИКОМ:

Elen Roaldset, *Talanta*, 1970, **17**, 593.

Резюме—Предложен метод вычисления относительных факторов чувствительности для редкоземельных элементов в геологическом материале. Обнаружена строгая функциональная связь между вычисленными относительными факторами чувствительности, массы изотопов, и первым потенциалом ионизации элементов. Точки расположены близко линии регрессии, которой можно пользоваться для определения относительных факторов чувствительности для всех редкоземельных элементов.

КОСВЕННОЕ ОПРЕДЕЛЕНИЕ ФТОРИДОВ ТИТРОВАНИЕМ САМАРИЯ С ЭДТА:

H. F. Combs and E. L. Grove, *Talanta*, 1970, **17**, 599.

Резюме—Фторидионы определяют оттитровыванием избытка самария с ЭДТА до светло-желтого конца титрования с метилтимоловым голубим. Фторид осаждают и дигерируют в растворе буфферированном при pH 2,5–3,0 с монохлоруксусным буффером. После дигерирования pH приводят к 5,6–5,8 пиридином и избыток самария титрируют в присутствии осадка в случае небольших количеств фторида. Метод применяли в анализе простих фторидов, борофторидов и некоторых других комплексов фтора.

Influence of pH in fluorescence and phosphorescence spectrometric analysis: S. G. SCHULMAN and J. D. WINEFORDNER, *Talanta*, 1970, **17**, 607. (Department of Chemistry, University of Florida, Gainesville, Florida 32601, U.S.A.)

Summary—An account is given of the theory of the effect of pH changes on fluorescence and phosphorescence of organic species which exhibit acid–base properties, and of the practical applications of the effect.

Determination of iridium in mafic rocks by atomic absorption: F. S. GRIMALDI and M. M. SCHNEPFE, *Talanta*, 1970, **17**, 617. (U.S. Geological Survey, Washington, D.C., U.S.A.)

Summary—Iridium is determined in mineralized mafic rocks by atomic absorption after fire-assay concentration into a gold bead. Inter-element interferences in the atomic-absorption determination are removed and Ir sensitivity is increased by buffering the solutions with a mixture of copper and sodium sulphates. Substantial amounts of Ag, Al, Au, Bi, Ca, Cd, Co, Cr, Fe, Ho, Hg, K, La, Mg, Mn, Mo, Ni, Pb, Te, Ti, V, Y, Zn and platinum metals can be tolerated in the atomic-absorption determination. The sensitivity and detection limits are 3·2 and 0·25 ppm of Ir, respectively.

Studies on nucleation from solution of some analytically important metal chelates: J. A. VELAZQUEZ and O. E. HILEMAN JR, *Talanta*, 1970, **17**, 623. (Department of Chemistry, McMaster University, Hamilton, Ontario, Canada.)

Summary—The combination of precipitation from homogeneous solution and Vonnegut's droplet technique is employed in the study of nucleation from solution of bis(1,2-cyclohexanedionedioximato)-Ni(II), bis(1,2-cycloheptanedionedioximato)Ni(II), bis(1,2-cyclohexanedionedioximato)Pd(II) and bis(1,2-cycloheptanedionedioximato)-Pd(II). Values of the kinetic constant, surface energy, critical radius and the number of molecules per critical nucleus are calculated and discussed in terms of the limitations of the classical theory of nucleation when applied to crystal nucleation from aqueous solutions of electrolytes.

ВЛИЯНИЕ pH В АНАЛИЗЕ МЕТОДАМИ ФЛУОРЕСЦЕНТНОЙ И ФОСФОРЕСЦЕНТНОЙ СПЕКТРОМЕТРИИ:

S. G. Schulman and J. D. Winefordner, *Talanta*, 1970, **17**, 607.

Резюме—Обсуждена теория влияния перемен pH на флуоресценцию и фосфоресценцию органических соединений, обладающих кислотно-щелочными характеристиками, и применение этого эффекта в практике.

ОПРЕДЕЛЕНИЕ ИРИДИЯ В МАФИЧЕСКИХ ГОРНЫХ ПОРОДАХ МЕТОДОМ АТОМНО-АБСОРБЦИОННОЙ СПЕКТРОМЕТРИИ:

F. S. Grimaldi and M. M. Schnepfe, *Talanta*, 1970, **17**, 617.

Резюме—Иридий определен в минерализованных мафических горных породах методом атодом атомно-абсорбционной спектрометрии после концентрирования в перле золота сухим путем. Межэлементные влияния в определении методом атомно-абсорбционной спектрометрии исключены и чувствительность метода для Ir повышена буфферированием растворов смесью сульфатов меди и натрия. Значительные количества Ag, Al, Au, Bi, Ca, Cd, Co, Cr, Fe, Ho, Hg, K, La, Mg, Mn, Mo, Ni, Pb, Te, Ti, V, Y, Zn, и платиновых металлов можно толерировать в определении методом атомно-абсорбционной спектрометрии. Чувствительность и предел обнаружения равны 3,2 и 0,25 мкг/л Ir, соответственно.

ИЗУЧЕНИЕ НУКЛЕАЦИИ ИЗ РАСТВОРОВ НЕКОТОРЫХ ВАЖНЫХ ДЛЯ АНАЛИТИЧЕСКОЙ ХИМИИ ХЕЛАТОВ МЕТАЛЛОВ:

J. A. Velazquez and O. E. Hileman, *Talanta*, 1970, **17**, 623.

Резюме—Использована комбинация осаждения из гомогенного раствора и методакапель Воннегута для изучения нуклеации из раствора бис(1,2-циклогександион-диоксимато)Ni(II) бис(1,2-циклогептандион-диоксимато)Ni(II), бис-(1,2-циклогександион-диоксимато)Pd(II) и бис(1,2-циклогептандион-диоксимато)Pd(II). Вычислены значения кинетической константы, поверхностной энергии, критического радия и числа молекул в критическом ядре и обсуждены в свете ограничений классической теории нуклеации, при мененной в нуклеации кристаллов из водных растворыо электролитов.

Determination of carbon monoxide in metal carbonyl complexes—II. Development of a volumetric finish: A. D. Campbell and P. E. Nelson, *Talanta*, 1970, **17**, 633. (Department of Chemistry, University of Otago, Dunedin, New Zealand.)

Summary—The method previously described for the determination of carbon monoxide in metal carbonyl complexes has been modified to provide an accurate volumetric finish.

Contributions to the analytical chemistry of osmium and ruthenium—IX. The dimercapto derivatives of asymmetric triazine as colour reagents for osmium: Gr. Popa, C. Lazar and C. Cristescu, *Talanta*, 1970, **17**, 635. (Laboratory for Analytical Chemistry of the Chemical Faculty, University of Bucharest, Romania.)

Summary—The parameters of the reaction of osmium with 3,5-dimercapto-6-(ethylcarboxy)-1,2,4-triazine have been studied and the optimum conditions for the spectrophotometric determination of osmium over the range 0·5–18·0 ppm determined. The coloured product contains the components in the ratio 1:2, metal:ligand.

Submicro determination of aluminium, bismuth and copper in organometallic compounds: R. Belcher, Barbara Crossland and T. R. F. W. Fennell, *Talanta*, 1970, **17**, 639. (Department of Chemistry, University of Birmingham, P.O. Box 363, Birmingham 15, U.K., and Royal Aircraft Establishment, Farnborough, Hants., U.K.)

Summary—Methods for the determination of aluminium, bismuth and copper in samples of organometallic compounds weighing 40–110 μg have been developed. Spectrophotometric determination following digestion with nitric and sulphuric acids in a sealed tube is recommended, all results obtained from the analysis of standard compounds being within ±0·3% absolute error. Digestion in an open tube with perchloric and sulphuric acids gives satisfactory results for bismuth compounds but erratic and often low results for aluminium and copper compounds.

ОПРЕДЕЛЕНИЕ ОКИСИ УГЛЕРОДА В МЕТАЛЛОКАРБОНИЛНЫХ КОМПЛЕКСАХ—II. РАЗРАБОТКА ВОЛУМЕТРИЧЕСКОГО МЕТОДА ИЗМЕРЕНИЯ:

A. D. CAMPBELL and P. E. NELSON, *Talanta*, 1970, **17**, 633.

Резюме—Раньше описанный метод определения окиси углерода в металлокарбонилных комплексах изменен включением точного волуметрического метода измерения.

ВКЛАД В АНАЛИТИЧЕСКУЮ ХИМИЮ ОСМИЯ И РУТЕНИЯ—IX. ДИМЕРКАПТОПРОИЗВОДНЫЕ АСИММЕТРИЧЕСКОГО ТРИАЗИНА В КАЧЕСТВЕ ЦВЕТНЫХ РЕАГЕНТОВ ДЛЯ ОСМИЯ:

GR. POPA, C. LAZAR and C. CRISTESCU, *Talanta*, 1970, **17**, 635.

Резюме—Изучены параметры реакции осмия с 3,5-димеркапто-6-(этилкарбокси)-1,2,4-триазином и определены оптимальные условия для спектрофотометрического определения осмия в области концентраций 0,5–18,0 частей на миллион. Отношение металла и лиганда в окращенном продукте равно 1:2.

СУБМИКРООПРЕДЕЛЕНИЕ АЛЮМИНИЯ, ВИСМУТА И МЕДЫ В ОРГАНОМЕТАЛЛИЧЕСКИХ СОЕДИНЕНИЯХ:

R. BELCHER, BARBARA CROSSLAND and T. R. F. W. FENNELL, *Talanta*, 1970, **17**, 639.

Резюме—Разработаны методы определения алюминия, висмута или меди в образцах органометаллических соединений 40–110 мкг. Предложено спектрофотометрическое определение после дигерирования азотной или серной кислотами в запаянной трубке. Вси результаты полученные в анализе эталонов имели ошибку меньше чем ±0,3 % абс. Дигерирование в открытой трубке с хлорной и серной кислотами дает удовлетворительные результаты для соединений висмута, но ошибочные и часто низкие результаты для соединений алюминия и меди.

Fällung des Wismuts als Bis(triphenylselenonium)-Pentachlorobismutat(III): Max Ziegler und Lüder Ziegeler, *Talanta*, 1970, **17**, 641. (Anorganisch-Chemisches Institut, der Universität, Göttingen, Deutschland.)

Summary—By precipitation as $[(C_6H_5)_3Se]_2[BiCl_5]$ in the presence of citrate, 15–50 mg of bismuth can be determined gravimetrically, and separated from moderate amounts of bi- and tervalent metals and from phosphate. Such metals can be identified by the formation of the triphenylselenonium salts of their various halide complexes.

Two new spectrophotometric reagents for copper: Lawrence Stookey, *Talanta*, 1970, **17**, 644. (Hach Chemical Company, P.O. Box 907, 713 South Duff, Ames, Iowa 50010, U.S.A.)

Summary—Two ferroin-type compounds are proposed as spectrophotometric reagents for copper(I): 6-methyl-2-pyridylhydrazidine, which forms a yellow complex with λ_{max} 426 nm and molar absorptivity 700 l.mole^{-1}.mm^{-1}, and 3-(6-methyl-2-pyridyl)-5,6-diphenyl-1,2,4-triazine, which forms a red-orange complex with λ_{max} 492 nm and molar absorptivity of 955 l.mole^{-1}.mm^{-1}. These reagents are specific for copper and the complexes can be extracted into isopentanol for increased sensitivity.

Amperometric titration of Cd(II), Hg(II) and Zn(II) in molten alkali thiocyanates with electrolytically generated sulphide ions: Paolo Cescon, Filippo Pucciarelli and Mario Fiorani, *Talanta*, 1970, **17**, 647. (Istituto Chimico dell'Università di Camerino, Camerino, Italy.)

Summary—The feasibility of the titration of some cations in molten sodium thiocyanate–potassium thiocyanate mixture with electrolytically generated sulphide ions has been tested at 443 K. Quantitative data are given for the titration of cadmium, mercury and zinc ions.

ОСАЖДЕНИЕ ВИСМУТА В ФОРМЕ БИС(ТРИФЕНИЛСЕЛЕНОНИЙ)-ПЕНТАХЛОРОВИСМУТАТА(III):

MAX ZIEGLER and LÜDER ZIEGELER, *Talanta*, 1970, **17**, 641.

Резюме—15–50 мг висмута определено весовым методом осаждением в форме $[(C_6H_5)_3Se]_2[BiCl_5]$ в присутствии цитрата, и отделено от умеренных количеств дву- и трехвалентных металлов и от фосфата. Эти металлы отождествлены образованием солей трифенилселенония их разных галоидкомплексов.

ДВА НОВЫХ СПЕКТРОФОТОМЕТРИЧЕСКИХ РЕАГЕНТА ДЛЯ МЕДИ:

LAWRENCE STOOKEY, *Talanta*, 1970, **17**, 644.

Резюме—Предложены два соединения типа ферроина в качестве реагентов для меди(I): 6-метил-2-пиридилгидразидин, образующий желтый комплекс с $\lambda_{\text{макс}}$ 426 нм и молярным светопоглощением 700 л.моль$^{-1}$.мм$^{-1}$, и 3-(6-метил-2-пиридил)-5,6-дифенил-1,2,4-триазин, который образует красно-оранжевый комплекс с $\lambda_{\text{макс}}$ 492 нм и молярным светопоглощением 955 л.моль$^{-1}$.мм$^{-1}$. Реагенты являются специфическим для меди, а комплексы извлекаемы изопентанолом для повышения чувствительности.

АМПЕРОМЕТРИЧЕСКОЕ ТИТРОВАНИЕ Cd, Hg(II) И Zn В РАСПЛАВЛЕННЫХ ТИОЦИАНАТАХ ЩЕЛОЧНЫХ МЕТАЛЛОВ С ЭЛЕКТРОЛИТИЧЕСКИМ ПУТОМ ОБРАЗОВАННЫМИ СУЛЬФИДИОНАМИ:

PAOLO CESCON, FILIPPO PUCCIARELLI and MARIO FIORANI, *Talanta*, 1970, **17**, 647.

Резюме—Испытана возможность титрования некоторых катионов в расплавленной смесе тиоцианатов натрия и калия при 443° К с электролитическим путом образованными сульфидионами Приведены количественные данные для титрации кадмия, ртути и цинка.

New chromogens of the ferroin type—VI. Some derivatives of 1- and 3-cyanoisoquinoline and substituted 2-cyanopyridines: Alfred A. Schilt, Wayne E. Dunbar, Bruce W. Gandrud and Steven E. Warren, *Talanta*, 1970, **17**, 649. (Department of Chemistry, Northern Illinois University, DeKalb, Illinois 60115, U.S.A.)

Summary—The chromogenic reactions with iron(II), copper(I) and cobalt(II) of 32 recently synthesized pyridazines, triazines, tetrazines and certain other compounds containing the ferroin grouping have been examined spectrophotometrically. Some interesting examples were found of steric and donor-atom selectivities in chelation of iron by ligands containing several ferroin groups. Of the various chromogens studied, the pyridyl and isoquinolyl derivatives of phenyl or pyridyl substituted 1,2,4-triazine show the most promising analytical utility.

Determination of alumina in sintered aluminium powder by activation with 14-MeV neutrons: Carlos E. Español and Ana María Marafuschi, *Talanta*, 1970, **17**, 653. (Facultad de Ingeniería, Universidad de Buenos Aires, Argentina.)

Summary—Fast neutrons of 14 MeV produced in the IMICAM CISE 150-kV generator by the (d, t) reaction in a tritium–titanium target, were used in the indirect determination of Al_2O_3. The samples were irradiated for 30 sec and the total ^{16}N activity was determined, by counting for ten 2-sec periods and graphically integrating. The standards were a known sintered aluminium powder and nylon pieces of identical shape. The method is competitive with the chemical one, because of its quickness, sensitivity and precision.

НОВЫЕ ХРОМОГЕНЫ ТИПА ФЕРРОИНА—VI. НЕКОТОРЫЕ ПРОИЗВОДНЫЕ 1- И 3-ЦИАНОИЗОХИНОЛИНА И ЗАМЕЩЕННЫХ 2-ЦИАНОПИРИДИНОВ:

Alfred A. Schilt, Wayne E. Dunbar, Bruce W. Gandrud and Steven E. Warren, *Talanta*, 1970, **17**, 649.

Резюме—Изучены спектрофотометрическим методом хромогенные реакции с железом(II), медью(I) и кобальтом(II) 32 новоситезированных пиридазинов, триазинов, тетразинов и некоторых других соединений содержащих ферроингруппу. Обнаружены интересные примеры стерической селективности и селективности на основе атома-донора в хелатообразовании с железом лигандов содержащих несколько ферроингрупп. Из исследованных хромогенов пиридил- и изохинолилпроизводные фенил- или пиридилзамещенного 1,2,4-триазина оказались наиболее полезными для применения в анализе.

ОПРЕДЕЛЕНИЕ ОКИСИ АЛЮМИНИЯ В СПЕКШЕМСЯ ПОРОШКОВИДНОМ АЛЮМИНИЕ АКТИВАЦИЕЙ С 14-МЭВ НЕЙТРОНАМИ:

Carlos E. Español and Ana Maria Marafuschi, *Talanta*, 1970, **17**, 653.

Резюме—Быстрые нейтроны произведенные в 150 кв генераторе IMICAM CISE реакцией (d, t) в щите трития-титана использованы для косвенного определения Al_2O_3. Образцы облучены в течение 30 сек. и определена общая ^{16}N активность, считанием в 10 периодов по 2 сек. и графическим интегрированием. Знакомые образцы спекшегося порошковидного алюминия и образцы найлона той же формы служили в качестве эталонов. Метод сравным с химическим методом по его быстроты, чувствительности и точности.

Talanta. 1970. Vol. 17, p. v. Pergamon Press. Printed in Northern Ireland

NOTICE

3RD ROMANIAN NATIONAL CONFERENCE ON ANALYTICAL CHEMISTRY

The Chemistry Department of the Romanian National Council of Engineers and Technicians will sponsor the 3rd National Conference on Analytical Chemistry between 22 and 26 September 1971 in Brașov, Romania.

The following sessions are planned.

A. Electrometric methods
B. Optical methods
C. Separation methods.

Further information on this meeting is available from the secretary: Dr. Constantin Luca, Consiliul Național al Inginerilor și Tehnicienilor, Conferința de Chimie Analitică, Calea Victoriei 118, București, Romania.

Talanta, 1970, Vol. 17, p v. Pergamon Press. Printed in Northern Ireland

NOTICE

ASSOCIATION OF OFFICIAL ANALYTICAL CHEMISTS

The 1970 meeting will take place on 12–15 October 1970 at Marriott Motor Hotel, Twin Bridges, Washington, D.C. 20001, on the theme of methods of analysis of materials and products important to health and agriculture, *i.e.*, drugs, pesticides, food, beverages, food additives, animal feeds, fertilizers *etc.*

Further details can be obtained from L. G. ENSMINGER, Executive Secretary, AOAC, Box 540, Benjamin Franklin Station, Washington, D.C. 20044.

Catalytic thermometric titrations in non-aqueous solvents by coulometrically generated titrant: VILIM J. VAJGAND, FERENC F. GAÁL and SMILJANA S. BRUSIN, *Talanta*, 1970, **17**, 415. (Institute of Chemistry, Faculty of Science, University of Belgrade, Studentski trg 16, Yugoslavia.)

Summary—Catalytic thermometric titrations have been developed for tertiary amines and salts of organic acids in acetic and propionic anhydride with titrant coulometrically generated at a mercury and/or platinum anode, hydroquinone being added to the solution titrated if the platinum anode is used. The results obtained are compared with those obtained by coulometric titration with the end-point detected either photometrically or potentiometrically.

Dosage protométrique des hydrogènes mobiles à l'aide de l'amidure de sodium: MARCEL MIOCQUE, JEAN-MICHEL VIERFOND and ANNICK REYNET: *Talanta*, 1970, **17**, 423. (Laboratoire de la Pharmacie, Hôpital Claude Bernard, Paris XIXème, and Laboratoire de Chimie Organique de la Faculté de Pharmacie de Paris.)

Summary—Sodium amide is decomposed by compounds containing active hydrogen, with stoichiometric release of ammonia, which can be determined by titration with acid. The proposed technique has been applied to representatives of various types of compound.

Estimation of thiosemicarbazide with chloramine-T: D. S. MAHADEVAPPA and A. S. ANANDA MURTHY; *Talanta*, 1970, **17**, 431. (Department of Postgraduate Studies and Research in Chemistry, Manasa Gangotri, Mysore-6, India.)

Summary—A rapid and accurate method for the estimation of thiosemicarbazide in aqueous solution has been developed based on its oxidation with chloramine-T at room temperature and pH 4. The effect of such variables as pH, mode of addition of reagents and concentration of chloride ion on the extent of oxidation has been studied.

SUMMARIES FOR CARD INDEXES

Atomic-fluorescence spectroscopy of lead: VÁCLAV SYCHRA and JAROSLAV MATOUŠEK, *Talanta*, 1970, **17**, 363. (Department of Analytical Chemistry, Technical University, Prague 6, Czechoslovakia.)

Summary—The fluorescence spectrum of lead excited with a high-intensity hollow-cathode lamp has been investigated and the probable mechanism of fluorescence transitions is suggested. It is confirmed experimentally that the most intense fluorescence line at 405·78 nm is mostly due to direct-line fluorescence. The premixed air–hydrogen flame, the separated air–acetylene flame, and the oxy-hydrogen flame diluted with argon have been used, the last mentioned giving a detection limit of 0·02 ppm with the line at 405·78 nm.

Substoichiometric determination of traces of palladium by neutron-activation analysis: G. B. BRISCOE and S. HUMPHRIES, *Talanta*, 1970, **17**, 371. (Department of Chemistry, The University of Aston in Birmingham, Gosta Green, Birmimgham, 4, England.)

Summary—A highly selective, rapid, one-step radiochemical separation procedure for palladium has been developed. It is based on the solvent extraction of palladium diethyldithiocarbamate from a 5*M* hydrochloric acid solution with a substoichiometric amount of copper diethyldithiocarbamate in chloroform. The separation has been applied to the determination of traces of palladium by neutron-activation analysis, in platinum, the rocks W-1 and PCC-1 and a biological material (kale). Amounts of palladium down to 10^{-8} g have been determined.

Further study of individual ion activities in pure aqueous sodium chloride: ADAM SHATKAY, *Talanta*, 1970, 381. (Isotope Department, Weizmann Institute of Science, Rehovot, Israel.)

Summary—The e.m.f. values between a chloride electrode and a reference electrode were measured in aqueous NaCl solutions between 10^{-5} and 6 m, saturated KCl and 1*M* KNO_3 bridges being used. The effect of the various liquid junctions is calculated and discussed. The consistency of the results is inspected, assuming either the MacInnes or the Guggenheim convention. The choice of different reference points for the standardization of the e.m.f.'s and for the activity coefficients is discussed. A comparison is made between the results obtained with an Ag/AgCl electrode of the second kind and a solid membrane chloride electrode.

ОПРЕДЕЛЕНИЕ СВИНЦА МЕТОДОМ АТОМНО-ФЛУОРЕСЦЕНТНОЙ СПЕКТРОСКОПИИ:

Vaclav Sychra and Jaroslav Matousek, *Talanta* 1970 **17**, 363.

Резюме—Изучен спектр флуоресценции свинца, возбужден высокоинтенсивной лампой с полым катодом и предложен вероятный механизм флуоресцентных переходов. Подтверждено опытом что наиболее интенсивная флуоресцентная линия при 405,78 нм является главным образом в результате флуоресценции непосредственной линии. Использованы предварительно смешанное пламя воздуха и водорода, отделенное пламя воздуха и ацетилена и разбавленное аргоном пламя кислорода-водорода. Последнее позволяет получить чувствительность 0,02 мг/л с использованием линии при 405,78 нм.

СУБСТЕХИОМЕТРИЧЕСКОЕ ОПРЕДЕЛЕНИЕ СЛЕДОВ ПАЛЛАДИЯ МЕТОДОМ НЕЙТРОННОАКТИВАЦИОННОГО АНАЛИЗА:

G. B. Briscoe and S. Humphries, *Talanta*, 1970, **17**, 371.

Резюме—Разработан высокоизбирательный, быстрый, одноэтапный радиохимический метод выделения палладия. Метод основан на извлечении диэтилдитиокарбамината палладия из раствора 5 *M* соляной кислоты с субстехиометрическим количеством диэтилдитиокарбамината меди в хлороформе. Метод применен в определении следов палладия методом нейтронноактивационного анализа в платины, горных породах W-1 и PCC-1 и в биологическом материале (кудрявой капусте). Определены следы палладия до 10^{-8} г.

ДАЛЬНЕЙШЕЕ ИЗУЧЕНИЕ ИНДИВИДУАЛЬНЫХ АКТИВНОСТЕЙ ИОНОВ В ЧИСТОМ ХЛОРИДЕ НАТРИЯ:

Adam Shatkay, *Talanta*, 1970, **17**, 381.

Резюме—Измерены величины э.д.с. между хлоридным электродом и электродом сравнения в водных растворах хлорида натрия в области концентрации 10^{-5} до 6 *M*, с использованием мостов из насыщенного KCl и 1 *M* KNO_3. Вычислен и обсужден эффект разных жидкостных мостов. Осмотрено постоянство результатов, предполагая конвенцию Макиннеса или Гуггенгейма. Обсужден выбор различных точек сравнения для стандартизации э.д.с. и коэффициентов активности. Сравнены результаты полученные с использованием электрода Ag/AgCl второго типа и хлоридого электрода с твердой мембраной.

Preparation of D-(−)-*trans*-1,2-diaminocyclohexane-*N*,*N*,*N*′,*N*′-tetra acetic acid and its use as a spectropolarimetric reagent for lead: P. E. Reinbold and K. H. Pearson, *Talanta*, 1970, **17**, 391. (Department of Chemistry, Texas A & M University, College Station, Texas 77843, U.S.A.)

Summary—D-(−)-*trans*-1,2-diaminocyclohexane-*N*, *N*, *N*′, *N*′-tetra-acetic acid [D(−)DCTA] was prepared stereospecifically in good yield by the condensation of the resolved diamine, D-(−)-*trans*-1,2-diaminocyclohexane, with sodium chloroacetate at 16°, followed by use of a strong cation-exchanger to obtain the free acid. Distinct differences were noted in the infrared spectra of the optically active acid and the racemate. The molecular rotation of D(−)DCTA showed strong dependence on the pH of the soluton. D(−)DCTA was used as a stereospecific chelometric reagent in the spectropolarimetrically monitored determination of lead.

EDTA titration of calcium and magnesium with a calcium-selective electrode: T. P. Hadjiioannou and D. S. Papastathopoulos, *Talanta*, 1970, **17**, 399. (Laboratory of Analytical Chemistry, University of Athens, Athens, Greece.)

Summary—Direct semi-automatic and automatic derivative potentiometric EDTA procedures for the determination of calcium and/or magnesium with a calcium-selective electrode are described. Calcium is titrated in the presence of magnesium at pH 12·0 and the total calcium and magnesium is determined at pH 9·7. Calcium in the range 1–8 mg and magnesium in the range 0·7–5 mg are determined semi-automatically with average errors of about 0·2 and 0·3% respectively and automatically with average errors of 0·4 and 0·7%. Titration times vary from a few seconds to a few minutes.

Determination of Co, Cu, Fe, Ga, W and Zn in rocks by neutron activation and anion-exchange separation: O. Johansen and E. Steinnes, *Talanta*, 1970, **17**, 407. (Institutt for Atomenergi, Isotope Laboratories, Kjeller, Norway.)

Summary—A neutron-activation method for the simultaneous determination of cobalt, copper, gallium, iron, tungsten and zinc in rocks is described. The method is based on anion-exchange separation in hydrochloric acid media. Chemical yield is higher than 97% for all elements, except for tungsten, where the recovery of the carrier is established by re-activation. The precision is about 1·3% for the iron determination and about 3% for cobalt, copper, gallium and zinc.

ПРИГОТОВЛЕНИЕ *D*-(-)-*транс*-1,2-ДИАМИНОЦИКЛОГЕКСАН-*N*,*N*,*N*′,*N*′-ТЕТРАУКСУСНОЙ КИСЛОТЫ И ЕЕ ИСПОЛЬЗОВАНИЕ В КАЧЕСТВЕ СПЕКТРОПОЛЯРИМЕТРИЧЕСКОГО РЕАГЕНТА ДЛЯ СВИНЦА:

P. E. Reinbold and K. H. Pearson, *Talanta*, 1970, **17**, 391.

Резюме—*D*-(-)-*транс*-1,2-диаминоциклогексан-*N*,*N*,*N*′,*N*′-тетрауксусная кислота (*D*)-(ДЦТА) приготовлена стереоспецифически с хорошим выходом конденсацией разрешенного диамина-*D*-(-)-*транс*-1,2-диаминоциклогексана-с хлороацетатом натрия при 16°, с последующим выделением чистой кислоты на сильном катионообменнике. Обнаружены характеристичные разницы в инфракрасных спектрах оптически активной кислоты и рацемата. Молекулярная ротация *D*(-)ДЦТА оказалась сильно зависимой от pH раствора. *D*(-)ДЦТА использована в качестве стереоспецифического хелатометрического реагента в спектрополяриметрическом определении свинца.

ТИТРАЦИЯ КАЛЬЦИЯ И МАГНИЯ С ЭДТА С ИСПОЛЬЗОВАНИЕМ СЕЛЕКТИВНОГО ДЛЯ КАЛЬЦЯ ЭЛЕКТРОДА:

T. P. Hadjiioannou and D. S. Papastathopolous, *Talanta*, 1970, **17**, 399.

Резюме—Описаны методы непосредственного полуавтоматического и автоматического дериватнвного потенциометрического титрования кальция и/или магния с ЭДТА, с использованием селективного для кальция электрода. Кальций титруют в присутствии магния при pH 12,0, а сумму кальция и магния определяют при pH 9,7. Кальций определяют полуавтоматическим способом в пределах 1–8 мг а магний в пределах 0,7–5 мг с средной ошибкой 0,2 и 0,3 %, соответственно, а автоматическим способом с средной ошибкой 0,4 0,7 %, соответственно. Продолжительность титрования колебается от несколько секунд до несколько минут.

ОПРЕДЕЛЕНИЕ Co, Cu, Fe, Ga, W И Zn В ГОРНЫХ ПОРОДАХ МЕТОДАМИ НЕЙТРОННОЙ АКТИВАЦИИ И ИОНООБМЕННОГО РАЗДЕЛЕНИЯ:

O. Johansen and E. Steinnes, *Talanta*, 1970, **17**, 407.

Резюме—Описан метод одновременного нейтронно-активационного определения кобальта, меди, галлия, железа, вольфрама и цинка в горных породах. Метод основан на анионообменном разделении металлов в солянокислых средах. Химический выход больше чем 97 % для всех элементов за исключением вольфрама. В этом случае восстановление носителя определяют реактивированием. Воспроизводимость определения около 1,3 % в случае железа и около 3 % в случае кобальта, меди, галлия и цинка.

КАТАЛИТИЧЕСКИЕ ТЕРМОМЕТРИЧЕСКИЕ ТИТРАЦИИ В НЕВОДНЫХ РАСТВОРИТЕЛЯХ С ИСПОЛЬЗОВАНИЕМ КУЛОНОМЕТРИЧЕСКОЙ ГЕНЕРАЦИИ ТИТРАНТА:

Vilim J. Vajgand, Ferenc F. Gaál and Smiljana S. Brusin, *Talanta*, 1970, **17**, 415.

Резюме—Разработаны методы термометрического титрования третичных аминов и солей органических кислот в ангидриде уксусной и пропионовой кислот, с использованием кулонометрической генерации титранта на ртутном и/или платиновом электроде, с добавлением раствору гидрохинона в случае использования платинового анода. Полученные результаты сравнены с результатами кулонометрического титрования с применением фотометрического или потенциометрического обнаружения конца титрования.

ПРОТОНОМЕТРИЧЕСКОЕ ОПРЕДЕЛЕНИЕ АКТИВНОГО ВОДОРОДА АМИДОМ НАТРИЯ:

Marcel Miocque, Jean-Michel Vierfond and Annick Reynet, *Talanta*, 1970, **17**, 423.

Резюме—Амид натрия разлагается действием соединений содержащих активный водород с стехиометрическим выделением аммиака, который может быть определен титрованием с кислотой. Предложенный метод применен на представители разных классов соединений.

ОПРЕДЕЛЕНИЕ ТИОСЕМИКАРБАЗИДА ХЛОРАМИНОМ Т:

D. S. Mahadevappa and A. S. Ananda Murthy, *Talanta*, 1970, **17**, 431.

Резюме—Разработан быстрый и точный метод определения тиосемикарбазида в водном растворе, основан на его окислении хлорамином Т при комнатной температуре и pH 4. Изучено влияние на степень окисления разных факторов-pH, способа добавления реагентов и концентрации хлоридиона.

Kinetochromic spectrophotometry—III. Determination of fluoride by catalysis of the zirconium–Methylthymol Blue reaction: R. V. HEMS, G. F. KIRKBRIGHT and T. S. WEST, *Talanta*, 1970, **17**, 433. (Chemistry Department, Imperial College, London, S.W.7, England.)

Summary—The determination of 0·5–4·75 μg of fluoride ion by its catalytic action upon the slow reaction between Methylthymol Blue and zirconium(IV) in aqueous solution is described. Calibration curves obtained after 60 min under optimal conditions are smooth, and yield an effective molar absorptivity of $3{\cdot}23 \times 10^4$ l.mole^{-1}. min^{-1} at 586 nm. There is considerably less cationic interference than in the alizarin complexan–cerium(III) or lanthanum procedure, but more serious anionic interference is encountered when phosphate, arsenate and, to a lesser extent, sulphate ions are present in the sample solution.

Composition of the thorium(IV)–8–hydroxyquinoline adduct compound: A. CORSINI and J. ABRAHAM, *Talanta*, 1970, **17**, 439. (Department of Chemistry, McMaster University, Hamilton, Ontario, Canada.)

Summary—The orange compound formed between thorium(IV) and 8-hydroxyquinoline by conventional precipitation is non-stoichiometric. The composition is very sensitive to experimental conditions; the average ratio of bound 8-hydroxyquinoline to thorium was found to be 4·9 : 1. The deficiency of 8-hydroxyquinoline is due either to partial hydrolysis of thorium, or to the presence of co-ordinated water. A simple procedure for the preparation of the pure tetrakis compound is described.

КИНЕТОХРОМНАЯ СПЕКТРОФОТОМЕТРИЯ—III. ОПРЕДЕЛЕНИЕ ФТОРИДИОНА НА ОСНОВЕ КАТАЛИЗА РЕАКЦИИ ЦИРКОНИЯ С МЕТИЛТИМОЛОВЫМ ГОЛУБИМ:

R. V. Hems, G. F. Kirkbright and T. S. West, *Talanta*, 1970, 17, 433.

Резюме—Описано определение 0,5–4,75 мкг фторидиона на основе его каталитического действия на медленную реакцию циркония(IV) с метилтимоловым голубим в водном растворе. В оптимальных условиях после 60 мин получаются ровные калибрационные крывые, давая эффективное молярное светопоглощение 3,23 × 10^4 л. $моль^{-1}$. $мм^{-1}$ при 586 нм. В этом методе встречается значительно меньше влияние катионов чем в методах основанных на реакции ализарин-комплексана с церием(III) или лантаном, но более серьезное влияние если в растворе пробы присутствуют фосфат-, арсенат- и—в меньшей мере—сульфатионы.

СОСТАВ АДДУКТА ТОРИЯ(IV) С 8-ОКСИХИНОЛИНОМ:

A. Corsini and J. Abraham, *Talanta*, 1970, 17, 439.

Резюме—Оранжевый аддукт образующийся из тория(IV) и 8-оксихинолина конвенциональным осаждением является нестехиометрическим. Состав аддукта сильно зависим от опытных условий; определено средное отношение связанного тория и 8-оксихинолина 4,9:1. Недостаток 8-оксихинолина вызван либо частичным гидролизом тория, либо присутствием координированной воды. Описан несложный метод приготовления чистого тетракис-аддукта.

SUMMARIES FOR CARD INDEXES

Nucleation and crystal growth of copper(II) 8-hydroxyquinolinate precipitated from mixed solvents: TONY RIHS, MARLAND C. THURSTON and LESTER C. HOWICK, *Talanta*, 1970, **17**, 123. (Department of Chemistry, University of Arkansas, Fayetteville, Arkansas 72701, U.S.A.)

Summary—The precipitation kinetics of copper(II) 8-hydroxyquinolinate, formed in water–acetone mixtures, have been studied in a stop-flow apparatus by spectrophotometric techniques. Three factors are found to be important in improving the physical characteristics of crystals precipitated from mixed solvents. Supersaturation and growth rate can be controlled uniformly by slow rate of change in solvent composition; the presence of acetone significantly reduces the number of effective nuclei; thirdly, large amounts of organic solvent cause a change in the crystal form and its growth mechanism. At room temperature, copper(II) 8-hydroxyquinolinate is precipitated as a dihydrate from water–acetone mixtures containing 0–60% acetone, and the crystal growth is limited by a diffusion-controlled process. Anhydrous copper(II) 8-hydroxyquinolinate is formed in 70% acetone solutions by a surface-controlled reaction.

Solvent extraction of Ga(III) and In(III) from aqueous halide media by Adogen-364: SH. A. SHERIF, A. S. ABDEL-GAWAD and A. M. EL-WAKIL, *Talanta*, 1970, **17**, 137. (National Research Centre, Dokki, Cairo, U.A.R.)

Summary—Adogen-364 has been used for the extraction of gallium(III) and indium(III) from halogen acid solutions, and the dependence of the extraction on chloride, bromide and iodide ion concentration studied. The separation of Ga(III), In(III) and Al(III) is reported and some conclusions have been drawn about the stoichiometry of the extracted species.

Versatile spectrophotometric method for the determination of silicon: FRANKLIN A. DUCE and STANLEY S. YAMAMURA, *Talanta*, 1970, **17**, 143. (Idaho Nuclear Corporation, Idaho Falls, Idaho 83401, U.S.A.)

Summary—A versatile spectrophotometric method is described for the determination of microgram levels of silicon, as molybdenum blue. It combines the desirable features of existing spectrophotometric methods with three pretreatment procedures, namely (*a*) the removal of cations with a cation-exchange resin in the H^+-form, (*b*) the conversion of all silicon species into the reactive monomer with an alkaline treatment, and (*c*) the decomposition of silicon fluoride with boric acid in the presence of cation-exchange resin. These pretreatments coupled with the colour development provide five procedures which are applicable to a wide variety of samples including natural and industrial water and solutions of various nuclear reactor fuels and components. Provisions are included for the selective determination of total silicon.

НУКЛЕАЦИЯ И РОСТ КРИСТАЛЛОВ 8-ОКСИХИНОЛИНАТА МЕДИ(II) ОСАЖДЕННЫХ ИЗ СМЕШАННЫХ РАСТВОРИТЕЛЕЙ:

Tony Rihs, Marland C. Thurston and Lester C. Howick, *Talanta*, 1970, **17**, 123.

Резюме—Кинетика осаждения 8-оксихинолината меди(II) в смесях воды и ацетона изучена спектрофотометрическим методом в приборе для остановки потока. Установлены три важных фактора для улучщения физических характеристик кристаллов осажденных из смешанных растворителей. Пересыщение и скорость роста поддерживается константным применением медленного изменения состава растворителя; присутствие ацетона в значительной мере снижает число эффективных ядер; в-третых, большие количества органического растворителя вызивают изменение формы кристалла и его механизма роста. При комнатной температуре 8-хинолинат меди(II) осаждается в форме дигидрата из смесях воды и ацетона содержащих 0–60% ацетона, а рост кристаллов ограничен регулированным диффузией процессом. Безводный 8-хинолинат мели(II) образуется в 70% тном ацетоне контроллированной поверхностью реакцией.

ИЗВЛЕЧЕНИЕ Ga(III) И In(III) ИЗ ВОДНЫХ ГАЛОИДНЫХ РАСТВОРОВ С АДОГЕНОМ-364:

Sh. A. Sherif, A. S. Abdel-Gawad and A. M. El-Wakil, *Talanta*, 1970, **17**, 137.

Резюме—Адоген-364 использован для извлечения галлия(III) и индия(III) из растворов галоидных кислот и изучена зависимость экстракции от концентрации хлорид-, бромид- и иодидионов. Приведены результаты разделения Ga(III), In(III) и Al(III) и сделаны выводы о стехоиометрии извлеченных ионов.

МНОГОСТОРОННЫЙ СПЕКТРОФОТОМЕТРИЧЕСКИЙ МЕТОД ОПРЕДЕЛЕНИЯ КРЕМНИЯ:

Franklin A. Duce and Stanley S. Yamamura, *Talanta*, 1970, **17**, 143.

Резюме—Описан многосторонный спектрофотометрический метод определения микрограммовых количеств кремния в форме молибденового голубого. Метод объединяет желательные характеристики имеющихся спектрофотометрических методов, именно (а) уклонение катионов с катионообменником в H^+ форме, (б) превращение всех кремниеьых соединений в реактивный мономер обработкой с щелочью и (в) разложение фторида кремния с боровой кислотой в присутствии катионообменника. Эти предварительные обработки вместе с проявлением окраски представляют собой пять процедур, применимых на ряд разнообразных образцов, включающих природные и промышленные воды и растворы различных топлив ядерных реакторов и их компонентов. Селективное определение общего кремния также принято во внимание.

End-point evaluation in instrumental titrimetry—I. Linear extrapolation of hyperbolic titration curves: J. Vřešťál and S. Kotrlý,® *Talanta*, 1970, **17**, 151. (Department of Analytical Chemistry, College of Chemical Technology, Pardubice, Slov. povstání 565, Czechoslovakia.)

Summary—A method is described for the estimation of a systematic titration error which is introduced by linear extrapolation of hyperbolic titration curves in amperometric, photometric, and other instrumental titrations. It is assumed that the titration is based upon a single-step ion-association reaction $mA + nB \rightleftharpoons A_mB_n$ and that the measured physical property falls within known minimum and maximum values. The procedure is suitable for end-point determination, even when the titration curves have extensive curvature, and for predicting the choice of optimum experimental conditions for a given titration.

α-(Phenylazo)-4-nitrobenzyl cyanide, a new acid-base indicator: László Légrádi, *Talanta*, 1970, **17**, 161. (Nitrokémia Works, Füzfögyártelep, Hungary.)

Summary—A new acid-base indicator, α-(phenylazo)-4-nitrobenzyl cyanide, is proposed. The indicator changes colour from yellow to violet in the presence of alkali owing to the formation of a nitronic acid structure. This indicator is applicable for the titration of weak acids in acetone and ethanol media or in a mixture of these organic solvents and water, with 0·1 M aqueous sodium hydroxide as titrant. The absorption spectra have been recorded for the indicator in 25%, 50% and 75% aqueous ethanol and acetone. By means of the spectra the dissociation constants in these media have been determined. The pK value of α-(phenylazo)-4-nitrobenzyl cyanide is 12·10 in water, and is decreased considerably in acetone but only slightly in ethanol. This behaviour is similar to that of positively charged weak acids and irregular for a weak acid carrying no charge or a negative charge.

Gas-chromatographic determination of ultramicro amounts of selenium in pure sulphuric acid: Yasuaki Shimoishi and Kyoji Tôei, *Talanta*, 1970, **17**, 165. (Department of Chemistry, Faculty of Science, Okayama University, Okayama, Japan.)

Summary—Ultramicro amounts of selenium in pure sulphuric acid are converted into selenous acid with a bromine–bromide redox buffer solution. The selenous acid reacts quantitatively with 4-nitro-*o*-phenylenediamine to form 5-nitropiaselenol which can be extracted into toluene. The extract is very sensitive to electron-capture detection in gas chromatography, and the sensitivity is higher than that of 5-chloro- or 4,5-dichloro-piaselenol. The calibration curve (peak heights) is linear up to 0·15 μg of selenium in 1 ml of toluene. Pure sulphuric acid, commercially available, contains $10^{-6} \sim 10^{-5}$% selenium.

ОПРЕДЕЛЕНИЕ КОНЦА ТИТРОВАНИЯ В ИНСТРУМЕНТАЛЬНОЙ ТИТРИМЕТРИИ—I. ЛИНЕЙНАЯ ЭКСТРАПОЛЯЦИЯ ГИПЕРБОЛИЧЕСКИХ ТИТРАЦИОННЫХ КРИВЫХ:

J. Vřešťál and S. Kotrlý, *Talanta*, 1970, **17**, 151.

Резюме—Описан метод определения систематической ошибки титрации, которая введена линейной экстраполяцией гиперболических титрационных кривых в амперометрической, фотометрической и других инструментальных титрациях. Принято, что титрация основана на ионоассоциационной, протекающей в одном шаге реакции

$$mA + nB \rightleftharpoons A_mB_n$$

и что измеренная физическая характеристика находится в диапазоне ограниченном знакомыми минимальными и максимальными величинами. Методом можно пользоваться для определения конца титрования, даже в случае сильно закривленных титрационных кривых и для предварительного отбора оптимальных опытных условий для данной титрации.

α-(ФЕНИЛАЗО)-4-НИТРОБЕНЗИЛЦИАНИД—НОВЫЙ КИСЛОТНОЩЕЛОЧНЫЙ ИНДИКАТОР:

László Légrádi, *Talanta*, 1970, **17**, 161.

Резюме—α-(фенилазо)-4-нитробензилцианид предложен в качестве нового кислотно-щелочного индикатора. Индикатор изменяет цвет из желтого в фиолетовый в присутствии щелочи, вследствие образования структуры на основе нитроновой кислоты. Этим индикатором может пользоваться для титрования слабых кислот в ацетоновых и спиртовых средах или в смесях этих органических растворителей и воды, с 0,1*M* водным раствором гидроокиси натрия в качестве титрованного раствора. Получены спектры светопоглощения индикатора в 25%, 50% и 75% водном растворе спирта и ацетона. На основе этих спектров вычислены константы диссоциации в этих средах. р*K* α-(фенилазо)-4-нитробензианлциида составляет 12,10 в воде, а снижается значительно в ацетоне, но только в небольшой мере в спирте. Это поведние похоже поведению положительно заряженных слабых кислот, а неправилно в случае слабой кислоты без заряда или отрицательно заряженной слабой кислоты.

ОПРЕДЕЛЕНИЕ УЛЬТРАМИКРОКОЛИЧЕСТВ СЕЛЕНА В ЧИСТОЙ СЕРНОЙ КИСЛОТЕ МЕТОДОМ ГАЗОВОЙ ХРОМАТОГРАФИИ:

Yasuaki Shimoishi and Kyoji Tôei, *Talanta*, 1970, **17**, 165.

Резюме—Ультрамикроколичества селена в чистой серной кислоте превращаются в селенистую кислоту с использованием окислительно-восстановительного буфферного раствора брома-бромида. Селенистая кислота реагирует количественно с 4-нитро-*о*-фенилендиамином с образованием 5-нитропиаселенола, который экстрагируют толуолом. Экстракт весьма чувствительный на электроннозахватывающий детектор газового хроматографа, и его чувствительность больше чем 5-хлор- или 4,5-дихлорпиаселенола. Калибрационная крыва (высота пиков) линейная до 0,15 мкг селена в 1 мл толуола. Чистая серная кислота (коммерческая) содержит 10^{-6} до 10^{-5}% селена.

Stability constants of lanthanide complexes with salicylhydroxamic acid: T. SESHADRI, *Talanta*, 1970, **17**, 168. (Regional Research Laboratory, Jorhat-6, Assam, India.)

Summary—The stability constants of La, Pr, Nd, Sm, Eu, Gd, Dy, Er, Yb and Y complexes of salicylhydroxamic acid have been determined potentiometrically in 3:1 v/v acetone–water medium at 25 ± 0·5° and at an ionic strength of 0·1 with respect to sodium perchlorate. The stability constants are comparable with those of other lanthanide complexes with oxygen-donating ligands such as benzoylacetone and benzoylphenylhydroxylamine.

Complexometric determination of molybdenum(VI): RUDOLF PŘIBIL and VLADIMÍR VESELÝ, *Talanta*, 1970, **17**, 170. (Laboratory of Analytical Chemistry, J. Heyrovský Polarographic Institute, Czechoslovak Academy of Sciences, Prague 1, Jilská 16, Czechoslovakia.)

Summary—In acidic medium molybdenum(VI) forms a stable complex on boiling with excess of DCTA and hydroxylamine hydrochloride. Molybdenum can then be determined by back-titration of the excess of DCTA either with zinc chloride at pH 5–5·5 or with thorium nitrate at pH 3–4·5, Xylenol Orange being used as indicator in both cases. A simple method for the determination of molybdenum in the presence of moderate amounts of tungsten is also described.

The dissociation constants of alizarin fluorine blue: C. K. LAIRD and M. A. LEONARD, *Talanta*, 1970, **17**, 173. (Department of Inorganic and Analytical Chemistry, Queen's University, Belfast, N. Ireland).

Summary—Dissociation constants for the analytical reagent alizarin fluorine blue (3-aminomethylalizarin-*N*,*N*-diacetic acid) have been determined by potentiometric titration at ionic strength 0·1, and are $k_1 = 1{\cdot}28 \pm 0{\cdot}30 \times 10^{-5}$; $k_2 = 2{\cdot}82 \pm 0{\cdot}24 \times 10^{-8}$; $k_3 = 3{\cdot}72 \pm 0{\cdot}19 \times 10^{-11}$; $k_4 = 6{\cdot}39 \pm 0{\cdot}12 \times 10^{-12}$.

КОНСТАНТЫ УСТОЙЧИВОСТИ КОМПЛЕКСОВ ЛАНТАНИДОВ С САЛИЦИЛГИДРОКСАМОВОЙ КИСЛОТОЙ:

T. Seshadri, *Talanta*, 1970, **17**, 168.

Резюме—Константы устойчивости комплексов La, Pr, Nd, Sm, Eu, Gd, Dy, Er, Yb и Y с салицилгидроксамовой кислотой определены потенциометрическим методом в растворе ацетон—вода 3:1 (по объему), при 25 ± 0,5° и ионной силы 0,1 в отношении на перхлорат натрия. Константы устойчивости сравниваемы с константами других комплексов лантанидов с кислород-подавающими лигандами, как на пример бензоилацетоном и бензоилфенилгидроксиламином.

КОМПЛЕКСОНОМЕТРИЧЕСКОЕ ОПРЕДЕЛЕНИЕ МОЛИБДЕНА (VI):

Rudolf Přibil and Vladimír Veselý, *Talanta*, 1970, **17**, 170.

Резюме—В кислых средах молибден(VI) образует устойчивый комплекс при кипячении с избытком ДЦТА и хлористоводородным гидроксиламином. Молбден определяют оттитровыванием избытка ДЦТА с хлоридом цинка при pH 5–5,5 или с нитратом тория при pH 3–4,5, пользуясь ксиленолоранжевым в качестве индикатора в обоих случаях. Также описан несложный метод определения молибдена в присутствии умеренных количеств вольфрама.

КОНСТАНТЫ ДИССОЦИАЦИИ АЛИЗАРИНФТОРОВОГО ГОЛУБОГО:

C. K. Laird and M. A. Leonard, *Talanta*, 1970, **17**, 173.

Резюме—Определены константы диссоциации аналитического реагента ализарнфторового голубого (3-аминометилализарин-*N*,*N*-диуксусной кислоты) методом потенциометрической титрации при ионной силе 0,1; они составляют $к_1 = 1,28 \pm 0,30 \times 10^{-5}$; $к_2 = 2,82 \pm 0,24 \times 10^{-8}$; $к_3 = 3,72 \pm 0,19 \times 10^{-11}$ и $к_4 = 6,39 \pm 0,12 \times 10^{-12}$,

Complexometric titration of total iron with *o*-mercaptobenzoic acid as indicator: L. M. Bhandari, M. M. L. Khosla and S. P. Rao, *Talanta*, 1970, **17**, 176. (Defence Laboratory, Jodhpur, India.)

Summary—The soluble deep blue complex of iron(II) with *o*-mercaptobenzoic acid in aqueous pyridine medium (pH 6·4–7·4) can be titrated with EDTA at room temperature with a sharp colour change from blue to light yellow. *o*-Mercaptobenzoic acid forms a 2:1 complex with iron(II), giving maximum absorption at 600 nm. Its stability constant was found to be $\log K = 7{\cdot}7$. With iron(III), a transient blue colour is first formed which soon becomes colourless and then on the addition of excess of reagent, the deep blue complex is formed on reduction of the iron(III). Iron can be titrated in the presence of copper, if the latter is masked with sodium thiosulphate. Cobalt and nickel interfere. Common anions such as chloride, tartrate, phosphate, oxalate, citrate and acetate give no interference.

Hydrolysis of substituted 8-acetoxyquinolines: E. J. Billo, R. P. Graham® and P. G. Calway, *Talanta*, 1970, **17**, 180. (Burke Chemical Laboratories, McMaster University, Hamilton, Ontario, Canada.)

Summary—In the absence of metal ions, the hydrolysis of 2-methyl-8-acetoxyquinoline and of 5-chloro-8-acetoxyquinoline follow the same reaction paths as those of the parent ester 8-acetoxyquinoline, including an intramolecular catalysis by the quinoline nitrogen. Unlike the hydrolysis of the other esters, that of the 2-methyl compound appears not to be catalysed by metal ions, and this is consistent with the view that catalysis by a metal ion involves the formation of a 7-membered chelate structure.

Acid dissociation and metal chelate formation equilibria of some halogenated diphenylthiocarbazones: Abdul R. Al-Salihy and Henry Freiser, *Talanta*, 1970, **17**, 182. (Department of Chemistry, University of Arizona, Tucson, Arizona 85721.

Summary—The acid dissociation constants (K_a) of di-*p*-fluoro-, di-*p*-chloro-, di-*p*-bromo-, di-*p*-iodo- and di-*m*-trifluoromethylphenylthiocarbazones and the equilibrium formation constants (K_{f_1}) of their 1:1 complexes with Co(II), Ni and Zn have been determined at 25° in 50% v/v aqueous dioxan at 0.10 M ionic strength. Each of the electron-withdrawing substituents gives a reduction in pK_a roughly proportional to its Hammett σ value, and log K_{f_1} increases linearly with pK_a.

КОМПЛЕКСОНОМЕТРИЧЕСКОЕ ТИТРОВАНИЕ ОБЩЕГО ЖЕЛЕЗА С ИСПОЛЬЗОВАНИЕМ *о*-МЕРКАПТОБЕНЗОЙНОЙ КИСЛОТЫ В КАЧЕСТВЕ ИНДИКАТОРА:

L. M. Bhandari, M. M. L. Khosla and S. P. Rao, *Talanta*, 1970, 17, 176.

Резюме—Темносиний растворимый комплекс железа(II) с *о*-меркаптобензойной кислотой в водном растворе пиридина (pH 6,4–7,4) можно титровать с ЭДТА при комнатной температуре с получением резкой перемены цвета из синего в слабожелтый. *о*-Меркаптобензойная кислота образует комплекс 2:1 с железом(II) с максимальным светопоглощением при 600 нм. Определена его константа устойчивости $\lg K = 7{,}7$. Железо(III) в первых образует преходящую синую окраску, раствор затем обесцвечивается, а добавлением избытка реагента образуется темносиний комплекс после восстановления железа(III). Железо можно титровать в присутствии меди если последный ион маскирован тиосульфатом натия. Кобальт и никель мешают определению. Обыкновенныё анионы хлорид, цитрат, тартарат, фосфат, оксалат и ацетат не мешают определению.

ГИДРОЛИЗ ЗАМЕЩЕННЫХ 8-АЦЕТОКСИХИНОЛИНОВ:

E. J. Billo, R. P. Graham® and P. G. Calway, *Talanta*, 1970, 17, 180.

Резюме—В отсутствии ионов металлов гидролиз 2-метил-8-ацетоксихинолина и 5-хлор-8-ацетоксихинолина следит смер реакции родственного эфира 8-ацетоксихинолина, включая интрамолекулярный катализ азотом хинолина. В отличии от гидролива других эфиров гидролиз 2-метилсоединения по-видимому не катализирован ионами металлов; этот факт в согласности с взглядом что катализ ионом металла включает в себя образование 7-членной хелатной структуры.

КИСЛОТНАЯ ДИССОЦИАЦИЯ И РАВНОВЕСИЯ ОБРАЗОВАНИЯ ХЕЛАТОВ МЕТАЛЛОВ НЕКОТОРЫХ ГАЛОИД-ЗАМЕЩЁННЫХ ДИФЕНИЛТИОКАРБАЗОНОВ:

Abdul Al-salihy and Henry Freiser, *Talanta*, 1970, 17, 182.

Резюме—Определены константы кислотной диссоциации (K_a) ди-п-фтор-, ди-п-хлор-, ди-п-бром-, ди-п-иод- и ди-м-трифторметилфенилтиокарбазонов и равновесные константы образования (K_{f_1})/их 1:1 комплексов с Co(II), Ni и Zn при 25° в 50% водном растворе диоксана (по объему) и ионной силы 0,10 *M*. Каждый из электронноудаляющих заместителей снижает pK_a грубо пропорционально значению σ Хамметта; $\log K_{f_1}$ увеличивается линейно с pK_a.

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SUMMARIES FOR CARD INDEXES

Comparative distribution coefficients and cation-exchange behaviour of the alkaline earth elements with various complexing agents: F. W. E. Strelow and C. H. S. W. Weinert, *Talanta*, 1970, **17**, 1. (National Chemical Research Laboratory, P.O. Box 395, Pretoria, S. Africa.)

Summary—Equilibrium distribution coefficients are presented for the alkaline earth metals Be(II), Mg(II), Ca(II), Sr(II) and Ba(II) with the complexing agents acetate, formate, lactate, citrate, tartrate, α-hydroxyisobutyrate, malonate, malate, acetylacetonate, EDTA, EGTA and DCTA, and the AG50W-X8 cation-exchange resin. Coefficients in HCl, HNO_3, $HClO_4$ and NH_4Cl are included for the sake of completeness. The merits of the various complexing agents for the separation of adjacent element pairs are discussed and experimental elution curves are presented for selected separations. Separation factors for adjacent elements are calculated at eluting agent concentrations corresponding to a distribution coefficient of 10 for the less strongly absorbed element and are presented together with the eluting agent concentrations to form a basis for comparison.

Analytical applications of ternary complexes—VIII. An improved reagent system for the spectrophotometric determination of aluminium: J. E. Chester, R. M. Dagnall and T. S. West, *Talanta*, 1970, **17**, 13. (Chemistry Department, Imperial College, London, S.W.7, U.K.)

Summary—Aluminium ions form a ternary complex with Catechol Violet (CV) and cetyltrimethylammonium bromide (CTAB) in which an Al^{3+}:CV:CTAB ratio of 1:2:5 is observed. The sensitivity of the binary complex between aluminium and Catechol Violet $\varepsilon_{615nm} = 1{\cdot}50 \times 10^3$ l. mole^{-1} . mm^{-1} is enhanced on ternary complex formation to $\varepsilon_{670nm} = 5{\cdot}30 \times 10^3$ l. mole^{-1} . mm^{-1}. The colour is formed instantaneously, stabilizes within 20 min, and may be used for the detection of aluminium in the range 0·27–54 pm in the presence of EDTA which prevents the interference of most ions. A benzoate extraction procedure for aluminium is used to prevent interference from hundredfold amounts of Cr(VI), Fe(II), Fe(III), Hg(II), Sb(III), Ti(IV) and acetate, but Be, Cr(III), rare earths, V(V), Zr and tartrate must be absent, as must high concentrations of phosphate and fluoride ions.

СРАВНИТЕЛЬНЫЕ КОЭФФИЦИЕНТЫ РАСПРЕДЕЛЕНИЯ И КАТИОНООБМЕННЫЕ ХАРАКТЕРИСТИКИ ЩЕЛОЧНОЗЕМЕЛЬНЫХ ЭЛЕМЕНТОВ С РАЗНЫМИ КОМПЛЕКСООБРАЗУЮЩИМИ АГЕНТАМИ:

F. W. E. Strelow and C. H. S. W. Weinert, *Talanta*, 1970, 17, 1

Резюме—Приведены равновесные коэффициенты распределения для щелочноземельных элементов Be(II), Mg(II), Ca(II), Sr(II) и Ba(II) с комплексообразующими агентами ацетатом, формиатом, лактатом, цитратом, тартаратом, α-оксиизобутиратом, малонатом, малатом, ацетилацетонатом, ЭДТА, ЭГТА и ДЦТА, икатионообменной смолой AG50W-X8. В качестве комплетности также включены коэффициенты в HCl, HNO_3, $HNClO_4$ и NH_4Cl, Обсуждены преимущества различных комплексообразующих агентов для разделения соседных пар элементов и приведены экспериментальные кривые элюирования для отобранных разделений. Вычислены факторы разделения соседных элементов для концентраций элюрующего агента отвествующих коэффициенту распределения 10 для менее сильно абсорбированного элемента и приведены вместе с концентрациями элюирующего агента, с целью послужить в качестве основы для сравнения.

ПРИМЕНЕНИЕ ТРОЙНИХ КОМПЛЕКСОВ В АНАЛИЗЕ—VIII. УЛУЧШЕННАЯ СИСТЕМА РЕАГЕНТОВ ДЛЯ ОПРЕДЕЛЕНИЯ АЛЮМИНИЯ СПЕКТРОФОТОМЕТРИЧЕСКИМ МЕТОДОМ:

J. E. Chester, R. M. Dagnall and T. S. West, *Talanta*, 1970, 17, 13.

Резюме—Ионы алюминия образуют троной комплекс с катехиновым фиолетовым (КФ) и цетилтриметиламмонийбромидом (ЦТАБ) в котором отношение Al^{3+}:КФ:ЦТАБ равно 1:2:5. Чувствительность двойного комплекса алюминия и катехинового фиолетового $\varepsilon_{615нм} = 1{,}50 \times 10^3$ л.моль$^{-1}$.мм$^{-1}$ повышается образованием тройного комплекса до $\varepsilon_{670mn} = 5{,}30 \times 10^3$ л.моль$^{-1}$.мм$^{-1}$. Окраска появляется мгновенно, стабилизируется в течение 20 мин и ее можно пользоваться для обнаружения алюминия в пределах 0,27–54 мг/л в присутствии ЭДТА который укланяет влияние большинства ионов. Экстракция алюминия бензоатом использована для уклонения влияния 100-кратного избытка Cr(VI), Fe(II), Fe(III), Hg(II), Sb(III), Ti(IV) и ацетата, но Be, Cr(III), редкоземельные элементы, V(V), Zr и тартарат надо отсутсвовать, так же как и высокие концентрации фосфат- и фторидионов.

Performance characteristics of analytical methods—I: A. L. Wilson, *Talanta*, 1970, **17**, 21. (Water Research Association, Ferry Lane, Medmenham, Nr. Marlow Bucks, U.K.)

Summary—The ever-increasing volume of analytical literature makes it important to be able to compare unambiguously the advantages and disadvantages of analytical methods. To this end, a set of consistent definitions and methods for determining quantitative performance-characteristics (*e.g.*, precision, sensitivity, bias) is needed. The aim of this series of papers is to review the definition and determination of such parameters, and to suggest criteria for general use. This first paper discusses the general problem, considers those general aspects of analytical methods that are important, and establishes the performance-characteristics to be considered in detail.

The performance-characteristics of analytical methods—II: A. L. Wilson, *Talanta*, 1970, **17**, 31. (Water Research Association, Ferry Lane, Medmenham, Nr. Marlow, Bucks. U.K.)

Summary—Statements on the errors of analytical results are an important aspect of characterizing the performance of analytical methods. The general nature of random and systematic errors is briefly discussed, and methods of numerically defining the former are considered. It is suggested that the standard deviation of analytical results be used exclusively as the quantitative measure of precision within the context of performance-characteristics. Techniques for, and precautions to be observed in, estimating standard deviation are critically discussed. On this basis, general principles are proposed that should be observed whenever possible in experimental tests to estimate standard deviation.

***N*-Acetylsalicyloyl-*N*-phenylhydroxylamine as an analytical reagent. Determination of niobium and tantalum in the presence of each other**: C. P. Savariar and Joy Joseph, *Talanta*, 1970, **17**, 45. (Department of Chemistry, University of Calicut, Kerala, India.)

Summary—*N*-Acetylsalicyloyl-*N*-phenylhydroxylamine is proposed for the separation of niobium(V) and tantalum(V) and their gravimetric determination. Niobium is precipitated at pH 5·5–6·5 by the reagent and the complex is weighed directly. Tantalum is precipitated from 1–2*M* hydrochloric acid solutions and the complex is ignited to tantalum pentoxide. The method is fairly selective. In the presence of thiocyanate the reagent forms an extractable complex with niobium. The reaction forms the basis of a selective and sensitive spectrophotometric determination of niobium.

ХАРАКТЕРИСТИКИ ВЫПОЛНЕНИЯ АНАЛИЧЕСКИХ МЕТОДОВ—I:

A. L. WILSON, *Talanta*, 1970, **17**, 21.

Резюме—Резко увеличивающийся объем аналитической литературы вызывает потребность сравнивать однозначно преимущества и невыгодности аналитических методов. В этом качестве надо иметь последовательные дефиниции и методы определения количественных характеристик выполнения (на пример точности, чувствительности, склонности). Цель этого ряда статей сделать обзор дефиниций и определения этих параметров и предложить критерии для общего применения. Предлежащая статья обсуждает общую проблему и важные общие виды аналитических методов, и обозначает изучаемые подробно характеристики выполнения.

ХАРАКТЕРИСТИКИ ВЫПОЛНЕНИЯ АНАЛИТИЧЕСКИХ МЕТОДОВ—II:

A. L. WILSON, *Talanta*, 1970, **17**, 31.

Резюме—Сообщение ошибок аналитических результатов представляет собой важный вид охарактеризования аналитических методов. Коротко обсужден общий характер случайных и систематических ошибок и сравнены методы цифрового определения этих ошибок. Предложено исключительное применение стандартного отклонения аналитических результатов в качестве количественной меры точности в смисле характеристик выполнения. Критически обсуждены методы определения стандартного отклонения и меры предосторожности в этом определении. На этой основе предложены общие принципы которые надо почитать—если обстоит возможность—в опытах определения стандартного отклонения.

N-АЦЕТИЛСАЛИЦИЛОИЛ-*N*-ФЕНИЛГИДРОКСИЛАМИН В КАЧЕСТВЕ АНАЛИТИЧЕСКОГО РЕАГЕНТА: ОПРЕДЕЛЕНИЕ НИОБИЯ И ТАНТАЛА ОДНОГО В ПРИСУТСТВИИ ДРУГОГО:

C. P. SAVARIAR and JOY JOSEPH, *Talanta*, 1970, **17**, 45.

Резюме—*N*-Ацетилсалицилоил-*N*-фенилгидроксиламин предложен для разделения ниобия(V) и тантала(V) и их определения весовым методом. Ниобий осаждают реагентом при pH 5,5–6,5 и комплекс прямо взвешивают. Тантал осаждают из 1–2*M* содянокислых растворов и комплекс обзоливают до пятиокиси тантала, Метод является довольно избирательным. В присутствии роданида реагент образует экстрагируемый комплекс с ниобием. На этой реакции основан селективный и чувствительный спекрофотометрический метод определения ниобия.

Determination of deuterium in heavy water by secondary deuteron activation: R. Pretorius and R. E. Wainerdi,® *Talanta*, 1970, **17**, 51. (Activation Analysis Research Laboratory, Texas A & M University, College Station, Texas, U.S.A.)

Summary—The deuterium concentration of heavy water was determined by utilizing recoiling deuterium nuclei from n–d collisions to induce the reaction $^{16}O(d, n)^{17}F$. The internal ratio of 66-sec fluorine-17 to 7·35-sec nitrogen-16 activity, formed by the reaction $^{16}O(n, p)^{16}N$, was found to vary linearly with deuterium concentration. When such an internal ratio of activities is measured, the neutron flux and sample weight need not be known. Deuterium was determined over the range from 2·6 to 94·5 atom%, with a relative standard deviation of 2·8%. The effect of sample size was investigated and it was found that the relative amount of fluorine-17 activity formed became less as sample size decreased, due to the loss of recoiling deuterons from the sample. A simple relationship to account for this effect was obtained.

Rapid spectrophotometric determination of boron in steel: Om P Bhargava and W. Grant Hines, *Talanta*, 1970, **17**, 61. (Chemical and Metallurgical Laboratories, The Steel Company of Canada Ltd., Wilcox Street, Hamilton, Ontario, Canada.)

Summary—A rapid spectrophotometric method is presented for the determination of boron in steel by use of the fluoborate–Methylene Blue complex. The method is in principle similar to that of Rosotte, but modifications simplify the operation, obviate contamination and avoid problems with emulsion formation. Up to 20% Cr, 10% Ni, and 1% each of V, Mo and W present either individually or collectively do not interfere in the determination, making it applicable to alloy steels. The determination limit of the method has been lowered from 5 to 0·2 ppm boron. Samples are dissolved at room temperature in polythene bottles, solubilizing all forms of boron including boron nitride, and avoiding loss of relatively volatile boron compounds. The precision of the method is good. Six samples can be analysed in less than 2 hr.

ОПРЕДЕЛЕНИЕ ДЕЙТЕРИЯ В ТЯЖЕЛОЙ ВОДЕ МЕТОДОМ ВТОРИЧНОЙ ДЕЙТЕРОННОЙ АКТИВАЦИИ:

R. Pretorius and R. E. Wainerdi®, *Talanta*, 1970, **17**, 51.

Резюме—Концентрация дейтерия в тяжелой воде определена использованием ядер дейтерия отдачи из $n - d$ сразов для индуцирования реакции $^{16}\mathrm{O}(d, n)^{17}\mathrm{F}$. Обнаружена линейная зависымость концентрации дейтерия от внутренного отношения активности 66-сек фтор-17 в 7,35-сек азот-16, образованной реакцией $^{16}\mathrm{O}(n, p)^{16}\mathrm{N}$. При измерении такого внутренного отношения активностей не надо определять поток нейтронов ни вес образца. Дейтерий определен в пределах 2,6 до 94,5 атомных %, с относительной стандартной ошибкой 2,8 %. Изучено влияние веса образца и обнаружено что относительная активность фтора-17 уменьшается с уменьшением веса образца в результате потер дейтеронов отдачи из образца. Обнаружено простое отношение для объяснения этого эффекта.

БЫСТРОЕ СПЕКТРОФОТОМЕТРИЧЕСКОЕ ОПРЕДЕЛЕНИЕ БОРА В СТАЛИ:

Om P. Bhargava and W. Grant Hines, *Talanta*, 1970, **17**, 61.

Резюме—Предложен быстрый спектрофотометрический метод определения бора в стали, пользующийся комплексом фторобората с метиленовым синим. В принципе метод похожий методу Розотта, но модификации упрощают процедуру, избежают загрязнение и проблемы образования эмульсий. До 20 % Cr, 10 % N:и 1 % V, Mo или W не мешают определению если присутствуют индивидуально или коллективно, этим образом позволяя применение метода в анализе легированных сталях. Чувствительность метода снижена от 5 до 0,2 мкг/г бора. Пробы растворяют при комнатной температуре в полиэтиленовых склянках, с растворением Всехформ бора включая нитрид бора, а избежая потери довольно летучих соединений бора. Метод дает хорошую воспроизводимость, а позволяет анализировать шесть проб в меньше чем 2 ч.

Anion-exchange separation and spectrophotometric determination of molybdenum and tungsten in silicate rocks: KAZUAKI KAWABUCHI and ROKURO KURODA, *Talanta*, 1970, **17**, 67. (Laboratory for Analytical Chemistry, Faculty of Engineering, University of Chiba, Yayoi-cho, Chiba, Japan.)

Summary—A combined ion-exchange spectrophotometric method has been developed for the determination of molybdenum and tungsten in silicate rocks. After the decomposition of samples with a mixture of sulphuric, nitric and hydrofluoric acids, traces of molybdenum and tungsten are separated from other elements by anion-exchange in acid sulphate media containing hydrogen peroxide. The adsorbed molybdenum and tungsten can easily be stripped from the column by elution with sodium hydroxide–sodium chloride solution. The adsorption and desorption steps provide selective concentration of molybdenum and tungsten, allowing the simultaneous spectrophotometric determination of the two metals with dithiol. Results on the quantitative determination of molybdenum and tungsten in the U.S. Geological Survey standard samples are included.

Use of 3-hydroxy-1,3-diphenyltriazine in the spectrophotometric determination of copper, palladium, iron, cobalt, nickel, and molybdenum: B. DAS and S. C. SHOME, *Talanta*, 1970, **17**, 75. (Chemical Laboratory, Presidency College, Calcutta, India.)

Summary—3-Hydroxy-1,3-diphenyltriazine (HDPTA) forms brightly coloured complexes with copper, palladium, iron, cobalt and nickel ions, which are readily extractable in benzene. The deep yellow molybdenum complex is completely soluble in 60% ethanol. All the chelates have a definite absorption maximum between 398 and 422 nm, the reagent absorption being negligible above 415 nm. The molar composition of the chelates is ML_2, except for iron and cobalt which form ML_3 complexes. Microquantities of these metals can be determined spectrophotometrically with HDPTA.

АНИОНООБМЕННОЕ РАЗДЕЛЕНИЕ И ОПРЕДЕЛЕНИЕ СПЕКТРОФОТОМЕТРИЧЕСКИМ МЕТОДОМ МОЛИБДЕНА И ВОЛЬФРАМА В СИЛИКАТНЫХ ГОРНЫХ ПОРОДАХ:

Kazuaki Kawabuchi and Rokuro Kuroda, *Talanta*, 1970, **17**, 67.

Резюме—Разработан комбинированный ионообменноспектрофотометрический метод для определения молибдена и вольфрама в силикатных горных породах. После разложения образцов с смесью серной, азотной и фтороводородной кислот, следы молибдена и вольфрама отделяют от других элементов анионным обменом в сернокислой среде, содержащей перекись водорода. Адсорбированные элементы молибден и вольфрам легко элюируют из колонки раствором гидроокиси натрия и хлорида натрия. Фазы адсорбции и десорбции позволяют селективное концентрирование молибдена и вольфрама и одновременное спектрофотометрическое определение этих металлов с дитиолом. Приведены результаты количественного анализа молибдена и вольфрама в эталонах U.S. Geological Survey.

ИСПОЛЬЗОВАНИЕ 3-ОКСИ-1,3-ДИФЕНИЛТРИАЗИНА ДЛЯ СПЕКТРОФОТОМЕТРИЧЕСКОГО ОПРЕДЕЛЕНИЯ МЕДИ, ПАЛЛАДИЯ, ЖЕЛЕЗА, КОБАЛЬТА, НИКЕЛЯ И МОЛИБДЕНА:

B. Das and S. C. Shome, *Talanta*, 1970, **17**, 75.

Резюме—3-Окси-1,3-дифенилгриазин (ОДФТА) образует яркоокрашенные комплексы с ионами меди, палладия, железа, кобальта и никеля, которые легко извлекаются бензолом. Темножелтый комплекс молибдена полностью растворимый в 60% спирте. Все комплексы имеют определенный максимум светопоглощения в пределах 398–422 нм, не принимая во внимание поглощение реагента выше 415 нм. Молекуля рный состав хелатов ML_2 исключая железо и кобальт, которые образуют комплексы ML_3. ОДФТА позволяет определять микроколичества этих металлов спектрофотометрическим методом.

A separation scheme for the analysis of multicomponent samples: James S. Fritz and Gary L. Latwesen, *Talanta*, 1970, **17**, 81. (Institute for Atomic Research and Department of Chemistry, Iowa State University, Ames, Iowa 50010, U.S.A.)

Summary—A sequential separation scheme has been devised for the quantitative analytical separation of 27 different metal ions. Five different chromatographic and ion-exchange columns are used to separate the metal ions into groups. The metal ions of each group are eluted separately from each column by means of selective eluents. Following separation, the metal ions are determined by titrimetry, flame spectrometry or other appropriate analytical methods. The reliability of the proposed scheme has been demonstrated by extensive testing, including the analysis of U.S. National Bureau of Standards samples. The scheme can be used for macro or micro quantities.

Metallextraktionen mit aliphatischen Alkoholen: Eugen Gagliardi and Peter Tümmler, *Talanta*, 1970, **17**, 93. (Institut für Anorganische und Analytische Chemie der Universität Graz, Österreich.)

Summary—A number of metal ions may be extracted quantitatively from iodide-containing sulphuric acid solutions by 2-ethyl-1-butanol, 4-methyl-2-propanol, or 1-butoxy-2-propanol, some partially extracted, and others not at all. There are many possibilities for separations, two of which—zinc–cadmium and indium–gallium—are described, and have been tested in technical products. The determination of the composition of the extracted metal complexes is described with reference to those of mercury, a conductimetric extraction titration being used.

Spectrophotometric determination of niobium(V) with n-propyl 3,4,5-trihydroxybenzoate: Fadhil Jasim, *Talanta*, 1970, **17**, 103. (Department of Chemistry and Food Technology, College of Agricutlure, University of Baghdad, Baghdad, Iraq.)

Summary—The use of n-propyl 3,4,5-trihydroxybenzoate (PTB) for the spectrophotometric determination of niobium is investigated. PTB yields a yellowish-orange ML_2 chelate with Nb(V) at pH 6·1. The formation constant at pH 6·1 is about 10^{10}. Beer's law is obeyed over the range 0–100 μg of Nb per ml.

СХЕМА РАЗДЕЛЕНИЯ ДЛЯ АНАЛИЗА МНОГОКОМПОНЕНТНЫХ ОБРАЗЦОВ:

James S. Fritz and Gary L. Latwesen, *Talanta*, 1970, **17**, 81.

Резюме—Разработана последовательная схема разделения для количественного аналитического разделения 27 различных ионов металлов. Использовано пять различных хроматографических и ионообменных колонок для разделения ионов металлов в группы. Ионы металлов каждой группы элюированы отделенно из каждой колонки с использованием селективных элюентов. После разделения ионы металлов определены титриметрическими или пламенно-фотометрическими методами или другими подходящими аналитическими. Прочность предложенной схемы подтвержена тщательным испытыванием, включая анализ образцов U.S. National Bureau of Standards. Схема применима на макро- или микрошкале.

ЭКСТРАКЦИЯ МЕТАЛЛОВ С АЛИФАТИЧЕСКИМИ СПИРТАМИ:

Eugen Gagliardi and Peter Tümmler, *Talanta*, 1970, **17**, 93.

Резюме—Ряд ионов металлов можно экстрагировать количественно из иодидсодержащих растворов серной кислоты 2-этил-1-бутанолом, 4-метил-2-пропанолом или 1-бутокси-2-пропанолом, некоторые ионы экстрагированы частично, некоторые совсем не экстрагированы. Даны многие возможности разделения, две из них—цинк-кадмий и индий-галлий—были испытаны на технических продуктах. Описано определение состава экстрагированных комплексов металлов, ссылаясь на комплексы ртути, с применением кондуктометрической экстракционной титрации.

СПЕКТРОФОТОМЕТРИЧЕСКОЕ ОПРЕДЕЛЕНИЕ НИОБИЯ(V) Н-ПРОПИЛ-3,4,5-ТРИОКСИБЕНЗОАТОМ:

Fadhil Jasim, *Talanta*, 1970, **17**, 103.

Резюме—Исследовано применение н-пропил-3,4,5-триоксибензоата (ПТБ) в спектрофотометрическом определении ниобия. ПТБ дает желтооранжевый ML_2 комплекс с Nb(V) при pH 6,1. Константа образования при pH 6,1 равна приблизительно 10^{10}. Закон Бера почитается в пределах 0–100 мкг/мл Nb.

Determination of gadolinium in sodium borate glasses: Renata Reisfeld and Ehud Biron, *Talanta*, 1970, **17**, 105. (Department of Inorganic and Analytical Chemistry, The Hebrew University of Jerusalem, Israel.)

Summary—A method for the determination of gadolinium in sodium borate glasses is described which utilizes the 312-nm fluorescence of gadolinium under 273-nm excitation. A linear dependence of fluorescence on concentration is found for the concentration range 10–20000 ppm. Quenching of gadolinium fluorescence by samarium is examined.

Polarographic determination of impurities in high purity phosphorus: T. Miwa, T. Kono, R. Isomura and A. Mizuike, *Talanta*, 1970, **17**, 108. (Faculty of Engineering, Nagoya University, Chikusa-ku, Nagoya, Japan.)

Summary—Square-wave and radio-frequency polarographic techniques in phosphoric acid–potassium chloride media are applied to the simultaneous determination of copper, lead and cadmium in high-purity red phosphorus down to a level of 0·1 ppm. In addition *ca.* 0·01 ppm of cadmium is determined by R.F. polarography in potassium sulphate base electrolyte after cation-exchange separation.

Submicro determination of cobalt, manganese or nickel in organometallic compounds: R. Belcher®, Barbara Crossland and T. R. F. W. Fennell, *Talanta*, 1970, **17**, 112. (Department of Chemistry, The University, P.O. Box 363, Birmingham 15, U.K.)

Summary—Methods for the determination of cobalt, manganese or nickel in samples of organometallic compounds weighing 30–100 μg have been developed. Spectrophotometric determination following digestion with nitric and sulphuric acids in a sealed tube is recommended, all results obtained from the analysis of standard compounds being within ±0·4% absolute error. Digestion in an open tube with perchloric and sulphuric acids gives slightly low results for cobalt and nickel compounds and is inappropriate for manganese compounds.

ОПРЕДЕЛЕНИЕ ГАДОЛИНИЯ В НАТРИЙБОРАТНЫХ СТЕКЛАХ:

Renetа Reisfeld and Ehud Biron, *Talanta*, 1970, **17**, 105.

Резюме—Описан метод определения гадолиния в натрийборатных стеклах, основан на флуоресценции гадолиния при 312 нм с возбуждением при 273 нм. Обнаружена линейная зависимость флуоресценции от концентрации в пределах 10–20000 частей на миллион. Изучено погашение самарием флуоресценции гадолиния.

ОПРЕДЕЛЕНИЕ ПРИМЕСЕЙ В ВЫСОКОЧИСТОТНОМ ФОСФОРЕ ПОЛЯРОГРАФИЧЕСКИМ МЕТОДОМ:

T. Miwa, T. Kono, R. Isomura and A. Mizuike, *Talanta*, 1970, **17**, 108.

Резюме—Полярографические методы квадратной волны и радиочастоты использованы в средах фосфорной кислоты и хлорида калия для одновременного определения меди, свинца и кадмия в высокочистотном красном фосфоре до концентрации 0,1 мкг/г. Кроме того можно определять около 0,01 мкг/г кадмия методом радиочастотной полярографии на фоне сульфата калия после выделения катионообменным методом.

СУБМИКРОМЕТОД ОПРЕДЕЛЕНИЯ КОБАЛЬТА, МАРГАНЦА ИЛИ НИКЕЛЯ В МЕТАЛЛООРГАНИЧЕСКИХ СОЕДИНЕНИЯХ:

R. Belcher®, Barbara Crossland and T. R. F. W. Fennell, *Talanta*, 1970, **17**, 112.

Резюме—Разработаны методы определения кобальта, марганца или никеля в 30–100 мкг пробы металлоорганических соединений. Предложено дигерирование с азотной и серной кислотами в закрытой трубке с последующим спектрофотометрическим определением; ошибка полученных на стандартных соединениях результатов составляла меньше чем ±0,4 % абс. Дигерирова нием в открытой трубке с хлорной и серной кислотами получаются незначительно низкие результаты в случае соединений кобальта и никеля, а метод неприменим в случае соединений марганца.

Spectrophotometric extractive titrations—VII. Titrations with di-2-naphthylthiocarbazone: A. Galík, *Talanta*, 1970, **17**, 115. (Lachema, N.C., Kaznějov, Czechoslovakia.)

Summary—An investigation of the possibilities of the use of di-2-naphthylthiocarbazone as titrant in spectrophotometric extractive titrations has been undertaken. A selective procedure for successive titration of silver in an ammoniacal medium has been developed and applied to the analysis of germanium dioxide. It has been established that the consecutive titration of mercury and zinc in the microgram range is possible. Because of low selectivity of this titration, a separation of mercury and zinc from other ions is necessary.

Determination of atmospheric iron particulates by X-ray fluorescence spectroscopy: Jae Y. Hwang, *Talanta*, 1970, **17**, 118. (Applications Laboratory, Instrumentation Laboratory Inc., 113 Hartwell Avenue, Lexington, Mass. 02173, U.S.A.)

Summary—A method is described for the determination of atmospheric iron particulates by X-ray fluorescence spectroscopy. Samples are collected, with a low-volume air sampler, on organic membranes which are used directly for measurement by comparison with standards prepared by precipitation of hydrous iron(III) oxide on similar membranes. The method is simple and rapid, and offers a precision and error of about 6% for the range 10–200 μg of iron.

ЭКСТРАКЦИОННО-СПЕКТРОФОТОМЕТРИЧЕСКИЕ ТИТРАЦИИ—VII. ТИТРАЦИИ С ДИ-2-ИАФТИЛТИОКАРБАЗОНОМ:

A. Galík, *Talanta*, 1970, **17,** 115.

Резюме—Изучена применимость ди-2-нафтилтиокарбазона в качестве титрадионного раствора для экстракционно-спектрофотометрических титраций. Разработан селективный метод последовательного титрования серебра в аммиачной среде и применен в анализе двуокиси германия. Последовательное титрование микрограммовых количеств ртути и цинка оказалось осуществимым. Вследствие низкой селективности этой титрации надо провести отделение ртути и цинка от других ионов.

ОПРЕДЕЛЕНИЕ ЧАСТИЦ ЖЕЛЕЗА В ВОЗДУХЕ МЕТОДОМ РЕНТГЕНОВСКОГО ФЛУОРЕСЦЕНТНОГО

Jae Y. Hwang, *Talanta*, 1970, **17,** 118.

Резюме—Описан метод определения частиц железа в воздухе методом рентгеновского флуоресцентного анализа. Пробы собирают при помощи прибора для пропускания небольших объемов воздуха на органических мембранах, которые служат для прямого измерения в сравнении с эталонами, приготовленными осаждением гидроокиси железа(III) на подобных мембранах. Метод является несложным и быстрым, его точность и ошибка равны 6% в области 10–200 мкг железа.