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DOSAGE ENTHALPIMETRIQUE DE TRACES DE MOLYBDENE(VI) ET DE TUNGSTENE(VI) PAR UNE METHODE CINETIQUE-CATALYTIQUE

R. FEYS, J. DEVYNCK® et B. TREMILLON

Laboratoire de Chimie Analytique et d'Electrochimie, Ecole Nationale Supérieure de Chimie de Paris, Université de Paris VI, 11, rue Pierre et Marie Curie, 75231 Paris Cedex 05, France

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Résumé—On décrit une méthode de dosage du molybdène(VI) et du tungstène(VI) dans laquelle les éléments à doser interviennent comme catalyseurs de la réaction d'oxydation des ions iodure, des ions thiosulfate ou de l'acide rubéanique par le peroxyde d'hydrogène. La réaction indicatrice est suivie par enthalpimétrie. On compare la limite de sensibilité (de l'ordre de 0,02 mg/l.) obtenue par cette méthode à celle des techniques habituellement mises en œuvre en analyse cinétique et on étudie les interférences.

L'utilisation de la cinétique chimique à des fins d'analyse quantitative connaît actuellement un regain d'intérêt, lié d'une part à la recherche de méthodes d'analyse de traces avec une sensibilité de plus en plus grande, d'autre part à la mise au point d'une instrumentation bien adaptée, grâce notamment aux dispositifs d'exploitation des données numériques à l'aide de calculateurs. Des revues bibliographiques récentes attestent du renouveau de ces méthodes et de très nombreux dosages sont maintenant basés sur la mesure de vitesse de réaction.[1–5]

Pour la plupart, ces méthodes reposent sur l'utilisation de l'élément à doser comme catalyseur d'une réaction lente; le principe consiste toujours à relier la vitesse de la réaction catalysée—qu'on appelle la réaction indicatrice—à la concentration du catalyseur. La limite de détection est fonction des propriétés catalytiques, mais il est courant de doser des expèces à des concentrations de l'ordre de 10^{-3} à 10^{-5} mg/l. (soit de l'ordre de 10^{-8} à $10^{-10}M$).

L'enthalpimétrie n'a été que peu utilisée jusqu'à présent comme méthode indicatrice instrumentale en analyse cinétique. Son caractère universel peut cependant en faire une méthode très intéressante puisqu'elle doit permettre de suivre la plupart des réactions indicatrices. C'est, en particulier, une technique bien adaptée aux réactions qui mettent en jeu des phénomènes d'oxydo-réduction, réactions qui sont caractérisées par la mise en oeuvre de quantités de chaleur importantes.[6]

L'étude que nous décrivons concerne l'analyse du molybdène(VI) et du tungstène(VI), par catalyse des réactions d'oxydation des ions thiosulfate ou iodure par le peroxyde d'hydrogène. Ces réactions ont déjà fait l'objet d'études absorptiométriques ou électrochimiques, portant principalement sur la détermination de la limite de sensibilité des dosages et sur l'étude des interférences.[7,8] Nous avons pour notre part recherché les possibilités de mise en application de l'enthalpimétrie pour suivre ces réactions indicatrices et comparé

les limites de détection obtenues par l'emploi de cette méthode avec celles résultant de l'emploi d'autres méthodes instrumentales.

De plus, nous avons essayé de préciser les possibilités de dosage du tungstène(VI) en utilisant comme réaction indicatrice l'oxydation de l'acide rubéanique par le peroxyde d'hydrogène.

PARTIE EXPERIMENTALE

Technique des mesures enthalpimétriques

Le montage expérimental schématisé sur la figure 1 comprend essentiellement une cellule sensiblement adiabatique et un dispositif de mesure des variations de température à thermistance.

Etant données les faibles variations de température qu'il est nécessaire de mesurer (de l'ordre de quelques centièmes de degré au cours d'une réaction), le dispositif expérimental nécessite un soin particulier. La cellule est un récipient du type vase Dewar d'une capacité utile d'environ 100 ml; l'ouverture est limitée au diamètre minimum qu'impose le passage des différents accessoires (thermistance, système d'agitation, dispositif d'addition de réactif et résistance chauffante pour l'étalonnage de la thermistance). La thermistance utilisée a une résistance de 900 Ω (à 25°) et un coefficient de température de $-0{,}025\ \Omega\,.\,\Omega^{-1}\,.\,\mathrm{deg}^{-1}$; elle constitue l'un des bras d'un pont de Wheatstone et fonctionne dans des conditions où le courant de déséquilibre du pont est proportionnel à la variation de la résistance.[6]

Le circuit d'étalonnage de la thermistance est constitué d'une résistance électrique de précision, placée dans la cellule et d'une alimentation stabilisée (chronoampérostat). La thermistance est étalonnée au voisinage de la température d'utilisation pour vérifier la proportionnalité des variations de température aux variations de résistance, proportionnalité qui n'est vérifiée que dans de faibles intervalles de température.

La cellule, ses accessoires ainsi que les différents réactifs sont totalement immergés dans un bain thermorégulé dont la température est maintenue constante avec une précision de 0,1°. L'inertie thermique de l'ensemble est suffisante pour que les fluctuations de température n'excèdent pas 0,001° dans la cellule pendant un intervalle de temps correspondant à la durée d'un titrage.

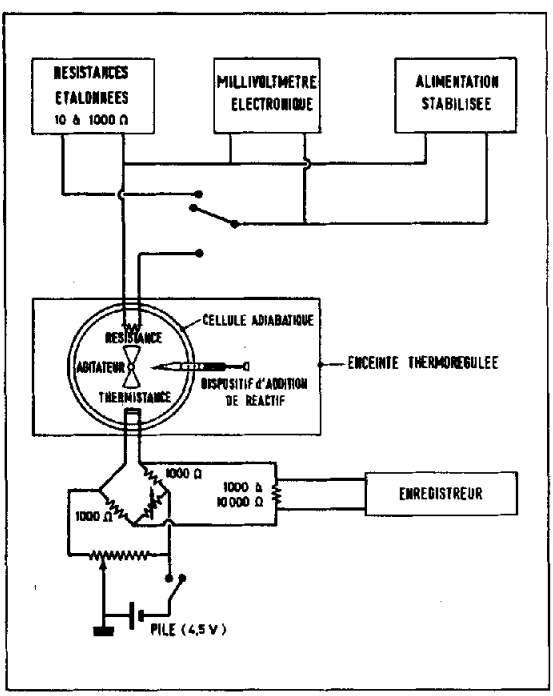

Fig. 1. Schéma du dispositif expérimental.

La réaction débute au moment de l'injection de l'un des réactifs dans la cellule. Ce réactif est ajouté à la seringue, en une seule fois; la durée de l'injection est négligeable devant celle du titrage et la fin de cette injection définit le temps $t = 0$ de l'expérience.

Un agitateur à palettes assure un mélange régulier des constituants.

REALISATION DES TITRAGES—RESULTATS EXPERIMENTAUX

Oxydation des ions thiosulfate par H_2O_2

Mode opératoire. Le molybdène(VI) catalyse l'oxydation des ions thiosulfate par H_2O_2, en milieu acide, suivant la réaction:

$$S_2O_3^{2-} + 4H_2O_2 \rightarrow 2SO_4^{2-} + 2H^+ + 3H_2O.$$

L'exploitation des propriétés catalytiques du molybdène(VI) consiste à choisir des conditions expérimentales telles que: d'une part soit observable une relation de proportionnalité entre la vitesse initiale de la réaction et la concentration du catalyseur; d'autre part, la vitesse de la réaction non catalysée soit suffisamment petite.

Alors que l'utilisation de solutions contenant les réactifs à des concentrations supérieures à $10^{-3}M$ environ permet de satisfaire à la première condition, l'emploi de concentrations inférieures à $10^{-2}M$ est imposé par la seconde.

Compte tenu de la nécessité d'imposer un rapport de concentration du thiosulfate de sodium et du peroxyde d'hydrogène correspondant approximativement à la stoechiométrie de la réaction, nous avons finalement réalisé un étalonnage au moyen de solutions de H_2O_2 $5.10^{-3}M$ et de thiosulfate de sodium $2.10^{-3}M$. De plus, le pH de la solution a été fixé à une valeur voisine de 3,4, au moyen de tampon acide acétique–acétate de sodium.

L'introduction des réactifs dans la cellule nécessite quelques précautions. Si l'on introduit d'abord l'eau oxygénée et les ions thiosulfate, en ne commençant les mesures qu'au moment de l'introduction du catalyseur, on aboutit à des résultats erronés; en effet, étant donné le temps de mise en équilibre thermique, la vitesse de la réaction non catalysée ne peut plus être négligée. D'autre part, il est déconseillé d'introduire en premier lieu le thiosulfate et le molybdène(VI): les réactions d'oxydation par l'eau oxygénée débutent souvent par la formation d'un peroxyde ou d'un complexe entre le catalyseur et l'oxydant, de sorte que, si cette première étape est lente, la réaction débute par une période d'induction.

Nous avons, par conséquent, opéré de la façon suivante: la solution d'H_2O_2, tamponnée à pH = 3,4, est placée dans la cellule en présence du catalyseur; lorsque l'équilibre thermique est pratiquement atteint, le thiosulfate de sodium est ajouté et la réaction commence, provoquant une élévation de température qui est enregistrée.

Résultats. Les courbes expérimentales obtenues, dont un exemple est représenté sur la figure 2, présentent trois parties:

(1) une ligne de base, correspondant à la mise en équilibre thermique (dans la cellule: eau oxygénée et catalyseur à doser).

(2) un décalage de la ligne de base au moment de l'injection de la solution de thiosulfate. Celle-ci est ajoutée rapidement en une seule fois; sa température peut être légèrement différente de la température de la cellule; d'autre part, la dilution est très endothermique ($\Delta H = 2{,}1 \pm 0{,}5$ kcal/mol).[9]

(3) une nouvelle partie linéaire caractéristique de la nouvelle mise en équilibre thermique; l'augmentation de température correspond au déroulement de la réaction indicatrice.

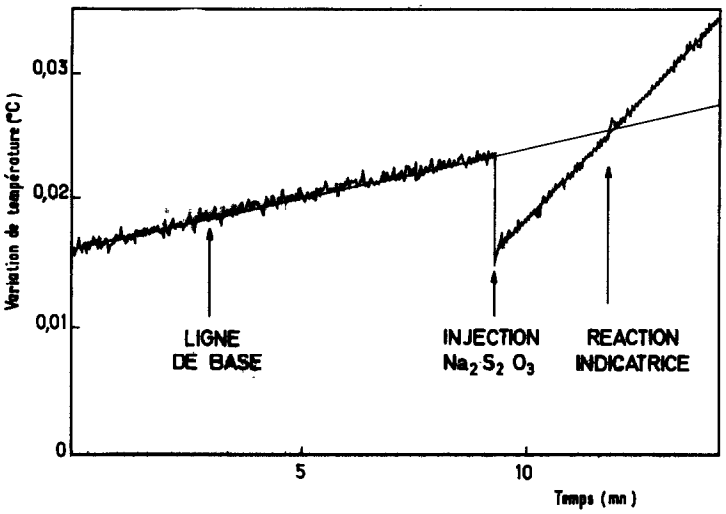

Fig. 2. Variation de température au cours de la réaction d'oxydation des ions thiosulfate ($2.10^{-3}M$) par H_2O_2 ($5.10^{-3}M$), en présence de molybdène(VI) $10^{-6}M$.

La vitesse de variation de la température mesurée (pente de la tangente au début de la courbe) est en principe proportionnelle à la vitesse de la réaction. La droite d'étalonnage est obtenue en portant cette valeur en fonction de la concentration de catalyseur.

Les points expérimentaux sont approximativement alignés; l'équation obtenue par la méthode des moindres carrés est la suivante:

$$y = (4{,}9 \pm 0{,}9)x + (0{,}28 \pm 0{,}09) \quad (1)$$

où y représente la vitesse [$10^4 \times$ (deg/sec)] et x la concentration de molybdène(VI) exprimée en mg/l.

Les limites d'incertitude correspondent à un taux de confiance de 95%. La variance résiduelle, qui caractérise la dispersion des points autour de la droite moyenne, est égale à 3.10^{-3}. L'écart-type de la valeur de l'essai à blanc, qui caractérise la limite de détection de la méthode, est voisin de 3 μg/l. (soit 3.10^{-8} M).

Oxydation des ions iodure par H_2O_2

La réaction d'oxydation des ions I^- en iode par H_2O_2 est également catalysée par le molybdène(VI) et peut donc servir à la détermination de ce dernier comme la réaction précédente.

Mode opératoire. Nous avons observé que, pour une concentration de chaque réactif supérieure à $10^{-2}M$, la vitesse mesurée est pratiquement celle de la réaction en l'absence de catalyseur, ce qui rend imprécise la détermination de traces de celui-ci.

D'autre part, lorsque les concentrations de H_2O_2 et d'iodure de potassium sont inférieures à $10^{-3}M$, la cinétique de la réaction n'est pas d'ordre zéro par rapport à ces deux réactifs même pendant une courte période après le début de la réaction (de l'ordre d'une minute environ).

Compte tenu de la nécessité d'imposer un rapport de concentration voisin de la stoechiométrie, nous avons finalement utilisé, pour réaliser l'étalonnage, des solutions con-

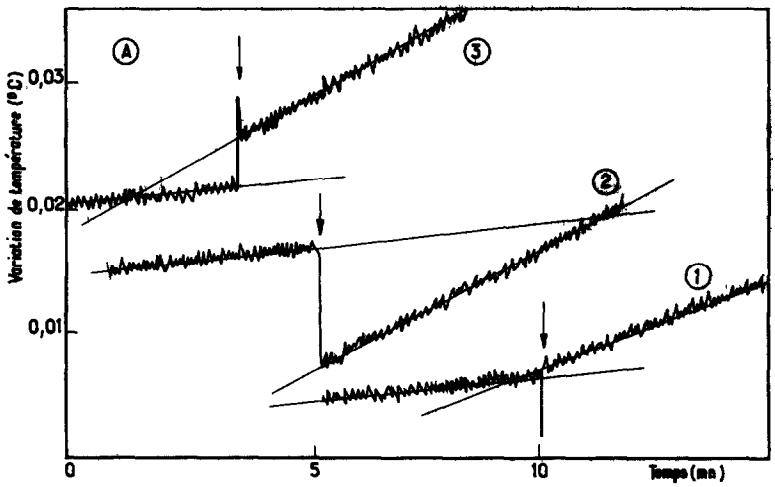

Fig. 3. Variation de température au cours de la réaction d'oxydation des ions iodure ($2.10^{-3}M$) par H_2O_2 ($10^{-3}M$) en présence de Mo(VI) à la concentration: (1) = 0; (2) = 0,12 mg/l.; (3) = 0,18 mg/l. (La flèche indique le moment de l'addition de l'iodure.)

tenant H_2O_2 $10^{-3}M$ et les ions iodure $2.10^{-3}M$, les solutions contenaient également de l'acide sulfurique $0{,}08M$.

Résultats. Les courbes expérimentales (Fig. 3) sont comparables à celles obtenues dans le cas de la réaction d'oxydation des ions thiosulfate; le même mode d'exploitation s'applique donc pour le tracé de la droite d'étalonnage. L'équation obtenue est la suivante:

$$y = (2{,}4 \pm 0{,}3)x + (0{,}06 \pm 0{,}03) \qquad (2)$$

ou y et x ont la même signification que dans l'équation (1).

La reproductibilité de la méthode au niveau de la limite de détection (écart-type de la valeur de l'essai à blanc) est de l'ordre de 20 μg/l.

Oxydation de l'acide rubéanique par H_2O_2

L'oxydation de l'acide rubéanique (ou dithiooxamide), $H_2(NHCS)_2$, conduit à un mélange de substances dont la composition est mal connue. Cette réaction est lente, mais peut être rendue plus rapide en présence de tungstène(VI).

L'expression de la vitesse v de la réaction, proposée par Pantaler:[10]

$$v = k[H_2(NHCS)_2][H_2O_2][H^+][W(VI)]$$

montre qu'il doit être possible de fixer des conditions opératoires permettant d'observer une relation de proportionnalité entre v et la concentration de tungstène(VI).

Mode opératoire. L'acide rubéanique est très peu soluble dans l'eau et se décompose en milieu acide, mais il est assez soluble dans l'éthanol (jusqu'à une concentration d'environ 5.10^{-2} M). De plus, l'expression de la vitesse de la réaction fait intervenir la concentration des ions hydrogène: comme ceux-ci sont probablement consommés au cours de la réaction, il est nécessaire de fixer leur concentration. Nous avons ainsi opéré dans un mélange à 90% d'éthanol (en volume) et 10% d'une solution aqueuse d'acide chlorhydrique pour imposer une concentration égale à $0{,}1M$.

Le choix des concentrations d'acide rubéanique et de peroxyde d'hydrogène est guidé, de la même façon que précédemment, par la nécessité de limiter la vitesse de la réaction en l'absence de catalyseur et de conserver une valeur constante aux concentrations de ces réactifs pendant un temps suffisant (de l'ordre de quelques minutes). Nous avons par suite utilisé des solutions d'acide rubéanique $2.10^{-3}M$ et de H_2O_2 $5.10^{-3}M$.

Résultats. Les courbes enthalpimétriques représentées figure 4 sont analogues à celles obtenues dans le cas de l'oxydation des ions thiosulfate et iodure; le même mode d'exploitation s'applique donc pour établir un étalonnage.

Pour comparer, nous avons également déterminé ici des courbes absorptiométriques de titrage. Elles ont été obtenues à 400 nm (maximum d'absorption de l'un des produits d'oxydation de l'acide rubéanique, la solution de référence étant une solution d'acide rubéanique). La variation d'absorbance en fonction du temps n'est pas linéaire; le tracé de la droite d'étalonnage a donc été réalisé en portant l'inverse du temps nécessaire pour obtenir une absorbance donnée en fonction de la concentration de catalyseur.

Les caractéristiques des droites d'étalonnage sont indiquées dans le tableau 1.

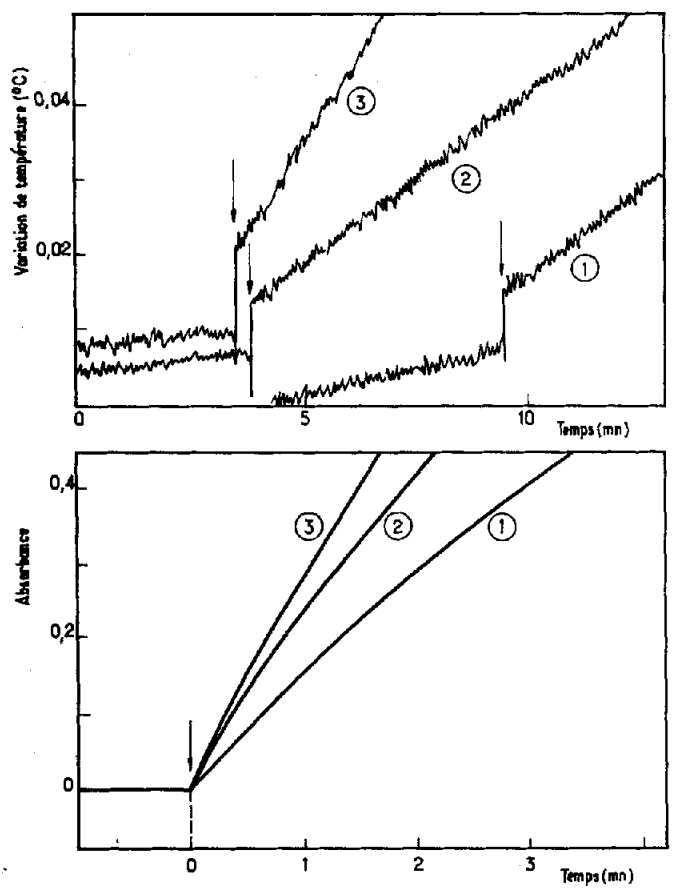

Fig. 4. Courbes enthalpimétriques et absorptiométriques d'oxydation d'acide rubéanique ($2.10^{-3}M$) par H_2O_2 ($5.10^{-3}M$), en présence de tungstène(VI) à la concentration: (1) = 0; (2) = $10^{-7}M$; (3) = $2.10^{-7}M$. (La flèche indique le moment de l'addition de l'acide rubéanique.)

Tableau 1. Variation de la vitesse de la réaction d'oxydation de l'acide rubéanique par H_2O_2 en fonction de la concentration de molybdène(VI). Caractéristiques des droites d'étalonnage obtenues par absorptiométrie et par enthalpimétrie

	Absorptiométrie	Enthalpimétrie
Domaine d'étalonnage, *mg/l.*	4.10^{-3} à 4.10^{-2}	$1{,}2.10^{-2}$ à 8.10^{-2}
Equation de la droite d'étalonnage*	$Y = (4{,}1 \pm 0{,}5)x.10^5$ + $(0{,}18 \pm 0{,}02)$	$Y = (0{,}20 \pm 0{,}02)x$ + $(5{,}5 \pm 0{,}3)\ 10^{-3}$
Variance résiduelle	$7{,}4.10^{-5}$	10^{-7}
Ecart-type de la valeur de l'essai à blanc, *mg/l.*	$2{,}4.10^{-3}$	$2{,}6.10^{-3}$

* x représente la concentration de tungstène(VI) exprimée en mg/l. et Y la vitesse en min^{-1} (absorptiométrie) ou deg/min (enthalpimétrie).

Etude d'interférences. L'activité catalytique manifestée par le tungstène(VI) pour la réaction d'oxydation de l'acide rubéanique par H_2O_2 est assez spécifique; nous avons en effet vérifié par enthalpimétrie l'absence d'interférences des ions suivants: alcalino-terreux, cobalt(II), nickel(II), plomb(II), manganèse(II), titane(IV) et lanthane(III), à la concentration de 1 ppm soit environ $10^{-5}M$. Nous avons en revanche mis en évidence, de la même façon, l'influence de traces de molybdène(VI), de vanadium(V) et de cuivre(II).

Le problème de l'interférence du cuivre(II) et du fer(III) illustre les avantages qu'offre l'utilisation conjointe de l'enthalpimétrie et de l'absorptiométrie comme méthodes indicatrices.

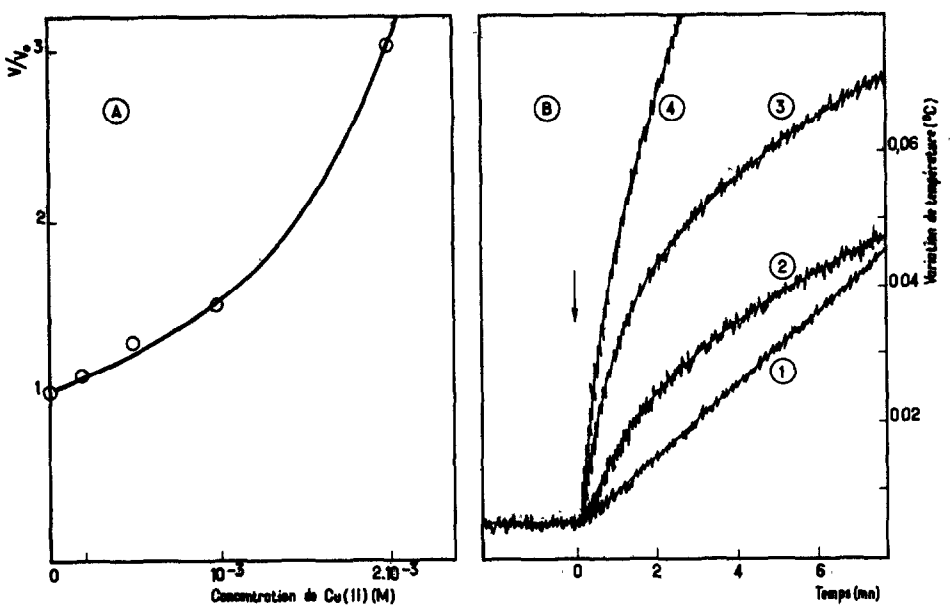

Fig. 5. Influence de la concentration de cuivre(II) sur la vitesse d'oxydation de l'acide rubéanique ($2.10^{-3}M$) par H_2O_2 ($5.10^{-3}M$).

(A)—variation relative apparente déduite des mesures absorptiométriques [V_0 = vitesse en l'absence de Cu(II)]. (B)—courbes enthalpimétriques; concentration de Cu(II): (1) = 0; (2) = $1{,}6.10^{-5}M$; (3) = $10^{-3}M$; (4) = $4.10^{-3}M$. (La flèche indique le moment de l'addition de l'acide rubéanique.)

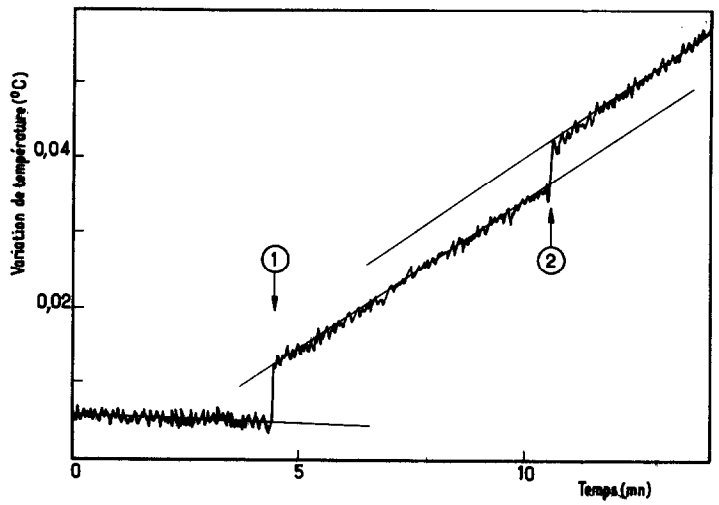

Fig. 6. Influence de l'addition de Fe(III) $10^{-5}M$ sur la vitesse de la réaction d'oxydation de l'acide rubéanique ($2.10^{-3}M$) par H_2O_2 ($5.10^{-3}M$). (1) Addition de l'acide rubéanique. (2) Addition du fer(III)

Les ions cuivre(II) forment avec l'acide rubéanique un complexe qui absorbe fortement à 400 nm (coefficient d'extinction voisin de 4.10^3 l.mol^{-1}.cm^{-1}); les mesures de vitesse de réaction par absorptiométrie sont donc perturbées par la présence de ce complexe et il n'est pas possible d'étudier l'influence du cuivre(II) sur la vitesse de la réaction indicatrice (Fig. 5). Par enthalpimétrie, nous avons, par contre, montré que la vitesse initiale dépend de la concentration de cuivre(II).

Ces résultats indiquent que le rubéanate de cuivre(II) est plus facilement oxydable par H_2O_2 que l'acide rubéanique lui-même et confirment—comme la formation de complexe le laissait prévoir—l'interférence des ions cuivriques dans le dosage du tungstène(VI).

L'étude absorptiométrique de l'influence du fer(III) sur la vitesse de la réaction montre que ces ions interfèrent, comme l'indiquent les résultats du tableau 2.

Tableau 2. Variation apparente relative de la vitesse V (déterminée par absorptiométrie) de la réaction d'oxydation d'acide rubéanique 2.10^{-3} M par H_2O_2 5.10^{-3} M, en fonction de la concentration de Fe(III). V_0 = vitesse en l'absence de Fe(III)

[Fe(III)]M	0	10^{-7}	5.10^{-7}	10^{-6}	10^{-5}	5.10^{-5}
V/V_0	1	0,96	0,74	0,60	0,63	0,66

Cependant, les courbes enthalpimétriques mettent en évidence le fait que l'addition de fer(III), à la concentration $10^{-5}M$, ne modifie pas la vitesse de la réaction (Fig. 6).

Les ions ferrique n'interviennent donc pas dans le dosage du tungstène(VI); les modifications apparentes observées par absorptiométrie (et déjà signalées par Pantaler)[10] ne sont donc dues qu'à une modification du spectre d'absorption en présence de fer(III).

CONCLUSION

L'analyse cinétique catalytique conduit à mettre en oeuvre des techniques expérimentales variées, les plus utilisées actuellement étant l'absorptiométrie et l'ampérométrie; l'en-

thalpimétrie n'a été que très rarement envisagée. Nos résultats montrent cependant que la mesure des vitesses de réaction à partir de variations de température permet le dosage de catalyseurs de réactions lentes dans un domaine de concentration et avec une sensibilité tout à fait comparables à ceux des méthodes plus courantes.

Ainsi, nous avons pu effectuer le dosage du molybdène(VI) catalyseur des réactions d'oxydation des ions iodure ou thiosulfate par le peroxyde d'hydrogène, dans le domaine de concentration compris entre 0,4 et 0,06 mg/l. De même, le dosage du tungstène(VI), catalyseur de la réaction d'oxydation de l'acide rubéanique par H_2O_2, a été réalisé dans le domaine de concentration 4.10^{-3} à 4.10^{-2} mg/l., par absorptiométrie, et 10^{-2} à 8.10^{-2} mg/l., par enthalpimétrie.

En ce qui concerne la limite de sensibilité, nous avons comparé, dans le tableau 3, nos résultats à ceux qui ont été publiés précédemment sur les mêmes dosages, suivis à l'aide de différentes autres techniques expérimentales.

Bien qu'il soit difficile d'établir les valeurs de cette limite de sensibilité dont la définition varie selon les auteurs, à partir des résultats expérimentaux, on peut conclure à une assez bonne concordance.

Les récents travaux de Vajgand *et al.*[11] confirment sensiblement nos résultats dans le cas de l'oxydation des ions iodure par H_2O_2.

Si les différentes techniques conduisent à des résultats comparables, le caractère universel de l'enthalpimétrie mérite cependant d'être souligné, car il augmente notablement le champ d'application de la méthode cinétique d'analyse.

L'enthalpimétrie est, par exemple, très facile à adapter au cas des milieux non-aqueux, et n'est pas perturbée, comme l'est l'absorptiométrie, par les phénomènes de précipitation ou de fluorescence.

La comparaison des résultats que nous avons obtenus par enthalpimétrie et par absorptiométrie dans le cas de l'oxydation de l'acide rubéanique par H_2O_2 illustre encore les avantages de l'enthalpimétrie dans l'analyse des interférences.

Tableau 3. Dosages de molybdène(VI) et de tungstène(VI) par la méthode cinétique-catalytique; limites de sensibilité comparées des différents systèmes indicateurs.

Réaction indicatrice	Element dosé	Méthode indicatrice (référence)	Limite de sensibilité, *mg/l.*
$H_2O_2 + I^-$	Mo(VI)	enthalpimétrie (1)*	2.10^{-2}†
		absorptiométrie	2.10^{-2}
		absorptiométrie (8)	10^{-2}
		absorptiométrie (12)	10^{-2} à 3.10^{-3}
		ampérométrie à potentiel constant (13)	10^{-2}
		ampérométrie avec deux électrodes indicatrices (7)	2.10^{-2}
		enthalpimétrie (11)	10^{-2}
$H_2O_2 + S_2O_3^{2-}$	Mo(VI)	enthalpimétrie*	3.10^{-3}†
		turbidimétrie (1)	10^{-3}
$H_2O_2 + H_2(NHCS)_2$	W(VI)	enthalpimétrie*	2.10^{-3}†
		absorptiométrie*	2.10^{-3}†
		absorptiométrie (10)	4.10^{-4}

* Nos résultats.

† Ecart-type de la valeur de l'essai à blanc.

Les limitations à l'utilisation de l'enthalpimétrie comme technique analytique en cinétique-catalytique ne sont donc pas liées à l'enthalpimétrie elle-même mais à l'utilisation de l'élément à doser comme catalyseur. La contre-partie de la très grande sensibilité est fréquemment un manque de sélectivité et des efforts sont actuellement faits dans la recherche de réactions où l'élément à doser agit sélectivement comme catalyseur.

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CONTROLLED POTENTIAL IODOMETRIC DETERMINATION OF NITRATE AFTER REDUCTION TO NITRITE BY COPPERED CADMIUM

RONALD KARLSSON and LARS-GUNNAR TORSTENSSON

Dept. of Analytical Chemistry, University of Lund, S-220 07 Lund 7, Sweden

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Summary—A controlled-potential coulometric iodometric method previously developed for the accurate determination of small amounts of nitrite has been extended for the determination of nitrate after its reduction on a coppered cadmium reductor. The conditions for quantitative reduction have been investigated with respect to type of reductor and pH. Nitrate-nitrogen in the range 0·01–100 μg/ml may be determined with high accuracy in less than 10 min, including the reduction step. The method has been applied with good results to a large variety of samples such as meat products, juices and waste waters.

Numerous methods have been proposed for the determination of small amounts of nitrate. Colorimetric methods are most commonly used, and most fall into one of two classes: oxidation by nitrate of an organic compound with specific chromophoric groups, such as strychnidine,[1] diphenylbenzidine[2] and diphenylaminesulphonic acid,[3] or by nitration of 2,6-xylenol,[4] 3,4-xylenol[5] or phenoldisulphonic acid.[6] Neither type of reaction is completely specific for nitrate. In most of these methods nitrite and organic matter interfere, and in some of them the colour stability is rather poor.

However, as nitrite can readily be determined colorimetrically by using different modifications of the Griess reagent,[7] several methods have been proposed for the determination of nitrate by reduction and subsequent determination as nitrite. Zinc[8] and zinc–manganese[9] have been used as reducing agents but the difficulty of ensuring stoichiometric reduction to nitrite, arising from the need for careful control of the reduction temperature, acidity and sequence of reagent addition makes these methods less attractive. Grau and Mirna[10] proposed cadmium for the reduction of nitrate to nitrite in alkaline medium and subsequent colorimetric determination of the nitrite formed. The cadmium reduction method was later improved by several workers[11–13] by the use of reductor columns of different designs.

Morris and Riley[14] studied the reductive action of finely divided cadmium and found that the most satisfactory yields of nitrite (91 ± 1%) were obtained with amalgamated cadmium. Gleason[15] found that improved conversion was obtained when analyses were performed at a pH near 10. Wood *et al.*[16] introduced a coppered cadmium reductor which was later modified for use in automatic nitrate analysers.[17] In all of these methods the nitrite is determined colorimetrically after diazotization, which makes the analysis dependent on rapid colour development and a stable coloured product.

Tests on different types of reductors performed by Henriksen and Olsen[18] have shown that the coppered cadmium reductor is to be preferred to the other kinds of cadmium reductors for many applications.

This paper describes an accurate method for the determination of nitrate based on conversion into nitrite in a coppered cadmium reductor followed by a coulometric determination according to a method described earlier by the authors.[19] This method makes it possible to perform accurate analyses, without special pretreatment, on strongly coloured and cloudy solutions for which the colorimetric methods often fail.

EXPERIMENTAL

Several procedures are proposed in the literature for preparing the cadmium used in the reductor columns. We tried three of the most common methods in order to investigate whether the way of preparing the cadmium would give rise to different reducing abilities.

Preparation of columns

(*a*) Prepare metallic cadmium by placing four zinc plates in a nearly saturated solution of cadmium sulphate and leaving the reaction to proceed overnight. Remove the growth of cadmium from the zinc plates and place the cadmium in a homogenizer for a few minutes. Sieve and retain the 20–25 mesh particles. Wash them with doubly-distilled water and store in 0·1*M* hydrochloric acid.

(*b*) Place two cadmium bars of 99·8% purity, 100 mm long and 10 mm in diameter, in a 10% cadmium sulphate solution and at least 200 mm from each other to prevent short-circuiting by the growth. Electrolyse for 8–10 hr between the two cadmium electrodes, using an external power supply. Treat the growth formed as in (*a*).

(*c*) Sieve and retain the 20-mesh particles from coarse cadmium powder. Rinse with 2*M* hydrochloric acid and wash repeatedly with distilled water. Store in 0·1*M* hydrochloric acid.

Coppering the cadmium

Shake about 6 g of the previously prepared cadmium with 100 ml of 2% copper sulphate solution (about 4 g of the coppered cadmium are required for each reductor column). Wash thoroughly with distilled water until all copper particles are removed. Store in distilled water.

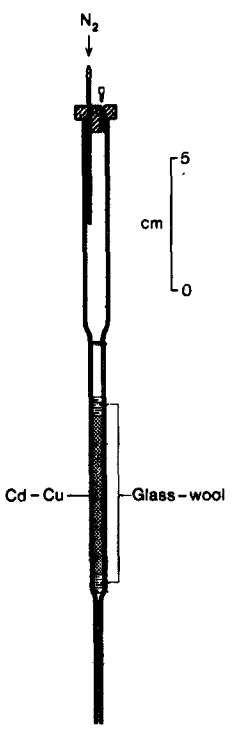

Fig. 1. Coppered cadmium reductor.

Reductor column

The reductor column shown in Fig. 1 is made of 1-mm thick Pyrex glass and equipped with a Teflon plug making a gas-tight seal with an O-ring. The hypodermic needle used as a nitrogen inlet can be moved up for driving samples through under nitrogen pressure or down for deaeration of the solutions.

Filling the reductor column

Place a plug of glass-wool at the bottom of the column and fill the column with distilled water. Introduce the prepared cadmium granules slowly to prevent entrapment of air bubbles and aerial oxidation of the granules. Insert a glass-wool plug on top of the filling and let 50–100 ml of 2% ammonium chloride buffer pass through the column. The pH of the wash solution is adjusted to 8·5–9·0, which effectively buffers samples with pH between 2 and 12.

Procedure

In order to avoid the risk of reducing any nitrate to a lower state of oxidation than nitrite, allow some hundred ml of distilled water to pass through the freshly prepared column before performing the nitrate determinations. After this, add 10 ml of the wash solution to the column reservoir and allow it to drain through until the solution stands about 0·5 cm above the cadmium filling. Then add a sample of 0·1–5 ml, depending on the nitrate content, to the column reservoir and when it has run nearly completely into the cadmium filling add 5–10 ml of wash solution to rinse the sample through the column. Collect the effluent in a 10- or 25-ml calibrated volumetric flask and make it up to the mark with distilled water or buffer solution.

To increase the flow-rate through the column, force the wash solutions through the column with compressed nitrogen. The optimum flow-rate for maintaining 100% reduction efficiency of the nitrate to nitrite was found to be 5–6 ml/min. To check the effectiveness of the reductor a sample with known nitrate content is tested twice daily.

After the reduction step the sample is analysed as a nitrite sample by the coulometric method developed by the authors.[19]

RESULTS AND DISCUSSION

Test of column fillings

Three reductors were set up, filled with coppered cadmium prepared according to the methods (*a*), (*b*) and (*c*), respectively. A series of nitrate reductions were performed with each reductor. The reductors prepared according to methods (*a*) and (*b*) showed a somewhat greater tendency than that of the method (*c*) column to reduce the nitrate to a lower oxidation state than nitrite. The flow-rate in the two first reductors decreased by about 30% after some days' use, but the flow-rate through the third reductor showed no significant decrease. This is probably due to the greater structural strength of the reductor filling prepared according to method (*c*), which prevented this filling from settling down to the same extent as the other two, especially when the flow-rate was increased by the application of compressed nitrogen. No significant differences between fillings (*a*) and (*b*) were noticed. Consequently, the use of reductor fillings prepared according to method (*c*) is to be preferred.

Variation of the reduction efficiency with pH was investigated for column (*c*). Ammonium chloride buffers adjusted to the desired pH-values with appropriate amounts of ammonia or hydrochloric acid were prepared. Samples (1 ml) containing 100·0 μg of nitrate in doubly-distilled water were reduced on the reductor at various pH's and then coulometrically analysed. The samples were all eluted with 2 × 4 ml of the buffer solution, collected in 10-ml volumetric flasks and made up to the mark with distilled water. In order to establish whether the reduction of nitrate to nitrite is exactly 100% complete, samples containing 100·0 μg of nitrite were treated in the same manner. Table 1 shows the results of these determinations. There is a small variation (<0·1%, not shown in Table 1) in the reducing efficiency of the reductor under optimum conditions.

Table 1. Effect of pH on the reduction of nitrate and nitrite on a coppered cadmium reductor

Solution pH	Nitrate reduced to nitrite, %	Nitrite reduced, %
10–6	100·0	0·0
5	99·8	0·1
4	99·1	0·8
3	98	4
2	55	45
1	22	83

As can be seen from Table 1 the reduction of nitrate to nitrite is practically 100% complete between pH 5 and 10, which is in good agreement with the observations made by Henriksen and Olsen.[18] Follet and Ratcliff[11] reported that the nitrate solution must be buffered at pH 9·5–9·7 to ensure complete reduction to nitrite. The strong pH-dependence found by these authors has to some extent been explained by Hatcher.[20]

The main reaction in the pH range 5–10 for the reduction of nitrate can be written:

$$Cd + NO_3^- + 2NH_3 + 2NH_4^+ \rightarrow Cd(NH_3)_4^{2+} + NO_2^- + H_2O \qquad (I)$$

Below pH 5 the reduction proceeds to a lower oxidation state than nitrite. Possible reactions for the nitrate and nitrite species are

$$3Cd + 2NO_3^- + 8H_3O^+ \rightarrow 3Cd^{2+} + 2NO + 12H_2O \qquad (II)$$

and

$$Cd + 2NO_2^- + 4H_3O^+ \rightarrow Cd^{2+} + 2NO + 6H_2O. \qquad (III)$$

There is of course a competition between reactions (I) and (II) but the lower the pH the more reaction (II) will dominate. Analysis for the amount of cadmium ions leaving the reductor also confirms the assumption that nitrate and/or nitrite are reduced to even lower states than that of nitric oxide, especially at very low pH. An ammonium chloride solution buffered with ammonia to a pH of about 8–9, which can buffer samples with pH from 2 to 12, seems suitable for obtaining accurate conversion of nitrate into nitrite in the reductor.

Water is often proposed in the literature for washing out the nitrite from the reductor but the reductor capacity will then decrease owing to the formation of cadmium oxide and cadmium hydroxide on the surface of the metal. Dissolved oxygen in the water will also react and form cadmium hydroxide. The reductor must in such cases be treated with a complexing agent in order to renew the cadmium surface.

In the reduction of nitrate to nitrite an equimolar amount of cadmium ions will be formed and eluted, together with the nitrite. Therefore a determination was performed to see if the cadmium ions could interfere with the iodine–iodide system used in the coulometric nitrite determination step. We oxidized 10·0 μmole of iodine, added 100 μmole of cadmium ions and waited 10 min. The subsequent reduction of iodine gave exactly 10·0 μmole, indicating the absence of interferences from the cadmium ions, which is in agreement with the standard electrode potentials.

A series of samples containing known amounts of nitrate and nitrite were analysed both directly and after passage through the reductor. The first determination gave the nitrite

content of the sample and the second the sum of nitrite and nitrate. All samples were prepared from *pro analysi* quality sodium nitrate and sodium nitrite and with doubly-distilled water. The wash solution for the reductor step was NH_4Cl–NH_3 solution at pH 8·5. The eluates were collected in 10-ml volumetric flasks and made up to the mark with pH 8·5 buffer. The results are given in Table 2. All results in the table are mean values of five determinations. The sample volumes were in the range 0·1–5 ml. The error in the determination of nitrogen after passage through the reductor was 5–7% in the lowest, 1–2% in the middle and 0·2–0·4% in the highest concentration range.

The accuracy in the determination of nitrite-nitrogen without the reductor was significantly better than that for the determination of total nitrogen. The lower accuracy of the determination of nitrogen with the reductor may arise from the dilution after passage through the reductor, caused by the wash solution required (a dilution factor of 2 is often a minimum) and from the conversion of nitrate to nitrite not always reaching 100·0%.

Applications

The method has been used for the determination of nitrate and nitrite in a large variety of samples.

Strongly coloured samples, for which the conventional colorimetric methods often fail, can be analysed by our method. A large number of coloured juices have been examined with very good results. Ascorbic acid, however, which is often added in large amounts to juices, especially to those intended for infants, caused some problem. As ascorbic acid reacts with nitrite to form nitric oxide, it must be removed before the reduction step. This can be achieved by shaking the juice with active carbon (e.g. Darco G60), then filtering before analysis in the usual manner. If large amounts of ascorbic acid are present, up to 10 hr shaking is needed in order to obtain >99% efficiency.

Meat samples are prepared in the same way as described for the determination of nitrite.[19] The solution of protein-free filtrate is first passed through the reductor and the eluate is then analysed for nitrite.

We have also tested the method for the determination of nitrate and nitrite in waste waters. Samples containing nitrate and nitrite in the range 0·1–20 ppm have been analysed. The determinations were done in parallel with analyses by a Technicon "AutoAnalyzer". Table 3 gives the results of a series of measurements on some very polluted waste waters. There can sometimes be interfering cations, in very polluted waste waters, which can disturb the coulometric nitrite determination, but these may be removed by passing the solutions through a cation-exchanger in the hydrogen form. The rather large discrepancy obtained for one of the samples in Table 3 is probably due to some substance interfering in the "AutoAnalyzer" determination. Otherwise the agreement is good.

Table 2. Analysis of samples containing nitrate and nitrite

Sample composition			Nitrogen found		
nitrate-nitrogen, μg/ml	nitrite-nitrogen, μg/ml	Total nitrogen, μg/ml	without reductor, μg/ml	with reductor, μg/ml	Nitrate-nitrogen by difference, μg/ml
0·018	0·023	0·041	0·025	0·044	0·019
0·088	0·115	0·203	0·113	0·201	0·088
0·176	0·230	0·406	0·232	0·405	0·173
1·76	2·30	4·06	2·30	4·04	1·74
8·80	11·50	20·30	11·53	20·33	8·80

Table 3. Determination of nitrate and nitrite content in some waste waters

Technicon "AutoAnalyzer"*	Nitrate and nitrite-nitrogen, μg/ml Cd/Cu-reductor + coulometry†	Difference
0·86	0·94	+0·12
2·1	2·10	+0·00
5·5	5·40	−0·10
8·6	9·06	+0·46
10·1	10·44	+0·34
16·4	12·31	−4·09
19·1	18·45	−0·65

* Single determination.
† Triple determination.

CONCLUSIONS

The controlled-potential iodometric method for determination of nitrite can easily be extended to cover the determination of nitrate. A coppered cadmium reductor is used for the reduction of nitrate to nitrite. Since the method is based on coulometric determination the results are directly related to the quantity of substance and there is no need for a calibration curve. With 5-ml samples the concentration range 0·2–100 ppm is covered with high accuracy. Lower concentrations down to 0·02 ppm can be determined with the sacrifice of some accuracy. The method has been applied to different kinds of samples, with very few interferences, many of which can in any case be eliminated.

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PRECISE COULOMETRIC DETERMINATION OF IRON IN IRON ORES WITH ELECTROGENERATED MANGANESE(III) FLUORIDE

TAKAYOSHI YOSHIMORI and TATSUHIKO TANAKA

Faculty of Engineering, Science University of Tokyo, Kagurazaka Shinjuku-ku, Tokyo

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Summary—Iron in Mohr's salt, electrolytic iron and iron ores has been determined by precision coulometric titration with electrolytically generated manganese(III) fluoride, with biamperometric end-point detection. The titration curve indicated the irreversibility of the electrode reaction of manganese(III) fluoride. Total iron in several standard samples of iron ores was determined with standard deviations of about 0·012%.

Precision coulometric titrimetry is a suitable technique for the direct determination of matrix constituents in samples, and has been used for about fifteen years for the evaluation of some standard reference materials (SRMs) for volumetric analysis, and of uranium compounds. Only a few papers, however, are to be found in the literature, describing applications to the analysis of technical samples.

The determination of iron in iron ore also belongs to the analysis of matrix components. The accuracy of an ordinary analytical procedure is not enough to justify four significant figures in the result. Therefore, several SRMs are needed for checking the accuracy of ordinary procedures.

The coulometric determination of iron has already been proposed by many authors. Several electrogenerated titrants such as cerium(IV), chromium(VI), vanadium(V), halogens, titanium(III), tin(II) and uranium(V) have been used for the determination of iron.[1–3] The disadvantages of these titrants are as follows: the current efficiency for the generation of cerium(IV) is somewhat less than 100%, and the efficiencies for the other titrants are not known with sufficient certainty for them to be suitable for precision coulometry.

Manganese(III) is a strong oxidizing agent. Many analysts have investigated this reagent and used it for the determination of iron.[4–10] In those studies, the relationship between current efficiency and current density has been measured and discussed for electrolytes of various composition. Buck[8] mentioned that 99·7% or greater efficiency is obtainable with an electrolyte 0·4*M* in manganese(III) sulphate and 4*M* in sulphuric acid with the current density between 0·4 and 3·7 mA/cm^2 at a platinum electrode. Atkinson and Brydon[11] showed that the addition of phosphoric acid to the electrolyte somewhat increased the efficiency to 99·8%. Electrogenerated manganese(III) is unstable in some electrolytes, which may make location of the end-point difficult. Such electrolytes are not suitable for use in high-precision analysis.

Katoh and Yoshimori[12] have recently proposed an electrolyte containing fluoride. They showed that the current efficiency for the generation of the fluoride complex of manganese(III) is high enough for precision coulometry. The optimum composition and con-

centration of the electrolyte were given as: manganese(II) sulphate 0·5*M*, potassium fluoride 0·5*M* and sulphuric acid 0·5*M*. The advantages of this electrolyte were discussed, and when a current density of 2–9 mA/cm^2 was used a current efficiency of more than 99·99% was obtainable. In the present investigation, the method was used for the accurate determination of iron in iron ore, for the determination of iron(II) in Mohr's salt (ferrous ammonium sulphate), total iron in electrolytic iron, and for the evaluation of standard samples of several iron ores. The electrode reaction of the fluoride complex of manganese(III) is discussed in conjunction with the biamperometric titration curve, and the probable sources of error are also considered.

EXPERIMENTAL

Apparatus

The instrumentation for the coulometric generation of titrant and for end-point location was similar to that described previously.[13] The *iR*-drop through a standard resistor (1 ohm) was measured with a potentiometer. In this case, it could be expected that the standard deviation of the error in the measurement of the generating current was less than 0·02%. The Faraday constant was taken as 96487·2 C/mole.

A column reductor (300 × 13 mm) containing cadmium was used for the reduction of iron(III). A polyethylene beaker (about 400 ml) was used as the electrolytic cell. The cathode compartment was a polyethylene test-tube which had many fine holes drilled through the bottom. The holes were plugged by a 10 mm layer of agar-agar gel saturated with potassium sulphate at the bottom of the tube. The generator anode was platinum foil (about 113 cm^2) and the cathode was a coiled platinum wire (about 10 cm long).

The end-point of the titration was located by a biamperometric procedure. Two platinum wires (0·5 mm diameter and 50 mm long) were used as the indicator electrodes, with an applied voltage of 580 mV. The indicator current was measured with a microammeter (full-scale deflection 10 μA). The indicator electrodes were frequently washed by dipping them into concentrated nitric acid for some time.

All electrodes were plugged and supported with polyethylene tubes.

The temperature of the electrolyte was maintained constant throughout the titration, because the current efficiency decreased significantly with increasing temperature.[6]

Reagents

The cadmium metal (5–10 mesh particles) for the column was better than 99·9% pure. Amalgamated cadmium (5% mercury) was also used.

The composition of the anolyte just before the titration was 0·5*M* in manganese sulphate, 0·5*M* in potassium fluoride and 0·5*M* in sulphuric acid. The final volume of the anolyte was about 300 ml.

All reagents were of analytical grade, and were used without further purification.

Preparation of sample solutions

Electrolytic iron. About 1 g of commercial electrolytic iron was weighed into a decomposition flask fitted with a reflux condenser[13] and dissolved in 20 ml of 1·5*M* sulphuric acid. After the dissolution was complete, 10 ml of 10% hydrogen peroxide solution were gradually added to complete the decomposition, and the excess was boiled off. The inside of the condenser was rinsed with small amounts of 0·5*M* sulphuric acid, the solution was evaporated to about 20 ml, and then most of the iron(III) was reduced to iron(II) by heating with a few chips of metallic cadmium. The reduced sample solution was cooled and then transferred to a weight-burette. The final volume of the sample solution in the burette was about 50 ml.

Iron ore (standard samples). Approximately 0·5 g of iron ore was dried at 105–110° for 2 hr, cooled, and weighed on a microbalance. All weights were corrected to absolute weights, and all weighings were corrected for air buoyancy.

The weighed iron ore was placed in a Teflon beaker, then decomposed without boiling, with 30 ml of 6*M* hydrochloric acid. Any acid-insoluble residue was filtered off, and washed with dilute hydrochloric acid and with water until free from iron. The filtrate and washings were evaporated to small volume (not to fumes).

The residue on the filter paper was ignited in a platinum crucible and siliceous materials removed by treatment with sulphuric and hydrofluoric acids. About 3 g of potassium pyrosulphate were added to the residue in the crucible and fused, and the cooled melt was extracted with small amounts of dilute hydrochloric acid. The extract was neutralized with aqueous ammonia, the excess of ammonia was boiled off and the solution filtered. The precipitate on the filter paper was washed several times with warm water, then dissolved in small amounts of 4*M* hydrochloric acid. The filter was washed several times with dilute hydrochloric acid and then with warm water until free from chloride.

The filtrate and washings were combined with the main solution. Five ml of 9*M* sulphuric acid were added to the combined solutions, and the mixture was evaporated repeatedly to fumes of sulphuric acid. The solution was diluted with water to give a sulphuric acid concentration of about 0·5*M*. Nearly all of the iron(III) was reduced by the addition of a few pieces of metallic cadmium as above.

Coulometric titration

About 130 ml of 1·2*M* manganese(II) sulphate solution and 5 ml of concentrated sulphuric acid were transferred to the titration cell. After the addition of 30 ml of 5*M* potassium fluoride, dissolved oxygen was removed from the anolyte by passage of oxygen-free nitrogen for about 30 min with vigorous stirring. Then the gas was allowed to flow over the anolyte, and was also introduced over the solution on the top of the column. The sample solution was transferred to the funnel on the column and allowed to flow through the column at a rate of about 1 ml/min. Then the column was washed thoroughly with 0·5*M* oxygen-free sulphuric acid. The column was washed until about 300 ml had collected in the cell. The sample solution was then electrolysed with a constant current of about 215 mA, corresponding to a current density of about 1·9 mA/cm^2. Near the end-point of the titration, the generating current was cut off and the current between two indicator electrodes was measured with the microammeter. Then the sample solution was electrolysed for several seconds and the indicator current was measured again. This procedure was repeated until several minutes after the end-point, which was then located graphically. A blank determination should be done, the complete procedure being applied.

RESULTS AND DISCUSSION

Cathode compartment

The plug of silicic acid gel used as the diaphragm for the assay of potassium dichromate[14] was not satisfactory for the electrolyte containing fluoride. The diaphragm made of polyethylene tube and agar-agar gel[15] was adopted for the present purpose.

Location of the end-point

The end-point of the titration was detected by a biamperometric procedure. Figure 1 shows an example of the titration curve. Although the indicator current was relatively small, the end-point could be located quite precisely. However, the indicator current decreased gradually after the generating current had been switched off. The indicator current was, therefore, read just 1 min after switch-off. From this titration curve of "dead stop" style, it can be proved that the electrode reaction of manganese(III) fluoride is "irreversible" and that of iron is "reversible" even in the presence of fluoride ion. The former conclusion agrees with the conclusions drawn by Katoh and Yoshimori.[12]

Assay of Mohr's salt

Iron(II) in an analytical-grade sample of Mohr's salt was assayed directly by the proposed method. In this case, the sample was weighed (on a semimicrobalance) directly into

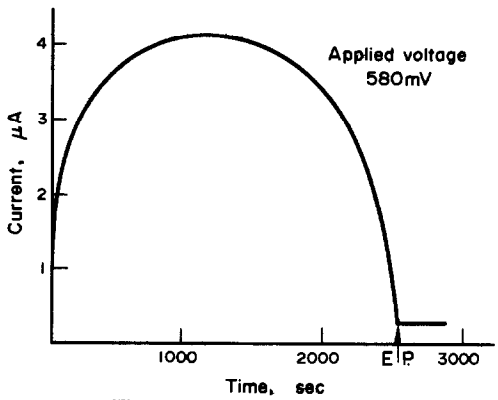

Fig. 1. Typical titration curve.

Table 1. Determination of iron in Mohr's salt

Nominal Fe(II) taken, *mg*	Fe(II) found, *mg*	Purity, %
279·98	278·58	$99{\cdot}50_0$
281·83	280·14	$99{\cdot}40_0$
282·37	280·27	$99{\cdot}25_6$
252·50	250·75	$99{\cdot}30_6$
289·05	287·02	$99{\cdot}29_8$
283·62	281·71	$99{\cdot}32_6$
267·29	265·42	$99{\cdot}30_0$
251·81	250·02	$99{\cdot}28_9$
290·83	289·19	$99{\cdot}43_6$
277·16	275·28	$99{\cdot}32_2$
		Mean = 99·34%
		Std. devn. = 0·077%

the cell. The results obtained are shown in Table 1. The purity of this salt was less than its guaranteed minimum value (99·5%). The sources of the difference are both the oxidation of iron(II) during the storage of the reagent and the variation of the water of crystallization in it. These results show that the present method is applicable to the direct assay of various reagents containing iron(II).

Determination of iron in electrolytic iron

Total iron in a sample of commercial electrolytic iron was determined by this method, and the results are shown in Table 2. The results in Table 2 were significantly lower than the value shown by the producer (99·9%). The main source of the error seems to be the presence of impurities adsorbed at the grain or crystal boundaries of the samples, since the metal was used without remelting. Furthermore, the results of each block of the sample differed appreciably. Thus this electrolytic iron does not meet the requirements for a standard substance for analytical chemistry.

Determination of total iron in iron ores

Total iron in iron(III) oxide and in six iron ores (standard samples certified by the Iron and Steel Institute of Japan) was determined by the proposed method. The results are shown in Tables 3 and 4. The standard values for these samples were determined titrimetrically with potassium dichromate. With only one exception, the values obtained by the proposed method were 0·03–0·06% lower than the certificate values.

Table 2. Purity tests of electrolytic iron

Sample block	No. of detns.	Mean purity, %	s_R^* %
A	4	$99{\cdot}55_7$	$0{\cdot}04_5$
	4	$99{\cdot}63_5$	$0{\cdot}08_2$
B	5	$99{\cdot}21_3$	$0{\cdot}05_4$
C	5	$99{\cdot}33_1$	$0{\cdot}02_3$

* Standard deviation calculated from the range.

Table 3. Determination of total iron in a standard sample* (Iron oxide, total Fe 69·99 ± 0·055%†)

Sample taken, *mg*	Total Fe found, *mg*	%
497·826	$348·05_0$	$69·91_4$
539·393	$377·27_9$	$69·94_5$
438·035	$306·26_2$	$69·91_7$
464·221	$324·58_8$	$69·92_1$
468·854	$328·03_2$	$69·96_5$
		Mean = 69·932%
		s_r = 0·019%

* Obtained from The Iron and Steel Institute of Japan.

† The 95% confidence interval for the certified value is based on 19 degrees of freedom.

The sources of bias in the results were considered as follows

First, there may be an error in the determination of the standard value. Each certified iron content was calculated from the results of eleven (or more) laboratories. Statistical treatment of the results shows that the 95% confidence interval for the mean is about ±0·058% and exceeds the difference between the certified values and the results of the present authors. Maxwell[12] has pointed out that results obtained for the iron content by titration will always be on the high side.

Secondly, incomplete reduction of iron(III) on the cadmium column was considered. The flow-rate through the column was slowed down to about 0·5 ml/min, but the iron content obtained by this procedure did not differ from that obtained by the ordinary procedure.

Thirdly, the influence of other components in the samples was also considered. Vanadium may be reduced to the bivalent state in the column.[17] Therefore, this element would shift the result to the high side, and cannot be the cause of low results. The vanadium contents in the samples were negligibly small, and not determined here. The sample of higher titanium content (Philippine Iron Sand, TiO_2 6·37%) produced much insoluble residue. Although the residue was treated and dissolved thoroughly, the end-point for the titration of this sample was not as clear as those of the other samples. This may be due to some interference with the reactions of the indicator electrodes, caused by the fluorotitanate

Table 4. Determination of total iron in standard iron ores*

Sample	Certified value and confidence interval† of total Fe, %	No. of detns.	Mean found, %	s_R, %
Rompin Hematite	62·92 ± 0·058	5	62·887	0·009
Indian	64·63 ± 0·037	5	64·589	0·014
Marcona Pellet	66·83 ± 0·059	4	66·791	0·007
Philippine Iron Sand	60·63 ± 0·075	4	60·601	0·016
Texada Magnetite	64·86 ± 0·051	4	64·857	0·014
Dungun Magnetite	61·84 ± 0·071§	4	61·890	0·017

* See footnote to Table 3.

† The 95% confidence intervals for the certified values are based on 21 degrees of freedom, unless otherwise shown.

§ For 17 degrees of freedom.

Table 5. Determination of iron in NBS 27d Iron Ore (total Fe 64·96%)

Sample taken, *mg*	Total Fe found, *mg*	%
530·463	$344{\cdot}58_8$	$64{\cdot}96_0$
711·258	$461{\cdot}83_3$	$64{\cdot}93_2$
643·308	$417{\cdot}73_7$	$64{\cdot}93_6$
505·293	$328{\cdot}01_8$	$64{\cdot}91_6$
500·039	$324{\cdot}72_7$	$64{\cdot}94_0$
		Mean = 64·937%
		s_R = 0·019%

complex. The interference, however, was not sufficient to affect the result of the iron determination. The rate of reduction of titanium(IV) by cadmium to titanium(III) is very slow under the present experimental conditions. Therefore, this element did not influence the results in practice.

Lastly, the drying of the sample may influence the results. However, the same drying procedure as that used to obtain the certified values, was followed in the present investigation. Chloride ion in the electrolyte interferes in this titration, causing low results to be obtained. Dissolved oxygen in the electrolyte and in the washing solution of the column must be carefully removed, because it readily oxidizes iron(II) in solutions containing fluoride ion and because it may be reduced to peroxide. To remove traces of oxygen in the nitrogen, it is advisable to bubble the gas through a chromium(II) chloride solution.[13]

From these considerations, the authors conclude that the most likely explanation for the apparently lower results lies in the certified values being on the high side.

Next, total iron in iron ore (NBS Standard Sample 27d) was determined by the proposed method. The results obtained are shown in Table 5 and indicate the reasonable accuracy of the present method.

Thus the coulometric titration using an electrolyte containing fluoride offers practically 100% current efficiency, high accuracy and high precision, and is consequently suitable for the precise determination of total iron in iron ores.

A statistical *F*-test (NBS 27d excluded) for comparison of the proposed method with the usual titrimetric procedures showed the present method to have a higher accuracy (99% confidence level). It should, however, be remembered that the standard deviations used for evaluation of the other procedures were based on interlaboratory comparisons. The proposed method possesses high accuracy and precision and is effective for the precise determination of total iron in iron ores.

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SEPARATION AND DETERMINATION OF SELENIUM IN ROCKS, MARINE SEDIMENTS AND PLANKTON BY DIRECT EVOLUTION WITH THE BROMIDE–CONDENSED PHOSPHORIC ACID REAGENT*

KIKUO TERADA®, TOMIKO OOBA and TOSHIYASU KIBA

Department of Chemistry, Faculty of Science, Kanazawa University, Kanazawa, Ishikawa, Japan

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Summary—A new method is presented for the quantitative separation and determination of selenium by direct evolution with the bromide–condensed phosphoric acid reagent (Br^-–CPA) from rocks, marine sediments and plankton. In the reaction with the Br^-–CPA, selenium(IV) and (VI) in the solid samples are evolved as selenium tetrabromide, and can be collected in an absorbing solution of 0·3*M* hydrochloric acid and 0·6*M* perchloric acid (1:1), and then determined spectrophotometrically with 4-substituted *o*-phenylenediamines followed by the extraction of the resulting 5-substituted piazselenol into toluene. Elemental selenium and selenide do not react with the Br^-–CPA, but can be determined after oxidation to selenite with potassium iodate. Therefore, successive distillations, the first with Br^-–CPA and the second with IO_3^-–Br^-–CPA, give a satisfactory means of differential determination of selenium(IV) and (VI), and elemental selenium and selenide. This method can be successfully applied for the separation of selenium in the neutron-activation analysis of standard rock samples, marine sediments and plankton, giving good and reliable results.

Although selenium is quite widely distributed in nature, it is invariably found in very small amounts, usually associated with sulphur and sulphur-containing minerals or ores such as sulphides. Owing to its low terrestrial abundance the element in natural materials can be determined only by a sensitive spectrophotometric method,[1] or by neutron-activation analysis.

For the determination of trace amounts of selenium several spectrophotometric reagents have been proposed, such as 3,3′-diaminobenzidine,[2,3] 2,3-diaminonaphthalene,[4] *o*-phenylenediamine[5] and 4-substituted *o*-phenylenediamines[6–9] *etc.* Tanaka and Kawashima[10] have presented a critical study of 4-methyl-, 4-chloro- and 4-nitro-*o*-phenylenediamine as spectrophotometric reagents for selenium, 5-substituted piazselenols being formed.

For many years, the reaction $H_2SeO_3 + 4HBr \rightarrow SeBr_4 + 3H_2O$ has been utilized for separating selenium from other elements,[11] but only in aqueous medium. The reaction has never been adopted directly for solid samples such as rocks, sediments and biological materials. Solid samples were brought into solution first, usually by alkaline or carbonate fusion followed by acid treatment of the fusion cake. In this fusion and dissolution process, however, some difficulties might arise; in the presence of sufficient oxidizing agent in the flux, all the selenium might be converted into selenium(VI), losing its original chemical form, and the fusion of low silica materials should be undertaken with caution because of their tendency to boil over, giving an appreciable loss of selenium.[12]

In our laboratory, Kiba *et al.*[13] have previously described a method for selenium in sulphide ores, in which tin(II) dissolved in condensed phosphoric acid (CPA) was used to

* Part of this work was performed at the Research Reactor Institute, Kyoto University.

evolve hydrogen selenide gas from selenium existing in various forms. For the determination of each form of selenium in the geological samples we have tested various reagent–CPA systems and found a new convenient method in which only selenium(IV) and (VI) react, evolving gaseous selenium tetrabromide from a solid matrix such as rocks, marine sediments and biological materials, by heating the samples with ammonium bromide in condensed phosphoric acid. Elemental selenium and selenides only react if oxidized to selenite first, *e.g.* by iodate. Therefore, only the total amount of selenium, and the sum of selenite and selenate or sum of elemental selenium and selenide can be determined spectrophotometrically.

EXPERIMENTAL

Reagents

Condensed phosphoric acid (CPA). Commercial orthophosphoric acid, extra-pure reagent grade (300–400 g), was placed in a 300-ml conical beaker, and dehydrated by heating on a 500-W electric heater until a thermometer dipped in the liquid indicated a temperature just below 300°. During the heating the vapour coming off was rapidly removed by suction. The syrupy liquid was stored in a closed vessel.

Standard selenium solution (1 mg/ml). Anhydrous sodium selenite (2·20 g) was dissolved in 1 litre of 0·1*M* hydrochloric acid, and the solution was standardized by iodometric titration.

Radioactive tracers. Selenium-75 was prepared by irradiation of pure selenium metal in the KUR, Research Reactor Institute, Kyoto University. The irradiated metal was dissolved in a small amount of nitric acid and the solution diluted with distilled water. ^{74}As, ^{82}Br, ^{59}Fe, ^{203}Hg, ^{54}Mn, ^{131}I, ^{192}Ir, ^{191}Os, ^{186}Re, ^{106}Ru, ^{124}Sb, ^{113}Sn and ^{99m}Tc were used as radioactive tracers.

Other chemicals. Ammonium chloride, ammonium bromide, sodium chloride, sodium bromide, potassium iodate, hydrochloric acid, perchloric acid and tin(II) chloride were of guaranteed reagent grade.

4-Chloro-o-phenylenediamine hydrochloride solution. A commercial product was purified as reported by Tanaka and Kawashima [7]. A freshly prepared aqueous 0·5% w/v solution was used.

Apparatus

Radioactivity measurements. A well-type γ-ray scintillation counter, Kobe Kogyo Co., Model STL-200[44 × 59 mm NaI(Tl) crystal] and a 2-cm³ Ge(Li) detector, ORTEC Model 8100–45, having a resolution of about 2·5 keV for the 1333-keV gamma-peak of ^{60}Co, coupled to a 400-channel pulse-height analyser, TMC Model 401D, together with a printer Model 500P, were used to measure radioactivity.

Reaction vessel and absorption tubes. The apparatus used is shown in Fig. 1; the reaction vessel (A) and absorption tubes (B) are connected together by ground-glass ball-joints. The reaction vessel is a round-bottomed flask having a glass cap fitted to its top and provided with inlet and outlet tubes. A glass tube closed at one end is inset in the cap to take a thermometer for measuring the temperature of the reaction medium. A few drops of silicone oil are put in the tube to reduce the time-lag of temperature indication.

Samples

Test solution. To establish general procedures several kinds of test solution were used. Radioactive tracers were used to estimate recoveries and separation factors.

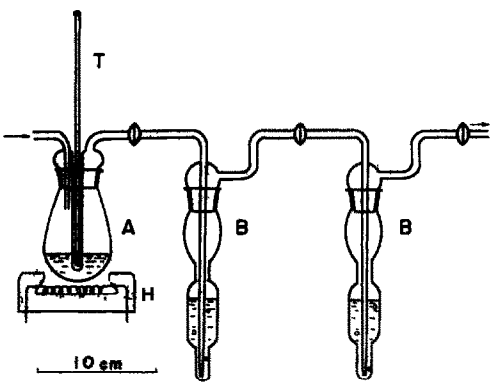

Fig. 1. Reaction vessel (A), absorbing tubes (B), electric heater (H) and thermometer (T).

Test samples. Marine sediments, standard rocks JG-1 and JB-1, and marine plankton were preferred for the study on neutron-activation analysis. The marine sediments were parts of cores collected from the bottom of the Japan Sea and Pacific Ocean, plankton was collected from Tsukumo-Bay, Noto Peninsula, and the rock samples were those distributed from the Japan Geological Survey. A synthesized selenide sample, Ag_3AsSe_3, which was prepared by the silica-tube method at the Department of Geology of our Faculty, was used for the spectrophotometric study.

Procedure

Place a test solution in the reaction vessel and add a few drops of dilute sodium hydroxide solution to keep the solution alkaline. Evaporate the solution to dryness on a water-bath. When a solid sample is to be analysed, place 0·5–1·0 g of the powdered sample in the reaction vessel.

Add about 30 g of CPA and about 0·1 g of ammonium bromide; put 10 ml of the absorption solution (10 ml of a 1:1 v/v mixture of 0·3*M* hydrochloric acid and 0·6*M* perchloric acid) into each of the absorption tubes and connect all the joints as shown in Fig. 1. Suck the air slowly from the last outlet tube with a pump and heat the reaction vessel with an electric heater to start the reaction. The time needed to complete the distillation is that needed to raise the temperature to that appropriate for selenium (250°). After the distillation, stop the heating and disconnect all the connections. Combine the absorption solutions in a 100-ml separating funnel, together with the washings, then make the solution to 0·1*M* hydrochloric acidic and add 1 ml of 0·5% 4-chloro-*o*-phenylenediamine solution. Let stand for 2 hr at room temperature, then extract the 4-chloropiazselenol with exactly 10 ml of toluene, the funnel being shaken for 5 min. Separate the two phases, wash the toluene phase once with 10 ml of 0·1*M* hydrochloric acid, and measure the absorbance of the toluene extract at 341 nm with toluene as reference.

After the determination of selenite and selenate as described above, put about 40 mg of potassium iodate and 0·1 g of ammonium bromide into the reaction vessel, which must be cooled to below 100° after the first distillation. Then repeat the procedure (distillation, extraction and measurement of absorbance) for the elemental selenium and selenide.

For the tracer method, transfer the contents of each absorption tube into a 25-ml volumetric flask and dilute to volume. Take a portion (usually 4 ml) of the solution for γ-counting.

When rock, marine sediments and plankton are to be analysed, dry the sample at 110° for an hour and grind it in an agate mortar; take a 0·5–1·0 g portion of the powder for the neutron-activation analysis. The analytical procedure is described below.

RESULTS AND DISCUSSION

Distillation of selenium

The choice of a suitable reagent for the CPA decomposition and distillation method was the first problem. Various solid chlorides and bromides were tested according to the procedure described above, and the amount of selenium distilled was determined radiometrically in each case. The amounts of selenium carrier added to the tracer were 2·5 μg, 20 μg, 1·0 mg and 10 mg, respectively. Ammonium bromide was found the most useful for the purpose, while ammonium chloride and sodium chloride gave insufficient distillation of selenium (50–80%).

Table 1. Effect of amount of ammonium bromide on distillation of selenium

NH_4Br, *mg*	Recovered, % Absorber (1)	Absorber (2)	Total	Undistilled, %	Total %
50	89·2	2·0	91·2	6·9	98·1
100	95·2	3·3	98·5	1·3	99·8
200	93·6	5·3	98·9	1·2	100·1
300	89·8	8·2	98·0	1·2	99·2
500	82·3	13·0	95·3	1·5	96·8

10 mg of Se(IV) were added together with ^{75}Se(IV) tracer.
Absorbing solution: 0·3*M* HCl + 0·6*M* $HClO_4$ (1:1 v/v).

Table 2. Effect of perchloric acid concentration on absorption of selenium bromide

HCl, 0·3*M*, *ml*	$HClO_4$, 0·6*M*, *ml*	Recovered, % Absorber (1)	Absorber (2)	Total	Undistilled, %	Total, %
Se(IV): 2·5 μg						
9·5	0·5	49·7	37·1	86·8	0·5	87·3
9·0	1·0	54·7	35·8	90·5	0·6	91·1
7·5	2·5	72·1	23·9	96·0	0·2	96·2
5·0	5·0	97·2	2·2	99·4	0·3	99·7
4·0	6·0	92·7	3·6	96·3	0·5	96·8
3·0	7·0	63·7	25·9	89·6	0·4	90·0
Se(IV): 10 mg						
9·5	0·5	30·4	6·6	37·0	2·9	39·9
9·0	1·0	75·5	8·7	84·2	1·3	85·5
7·5	2·5	82·5	5·6	88·1	1·4	89·5
5·0	5·0	95·2	3·3	98·5	1·3	99·8
4·0	6·0	92·4	2·7	95·1	1·5	96·6
3·0	7·0	78·4	9·5	87·9	1·6	89·5

^{75}Se(IV) tracer was added.

The recovery of selenium by the use of ammonium bromide is shown in Table 1, from which 100–300 mg (2–6 equivalents for 10 mg of selenium) of the salt seems appropriate. When less than 100 mg of reagent are used recovery of selenium is insufficient, but if over 300 mg are used a small part of the distilled selenium is liable to pass through the absorption solution, leading to low results. As shown in Table 1, the fraction of the total absorbed selenium in the absorption tube No. 2 increases with increase in amount of ammonium bromide used.

Next, various kinds of absorption solution were examined for quantitative trapping of the distilled selenium tetrabromide. An aqueous mixture of hydrochloric and perchloric acids was found to give the best results. Table 2 shows that a 1:1 v/v mixture of 0·3*M* hydrochloric acid and 0·6*M* perchloric acid is best for 2·5 μg–10 mg of selenium.

For Se(VI), the spectrophotometric method for yield determination was used, but not the radioactive tracer method. From the results, it seems that the bromide reduces the Se(VI), and Se(IV) bromide evolves from the CPA medium, because the selenium in the absorption solution directly reacts with 4-chloro-*o*-phenylenediamine which can react with Se(IV) but not Se(VI).[10] The distillation of Se(VI) was similar to that of Se(IV).

Table 3. Recovery of selenium at various temperatures of Br^-–CPA medium

Temp., °C	Recovered, % Absorber (1)	Absorber (2)	Total	Undistilled, %	Total, %
200	70·3	2·8	73·1	22·6	95·7
220	82·2	3·7	85·9	12·8	98·7
240	91·3	3·0	94·3	4·6	98·9
250	95·2	3·3	98·5	1·3	99·8
260	90·1	7·4	97·5	1·2	98·7
270	77·9	17·2	95·1	1·6	96·7

10 mg of Se(IV) were added together with ^{75}Se(IV) tracer

Table 4. Effect of heating time on recovery of selenium

Heating time, *min*	Recovered, % Absorber (1)	Absorber (2)	Total	Undistilled, %	Total, %
Se(IV): 2·5 μg					
10	80·5	4·7	85·2	0·3	85·5
20	89·7	4·1	93·8	0·5	94·3
30	97·2	2·2	99·4	0·3	99·7
45	93·4	4·5	97·9	1·0	98·9
75	79·3	9·6	88·9	0·7	89·6
Se(IV): 10 mg					
10	89·9	4·9	94·8	1·9	96·7
20	92·7	4·6	97·3	1·4	98·7
30	95·2	3·3	98·5	1·3	99·8
45	95·0	4·1	99·1	1·2	100·3
75	92·6	4·9	97·5	1·2	98·7

^{75}Se(IV) tracer was added.

Temperature control

Precise temperature control during the process was not necessary, as the temperature was simply raised from room temperature to the highest appropriate to the CPA reagent. Decomposition of samples and distillation of selenium tetrabromide proceeded as the temperature rose and was complete by the time the temperature reached its highest point. In Table 3 the recovery of selenium is given as a function of temperature, and it is seen that selenium has been completely distilled when the temperature has reached about 250°.

Furthermore, the time taken to raise the temperature seems to affect the recovery of selenium tetrabromide. As shown in Table 4, too fast and too slow heating gave poor recovery of selenium. Therefore, the heating should take between 30 and 50 min. This can be achieved by using a transformer to control the heating block.

Recovery of elemental selenium and selenide

Under the conditions established above, only selenium(IV) and (VI), namely selenite and selenate, could be converted into gaseous selenium tetrabromide, but elemental selenium and selenide were not affected. Hence, differential determination between selenium in higher and lower oxidation states seemed possible: in the first step selenite and selenate would be determined by the ammonium bromide–CPA distillation method, and then elemental selenium and selenide would be oxidized to higher oxidation states in the residual CPA medium by addition of an appropriate oxidizing agent. Various oxidizing agents were tested and potassium iodate was found the most adequate. The oxidation-reduction

Table 5. Effect of amount of potassium iodate on distillation of elementary selenium

KIO_3, *mg*	Recovered, % Absorber (1)	Absorber (2)	Total	Undistilled, %	Total, %
25	83·6	2·6	86·2	13·3	99·5
30	88·1	3·1	91·2	7·6	98·8
40	95·3	3·2	98·5	0·9	99·4
50	93·7	4·6	98·3	1·0	99·3

10 mg of Se(IV) [containing ^{75}Se(IV)] were added and reduced to elementary selenium with sodium sulphite.

Table 6. Recovery of elementary selenium after distillations with Br^-–SPA and IO_3^-–Br^-–CPA

Se taken	Recovered, % Br^-–CPA	IO_3^-–Br^-–CPA
2·5 μg	<1	98·1
2·5	<1	98·7
2·5	<1	98·5
1·0 mg	<1	98·6
1·0	<1	98·5
10·0 mg	<1	98·3
10·0	<1	98·5
10·0	<1	98·6

[75]Se was added as a radioactive tracer.

potentials justify the choice: there is a difference of 0·46 V between the redox potentials of $IO_3^- + 6H^+ + 5e^- = 1/2I_2 + 3H_2O$ (1·20 V) and $H_2SeO_3 + 4H^+ + 4e^- = Se + 3H_2O$ (0·74 V). The recovery of 10 mg of elemental selenium heated with various amounts of potassium iodate in the NH_4Br–CPA is shown in Table 5. About 40–50 mg of iodate were found enough for less than 10 mg of selenium.

The experiments were carried out as follows. A definite amount of slightly acidic sodium selenite solution containing radioactive tracer was put in the reaction vessel, and sodium sulphite solution was added to reduce the selenite to elemental selenium. The solution was evaporated to dryness on a water-bath, and the Br^-–CPA distillation was performed. No selenium was found in the absorption solution. The reaction vessel was cooled to below 100°C, 40 mg of potassium iodate and 0·1 g of ammonium bromide were added, and the distillation started again. The amounts of selenium trapped in the absorption solution were determined by γ-counting. Table 6 shows the results.

For selenide tests, a synthesized Ag_3AsSe_3 sample was used. The results obtained were similar to those for elemental selenium. This two-step distillation could form the bases of a differential determination of selenium in various oxidation states, but unfortunately several sulphide ores such as pyrites, chalcopyrites and galena are incompletely decomposed by the IO_3^-–Br^-–CPA reagent under the present conditions, and for application of the method to such sulphide ores, further investigation is required.

Behaviour of other elements

Other elements giving volatile bromides were submitted to the Br^-–CPA and the IO_3^-–Br^-–CPA treatment. Table 7 shows that Fe(III), Ir(IV), Mn(II), Os(III), Re(VII), Ru(III) and Tc(VII) are not distilled at all, but that more than 95% of arsenic(III), bromide, mercury(I,II) and iodide, and 2–3% of antimony(III,V) and tin(II,IV) are distilled from samples containing 1 mg of each.

Spectrophotometric determination of selenium after distillation

In the present study 4-chloro-*o*-phenylenediamine was chosen as the spectrophotometric reagent for selenium because it has not only high sensitivity and stability but also a wide pH range for complete formation of the piazselenol, extending to low pH. After the decomposition and distillation, the absorption solution contains hydrochloric acid, perchloric acid, hydrobromic acid, and any selenium tetrabromide, iodide, mercury and

Table 7. Distillation of various elements from CPA in the presence of bromide

Element*	by Br^-–SPA %	by IO_3^-–Br^-–SPA %
As(III)	>95	>95
Br^-	>95	>95
Fe(III)	0	0
Hg(I,II)	>95	>95
I^-	>95	>95
Ir(IV)	0	0
Mn(II)	0	0
Os(III)	0	0
Re(VII)	0	0
Ru(III)	0	0
Sb(III,V)	≃2	0
Sn(II,IV)	≃3	≃3
Tc(VII)	0	0

* 1 mg of each was added together with its radioactive tracer.

arsenic present. The effect of these species was examined as follows: 1·0 mg of each was added to the reaction vessel containing 20 μg of selenium, and the complete procedure was applied. The absorption spectrum of the final toluene phase and the absorbance measured at 341 nm completely agreed with those obtained for extraction of the piazselenol from a 0·1*M* hydrochloric acid solution containing 20 μg of selenium as selenite, confirming that selenium could be determined without interference from other volatile species and the acid medium used.

Neutron-activation analysis of rocks, marine sediments and marine plankton for selenium

A sample of 0·5–1·0 g of the finely-ground rock, sediment or plankton was accurately weighed and sealed in a clean silica tube. For the standard, about 0·01 ml of 500-ppm standard selenium solution was placed in a similar tube by microsyringe, dried, weighed and sealed. The samples and the standards were irradiated with a thermal-neutron flux of $4{\cdot}65 \times 10^{13}$ n. cm^{-2} . sec^{-1} for 80 hr.

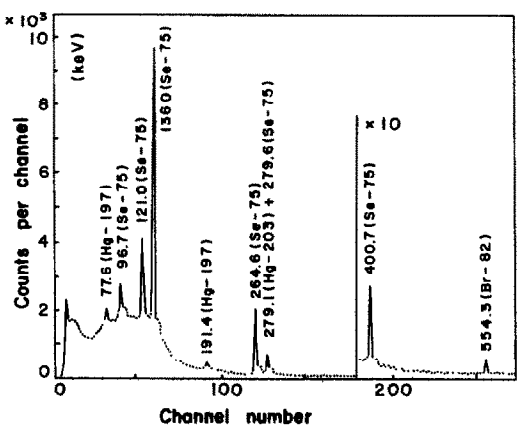

Fig. 2. γ-Spectrum of selenium fraction after separation by the CPA-method, obtained by Ge(Li) detector with 400-channel pulse-height analyser. Sample: irradiated marine sediment.

Table 8a. Selenium contents of the standard rocks JG-1 and JB-1*

JG-1, *ppm*	JB-1, *ppm*
0·0027 ± 0·0002	0·026 ± 0·002
0·0028 ± 0·0002	0·024 ± 0·002
0·0027 ± 0·0002	0·026 ± 0·002
0·0027 ± 0·0002	0·027 ± 0·002
0·0026 ± 0·0002	0·027 ± 0·002
av. 0·0027 ± 0·0002	av. 0·026 ± 0·002

* Data were obtained by neutron-activation analysis.
Elementary selenium and selenide could not be detected.

Table 8b. Selenium contents of marine sediments and plankton

Location of the sample collected	Depth, *m*	By neutronactivation, *ppm* Se(IV) + (VI)	Se(0) + (II)	By spectrophotometry, *ppm*
Sediments				
0°00′00″ N 150°04′07″ E	5135	$0{\cdot}4_7$	—*	—
0°48′08″ N 163°59′05″ E	4330	$0{\cdot}8_7$	—*	—
37°24′ N 132°03′ E	2100	2·6	1·6	4·5†
36°11′ N 131°08′ E	1810	8·5	1·3	9·6†
Plankton				
Tsukumo Bay, Noto Peninsula	10	$0{\cdot}1_9$	$0{\cdot}2_8$	—

* Elementary selenium and selenide were not determined.
† Total selenium were determined by the IO_3^-–Br^-–CPA method.

After cooling for 5–7 days, the sample was transferred into the CPA reaction vessel together with non-radioactive carrier. After the decomposition and distillation, the absorption solution and washings were combined in an Erlenmeyer flask (100-ml), made about 6*M* in hydrochloric acid, heated on the water-bath, treated with about 3 ml of 10% tin(II) chloride solution (in concentrated hydrochloric acid) and digested for 1 hr. The precipitate was filtered off on a previously weighed glass-fibre filter paper (Toyo Roshi, GB-60), washed successively with 6*M* hydrochloric acid, distilled water and ethyl alcohol, then dried at 110° and weighed; the chemical yield of the selenium carrier was calculated.

The final precipitate was wrapped in a "Mylor" film or paraffin-waxed paper and the 136·0 or 264·6 keV photopeaks of ^{75}Se (121 d) were counted with a Ge(Li) solid-state detector coupled to a 400-channel pulse-height analyser. A typical spectrum is shown in Fig. 2.

An outstanding feature of the spectrum shown in Fig. 2 is the excellent separation of both the photopeaks of ^{75}Se; the 279·6-keV photopeak may be overlapped by the 279·1-keV photopeak of ^{203}Hg (46·9 d).

Table 8a shows the results of the neutron-activation analysis of the standard granodiolite JG-1 and basalt JB-1 for selenium. In Table 8b are presented some analytical results for marine sediments and plankton together with those obtained by spectrophotometric analysis; the results are in good agreement.

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GRAVIMETRIC DETERMINATION OF SELENIUM FROM PERCHLORIC ACID SOLUTION WITH HYDRAZINE

SHIGEKI OOBA* and SEIICHI UNEO

National Institute for Researches in Inorganic Materials, Kurakake, Sakura-mura, Niihari-gun, Ibaraki, 300-31, Japan

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Summary—The gravimetric determination of selenium, by reduction of selenious acid in perchloric acid solution with hydrazine hydrate, has been studied in detail. Elemental selenium is completely precipitated in 3·2–5·1*M* perchloric acid at room temperature or 100°C. One mole of selenious acid reacts with one mole of hydrazine hydrate to give elemental selenium.

Various reducing agents have been used for the gravimetric determination of selenium based on the reduction of selenite and selenate to elemental selenium in hydrochloric acid. They include sulphur dioxide,[1,2] 1-amidino-2-thiourea,[3] copper(I) chloride,[4] hydroxylamine,[5] hypophosphite,[6] thiourea,[7] tin(II) chloride[8] and mercury(I) chloride.[9] Hydrazine has been used for the volumetric determination of selenium.[10] It has also been used for the gravimetric determination of selenium in hydrochloric[11] and in tartaric acids.[12] Hovorka[13] determined selenium by treatment with hydrazine hydrate or hydrazine sulphate in hydrochloric, perchloric, sulphuric, phosphoric, phosphorous, formic, acetic, citric and tartaric acids, but the determination of selenium in perchloric acid was unsatisfactory. Perchloric acid[2] has been used to remove any residual nitric acid which had been used to dissolve elemental selenium, and its influence on the determination of selenium in hydrochloric acid discussed. For the determination of total selenium in rubber, a mixture of fuming nitric and perchloric acids[14] has been used for the oxidation of the rubber. Perchloric and sulphuric acids have also been used in the determination of selenium with sulphur dioxide.[15] However, no systematic studies have been made on the determination of selenium in the presence of other chalcogenide elements. A gravimetric determination of selenium in chalcogenide glasses containing arsenic, sulphur, selenium and tellurium is described below. It is based on the reduction of selenium(IV) and (VI) in perchloric acid with hydrazine.

EXPERIMENTAL

Reagents

Selenious acid solution. Metallic selenium (99·999% pure) was dissolved in nitric acid and the solution was evaporated to dryness on a water-bath; perchloric acid was added and the mixture heated on the water-bath to give a standard selenium solution (Se 10 mg/ml). Another standard solution (also 10 mg/ml) was prepared from analytical-reagent grade selenious acid.

Perchloric acid, 60%. Specially pure.

Hydrazine hydrate solution, 10%. Other reagents used were of analytical-reagent grade and used without further purification.

General procedure

The selenium sample solution was diluted to 100 ml with water, 40 ml of 60% perchloric acid and 8 ml of 10% hydrazine hydrate solution were added, and the mixture was heated on a water-bath for 3 hr, and allowed to stand overnight until all the precipitate of elemental selenium settled. The precipitate was then filtered off on a weighed sintered-glass filter (porosity 4), washed with water, dried at 100° for 2 hr and weighed.

RESULTS AND DISCUSSION

Duval *et al.*[16] have studied the thermolysis of selenium precipitated with various reducing agents[11,13] from various acids other than perchloric acid. We deduce from these results that the selenium precipitated from perchloric acid may not be the same in nature as that from other acid solutions. To find the best drying conditions for the selenium, the weight of selenium obtained by the standard drying procedure was compared with that obtained by vacuum drying at room temperature and at 110°. Drying conditions and the results obtained are summarized in Table 1.

As shown in Table 1, there was little difference between the weight of selenium when dried at 110° from either the wet or the dry state. No increase in weight is brought about by drying at 110° in air. It is clear that selenium is not oxidized by this standard drying procedure. The vacuum drying takes so much time to remove any traces of water that it was preferred in the present study to dry the precipitate at 110° for 2 hr in air.

Perchloric acid concentration

Kimura[1] showed that the reduction of selenious acid with sulphur dioxide is complete when the concentration of hydrochloric acid is higher than 30% v/v. We intended to use the filtrate for the determination of arsenic by the Volhard method, in which case hydrochloric acid interferes. It was decided to see whether perchloric acid could be used instead of hydrochloric acid. The experiments were made by taking 0·1 g of selenium as selenious acid solution, adding from 0 to 55 ml of 60% perchloric acid and 8 ml of 10% hydrazine hydrate solution. The solution was brought to a total volume of 100 ml, and was heated on a water-bath (100°) for 3 hr and then left to stand overnight. The precipitate was filtered off on a sintered-glass filter (porosity 4), washed with water and, after drying at 110° for 2 hr, was weighed. The results obtained by using perchloric acid were compared with

Table 1. Method of drying

Drying conditions	Selenium		
	Taken, *mg*	Found, *mg*	Recovery, %
a at room temp. in vacuum	99·76	$100·2_7$	100·5
a' at room temp. in vacuum	99·76	$100·7_2$	101·0
b at 110°C in vacuum*	99·76	$99·2_9$	99·5
b' at 110°C in vacuum*	99·76	$99·6_7$	99·9
c at room temp. in vacuum	100·56	$101·5_8$	101·0
c' at room temp. in vacuum	100·56	$101·5_7$	101·0
d at 110°C in air†	100·56	$100·8_0$	100·2
d' at 110°C in air†	100·56	$100·4_8$	99·9
e at 110°C for 1 hr	100·56	$100·5_3$	100·0
e' at 110°C for 1 hr	100·56	$100·9_1$	100·4
f at 110°C for 2 hr	99·76	$99·8_5$	100·1
f' at 110°C for 2 hr	99·76	$100·2_3$	100·5

* *b* and *b'* were performed after *a* and *a'*, respectively.
† *d* and *d'* were performed after *c* and *c'*, respectively.

those obtained by using hydrochloric acid. They showed that the reduction of selenious acid to elemental selenium is accomplished in the presence of 35–55 ml of 60% perchloric acid, and it was decided to use 40 ml of 60% perchloric acid in the total volume of 100 ml.

Time and temperature of reduction of selenious acid

Reduction of selenious acid was carried out (1) at room temperature for 1 hr, 2 hr and overnight, (2) at 100° for 1 hr, 2 hr and 3 hr, (3) at 100° for 1 hr, 2 hr and 3 hr. In this case the solution was let stand overnight after reduction.

Satisfactory results were obtained under the conditions specified in (2) or (3). It should be noted that the selenium which was precipitated at room temperature was red and that heated on the water-bath was black. Good and consistent results were obtained irrespective of the colour of the precipitate.

The reaction between selenious acid and hydrazine in perchloric acid solution

The reaction between selenious acid and hydrazine in hydrochloric acid solution[10] has been established as

$$H_2SeO_3 + N_2H_4 \rightarrow Se + N_2 + 3H_2O$$

To ascertain whether this reaction is the same in perchloric acid solution or not, the following experiment was carried out; 0·1 g of selenium as selenious acid, 40 ml of 60% perchloric acid and a known amount of hydrazine hydrate were diluted to 100 ml with water and the reaction was carried out at 30° overnight with nitrogen being bubbled through the solution during the whole reaction. The same experiment was made with hydrochloric instead of perchloric acid. In both experiments, the excess of hydrazine in the filtrate was titrated with potassium iodate[17] and the amount of selenium was calculated from the amount of hydrazine reacted.[10] The results obtained showed that the reaction scheme of selenious acid with hydrazine in perchloric acid solution is the same as that in hydrochloric acid solution.

Recovery of selenium

Solution containing various amounts of selenium were treated by the standard method. The results obtained are shown in Table 2 together with the results obtained for hydrochloric acid solutions. Satisfactory results can be obtained for as little as 20 mg of selenium, with an overall recovery of 99·4–100·2%.

Table 2. Determination of various amounts of selenium

Taken, *mg*	Selenium Found, *mg*	Recovery, %	Taken, *mg*	Selenium Found, *mg*	Recovery, %
150·03	$150·2_3$	100·2	10·00	$9·9_3$	99·3
99·76	$99·6_7$	99·9	10·00	$9·8_6$	98·6
99·76	$99·5_3$	99·8	150·03*	$149·8_6$	99·9
70·01	$70·0_0$	100·0	100·02*	$100·0_2$	100·0
50·01	$49·8_0$	99·6	105·82*	$105·5_3$	99·7
50·01	$49·9_3$	99·8	105·82*	$105·7_2$	99·9
20·00	$19·8_8$	99·4			

* In hydrochloric acid medium.

Table 3. Effect of coexistent substances

Substance	Amount	Selenium		
		Taken, *mg*	Found, *mg*	Recovery, %
$Na_2HPO_4.12H_2O$	2·5 g	100·56	$100·5_1$	100·0
$NaClO_4$	2·5 g	100·56	$100·1_4$	99·6
CH_3COONa	2·5 g	99·76	$99·6_1$	99·9
Na_2SO_4	2·5 g	99·76	$99·4_3$	99·7
$NaAsO_2$	1·0 g	100·02	$99·9_5$	99·9
$NaTeO_3$	1·0 g	100·02	$100·3_5$	100·4
CH_3COOH	2 ml	100·56	$100·4_2$	99·9
HCl	2 ml	100·56	$100·6_3$	100·1
HNO_3	2 ml	100·56	$14·4_8$	14·4

Effect of coexistent substances

The effects of coexisting substances which may be present in chalcogenide glass, such as sulphur, selenium, tellurium, and arsenic, were studied (Table 3). The constituent elements of chalcogenide glass do not interfere in the determination of selenium, but nitric acid does.

Determination of selenium in chalcogenide glass

From the results obtained above, the following analytical procedure was established for the determination of selenium in chalcogenide glass (As–S–Se system).

Dissolve the sample in a mixture of sodium hydroxide and hydrogen peroxide on the water-bath. Neutralize the resulting solution with perchloric acid and add 40 ml of 60% perchloric acid. (Alternatively, dissolve the sample in 5 ml of nitric acid and 10 ml of perchloric acid, on the water-bath, then heat the resulting solution on the water-bath to eliminate any nitric acid and add 30 ml of 60% perchloric acid, or dissolve the sample in a mixture of sodium hydroxide and hydrogen peroxide on the water-bath, neutralize the resulting solution with hydrochloric acid and add 40 ml of hydrochloric acid.) Determine the selenium according to the standard procedure.

Typical results are summarized in Table 4, which indicates that selenium in chalcogenide glass can be determined successfully by use of any of the dissolution procedures.

Table 4. Determination of selenium in chalcogenide glass

Dissolution procedure	Selenium found, %
(1) NaOH, H_2O_2, $HClO_4$	$30·9_0$
(2) HNO_3, $HClO_4$	$30·7_6$
(3) NaOH, H_2O_2, HCl	$30·6_9$

This glass contained 30·8% of selenium.

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NEW REDOX TITRANTS IN NON-AQUEOUS OR PARTIALLY AQUEOUS MEDIA—V*

POTENTIOMETRIC TITRATIONS WITH IODOSOBENZENE DIACETATE IN ACETIC ACID MEDIUM

V. N. SIVASANKARA PILLAI and C. G. RAMACHANDRAN NAIR

Department of Chemistry, University of Kerala, Trivandrum-695001, India

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Summary—A stable new redox titrant, *viz.*, iodosobenzene diacetate in anhydrous acetic acid medium, is proposed for the potentiometric determination of a number of reductants such as As(III), I^-, Fe(II), N_2H_4, $[Fe(CN)_6]^{4-}$, Tl(I), Sb(III), hydroquinone, ascorbic acid, phenol, aniline and oxine.

In the course of our investigations on new organic oxidimetric titrants for use in non-aqueous media, it was found that iodosobenzene diacetate (also known as iodobenzene diacetate or phenyl iodosodiacetate; hereafter abbreviated as IBDA) is ideally suited for this purpose. Its solutions in acetic acid were found to be very much more stable than those of dichloramine-T[1–3] (DCT) and iodosobenzene dichloride[4] (IBDC), studied earlier. The solid compound is also quite stable on storage and is commercially available. In this communication, we wish to report on the potentiometric titrations of some typical inorganic as well as organic reductants with IBDA.

EXPERIMENTAL

Apparatus

The apparatus and electrodes used were the same as described earlier.[2]

Reagents

Iodosobenzene diacetate was prepared by the procedure of Pausacker[5] as well as by the procedure described by Sharefkin and Saltzman.[6] While both procedures were found to be satisfactory, that of Pausacker was found to be simpler and more convenient. The product was recrystallized from anhydrous acetic acid and was freed from the adhering solvent under suction with dry air and was stored in a vacuum desiccator, m.p. 160·5° (literature value 159–161°C). In an assay of the purity, known weights were dissolved in acetic acid (5–10 ml), 20 ml of 10% potassium iodide solution were added and after dilution to 100 ml with water, the liberated iodine was titrated with standard sodium thiosulphate solution. Samples of 99·5% purity could easily be prepared.

Preparation and standardization of stock solution. Stock solutions were prepared in anhydrous acetic acid and were preserved in amber-coloured bottles attached to automatic burettes, with precautions for the exclusion of moisture as described earlier.[2] The solutions were standardized by the usual procedure.[2]

Stability of the stock solutions. The stability of IBDA solution in anhydrous acetic acid was studied in detail. The solutions are remarkably stable when kept in amber-coloured bottles, their strengths remaining unchanged for more than 30 days. Even with clear glass bottles for the storage, the stability is reasonable (stable up to 7 days). It may be pointed out that solutions of DCT and IBDC deteriorate quickly when kept in clear glass bottles; even in amber-coloured bottles they deteriorate, albeit slowly. Thus IBDA is superior to DCT and IBDC in this respect.

* Parts I–IV see references 1–4.

Other reagents. Acetic acid was refluxed with chromium trioxide and distilled.[7] The addition of acetic anhydride, necessary in the case of DCT and IBDC solutions, was found not to be required. All other reagents were of analytical-reagent grade.

Standard solutions of ascorbic acid, phenol, hydrazine sulphate, potassium ferrocyanide, potassium iodide and thallium(I) nitrate were prepared in water; those of aniline and arsenic(III) were prepared in 0·5*M* hydrochloric acid, that of iron(II) in 2*M* sulphuric acid and that of oxine in 8*M* acetic acid. Solutions of hydroquinone were prepared in 0·5*M* sulphuric acid to give a stable solution as recommended by Miraz, Simon and Zýka.[8] These solutions were all checked by the usual methods.[9]

General procedure for potentiometric titrations

Our previous experience with DCT and IBDC had shown that there is no advantage in removing the water present in the titrand by the addition of acetic anhydride, but that, on the contrary, the presence of small amounts of water is advantageous in facilitating quicker equilibration. The same was found to be the case with IBDA. Therefore, titrations were carried out in a partially aqueous medium, the titrand usually being an aqueous solution and the titrant a non-aqueous solution.

Titration cells (100-ml capacity) provided with lids having holes for the introduction of the electrodes, microburettes, *etc.*, were employed. Measured aliquots of the titrand solutions were taken in the cells and other reagents (if required) were added. The solutions were magnetically stirred and the titrant was added from a burette. Stirring was stopped temporarily before potential readings were taken. All the titrations were carried out at 28 ± 2°.

Titration of inorganic materials

As(III), I^-, Fe(II). The titration of these was found to be the simplest case, the addition of no other reagent or catalyst being necessary. An inert atmosphere was found to be advantageous for I^- and Fe(II).

To 5–10 ml of the reductant solution add 10 ml of water. In the case of I^- and Fe(II), displace the air in the titration cell with pure nitrogen, maintain a slow stream of nitrogen and titrate with IBDA solution. [Potential break at end-point = 400 mV for As(III), 250 mV for Fe(II) and 120 mV for I^-, per 0·05 ml of 0·1*N* IBDA solution.]

Hydrazine and potassium ferrocyanide. Direct titration was found to be unsatisfactory; however, in presence of bromide, accurate titrations were possible. Further, the addition of hydrochloric acid improved the titration of hydrazine whereas the ferrocyanide titration was improved by the addition of acetic acid.

To 5–10 ml of the reductant solution add 0·5 g of potassium bromide and 2 ml of 2*M* hydrochloric acid (for hydrazine) or 10 ml of 5*M* acetic acid (for ferrocyanide) and titrate with IBDA solution. (Potential break at end-point = 200 mV for hydrazine and 290 mV for ferrocyanide per 0·05 ml of 0·1*N* IBDA.)

Tl(I) and Sb(III). Direct titration was found to be very slow; the addition of bromide (or more satisfactorily, chloride) improved the titration of Tl(I). In the case of Sb(III), addition of bromide improved the speed, but caused a lowering of the break. Addition of chloride did not help. The addition of a catalyst such as osmic acid improved the speed and also gave a satisfactory potential break. A catalyst correction was applied by carrying out titrations at various catalyst concentrations and extrapolating to zero catalyst concentration.

To 5–10 ml of the solution add 10 ml of 2*M* hydrochloric acid (and 0·05 ml of 0·2% aqueous osmic solution in the case of Sb) and titrate with IBDA solution. Apply a catalyst correction as indicated above [potential break at end-point = 230 mV for Tl(I) and 170 mV for Sb(III) per 0·05 ml of 0·1*N* IBDA.]

Titration of organic materials

Hydroquinone and ascorbic acid. Direct titration is quite satisfactory. Dilute 5–10 ml of the reductant solution with 10 ml of water and titrate with IBDA solution. [Potential break at end-point = 160 mV for hydroquinone and 340 mV for ascorbic acid, per 0·05 ml of 0·1*N* IBDA.]

Phenol, aniline and oxine. The titrations were unsatisfactory in the absence of bromide, but proceeded smoothly when it was added. The addition of a 10% solution of pyridine in glacial acetic acid improves the titration of phenol.[10] It was also found that the addition of sodium acetate improves the titration of oxine slightly and that of aniline remarkably.

To 5–10 ml of the titrand solution add 0·5 g of potassium bromide and 10 ml of water. In the case of aniline and oxine, add 0·5 g of sodium acetate. In the case of phenol, add 1 ml of a 10% solution of pyridine in glacial acetic acid. Titrate with IBDA solution. [Potential break at end-point = 220 mV for 0·05 ml of 0·1*N* IBDA.]

RESULTS AND DISCUSSION

Direct, first derivative and second-derivative potentiometric titration curves were drawn. The end-points were checked also by using the Hostetter–Roberts equation[11] and the Yan equation.[12] Typical results are presented in Tables 1 (inorganic materials) and 2 (organic materials).

Table 1. Determination of inorganic materials

Reductant	Taken, *mmole*	No. of expts. done	Found, *mmole* (average)	Standard deviation, *mmole*
[b]As(III)	0·3845	6	$0{\cdot}384_8$	$8{\cdot}9 \times 10^{-5}$
	0·7690	7	$0{\cdot}769_1$	$2{\cdot}5 \times 10^{-4}$
[a]I^-	0·6023	6	$0{\cdot}603_5$	$1{\cdot}3 \times 10^{-4}$
	1·204	5	1·203	$7{\cdot}0 \times 10^{-4}$
	1·437	5	1·442	$3{\cdot}0 \times 10^{-3}$
[a]Fe(II)	0·6413	7	$0{\cdot}644_0$	$3{\cdot}2 \times 10^{-4}$
	0·8039	6	$0{\cdot}800_8$	$2{\cdot}4 \times 10^{-3}$
[c]N_2H_4	0·1146	7	$0{\cdot}114_2$	$5{\cdot}8 \times 10^{-5}$
	0·2292	4	$0{\cdot}229_1$	$1{\cdot}2 \times 10^{-4}$
	0·2523	6	$0{\cdot}252_5$	$7{\cdot}7 \times 10^{-4}$
[a]$[Fe(CN)_6]^{4-}$	0·6406	6	$0{\cdot}641_0$	$1{\cdot}0 \times 10^{-3}$
	0·7929	6	$0{\cdot}792_4$	$1{\cdot}7 \times 10^{-4}$
	1·519	6	1·527	$2{\cdot}6 \times 10^{-4}$
[b]Tl(I)	0·2515	6	$0{\cdot}251_2$	$1{\cdot}9 \times 10^{-4}$
	0·3440	7	$0{\cdot}344_1$	$2{\cdot}6 \times 10^{-4}$
[b]Sb(III)	0·2225	6	$0{\cdot}222_4$	$3{\cdot}5 \times 10^{-4}$
	0·2273	8	$0{\cdot}226_0$	$4{\cdot}5 \times 10^{-4}$
	0·4934	7	$0{\cdot}491_1$	$4{\cdot}2 \times 10^{-4}$

a, b, c: Assuming that the number of equivalents of the oxidant consumed per mole of the reductant is 1 for (a), 2 for (b) and 4 for (c).

It may be seen from Table 1 that the inorganic reductants studied indicate quantitative oxidation in accordance with the following equations.

$$C_6H_5I(CH_3COO)_2 + 2e^- \rightarrow C_6H_5I + 2CH_3COO^-$$
$$As^{3+} \rightarrow As^{5+} + 2e^-$$
$$2I^- \rightarrow I_2 + 2e^-$$
$$Fe^{2+} \rightarrow Fe^{3+} + e^-$$
$$N_2H_4 \rightarrow N_2 + 4H^+ + 4e^-$$
$$[Fe(CN)_6]^{4-} \rightarrow [Fe(CN)_6]^{3-} + e^-$$
$$Tl^+ \rightarrow Tl^{3+} + 2e^-$$
$$Sb^{3+} \rightarrow Sb^{5+} + 2e^-$$

The organic reductants examined undergo quantitative oxidation (or bromination in the presence of bromide) when titrated with IBDA (Table 2). Hydroquinone and ascorbic acid are oxidized to quinone and dehydroascorbic acid respectively. Phenol, aniline and oxine are brominated by IBDA in the presence of bromide to give tribromo derivatives (for phenol and aniline) or dibromo derivative (oxine). The reactions are represented below:

$$C_6H_4(OH)_2 \rightarrow C_6H_4O_2 + 2H^+ + 2e^-$$
$$C_6H_8O_6 \rightarrow C_6H_6O_6 + 2H^+ + 2e^-$$
$$C_6H_5OH + 3Br_2 \rightarrow C_6H_2Br_3OH + 3H^+ + 3Br^-$$
$$C_6H_5NH_2 + 3Br_2 \rightarrow C_6H_2Br_3NH_2 + 3H^+ + 3Br^-$$
$$C_9H_6NOH + 2Br_2 \rightarrow C_9H_4Br_2NOH + 2H^+ + 2Br^-$$

The role of bromide in these titrations is similar to its role in DCT titrations.[2]

Table 2. Determination of organic materials

Reductant	Taken, *mmole*	No. of expts. done	Found, *mmole* (average)	Standard deviation, *mmole*
[a]Hydroquinone	0·2700	6	$0·269_5$	$9·6 \times 10^{-4}$
	0·4050	6	$0·404_3$	$3·6 \times 10^{-4}$
	0·5400	5	$0·537_9$	$1·8 \times 10^{-3}$
[a]Ascorbic acid	0·2537	6	$0·253_0$	$1·7 \times 10^{-3}$
	0·2750	6	$0·273_4$	$1·4 \times 10^{-3}$
	0·7555	5	$0·757_0$	$1·4 \times 10^{-3}$
[c]Phenol	0·0548	6	0·0548	$2·4 \times 10^{-4}$
	0·1096	6	$0·109_0$	$6·2 \times 10^{-4}$
	0·1301	8	$0·129_2$	$4·5 \times 10^{-4}$
[c]Aniline	0·0851	8	$0·084_9$	$2·3 \times 10^{-5}$
	0·1688	7	$0·167_3$	$8·2 \times 10^{-5}$
	0·1700	6	$0·169_7$	$8·9 \times 10^{-5}$
[b]Oxine	0·1004	7	$0·100_5$	$2·7 \times 10^{-4}$
	0·2007	6	$0·201_2$	$7·5 \times 10^{-4}$
	0·2605	5	$0·259_7$	$2·7 \times 10^{-4}$

a, b, c: Assuming that the number of equivalents of oxidant consumed per mole of the reductant is 2 for (a), 4 for (b) and 6 for (c).

It may be mentioned that while IBDA titrations were found to be as satisfactory as titrations with DCT or IBDC, the superior stability of IBDA solution makes daily standardization (recommended in the case of solutions of DCT and IBDC) quite unnecessary here; this is a definite advantage of this new titrant.

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SPECTROPHOTOMETRIC AND FLUOROMETRIC DETERMINATION OF TRACES OF MOLYBDENUM IN SOILS AND PLANTS

P. R. HADDAD, P. W. ALEXANDER and L. E. SMYTHE

Department of Analytical Chemistry, University of New South Wales, P.O. Box 1, Kensington, N.S.W. 2033, Australia

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Summary—The reaction of the molybdenum oxypentathiocyanate ion with the dyestuff Rhodamine B (RhB) produces the ternary complex $MoO(SCN)_5(RhB)_2$. The formation of this complex is accompanied by a colour change and by extinction of the fluorescence of RhB. A spectrophotometric and fluorometric method for the determination of Mo has been developed from these observations. The method is free from interferences and has detection limits of 0·1 μg and 0·05 μg of Mo for absorption and fluorescence measurements, respectively. The spectrophotometric method is applicable to the determination of Mo in soils and the fluorometric method is suited to the determination of Mo in plants.

Early colorimetric methods for the determination of molybdenum in soils, while being adequate for analysis of samples of high molybdenum content, were not suitable for Mo-deficient soils containing less than 2 ppm of molybdenum. The analysis of plant materials for molybdenum in the sub-ppm range has, however, been successfully achieved by Ssekaalo,[1] using toluene-3,4-dithiol, with the complex being extracted into carbon tetrachloride.

Direct atomic-absorption determination of molybdenum is subject to large amounts of interference from acids[2] and, as such, has not found wide usage for low concentrations of molybdenum. A method recently developed in this laboratory,[3] however, employs solvent extraction of the molybdenum thiocyanate complex coupled with an AAS finish and gives the best reported detection limit and precision for an AAS method. The photometric (or alternative fluorometric) procedure described here gives comparable precision and sensitivity, and is designed as an alternative to the AAS method. However, this photometric method has the advantage of being a non-extraction technique, and so requires less manipulation than that needed for the AAS procedure.

Ternary complexes, wherein a metal ion reacts with two separate ligands, have been used extensively over recent years,[4–6] with the majority of examples reported being of the ion-association type. In such a complex, the metal ion reacts with a ligand to produce a charged binary complex which then forms an ion-association complex with a second ligand of opposite charge, usually a dyestuff. A ternary complex so formed normally exhibits enhanced selectivity, precision and sensitivity over the equivalent binary complex.[7] There are few examples of ternary molybdenum complexes, although the molybdophosphate ion has been used with the dyes Rhodamine B[8] and Crystal Violet[9] to determine phosphorus, and the silicomolybdate ion with Rhodamine B[10] for silicon determination. Ganago and Ivanova[11] have reported a ternary complex formed by association of the molybdenum thiocyanate complex with the dye cation Crystal Violet. This complex is

floated with toluene before being dissolved in ethanol. No information on interferences or analytical applications of the method is given.

This paper describes the formation of a 1:5:2 complex of molybdenum, thiocyanate and Rhodamine B (RhB). The formation of this complex may be represented by the equation

$$[MoO(SCN)_5]^{2-} + 2RhB^+ \rightleftharpoons \underset{\text{pink, fluorescent}}{MoO(SCN)_5(RhB)_2} \quad (1)$$

blue, non-fluorescent

This ternary complex absorbs strongly at 600 nm, forming the basis of a spectrophotometric method. In addition, the fluorescence of RhB is quenched by the formation of the non-fluorescent ternary complex, thereby providing foundation for a fluorescence-quenching method. Both of these methods have been successfully developed and applied to the determination of traces of molybdenum in soils and plants.

EXPERIMENTAL

Apparatus

All absorption measurements were taken on a Perkin–Elmer PE 124 recording spectrophotometer, and fluorescence measurements were taken with an Hitachi Perkin–Elmer MPF-2A fluorescence spectrophotometer. Wavelengths used were 600 nm for absorption and 350 and 578 nm for fluorescence excitation and emission, respectively.

Reagents

Standard Mo solution. A 1000-ppm stock solution was prepared by dissolving 1·84 g of analytical grade ammonium molybdate [$(NH_4)_6Mo_7O_{24}\ 4H_2O$] in distilled water. More dilute standards were made up as required in 2*M* hydrochloric acid, this acidity being equal to that used in sample digests.

Rhodamine B. A 0·004% solution in water was prepared from commercial reagent (E. Merck and Co.). This dye was not recrystallized before use.

All other reagents used were of analytical grade and distilled water was used to make up solutions.

Dissolution of samples

Soils were dissolved by using the method of Kim *et al.*[3] with the exception that 1 g of sample was used in all cases. This sample weight necessitated a second addition of concentrated hydrofluoric acid before the evaporation to dryness. The residue so obtained was redissolved in 5 ml of 10*M* hydrochloric acid and the solution made up to 25 ml in a standard flask with distilled water. Complete dissolution of all samples was obtained by this process.

Plant samples were digested by addition of 15 ml of concentrated nitric acid to 1 g of sample in a 100-ml Kjeldahl flask, followed by gentle heating until evolution of brown fumes had ceased. When all organic matter had dissolved, 5 ml of 72% perchloric acid were added and the solution was heated strongly until all acids had been removed. During this process, the flask was rotated regularly to ensure that all sample was washed down by the refluxing acid. The residue remaining after evaporation was redissolved in 5 ml of 10*M* hydrochloric acid and the solution transferred to a 25-ml volumetric flask before being diluted to the mark with distilled water.

Analysis of samples

A 10-ml portion of the soil or plant-digest solution was added to a 25-ml volumetric flask containing about 0·1 g of solid ascorbic acid and the flask shaken to remove all traces of the yellow colour of Fe(III). Additional ascorbic acid was added if required. The following additions were then made, in the order given: 1 ml of 10% sodium tartrate solution, 4 ml of 10*M* sulphuric acid, 1 ml of 1% copper sulphate solution and 1 ml of a freshly prepared 10% thiourea solution. The flask was then agitated for 1 min to ensure complete conversion of Mo(VI) into Mo(V). Potassium thiocyanate solution (10%, 2 ml) was added and the flask allowed to stand for 20 min. After this time, 5·0 ml of 0·004% RhB solution were added and the solution diluted to the mark with distilled water. A blank solution and a series of standards were carried through the entire procedure.

The solutions were centrifuged at moderate speed for 30 sec before having their absorbance and fluorescence measured at the optimal wavelengths. Any extraneous quenching of fluorescence was detected by using a sample carried through the procedure but with no thiocyanate added. The fluorescence of this solution was compared with that of an equivalent RhB solution in distilled water, and a quenching factor calculated. This factor was applied to all subsequent samples of the same soil or plant.

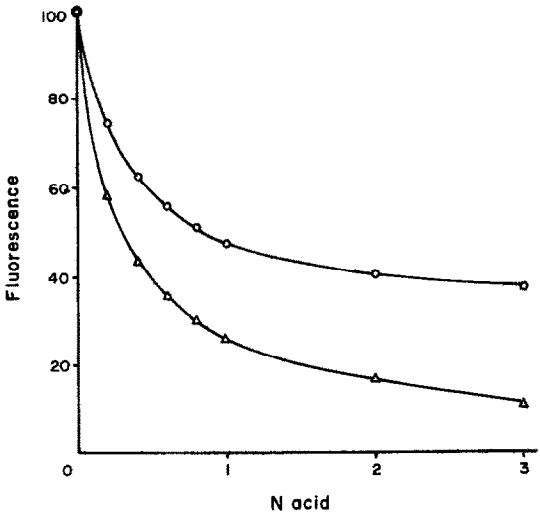

Fig. 1. Effect of acidity on fluorescence of RhB; ○ H_2SO_4, △ HCl.

RESULTS AND DISCUSSION

Conditions for formation of $[MoO(SCN)_5)]^{2-}$

Before investigating the formation of the ternary complex, it was necessary to establish the optimum conditions required for formation of the binary complex $[MoO(SCN)_5]^{2-}$. Additionally, it was essential that these conditions, and the reagents used, be compatible as far as possible with those conditions suited to the formation of the ternary complex. There was no previously published procedure for formation of $[MoO(SCN)_5]^{2-}$ which fulfilled these criteria. A study was made of the effects of various commonly used reagents on the fluorescence and absorbance of RhB.

The fluorescence of RhB was found to depend markedly on acid concentration, this effect being more pronounced for hydrochloric acid solutions than for sulphuric acid solutions. The dependence of fluorescence is shown in Fig. 1. It is evident that, for maximum fluorescence, acidity of the solution should be kept as low as possible and that sulphuric acid is preferable to hydrochloric acid. Acidity had very little effect on the absorbance of RhB solutions once an acid concentration of 1*N* was exceeded.

Thiocyanate in high concentrations had some effect on RhB, in that increasing the amount of thiocyanate caused increased absorbance at 600 nm and decreased fluorescence. This effect was less pronounced at higher acidities and disappeared completely at an acidity $>2N$ sulphuric acid.

The most common reductant used for the conversion of Mo(VI) into Mo(V) is stannous chloride in acid solution.[12] This reagent was investigated and was found to have no effect alone, but in conjunction with thiocyanate it caused increased absorbance and decreased fluorescence. Again, this effect was reduced when the acidity was increased but remained evident to a small degree in 2*N* sulphuric acid. This interference was attributed to the formation of an ion-association ternary complex between Sn(II), thiocyanate and RhB; the complex being less stable at the higher acidities.

It was apparent that stannous chloride could be employed as reductant provided high acid concentrations were used, but this condition has been shown to be detrimental to the

planned fluorescence-quenching method. An alternative reducing agent was therefore sought.

Reducing agents for conversion of Mo(VI) into Mo(V) include ascorbic acid,[11] hydrazine sulphate,[13] dihydroxymaleic acid[14] and thiourea with Cu(II).[14] These were examined and the best with regard to efficiency of reduction and freedom from interference with RhB was the thiourea–Cu(II) system. These reagents together produced no effect on RhB in the presence of thiocyanate in 2*N* sulphuric acid solution.

For the selected reducing mixture, the minimum concentrations of reagents for formation and stability of $[MoO(SCN)_5]^{2-}$ were found to be 2·0*N* sulphuric acid, 0·8% thiocyanate, 0·04% Cu(II), 0·4% thiourea and a development time of 20 min. These concentrations can be exceeded without detriment and represent only the minimum concentrations required.

Formation of the ternary complex

Addition of RhB to a stable solution of $[MoO(SCN)_5]^{2-}$ produced a blue colour, the intensity of which was dependent on the concentration of Mo. RhB solutions normally exhibit a pink colour under the conditions of acidity used. The absorbance spectra of RhB alone and in the presence of 0·3 ppm Mo as $[MoO(SCN)_5]^{2-}$ are given in Fig. 2. The fluorescence spectra for the same two solutions are shown as Fig. 3.

It is noteworthy that when high concentrations of molybdenum were present (in excess of 4 μg/ml) the solutions became turbid owing to precipitation of the sparingly soluble ternary complex. At the 0·3-ppm concentration, however, the solutions were quite transparent. The centrifuging step in the experimental procedure was included to remove any undissolved soil *etc.* which could have been present.

At the wavelength of maximum absorption of 600 nm, linear calibration curves were obtained in the range 0·1–10 μg Mo/25 ml, indicating that the method was suitable for molybdenum determinations within this range.

The spectra shown in Fig. 3 are not corrected for instrumental variations, and hence are applicable to one instrument only. Optimum excitation and emission wavelengths

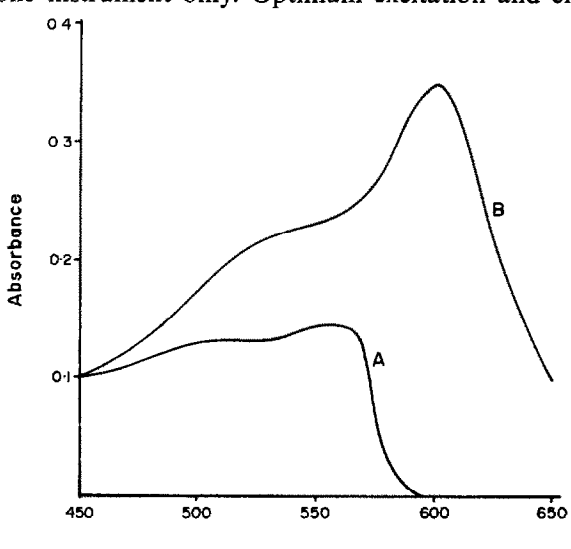

Fig. 2. Absorption spectra for RhB alone (A) and in the presence of 0·3 ppm Mo as $MoO(SCN)_5^{2-}$ (B).

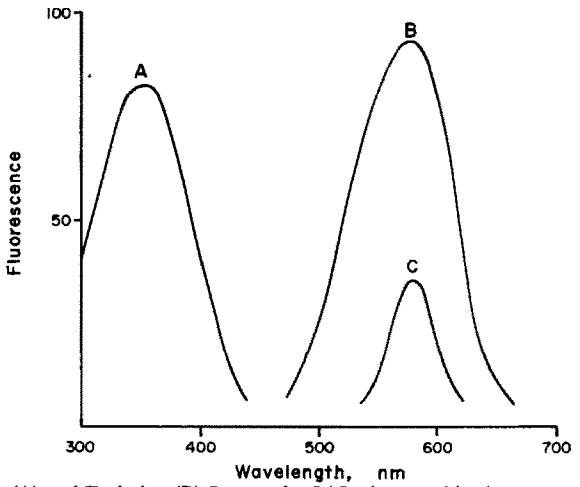

Fig. 3. Excitation (A) and Emission (B) Spectra for RhB alone and in the presence of 0·3 ppm Mo as $MoO(SCN)_5^{2-}$ (C).

should be determined by each operator for his own particular instrument. Figure 3 shows that addition of $[MoO(SCN)_5]^{2-}$ to RhB does not alter the shape of the emission curve but merely reduces the height of the peak at 580 nm. This behaviour can be attributed to the removal of RhB from the solution in accordance with equation (1). Plotting concentration of molybdenum against fluorescence quenching at 580 nm yielded linear calibration curves in the range 0·05–5 μg/25 ml. At Mo concentrations above 5 μg/25 ml, self-absorption effects due to the strongly coloured solution became evident. The fluorescence-quenching method was suitable for determinations in the range 0·05–5 μg of Mo.

The degree of formation of the ternary complex was found to depend on acidity, although the effect was not very marked. As expected, decomposition of the complex at higher acidities resulted in reduced absorbance at 600 nm. This aspect is discussed more fully in the *Interferences* section.

Composition of the ternary complex

Both absorbance and fluorescence techniques were used to elucidate the nature of the ternary complex. Job's method of continuous variation, with $5 \times 10^{-5} M$ solutions of RhB and Mo under optimum conditions for formation of the complex, yields an RhB:Mo ratio of 2·1:1. Job's method was not applicable to the fluorescence measurements since a quenching process was involved. The mole-ratio method, however, was suitable for both absorbance and fluorescence techniques, and with a fixed [Mo] of $10^{-5} M$ with varying [RhB], both methods gave the RhB:Mo ratio as 2·1:1.

These results indicate that the formula of the ternary complex is $MoO(SCN)_5(RhB)_2$, the slight discrepancy between the theoretical and observed mole ratios probably being due to dye impurity. The mole-ratio curve for the absorbance values was used to calculate that the molar absorptivity (ϵ) for the complex was $1{\cdot}09 \times 10^5$ l.mole^{-1}.cm^{-1}.

Interferences

The effect of interfering ions is illustrated in Table 1, which refers to a final acidity of 2·0*N* sulphuric acid. At this acidity, interferences from iron(III) and tungstate were masked with ascorbic acid and tartrate, respectively. The ascorbic acid was necessary to reduce

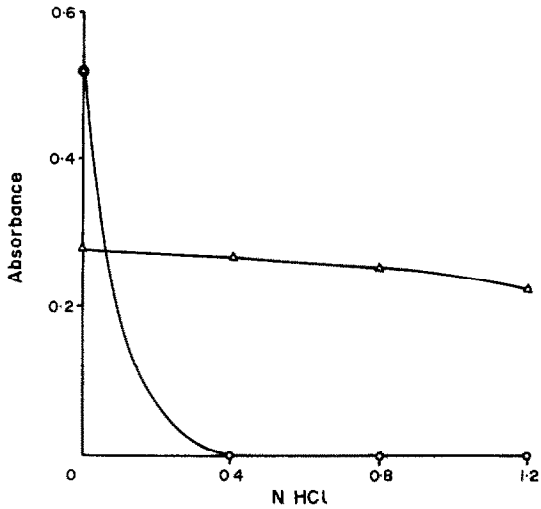

Fig. 4. Absorbances of Mo and Zn ternary complexes with SCN^- and RhB in HCl–H_2SO_4 mixtures. △ $MoO(SCN)_5$ $(RhB)_2$ in 1·6N H_2SO_4 ([Mo] = 0·2 ppm) ○ Zn–SCN–RhB in 1·6N H_2SO_4 ([Zn] = 80 ppm).

iron(III) since the thiourea–Cu(II) system will not achieve this reduction in sulphuric acid media.[15] The tungstate interference is assumed to be due to the formation of a simple binary complex between this ion and RhB. The reducing conditions used were not sufficiently strong to convert W(VI) into W(V), which could form a thiocyanate complex equivalent to $[MoO(SCN)_5]^{2-}$. This assumption regarding tungstate interference was verified by the fact that tungstate still interfered even in the absence of thiocyanate or reducing agent.

The interference of zinc is due to the formation of a ternary complex between zinc, thiocyanate and RhB; such a complex has previously been reported.[16, 17] This complex was subject to instability at high acidities and Fig. 4 shows the behaviour of the zinc and molybdenum ternary complexes in sulphuric acid–hydrochloric acid mixtures.

From Fig. 4 it can be seen that by use of concentrations of 1·8*N* sulphuric acid and 0·8*N* hydrochloric acid, the interference of 2000 μg of zinc is completely removed, while the absorbance of the $MoO(SCN)_5(RhB)_2$ complex is reduced by only 15%. The breakdown of the zinc complex was due to the total acidity, and a mixture of acids was used in order to maximize the fluorescence of RhB (see Fig. 1). This acid mixture was used for all determinations since the loss in sensitivity of the fluorescence method is outweighed by the advantage gained in obviating the need for separation of molybdenum. The correct conditions of acidity were readily achieved by dissolving sample digests and standards in 2*M* hydrochloric acid and using 10-ml portions for analysis, with subsequent addition of the sulphuric acid.

Precision

Under the acidity conditions described above, the precisions of the spectrophotometric and fluorometric procedures were estimated for a molybdenum concentration of 0·2 μg/ml. Fluorescence precision was determined by setting the scale reading to 100 for a blank RhB solution (containing all reagents except molybdenum) and measuring the amount of fluorescence-quenching of 7 identical molybdenum solutions. The relative standard deviation (RSD) of these values was then calculated. These same solutions were used for absorbance

Table 1. Effect of diverse ions on the fluorescence-quenching and absorbance of $MoO(SCN)_5(RhB)_2$. Molar ratio to Mo is indicated in brackets

Ion	Added as	Change in fluorescence, %*	Change in absorbance, %*
Ag^+ (200)	$AgNO_3$	—	—
Al^{3+} (200)	$Al(NO_3).9H_2O$	—	—
Co^{2+} (200)	$Co(NO_3)_2.6H_2O$	—	—
Cr^{3+} (200)	$Cr(NO_3)_3.9H_2O$	—	—
Fe^{3+} (10,000)	$FeNH_4(SO_4)_2.12H_2O$	−95	+200
(10,000)	$FeNH_4(SO_4)_2.12H_2O$	—†	—†
Hg^{2+} (200)	$Hg(NO_3)_2.H_2O$	—	—
K^+ (200)	KNO_3	—	—
Mg^{2+} (200)	$Mg(NO_3)_2.6H_2O$	—	—
Mn^{2+} (200)	$Mn(NO_3)_2.6H_2O$	—	—
Na^+ (200)	$NaNO_3$	—	—
NH_4^+ (200)	NH_4NO_3	—	—
Ni^{2+} (200)	$Ni(NO_3)_2.6H_2O$	—	—
Pb^{2+} (200)	$Pb(NO_3)_2$	(ppte)—§	(ppte)—§
ReO_4^{2-} (200)	$(NH_4)_2ReO_4$	—	—
Sr^{2+} (200)	$Sr(NO_3)_2.4H_2O$	—	—
Th^{4+} (200)	$Th(NO_3)_4.4H_2O$	—	—
V(V) (200)	NH_4VO_3	—	—
WO_4^{2-} (1,000)	Na_2WO_4	−56	+81·5
(1,000)	Na_2WO_4	—‡	—‡
Zn^{2+} (200)	$Zn(NO_3)_2.6H_2O$	−64	104
(50)	$Zn(NO_3)_2.6H_2O$	−25	32
(10)	$Zn(NO_3)_2.6H_2O$	−12	10
Br^- (200)	NaBr	—	—
CH_3COO^- (200)	CH_3COONa	—	
Cl^- (200)	NaCl	—	—
ClO_4^- (200)	$NaClO_4$	—	—
F^- (200)	NaF	—	—
PO_4^{3-} (200)	Na_3PO_4	—	—
SeO_4^{2-} (200)	Na_2SeO_4	—	—

* Changes of 5% or less are not listed.
† In the presence of ascorbic acid.
§ Solution was centrifuged before absorbance and fluorescence measurements were taken.
‡ In the presence of tartrate.

Table 2. Analysis of soil and plant samples

Material	No. of detns.	Mean, *ppm*	RSD, %	Previous analyses, *ppm*	Reference
Soil 1	10	133	1·86	136*	
Soil 2	6	28·0	2·96	25·8*	
USGS Gossan	4	6·35	4·30	6·3*	3
Soil 3	4	1·2	7·88	1·2*	
Standard kale	4	2·42	6·11	2·33 ± 0·47	18

* Value determined by the method of Kim *et al.*[3] (4 replicates were used.)

measurements to indicate the precision of the spectrophotometric method. Values obtained for RSD were 0·46% and 0·71% for the fluorescence and absorbance methods, respectively.

This precision is considered excellent for the low concentration used.

Analysis of samples

Soil samples containing 1·2–133 ppm molybdenum were digested and analysed by the proposed experimental procedure. The standard kale material of Bowen[18] was also analysed as a representative plant sample to test the efficiency of the method for plant material.

The soil samples gave consistently high fluorescence-quenching factors (usually about 35–40%) which was considered unsuitable for trace analysis. The spectrophotometric method, however, gave good results for the soils and is the preferred method. The soil analyses in Table 2 were done by this method. Plant samples, owing to their low inorganic content, gave virtually no extraneous fluorescence quenching, and employment of quenching factors was not necessary. The fluorometric method was therefore used for analysis of standard kale.

Good agreement was obtained between results from the proposed method and those from previous methods. The procedure is therefore considered suitable for the analysis of plants and soils for traces of molybdenum. The detection limits are 0·1 μg of Mo for the spectrophotometric method and 0·05 μg of Mo for the fluorometric method. These values correspond to 0·004 and 0·002 ppm molybdenum, respectively, in the final 25 ml of solution.

CONCLUSION

The high sensitivity and selectivity of the proposed method ensure that it is applicable to the analysis of plants and soils for molybdenum. Of the two types of sample, plants are more readily analysed by the fluorometric method because the low inorganic content leads to minimal extraneous fluorescence quenching. The spectrophotometric method, however, is preferred for soil samples. These methods compare favourably with existing procedures in terms of sensitivity, selectivity and precision, but have the additional advantage of being non-extraction techniques.

The unusually high stability of the ternary complex $MoO(SCN)_5(RhB)_2$ in strongly acidic solution is the main factor contributing to the lack of interferences in the method. This behaviour is consistent with the trend towards higher stability generally exhibited by ternary complexes.

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SHORT COMMUNICATIONS

DETERMINATION OF METALS BY SOLID–LIQUID SEPARATION AFTER LIQUID–LIQUID EXTRACTION

POLAROGRAPHIC DETERMINATION OF INDIUM AFTER EXTRACTION WITH OXINE INTO MOLTEN NAPHTHALENE

(*Received* 9 *April* 1974. *Accepted* 16 *May* 1974)

Indium may be determined polarographically[1] and the selectivity may be improved by the use of various masking agents, though their use may also introduce the disadvantages of changing the composition of the electrolyte, diluting the sample, producing insoluble chelates, or simply not being sufficiently selective. Solvent extraction may help to overcome some of these difficulties, but not that of dilution, as the electrolyte must still be added to the organic phase. The technique of extraction at high temperature into a liquid phase of small volume which solidifies on cooling, has been shown to overcome these problems. Moreover, at the elevated temperature, equilibrium is attained more rapidly than at room temperature. Metals have been extracted as chelates and estimated spectrophotometrically after dissolution of the solid phase in a suitable solvent.[2–4] A polarographic finish has been used for the determination of cadmium and lead,[5] and of molybdenum.[6] This communication describes the extraction of indium with 8-hydroxyquinoline into molten naphthalene, and its subsequent determination by polarography after dissolving the naphthalene in dimethylformamide and adding pyridinium perchlorate as supporting electrolyte.

EXPERIMENTAL

Reagents

Indium sulphate was dissolved in distilled water containing a few drops of sulphuric acid and standardized complexometrically.[7] The concentration was 11·5 mg/ml.

8-*Hydroxyquinoline* was dissolved in ethanol to give a 0·1*M* solution.

Perchloric acid and *pyridine* solutions in dimethyl formamide and water respectively, were each 2*M*.

Naphthalene and *DMF* were checked polarographically for impurities.

Apparatus

Polarograms were recorded at 25° ± 0·5° with a Yanagimoto P8 three-electrode polarograph. An H-type cell with fine porosity sintered-glass disk between the compartments was used. A saturated calomel electrode was connected to the polarographic cell *via* a potassium chloride–agar bridge. The parameters for the mercury drop in open circuit were $m = 1{\cdot}52$ mg/sec, $t = 4{\cdot}78$ sec, $h = 60$ cm. All solutions were deaerated by passing nitrogen through them for 5 min.

Indium oxinate standard in DMF

An aliquot of indium sulphate solution was taken and the indium precipitated by addition of oxine according to Geilmann.[8] The precipitate was filtered off, washed, and dissolved in 100 ml of DMF. This solution was used for studying the polarographic behaviour of indium oxinate in DMF.

General procedure

An aliquot of indium solution was transferred to a 100-ml round-bottomed flask along with 0·5 ml of the oxine solution, diluted to 30–40 ml with distilled water, and the pH adjusted if necessary to within the range 3–12 by addition of ammonia solution. The stoppered flask was warmed in a water-bath at about 60°, 2 g of naphthalene were added, and the flask was heated till the naphthalene melted (m.p. 80°) and formed a separate layer. This solution was stirred while being allowed to cool till the naphthalene separated out as a solid mass. The flask was again heated, shaken vigorously and allowed to stand. The lump of solid naphthalene was separated by filtration, dried on filter paper, and dissolved in DMF in a 20-ml flask. One ml of pyridine solution and one ml of perchloric acid were added and the solution was diluted to 20 ml. After deaeration the polarogram was recorded.

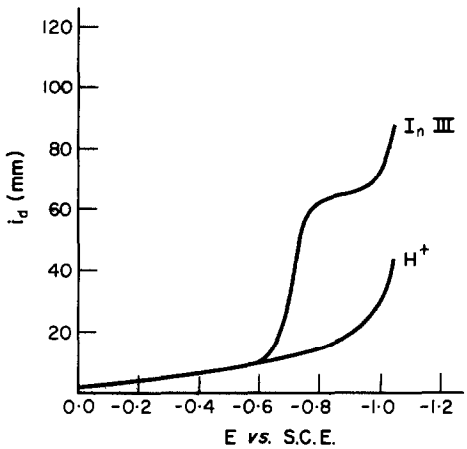

Fig. 1. Typical polarogram of indium oxinate in DMF in the presence of naphthalene (72 μg of indium in 20 ml of 0·1*M* pyridinium perchlorate in DMF containing 1 g of naphthalene.).

Polarography of indium oxinate

A well-defined wave was recorded under the conditions described, with the 0·1*M* pyridine–0·1*M* perchloric acid electrolyte. Whilst aqueous pyridine and DMF perchloric acid solutions were preferred, the respective solvents could be interchanged, so long as the amount of water in the final solution remained the same, as too high a water concentration restricts the solubility of the naphthalene. The pyridine should be added before the acid. When no water is added, distorted waves are recorded.

Effect of the naphthalene concentration

Amounts of naphthalene from 0 to 2·4 g, as a 30% solution in DMF, were added to the test solution, and found to have no effect on the diffusion current. The upper limit was determined by the solubility of the naphthalene.

Effect of water and oxine concentrations

The results obtained from separate series of experiments are summarized in Tables 1 and 2.

The electrode reaction

The wave-height was found to be proportional to the square root of the height of the mercury column over the range 33–73 cm, indicating that the electrode process is diffusion-controlled. A plot of log $i/(i_d - i)$ *vs.* E gave a straight line with slope of 61 mV and intercept −0·715 V, which does not correspond to a reversible three-electron reduction of the indium. However, indium in aqueous perchlorate solutions does not undergo reversible reduction either, and in the non-aqueous medium the presence of the solvent molecules around the electrode may well lead to preferential adsorption of these species, thus hindering the process of electron-transfer and slowing down the reaction considerably.[9]

Table 1. Effect of the amount of reagent on the polarograms of indium oxinate

Reagent added, *mg*	i_d, *mm*	$E_{\frac{1}{2}}$, $-V$(SCE)	Remarks
0·00	56	0·72	
3·75	56	0·75	
7·50	56	0·76	
11·25	56	0·78	
15·00	55	0·80	
22·50	48	0·80	
30·00	42	0·85	Upper plateau slightly distorted

Amount of indium oxinate taken was equivalent to 72 μg of indium. Pyridinium perchlorate 0·1*M*. Naphthalene added: 1·0 g.

Table 2. Effect of water on the polarograms of indium oxinate

Water added, *ml*	i_d, *mm*	$E_{\frac{1}{2}}$, *V* (SCE)	Remarks
0·00	56	0·72	
0·20	56	0·72	
0·40	56	0·72	
0·50	56	0·72	
0·70	54	0·72	
1·00	46	0·74	
1·20	44	0·74	Slight turbidity appeared
1·50	40	0·74	Precipitate appeared

Conditions as for Table 1.

The wave-height was measured by the extrapolation method and found to be proportional to the indium concentration over the range 0·7–21·5 μg/ml. The diffusion current constant from the Ilkovič equation, $I = i_d . C^{-1} m^{-2/3} . t^{-1/6}$ was 6·07, confirming that the method is as sensitive as most polarographic methods in aqueous media. The average relative error over the working range was 1·1%. The effect of pH on the efficiency of the extraction is shown in Fig. 2. Extraction was complete as long as more than 1·25 mg of oxine was used. As amounts greater than 15 mg affected the height of the wave, a value of 7·5 mg was adopted for the procedure. The minimum amount of naphthalene for quantitative extraction was 0·5 g.

The extraction was usually from less than 50 ml of aqueous solution into 2 g of naphthalene. When aliquots containing 144 μg of indium were taken, the recovery was ⩾99% for up to 350 ml of aqueous phase, but fell for larger volumes.

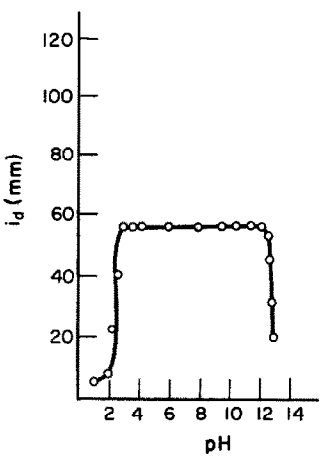

Fig. 2. Effect of pH on the extraction of indium(III).

Interferences

A number of anions and cations were tested for possible interference effects on the method, with 50 mg of salts of the anions being taken, and 1 mg of salts of the cations, as many other metals do extract under these conditions. Only EDTA was found to interfere; citrate, phosphate, azide, fluoride, borate, oxalate, thiocyanate, tartrate, chloride, bromide, iodide, thiosulphate, and carbonate did not, for 144 μg of indium.

The following metal salts (1 mg of each) did not affect the determination of 144 μg of indium: uranyl acetate, lead nitrate, sodium tungstate, chromium nitrate, iron(III) chloride, copper sulphate, sodium vanadate, bismuth nitrate, thallium(I) nitrate, silver nitrate, mercury(II) chloride, sodium molybdate, nickel chloride, zinc nitrate, potassium titanium oxalate, tin(IV) chloride and cadmium chloride.

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Department of Chemistry
Faculty of Science
Kyoto University
Kyoto, Japan
T. FUJINAGA

Department of Chemistry
Punjabi University
Patiala
Punjab, India
B. K. PURI

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Summary—Indium has been extracted as its oxinate into molten naphthalene, the naphthalene allowed to solidify and then separated and dissolved in dimethylformamide, and the indium determined polarographically in dimethylformamide medium with pyridium perchlorate as supporting electrolyte.

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DETERMINATION OF CYSTEINE, 3-MERCAPTOPROPIONIC, AND MERCAPTOSUCCINIC ACID WITH NEUTRAL HEXACYANOFERRATE(III)

(*Received* 22 *October* 1973. *Accepted* 12 *April* 1974)

Hexacyanoferrate(III) has been extensively employed for quantitative determination of mercaptans according to the reaction:[1–4]

$$2RSH + 2[Fe(CN)_6]^{3-} \rightarrow RSSR + 2H^+ + 2[Fe(CN)_6]^{4-}.$$

The unreacted reagent is then determined iodimetrically.[4] However, error can arise from the partial reaction of liberated iodine. This disadvantage is avoided in the proposed procedure by reducing the excess of hexacyanoferrate(III) with ascorbic acid and titrating the excess of ascorbic acid with iodine or by titrating the excess of hexacyanoferrate(III) directly with ascorbic acid.

EXPERIMENTAL

Reagents

Potassium hexacyanoferrate(III) solution, 0·05M. Prepared daily by dissolving accurately weighed analytical-grade reagent in distilled water, and stored in the dark. Standardized by the experimental procedure, and by iodimetric assay.[5]

Samples. Cysteine hydrochloride, 3-mercaptopropionic and mercaptosuccinic acid.

Buffer solution. Phosphate buffer (pH 7) prepared by dissolving 117·7 g of K_2HPO_4 and 44·1 g of KH_2PO_4 in 1 litre of water.

All other chemicals were reagent grade.

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Department of Chemistry
Faculty of Science
Kyoto University
Kyoto, Japan
T. FUJINAGA

Department of Chemistry
Punjabi University
Patiala
Punjab, India
B. K. PURI

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All other chemicals were reagent grade.

Procedures

1. To a 10-ml portion of sample solution in distilled water containing 0·05–1·0 mmole of mercaptan, add 5 ml of phosphate buffer. Swirl the solution whilst adding 25 ml of hexacyanoferrate(III) solution. Continue the swirling for about 1 min, then add a measured excess of 0·05*M* ascorbic acid, 1 g of zinc sulphate and 5 ml of 1*M* hydrochloric acid; titrate the residual ascorbic acid with 0·04*N* iodine in the usual manner. Do a blank determination.
2. Alternatively titrate the residual hexacyanoferrate(III) with 0·02*M* ascorbic acid after adding 1 ml of 0·1% sodium 2,6-dichlorophenolindophenol solution to the reaction mixture; at the end-point the dye is bleached. An indicator blank correction must be applied.

RESULTS

In Table 1, results for the determination of three mercaptans with hexacyanoferrate(III) and those obtained with established methods are given. Procedure 1 is convenient and well suited for routine analysis. A solution of mercaptosuccinic acid shown to be 0·03952*M* by procedure 1, when analysed by procedure 2 had a mean value of 0·03950*M* (8 determinations, relative standard deviation 0·1%).

With *o*-mercaptobenzoic acid the results were low and the method is not recommended for this mercaptan.

Table 1. Determination of mercaptans with hexacyanoferrate(III)

Mercaptan	Apparent purity, % Present method*	Comparison method	No. of detns.
Cysteine	98·6	98·9 *o*-iodosobenzoate oxidation[6,7]	10
3-Mercaptopropionic acid	99·7	99·5 Hg^{2+} titration[8]	6
Mercaptosuccinic acid	98·3	98·2 Hg^{2+} titration[8]	8

* Mean deviations for the three mercaptans tested were in the range 0·2–0·3% (Procedure 1).

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Department of Chemistry
University of Jabalpur
Jabalpur, India

KRISHNA K. VERMA
SAMEER BOSE*

* Present address, 310 Napier Town, Jabalpur, India.

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Summary—Two procedures are proposed for the determination of –SH groups. In both a known amount of hexacyanoferrate(III) is added to the sample and the excess is then determined. In one procedure an excess of ascorbic acid is added and the excess of that is titrated with iodine. In the other, the excess is determined by direct titration with ascorbic acid. Both procedures avoid errors resulting from side-reactions of iodine which takes place if the excess of hexacyanoferrate(III) is reacted with potassium iodide.

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EXTRACTION TITRIMETRIC DETERMINATION OF COPPER

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Exchange reactions between metal dithiocarbamates and certain other metals have been reported. Lead diethyldithiocarbamate has been used for the determination of copper,[1–3] and there is one reference to exchange reactions of xanthates.[4] Lead xanthate solution in carbon tetrachloride is colourless and that of copper xanthate is dark brown. Thus this system is suitable for extractive titration, the end-point corresponding to the stage when no copper is left in the aqueous phase to participate in the exchange reaction, *i.e.*, no brown colour appears in the organic phase.

EXPERIMENTAL

Reagent

Lead xanthate. Prepared by mixing solutions of lead acetate and twice crystallized potassium ethyl xanthate [first from acetone–benzene (1 : 4 v/v), then from acetone–petroleum ether (1 : 8 v/v)] in stoichiometric amounts. Wash the lead xanthate thoroughly with distilled water, recrystallize it twice from chloroform and dry it *in vacuo*. Check the purity by decomposing a sample with nitric acid (1:2), diluting and titrating with standard EDTA solution at pH 5–6 (hexamine buffer. Xylenol Orange as indicator). Prepare a $2{\cdot}5 \times 10^{-4}M$ solution in carbon tetrachloride.

Procedure

Take an aliquot of sample solution, containing 60–750 μg of copper, in a separating funnel, dilute it to 25–35 ml with distilled water, and adjust the pH to 2–5 if necessary. Add the titrant in 1-ml portions, shaking for about 30 sec and separating the extract after each addition. Continue until the extract is colourless. Repeat the titration, adding (in one portion) 1 ml of reagent less than that used in the first titration, then continue, with addition of reagent in 0·1-ml portions until the extract is colourless. Add about 0·5 ml of carbon tetrachloride along with the reagent to ensure proper mixing of the phases.

Procedure for the analysis of alloys

From knowledge of the expected amount of copper in the alloy, enough sample to give a 0·0005–0·001*M* copper solution is dissolved in nitric acid, the solution is digested on a water-bath, any hydrous stannic oxide is filtered off, and the solution is diluted to the appropriate standard volume. Copper is determined in an aliquot by the procedure given above. Results for some real samples are given in Table 3.

RESULTS AND DISCUSSION

A fast exchange reaction takes place between copper(II) and lead xanthate. The stoichiometry of the reaction is always 1 : 1. The solution of lead xanthate is quite stable and its strength does not change on storage or on treatment with dilute solutions of mineral acids (pH > 1) or sodium hydroxide (pH < 10). It was found that the exchange is very fast at pH 2–5 and about half a minute is required for complete exchange. However, with further increase of pH, the reaction becomes slow and the separation of the phases becomes difficult.

Accuracy and precision

Amounts of 60–750 μg of copper in a volume of 20–35 ml can be determined with an error of < 1% (Table 1). Twelve replicate determinations of 127 μg of copper never gave a deviation of more than 1·3%.

Interferences

Interferences were studied by titrating 127 μg of copper in the presence of other metal ions, and the results are tabulated in Table 2. Under the conditions used, nickel, cobalt, iron, manganese, zinc and lead give no

Table 1. Determination of copper

Copper taken, μg	Copper found, μg
64	63
127	126
254	255
508	509
762	763

Table 2. Interferences in determination of 127 μg of copper

Interfering metal ion added, *mg*	Copper found, *μg*	Interfering metal ion added, *mg*	Copper found, *μg*
Co(II) 40	128	Mn(II) 40	128
Ni(II) 40	128	Zn(II) 40	128
Fe(III) 40	128	Pb(II) 40	129
Cd(II) 40	128	Tl(I) 5	129

Table 3. Analysis of some samples

Sample	Copper content, % (certificate value)	Other important constituents, %	Copper found, %
TISCO	86·5*	Sn 8·77; Zn 1·5; Pb 1·48; Ni 1·16; Fe 0·40	86·4; 87·0; 87·0
NBS 162	28·9	Ni 66·38; Mn 2·34	28·5; 28·5; 28·7
BCS 183	85·5	Sn 9·96; Zn 1·86; Pb 1·83; P 0·25; Sb 0·24; Fe 0·07; Ni 0·04; As 0·06	85·0; 85·0; 85·6

* Standardized according to Šedivec and Vašák[1].

exchange with lead xanthate and so do not interfere, making the method selective for the determination of copper in alloys and ores.

Silver, mercury and bismuth interfere strongly.

Chemistry Department
Punjabi University
Patiala -147002, India

A. L. J. Rao
Chander Shekhar
Surinder Singh

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Summary—Lead xanthate undergoes a quantitative, stoichiometric and fast exchange reaction with copper(II), even near the equivalence point, making it a suitable reagent for an extraction titration of copper. Many other metal ions do not participate in exchange reactions with lead xanthate, making this method selective for copper.

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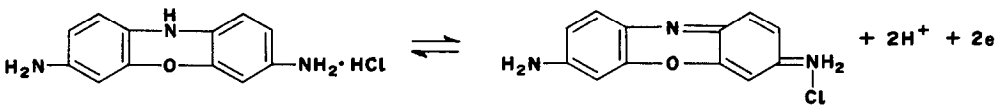
NILE BLUE AND BRILLIANT CRESYL BLUE AS REDOX INDICATORS IN IRON(II) TITRATIONS

(*Received* 17 *July* 1973. *Revised* 15 *July* 1974. *Accepted* 24 *August* 1974)

Both Nile Blue (NB) (C.I. No. 51180) and Brilliant Cresyl Blue (BCB) (C.I. No. 51010) are related to diaminophenoxazine. Their indicator properties have been reported[1–3] earlier; they conform to an oxidation-reduction equilibrium similar to the one for the parent compound



Colourless form Coloured dye

with or without detectable formation of an intermediate. They generally find application as indicators with strong reducing titrants such as titanous chloride. The present communication describes the use of these two compounds as redox indicators in titrations of iron(II) with some common oxidizing titrants. The colour change in these titrations depends on an oxidative mechanism of the coloured dye.

EXPERIMENTAL

Reagents

Potassium dichromate, cerium(IV) sulphate and sodium vanadate solutions were prepared and standardized as already described.[4] Cerium(IV) ammonium nitrate solution, 0·05*M* was prepared in 1*M* perchloric acid and standardized against sodium oxalate. Potassium permanganate solution, 0·05 *N* was prepared with water that had been distilled over permanganate, and was standardized against sodium oxalate. Iron(II) ammonium sulphate solution, 0·1*M* was prepared in 1*N* sulphuric acid from analytical-reagent grade material. Aqueous 0·1% solutions of Nile Blue and Brilliant Cresyl Blue were prepared from commercial samples without further purification. The indicator solutions are stable for more than 6 months.

Most of the information concerning the results of the various iron(II) titrations has been included in Table 1. A 0·05–0·10-ml amount of NB or 0·10–0·20 ml of BCB is generally used per 50 ml of titration mixture. Titrations of 1·5–28 mg of iron(II) with use of either indicator have given results which are correct to within ±0·2%. The colour changes are sharp, vivid and complete although the end-point colours are not permanent and last for only a few seconds (2–120). In titrations with cerium(IV) ammonium nitrate in perchloric acid medium, a permanent pale-pink colour (irreversible) that results at the end is, however, without effect on the sharpness of the usual colour change. In titrations in fairly concentrated sulphuric acid medium the titration mixture is occasionally cooled to obviate the effect of the temperature rise during titration. Since in this medium the life of the pink intermediate is somewhat increased, a few titrations using the oxidant as titrand are possible but only if the indicator is added close to the equivalence point; they do not seem, however, to be of any practical application. The indicator corrections range from 0·03 to 0·08 ml of 0·01*N* titrant but it is best to determine the indicator correction in every case under the exact conditions of titration, owing to possible variation in the composition of the commercial products used as indicators.

Cerium(IV) sulphate titration of iron(II) obtained from iron(III) by the stannous chloride–mercuric chloride method or the Jones method can also be done satisfactorily, using either indicator.

Interferences

Amounts of 14 mg of cobalt(II), 25 mg of nickel(II) and 9 mg of arsenic(III) did not interfere in the titration of iron(II) with cerium(IV) sulphate. Tungstates hindered the colour change but this could be overcome by titration in 20 *N* sulphuric acid medium.

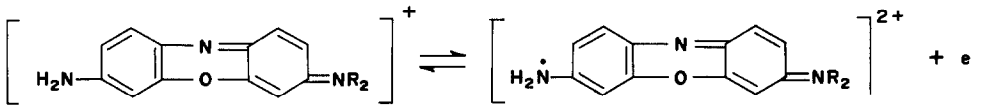
Table 1.

Titration in which the indicator is used	Titration medium	Nile Blue			Brilliant Cresyl Blue		
		Acidity, *N*	Colour change	Transition potential (*vs.* NHE, 30°C), *V*	Acidity, *N*	Colour change	Transition potential (*vs.* NHE, 30°C), *V*
Fe(II)–Ce(IV)	H_2SO_4	1–20	blue-green/light yellow* to pink	0·95–0·90	1–20†	blue/blue-green* to pink	0·96–0·91
Fe(II)–Ce(IV)	HCl	0·5–2·0	apple green to red-brown	—	0·5–2·0‡	apple green to red-brown	—
Fe(II)–Ce(IV)	$HClO_4$	1–4	light yellow to pink	0·98–1·05	1–4	blue–green to pink	0·98–1·04
Fe(II)–Cr(VI)	H_2SO_4	14–20	light green-yellow to pink	0·95–0·93	16–20§	blue-green to pink/grey‖	0·94–0·93
Fe(II)–V(V)	H_2SO_4	18–22	light green-yellow to pink/grey‖	—	—	not satisfactory	—
Fe(II)–Mn(VII)¶	H_2SO_4	1–10§	blue-green/light yellow to pink	—	6–10§	blue-green to pink	—

* Colour change in strong acid medium.
† Acidity range is 10–20 *N* when 0·01 *N* titrant is used.
‡ Titrations not possible when 0·01*N* titrant is used.
§ Indicator to be added ~0·5 ml before the end-point.
‖ Colour change when the concentrations of Cr(III) and V(IV) exceed $1{\cdot}5 \times 10^{-3}$ *M* and 5×10^{-3} *M* respectively.
¶ Titrations done with 0·01 *N* solutions only.

DISCUSSION

The colour change at the end-point with either NB or BCB as indicator depends on the oxidation of the dye to a coloured intermediate which can undergo a reversible reduction or an irreversible oxidation. The oxidation mechanism of these dyes may be compared to the stepwise oxidation of aromatic diamines leading to strongly coloured substances which are designated as free radicals.[5–7] The oxidation of a diaminophenoxazine derivative may then be formulated as



Coloured dye — Intermediate oxidation product (pink)

the free radical being stabilized by resonance. On further oxidation, the free radical seems to yield a very labile di-imonium compound which apparently passes into colourless products. The relative stability of the intermediate in a strong acid medium may be attributed to the protonated species, *viz.*, a doubly-charged free radical cation with a symmetrical charge distribution, being favoured relative to the unprotonated form.

A spectrophotometric study was made to establish that the indicator mechanism involves a reversible redox change. A quickly reduced intermediate oxidation product in 18 *N* sulphuric acid was identified as the original dye (NB) by determination of the absorption spectrum (λ_{max} = 450 nm), but the recovery of the dye was low presumably owing to some irreversible oxidation.

NB can be used in the titration of iron(II) with various oxidizing titrants, but both NB and BCB are useless in the reverse titrations. They work in the iron(II)–cerium(IV) titration over the range 1–20 *N* sulphuric acid medium. Ferroin and *N*-phenylanthranilic acid[4] do not work in a sulphuric acid medium more concentrated than 14 and 6 *N* respectively; the dicarboxylic acids of diphenylamine, which are recommended[8,9] for titrations in 15–20 *N* sulphuric acid medium, need large indicator corrections. In view of their vivid colour change NB and BCB can be used in titrations even in the presence of coloured ions; they are to be preferred to triphenylmethane dyes in these titrations because of their smaller indicator corrections. Further, they can also be used in the determination of iron(III) after its reduction with stannous chloride or zinc.

Department of Chemistry K. SRIRAMAM
Andhra University Postgraduate Centre
Guntur 522005, Andhra Pradesh, India

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Summary—Nile Blue and Brilliant Cresyl Blue, two compounds related to diaminophenoxazine, have been studied as indicators in titrations of iron(II) with cerium(IV) (in hydrochloric, sulphuric and perchloric acid media), dichromate, vanadate and permanganate. They are particularly suited for titrations in a fairly concentrated sulphuric acid medium and for titrations with dilute solutions. A probable indicator mechanism is suggested.

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ANION-EXCHANGE SEPARATION OF Te(IV) FROM Te(VI), Se(IV) AND Se(VI) ON DEAE-CELLULOSE IN MIXED HYDROCHLORIC–ACETIC ACID MEDIA

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Only a few metals have been found to be adsorbed on DEAE-cellulose strongly enough to allow column separations from aqueous mineral acid media.[1–5] However, enhanced ion-exchange adsorption of metals on DEAE-cellulose has been obtained by the addition of an organic protic solvent to the aqueous mineral acid media such as hydrochloric acid,[6] nitric acid[7,8] and hydrochloric acid–thiocyanate solutions.[9] Previously methanol has been used as the protic solvent in mixed media involving hydrochloric acid[6] nitric acid[7] and hydrochloric acid–thiocyanate solutions.[9] A mixed nitric acid–acetic acid medium allowed greater ion-exchange adsorption of nitrate complexes on DEAE-cellulose than did mixed nitric acid–methanol media.[8]

In this study we found that Te(IV) was not adsorbed on DEAE-cellulose to any great extent from aqueous hydrochloric acid solutions, but the introduction of acetic acid enabled Te(IV) chloro-complexes to be adsorbed strongly. This provided a basis for the separation of Te(IV) from Te(VI) as well as Se(IV) and Se(VI). Recent progress in ion-exchange separations of Te(IV) on exchange resins has been reviewed by Korkisch.[10]

EXPERIMENTAL

Selectacel DEAE-cellulose (diethylaminoethylcellulose), 0·95 meq/g (Brown Co., Berlin, N.H., U.S.A.) was used. Ten g of DEAE-cellulose were slurried with 200 ml of 0·12*M* hydrochloric acid, placed in a conventional column and washed with 0·12*M* hydrochloric acid–1*M* ammonium chloride solution. The DEAE-cellulose in the chloride form was then washed by centrifugation with demineralized water until the pH of the supernatant was 2·5–3·5. After thorough washing with methanol to remove the adsorbed water, the DEAE-cellulose was dried at 40° for 5 hr and stored in a desiccator containing saturated potassium bromide solution.

Stock solutions of Te(IV) and Se(IV) were prepared from weighed amounts of the elements to contain ~7 mg of Te(IV) per ml of 1*M* hydrochloric acid and ~40 mg of Se(IV) per ml of water respectively. Solutions of Te(VI) and Se(VI) were prepared by dissolving sodium tellurate and sodium selenate in 1*M* hydrochloric acid to yield ~5 mg of Te(VI) per ml and ~40 mg of Se(VI) per ml, respectively. The stock solution of Te(VI) was standardized by taking an aliquot, reducing to metal with hydrazine dihydrochloride, dissolving the product in *aqua regia* and determining colorimetrically with stannous chloride.[11] The stock solution of Se(VI) was standardized chelometrically as outlined later.

The distribution coefficient of Te(IV) was determined by a batch equilibrium method. The DEAE-cellulose (1·0 g) was weighed and placed in glass-stoppered Erlenmeyer flasks containing 5 μmole of Te(IV) and 40·0 ml of appropriate hydrochloric acid–acetic acid mixtures of varied composition. The mixtures were shaken mechanically for 24 hr at 25·0 ± 0·1°. The separated aqueous phases were analysed for tellurium and the distribution coefficient K_d was computed according to:

$$K_d = \frac{\text{(amount of Te in DEAE-cellulose phase/g of DEAE-cellulose)}}{\text{(amount of Te in solution phase/ml of solution)}}$$

The coefficients for Te(VI), Se(IV) and Se(VI) were determined by a column method. One ml of solution containing 5 μmole of the element was loaded onto a column (1·5 × 7·5 cm) containing 1 g of DEAE-cellulose, and eluted with a mixture of hydrochloric acid and acetic acid of varied composition at a flow-rate of 2 ml/min. The coefficient was calculated by means of the equation $K_d = (V_{max} - V_o)/M$, where V_{max} is the retention volume (ml), V_o the void space (ml), and M the weight of DEAE-cellulose used (g).

Absorbance measurements at fixed wavelengths were made with a Hitachi Perkin-Elmer 139 Spectrophotometer. For the construction of absorption curves a Hitachi 124 Double Beam Spectrophotometer was used.

Procedure

Slurry 1 g of DEAE-cellulose with 50 ml of a mixture of 1*M* hydrochloric acid and acetic acid (1:9, v/v), and pour the slurry into a conventional column (bore 1·5 cm), the bed being 7·5 cm long. Load 10–30 ml of a sample

solution, in the mixed solvent of ~1*M* hydrochloric acid and acetic acid (1:9, v/v), on to the top of the column and allow it to percolate at a flow-rate of 2 ml/min. Wash the column with about 45 ml of the same mixed acid to remove Te(VI), Se(IV) and Se(VI). Strip Te(IV) by elution with 45 ml of 0·1*M* hydrochloric acid.

Effluent analysis. Determine Te(IV) and Se(IV) spectrophotometrically with stannous chloride[11] and 3,3′-diaminobenzidine,[11] respectively. For Te(VI), reduce first with hydrazine dihydrochloride to the element, dissolve this in *aqua regia*, treat with hydrochloric acid, and subsequently determine spectrophotometrically with stannous chloride. When a large quantity of Se(IV) or Se(VI) is involved, evaporate the effluent to dryness, treat with potassium permanganate, and precipitate lead selenate at pH 2 ~ 3 by adding lead nitrate solution. Add ethanol to yield a 30% ethanolic solution and let stand for 30 min to complete the precipitation. Dissolve the precipitate in excess of EDTA and back-titrate with 0·01*M* manganese(II) sulphate, with Eriochrome Black T as indicator.[12]

RESULTS AND DISCUSSION

In Table 1 the distribution coefficients of Te(IV), Te(VI), Se(IV) and Se(VI) on DEAE-cellulose in ~1*M* hydrochloric acid–acetic acid media are given as a function of acetic acid concentration. The coefficient increases regularly with increasing concentration of acetic acid, but the adsorption is generally low for Te(VI), Se(IV) and Se(VI) over the acetic acid concentration range tested. Te(IV) is adsorbed strongly on DEAE-cellulose at higher concentrations of acetic acid. The adsorption of Te(IV) is affected to a lesser extent by the concentration of hydrochloric acid, as shown in Table 1*b*. The adsorption behaviour of Te(IV), Te(VI), Se(IV) and Se(VI) in mixed hydrochloric acid–acetic acid media will provide a basis for the selective separation of Te(IV) from the other three species. For the pairs Te(IV)–Te(VI), Te(IV)–Se(IV) and Te(IV)–Se(VI) in various proportions, quantitative separations were conducted on DEAE-cellulose columns by adsorption of Te(IV) from ~1*M* hydrochloric acid–acetic acid (1:9, v/v). The results are summarized in Table 2. About 6 μmole (0·749 mg) of Te(IV) can be quantitatively separated from 10 times as much Te(VI), 1000 times as much Se(IV) and 100 times as much Se(VI) (on a mole basis). The limited solubility of sodium tellurate in the mixed acid did not increase the permissible ratio of Te(VI) to Te(IV).

Table 1. Distribution coefficients of Te(IV), Te(VI), Se(IV) and Se(VI) on DEAE-cellulose

a 0·93*M* HCl–acetic acid media

	Acetic acid, % v/v					
	95	90	80	70	60	40
Te(IV)	$>10^3$	550	67	13	<5	<5
Te(VI)	17	8	~5	<5	<5	<5
Se(IV)	<5	<5	<5	<5	<5	<5
Se(VI)	27	14	10	~5	<5	<5

b HCl–acetic acid media (1:9, v/v)

	[HCl], *M*					
	0·47	0·93	1·9	3·9	5·8	7·7
Te(IV)	710	550	530	470	310	280

Runs 6–8 show the effect of increasing the loading of Te(IV) (on a 1-g DEAE-cellulose column) while keeping the amount of Se(IV) constant. A load as high as 22·1 mg of Te(IV), was held on the column, being separated effectively from 42·7 mg of Se(IV). Further increase of Te(IV) resulted in breakthrough, causing incomplete recovery (run 8).

Because of the transparency of swollen DEAE-cellulose, we attempted to record the spectrum of the greenish yellow Te(IV) species adsorbed on the DEAE-cellulose. DEAE-cellulose swollen in the same medium was used as a reference and the spectrum obtained is illustrated in Fig. 1. The absorption curve in the short wavelength region was not recorded because of the scattering of the ultraviolet light by solid DEAE-cellulose.

For the purpose of comparison the visible-region spectrum of Te(IV) chloro-complexes in 11·6*M* hydrochloric acid and successive spectra of Te(IV) species in the mixed hydrochloric acid–acetic acid solutions are given. All the spectra resemble each other closely, with an absorption maximum at around 374 nm. Even though the overall chloride concentrations are as low as 1·16–0·29*M* for the mixed acid solutions tested (curves 3–6), the chloro-complexes formed in them are likely to correspond to those formed in concentrated hydrochloric acid solutions (9–12*M*).[13] In pure aqueous hydrochloric acid as dilute as 1·16*M* the absorption maximum at 374 nm did not develop at all (curve 8). Therefore, we see that Te(IV) chloro-complexes in solution are stabilized in the presence of acetic acid.

Table 2. Separation of Te(IV)

Run	Te(IV) Added, *mg*	Te(IV) Recovery, %	Species	Foreign species Added, *mg*	Foreign species Recovery, %
1	0·749	99·6	Te(VI)	0·560	102·7
2	0·749	100·3	Te(VI)	5·60	104·8
3	0·749	99·5	Se(IV)	0·427	97·9
4	0·749	100·5	Se(IV)	42·7	99·8
5	0·749	99·9	Se(IV)	427	99·5
6	7·37	99·9	Se(IV)	42·7	99·8
7	22·1	99·5	Se(IV)	42·7	99·8
8	36·8	88·3	Se(IV)	42·7	*
9	0·749	99·5	Se(VI)	4·14	97·6
10	0·749	98·7	Se(VI)	41·4	100·0

* Not determined.
Averages of three determinations listed.

In ~1*M* hydrochloric acid–acetic acid (1:9, v/v) the peak at 374 nm disappeared (curve 7), but Te(IV) complexes were adsorbed to a significant extent from this medium on DEAE-cellulose (Table 1*a*), the adsorbed species exhibiting an absorption curve (curve 1) similar to those obtained in the other media (curves 2–6). This is evidently due to the presence of a high concentration of chloride ions in the swollen DEAE-cellulose phase and subsequent formation and stabilization of chloro-complexes in the DEAE-cellulose phase.

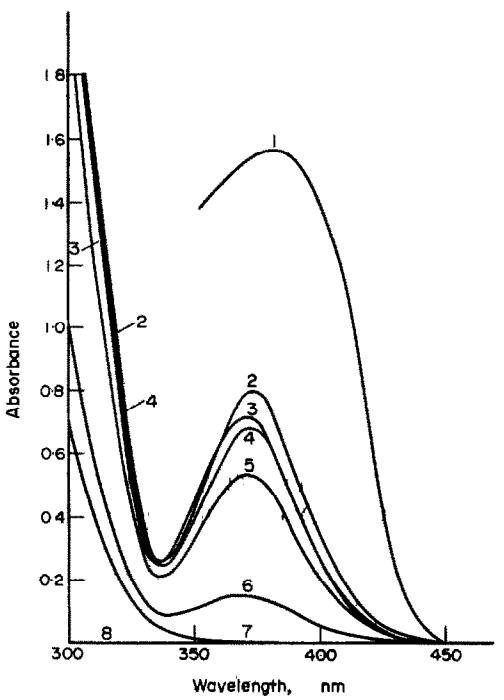

FIG. 1. Absorption spectra: 1: Te(IV) adsorbed batchwise on DEAE-cellulose from 0·93*M* hydrochloric acid–acetic acid (1:9, v/v); approximately 25 μg of Te(IV) per ml of swollen DEAE-cellulose; 2: Te(IV) chloro-complexes in 11·6*M* hydrochloric acid; Te(IV) 40 μg/ml; 3–7: Te(IV) chloro-complexes in *x M* hydrochloric acid–acetic acid (1:9, v/v); Te(IV) 40 μg/ml. Hydrochloric acid concentrations were: 11·6*M* for curve 3, 8·7*M* for curve 4, 5·8*M* for curve 5, 2·9*M* for curve 6 and 0·93*M* for curve 7; 8: Te(IV) species in 1·16*M* hydrochloric acid solution; Te(IV) 40 μg/ml.

In order to have stable Te(IV) chloro-complexes form in aqueous solution, it is necessary either to keep the hydrochloric acid concentration high or to add enough protic solvent such as acetic acid to the hydrochloric acid solution, enabling the chloro-complexes to be formed at a lower concentration of hydrochloric acid. In the ion-exchange system, however, chloride ions compete for the ion-exchange sites with chloro-complexes, so it is a primary requirement to keep the competitive chloride concentration as low as possible without appreciable dissociation of the chloro-complexes. This can be accomplished in mixed hydrochloric acid–acetic acid media (Table 1*a*). A lower concentration of hydrochloric acid is sufficient for the anion-exchange in the mixed media, which is in accord with the slight dependence of the distribution coefficients of Te(IV) on hydrochloric acid concentrations (Table 1*b*).

Laboratory for Analytical Chemistry
Faculty of Engineering
University of Chiba
Yayoi-cho, Chiba, Japan

ROKURO KURODA
NOBUTAKA YOSHIKUNI

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Summary—Te(IV) can be separated from Te(VI), Se(IV) and Se(VI) by adsorption of Te(IV) on a DEAE-cellulose column from a mixed 1*M* hydrochloric acid–acetic acid solution (1:9, v/v). This allows a selective separation of Te(IV) from the other three species in widely different mole ratios.

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DETERMINATION OF TRACES OF OXYGEN IN CHALCOGENIDE GLASSES

(*Received* 23 *July* 1974. *Accepted* 25 *August* 1974)

Chalcogenide glasses ($Ge_{28}Sb_{12}Se_{60}$ or $Ge_{33}As_{12}Se_{55}$) are known to have optical properties which make them well suited for use as windows in high-intensity CO_2 lasers.[1,2] Their quality is, in part, dependent on the levels of impurities found in the finished product. Among possible contaminants, oxygen is most likely to affect the performance of the infrared optical material and is also most likely to be present as an impurity, either from trace oxides introduced during the preparation step or already present in the starting reactants. From the analyst's standpoint, this poses a challenging problem of measuring trace levels of oxygen in chalcogenide materials. Therefore, to be suitable, an analytical procedure must be sensitive, selective and free from reagent blanks. In this respect, of the currently available techniques, charged-particle activation analysis (CPAA) appears best suited in this case. CPAA, and more specifically ^{3}He activation, has already been applied successfully for sub-ppm oxygen determinations in many high-purity materials.[3–11]

In order to have stable Te(IV) chloro-complexes form in aqueous solution, it is necessary either to keep the hydrochloric acid concentration high or to add enough protic solvent such as acetic acid to the hydrochloric acid solution, enabling the chloro-complexes to be formed at a lower concentration of hydrochloric acid. In the ion-exchange system, however, chloride ions compete for the ion-exchange sites with chloro-complexes, so it is a primary requirement to keep the competitive chloride concentration as low as possible without appreciable dissociation of the chloro-complexes. This can be accomplished in mixed hydrochloric acid–acetic acid media (Table 1*a*). A lower concentration of hydrochloric acid is sufficient for the anion-exchange in the mixed media, which is in accord with the slight dependence of the distribution coefficients of Te(IV) on hydrochloric acid concentrations (Table 1*b*).

Laboratory for Analytical Chemistry
Faculty of Engineering
University of Chiba
Yayoi-cho, Chiba, Japan

ROKURO KURODA
NOBUTAKA YOSHIKUNI

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In this paper we report on the application of CPAA to the non-destructive determination of oxygen in chalcogenide glasses. Attention was focused in particular on the optimization of the ^{3}He bombardment energy and the validity of the post-irradiation chemical etch used for removing surface oxygen contamination.

EXPERIMENTAL

Irradiations

Irradiation with ^{3}He ions was carried out at the Texas A & M University variable-energy cyclotron. Typical irradiation conditions were nominal beam energies of ~8 MeV for 2 hr at beam intensities of 0·2 μA. The low beam intensity was found to be necessary to avoid sample damage by fracturing or melting. The experimental arrangement has been previously described in its entirety.[3]

Samples

The chalcogenide glasses of chemical composition either $Ge_{28}Sb_{12}Se_{60}$ (No. 1173) or $Ge_{33}As_{12}Se_{55}$ (No. 20) were supplied by Texas Instruments Inc., Dallas, Texas. Thin mica foils (muscovite) were irradiated along with the samples and served as oxygen standards for quantitation.

Etching

A post-irradiation etch has been found necessary to remove surface and recoil contamination. This was accomplished by several etchings of the irradiated surface with 5–10*M* potassium hydroxide to a total depth of 10–15 μm. Etching times typically totalled 5 min. The validity of the chemical-etch procedure was verified by comparison of oxygen values found on different samples of the same glass, each being etched at different depths. The results will be discussed later.

Counting and quantitation

The β^+ annihilation radiation (0·511 MeV) from ^{18}F produced *via* the ^{16}O(^{3}He, p)^{18}F reaction was monitored with a γ-γ coincidence system employing two 3 × 3 in. NaI(Tl) detectors. The presence and identity of other matrix activities was checked by counting with a Ge(Li) γ-spectrometer system.

This counting combination aided in the decay-curve resolution for the 110-min (^{18}F) component. Quantitative calculations based on use of mica monitor foils as standards were carried out by the equivalent thickness method described by Engelmann.[12]

RESULTS AND DISCUSSION

Optimization of experimental beam energy

Since the oxygen levels were expected to be greater than 1 ppm, non-destructive determination was attempted. The only way we could see to accomplish this was to keep the ^{3}He energy below the Coulomb barrier of the

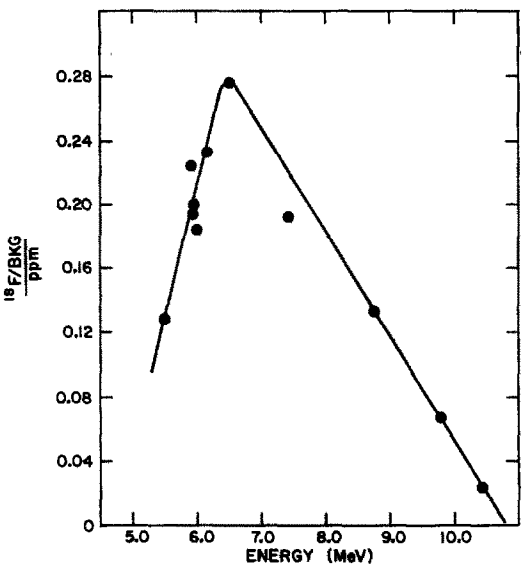

Fig. 1. Optimization of ^{3}He bombardment energy for non-destructive oxygen determination in chalcogenide glasses.

Table 1. Results of oxygen determinations in chalcogenide glasses

Glass No.	Oxygen content, *ppm, μg/g*
No. 1173–109	4·5 ± 2·0
No. 1173–107	5·5 ± 2·0
No. 1173–92	5·3 ± 2·0
No. 1173–P	4·0 ± 2·0
No. 20–102	8·8 ± 2·0
No. 20–98	5·5 ± 2·0
No. 20–P	6·0 ± 2·0

glass constituents (~ 11 MeV for Ge). This approach has been reported previously for non-destructive analysis for oxygen in germanium with 6·5-MeV ^{3}He beams.[13,14]

The optimum beam energy was considered to be a compromise dictated by the lower matrix activity at lower energies and the larger sample volume activated at high energies. To arrive at the best experimental energy, several samples of No. 1173 glass were irradiated at ^{3}He energies of 5·5–10·5 MeV and values for oxygen were calculated as usual.

Figure 1 shows the results of these optimization experiments. As the energy approaches 6–7 MeV a maximum is reached in the ratio of ^{18}F count-rate to long-lived background count-rate at a given oxygen content. At higher energies, the ratio is lowered owing to an increase in matrix activity (some tunnelling must certainly be occurring).

Sample analysis

On the basis of the experiments above, the chalcogenide glasses were analysed for oxygen, with beam energies of ~6·5 MeV. The analytical results are given in Table 1. Only glass No. 20–102 was significantly higher in oxygen. The others can be said to be equal, within experimental error. Seven separate oxygen determinations were performed to check the precision of the value obtained on sample No. 20–102 and the method in general. The validity of the chemical etching procedure was also verified by these additional determinations since a non-uniform chemical etch could lead to high oxygen values owing to incomplete removal of surface oxide contamination.

The results of this study on glass No. 20–102 are presented in Table 2. No systematic trend seems to occur when the etch is made to any depth between 6 and 22 μm.

The precision calculated from these measurements indicates a 23% relative standard deviation at an oxygen level of 8·8 ppm. Since the remaining glasses were only analysed in duplicate, a larger error has been reported.

CONCLUSION

This paper reports another case in which the rather novel analytical technique of charged-particle activation analysis has been found very applicable in evaluation of developmental materials research and production processes. By optimization of the ^{3}He irradiation energy and careful investigating of the chemical etching of irradiated glasses, it has been found possible to detect as little as 1 ppm oxygen in chalcogenide glass material.

Table 2. Glass No. 20–102 etching study, using 10*N* KOHM

Depth of etch, *μm*	Oxygen found, *ppm*
6·3	7·6
6·3	10·4
10·0	8·0
12·0	6·3
12·5	11·3
20·3	10·7
21·7	7·5
	Mean 8·8
	Std. devn. 2·0

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Center for Trace Characterization
Texas A & M University
College Station, Texas, U.S.A.

D. L. SWINDLE
E. A. SCHWEIKERT

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Summary—The ^{3}He activation method for oxygen determination was applied to chalcogenide materials such as $Ge_{28}Sb_{12}Se_{60}$ and $Ge_{33}As_{12}Se_{55}$. Attention was focused on the optimization of the ^{3}He bombardment energy for non-destructive oxygen determination and the validity of the post-irradiation chemical etch used for removing surface oxygen contamination. The procedure developed was tested on a series of chalcogenide glasses. The detection limit for this non-destructive technique using ~ 6-MeV ^{3}He is estimated at ~1 ppm of oxygen.

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ANALYTICAL DATA

FORMATION CONSTANTS OF MERCURY(II) WITH SOME BUFFER/MASKING AGENTS AND THE FORMATION OF MIXED-LIGAND COMPLEXES

(*Received* 4 *June* 1974. *Accepted* 24 *August* 1974)

In our work on the determination of mercury by means of complexometric titrations we have found a lack of sufficiently consistent information in the literature[1,2] about the interaction between mercury(II) and several buffers and/or masking agents. Therefore some of these stability constants have been determined. The procedure followed was the same as described in our study on amino-acids.[3]

Only a few data are available on the formation of mixed-ligand complexes with chelating agents such as EDTA *etc.* in solutions containing buffers and/or masking agents. The procedure introduced by Harju[4] was applied for the determination of the stability constants in this case.

EXPERIMENTAL

All chemicals were of "*pro analyse*" quality and used without further purification. The concentrations of the stock solutions were checked by titrations with standardized solutions. Sodium nitrate was added to the solutions to bring the ionic strength to 0·1 at the beginning of all experiments. Because of the titration technique used a change of the ionic strength from 0·1 to 0·12 had to be accepted. The temperature was kept at 25°.

The mercury electrode was a gold electrode covered by a thin layer of mercury. Potential differences between the mercury electrode and a SCE were measured with a Radiometer PHM 4c compensation pH/mV-meter; pH measurements were made with a Radiometer expanded-scale pH-meter. The pH was varied by addition of sodium hydroxide solution or nitric acid from a piston-type burette (25 ml). In the calculations a correction was made for the dilution caused by the titration.

RESULTS

Table 1 shows the results obtained with some buffer/masking agents. Generally a pH range between 2·5 and 9·5 was examined. The error is approximately 0·1 in the logarithmic value.

In Table 2 the experimentally obtained stability constants of the mercury(II) chelates and their monoprotonated forms are given. A summary of literature values is included in this table, with the restriction that for values reported before 1962–63 the values selected by Ringbom[5] are given.

Table 3 shows formation constants of some mixed-ligand complexes. If no difference was observed between the potential *vs.* pH curves in the presence and absence of the buffer/masking agents "no ev." is inserted in the columns. A dash means that no measurements were made.

DISCUSSION

The values summarized in Table 1 almost all differ to a greater or lesser extent from previously published data. It is difficult to explain these discrepancies. We feel, however, that generally speaking measurement of both pH and pHg should yield more reliable information on composition and stability of mercury complexes. Moreover our results cover a large range of pH values.

The stability constants given in Table 2 deviate in some cases to some extent from the values found in the literature. In particular the values for the monoprotonated species are all slightly larger than those published earlier. As stated already by Schwarzenbach[21] there is evidence that his value for the mercury(II)–TRIEN complex has to be attributed to a mixed TRIEN–halogen complex with mercury. This may explain why we found a smaller value in the absence of halogen ions.

In our study on mixed-ligand complexes by Harju's method we checked the values obtained by Reilley and Schmid[23] on EDTA complexes. The agreement is quite satisfactory.

In conclusion, several titrations of mercury(II) with the different chelating agents under several conditions have been performed. The experimentally obtained titration curves coincided with the theoretical curves calculated with the constants obtained: deviations were less than a few mV.

Table 1. Logarithmic values of stability constants (I = 0·10–0·12; T = 25°C)

Compound	$K^{H,L}_{HL}$	$K^{H,HL}_{H_2L}$	$K^{H,H_2L}_{H_3L}$	$K^{H,H_3L}_{H_4L}$	$K_1 \equiv K^{L,M}_{ML}$	$K_2 \equiv K^{L,ML}_{ML_2}$	$K^{H,ML}_{MHL}$	$K^{H,MHL}_{MH_2L}$	pH-range examined	Other values found in the literature	Ref.
Acetic acid	4·65*	—	—	—	6·1	2·5	—	—	2·5–5·0	$\beta_2 \equiv K_1 . K_2$ = 8·42	6
										K_1 = 5·55; β_2 = 9·30; β_3 = 13·28; β_4 = 17·06	7
										K_1 = 5·85 ± 0·07	8
Citric acid	10·82†	5·67†	4·39†	2·96†	13·3	5·5	6·1	4·1	2·8–9·5	K_1 = 10·9 ± 0·2	9
Tartaric acid	3·96†	2·80†	—	—	7·0		—	—	2·5–9·0	$K_1 < 4$	10
										$K^{HL,M}_{MHL}$ = 5·6	11
Iminodiacetic acid	9·45‡	2·65‡	—	—	13·1	7·1	—	—	2·5–9·0	K_1 = 11·76	12
Acetylacetone	8·8†	—	—	—	12·9	7·2	—	—	2·0–8·5	—	—

* Protonation constant taken from ref. 5.
† Protonation constant taken from refs. 1 and 2.
‡ Protonation constant taken from ref. 13.

Table 2. Logarithmic values of stability constants (I = 0·10–0·12)

	Present paper; T = 25°C		Suppl. literature data; T = 20–25°C		
Ligand	$K^{M,L}_{ML}$	$K^{H,ML}_{MLH}$	$K^{M,L}_{ML}$	$K^{H,ML}_{MLH}$	Ref.
EDTA	22·04	3·38	21·8	3·1	5
			21·47 ± 0·05	3·19*	14
			21·7 ± 0·2	3·19	15
			21·8	—	16
DTPA	26·60	4·59	27·0	3·6	5
			26·59	4·10	15
			28·4 ± 0·4	—	17
			25·4	—	18
EGTA	23·66	3·17	23·2	3·0	5
			23·2	3·06	16
			23·47	—	19
DCTA	23·85	4·00	24·3	3·1	5
			23·77	—	20
			23·59	3·51	15
TRIEN	24·65	no ev.	25·26		5; 21
NTA	15·4	2·3	12·7		5
			14·6 ± 0·1		9
			16·6		22

* Calculated as $\log K^{H,ML}_{MLH} = \log K^{H,M,L}_{MLH} - \log K^{M,L}_{ML}$ = 24·66 − 21·47 = 3·19.
† Calculated as $\log K^{H,ML}_{MLH} = \log K^{M,HL}_{MLH} + \log K^{H,L}_{HL} - \log K^{M,L}_{ML}$ = 16·8 + 9·46 − 23·2 = 3·06.

Table 3. Logarithmic values of the stability constants of mixed-ligand complexes: log $K_{HgYX}^{X,HgY}$ ($HgY + X \rightleftharpoons HgYX$) ($I$ = 0·1–0·12; T = 25°C)

X	Y	EDTA*	DTPA*	EGTA*	DCTA†	TRIEN†	NTA*	
—	log $K_{HgY}^{Hg,Y}$	22·04	26·60	23·66	23·85	24·65	15·4	log $K_{Hg(NTA)_2}^{NTA,HgNTA}$ = 7·1
H		3·38	4·59‖	3·17	4·00	no ev.	2·3	log $K_{Hg(NTA)_2H}^{H,Hg(NTA)_2}$ = 4·7
NH_3		6·3 (6, 4)‡	no ev.	no ev.	no ev.	no ev.	8·9	
TRIS		5·2 (5, 2)‡	no ev.	—	—	no ev.	6·7	
Glycine		5·4	no ev.	no ev.	—	no ev.	7·3	
Ethylenediamine		5·4§	no ev.	—	—	—	5·5§	
Ethanolamine		5·7	no ev.	—	—	—	9·5	
Pyridine		4·4 (4, 3)‡	—	—	—	—	—	
Hexamethylenetetramine		4·0 (4, 1)‡	no ev.	—	—	—	—	
Acetic acid		no ev.	no ev.	no ev.	—	—	—	
Acetylacetone		¶	no ev.	—	—	—	—	

* Protonation constants taken from ref. 13.
† Protonation constants taken from refs. 1 and 2.
‡ Values obtained by Reilley and Schmid.[23]
§ X = HL.
‖ $K_{MLH_2}^{H,MLH}$ = 3·15.
¶ Slight evidence for formation of $HgY(X)_3$.

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Laboratory for Analytical Chemistry
University of Amsterdam
Nieuwe Achtergracht 166
Amsterdam, The Netherlands

W. E. VAN DER LINDEN
C. BEERS

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Summary—Values are given for the formation constants of complexes of mercury(II) with some buffer/masking agents. The mixed-ligand complex formation of mercury(II)-chelates with other complexing agents has also been studied.

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ANNOTATION

DICHROMATE TITRATION OF THALLIUM(I)

(*Received* 18 *December* 1973. *Accepted* 8 *May* 1974)

The standard redox potential of the thallium(III)–thallium(I) couple is reported[1] to be 0·89 V, which is very nearly the same as that of the chromium(VI)–chromium(III) couple.[2] Though this potential is sufficiently high for the absence of oxidation of thallium(I) salts by atmospheric oxygen, several workers have observed the oxidation of thallium(I) salts by atmospheric oxygen in the presence of halide ions.[3–6] Thus the loss of luminescence of thallium(I) salt solutions under ultraviolet light in the presence of chloride and hydrogen ions was found to be due to the aerial oxidation of the thallium(I) salts.[4] Oxidation of thallium(I) to thallium(III) in aqueous medium at pH less than 6 in the presence of chloride and bromide ions has also been reported.[5] Daiev *et al.*[6] thought it necessary to use an inert atmosphere to prevent aerial oxidation of thallium(I) to thallium(III) in media containing hydrochloric acid at high concentrations. Rao[7] attempted a potentiometric titration of thallium(I) with chromium(VI) but thought that the titration was non-stoichiometric though there is a considerable potential difference between the two redox systems (in media of high hydrochloric acid concentration). According to him the potentiometric titration is not satisfactory even in the presence of iodine monochloride as catalyst. Buzás and Erdey[8] on the other hand reported a satisfactory potentiometric titration of thallium(I) with chromium(VI) at hydrochloric acid concentration > 5*M*, but did not find it necessary to use an inert atmosphere for the titration. All the oxidimetric titration methods for thallium(I) require the presence of chloride ions.[9] In view of these findings a study of the reaction between thallium(I) and chromium(VI) in hydrochloric acid medium was undertaken.

EXPERIMENTAL

Reagents

The thallium(I) and thallium(III) solutions were prepared from thallous carbonate and standardized, as described earlier.[10] Other reagents used were analytical-reagent grade.

Apparatus

In the potentiometric titrations the potentials were measured with use of a bright platinum wire indicator electrode and a saturated potassium chloride–agar bridge. During all experiments the thallium solutions were kept under an inert atmosphere, as otherwise there was considerable oxidation of thallium(I) with atmospheric oxygen, especially in solutions containing hydrochloric acid at high concentrations.

Formal redox potentials

The formal redox potentials of the thallium(III)–thallium(I) couple were measured in solutions of various hydrochloric acid concentration and 0·025*M* in both thallium(I) and thallium(III). Air was expelled from these solutions by saturating the solutions with nitrogen and keeping them under a nitrogen atmosphere. The potentials attained by the platinum electrode after 10–15 min were stable and were recorded.

Titration procedure

A mixture of 50 ml of concentrated hydrochloric acid and 40 ml of water in a 150-ml titration vessel is saturated with carbon dioxide by passage of the gas for a few minutes. An aliquot of thallium(I) solution is added and the potential acquired by a bright platinum electrode inserted in the mixture is measured against a saturated calomel electrode. The potential is then recorded after each addition of titrant and the equivalence-point is found in the usual way.

Reasonably stable potentials are attained rapidly by the indicator electrode until near the equivalence point. At the equivalence point the stabilization of potential is rather slow, a few minutes wait being necessary before the measurement. The potential break at the equivalence point is about 150 mV for the addition of 0·05 ml of 0·05*N* chromium(VI).

Among other methods of detecting the end-point of this titration the extractive end-point method of Rao[11] and the chemiluminescent method of Buzás and Erdey[8] may be mentioned. No reversible redox indicator seems to have been reported. Ferroin, which is widely used in titrations with cerium(IV), has a formal oxidation potential of 1·06 V,[12] and might function as a reversible indicator in the present titration. Experiments have shown

Table 1. Determination of thallium(I) by titration with potassium dichromate in 6*M* hydrochloric acid medium

Thallium(I), *mmole* Taken	Found	Method of detecting the end-point
0·0844	0·0848	Potentiometry
0·1688	0·1682	
0·2532	0·2524	
0·3376	0·3372	
0·4220	0·4208	
0·6330	0·6300	
0·0485	0·0483	Indicator
0·1309	0·1315	
0·1455	0·1448	
0·1746	0·1744	
0·1940	0·1932	
0·2425	0·2423	

that ferroin is rapidly oxidized by dichromate, and ferriin is rapidly reduced by thallium(I) in media > 5*M* in hydrochloric acid, and the indicator gives satisfactory results (Table 1).

Tartrate and iron(II) interfere in this titration of thallium(I) with dichromate. Other reducing agents which react with dichromate must also be absent.

RESULTS AND DISCUSSION

The formal redox potentials of the thallium(III)–thallium(I) couple, as determined in the present study, and those reported[2] for the chromium(VI)–chromium(III) couple, in media of various hydrochloric acid concentration, are presented in Fig. 1. From these results it is clear that while the formal potentials of the chromium system increase, those of the thallium system decrease with increase in the concentration of hydrochloric acid. Thus though the formal redox potentials of the two systems are comparable at low acidity, the difference between them increases considerably at high hydrochloric acid concentration, allowing a satisfactory oxidimetric titration of thallium(I) with chromium(VI).

Besides the thermodynamics, the kinetics of the reaction must also be favourable if the titration is to be satisfactory. The rates of the reduction of chromium(VI) by thallium(I) were studied spectrophotometrically. The absorption spectra of chromium(VI) and chromium(III) between 340 and 600 nm do not vary much with variation in

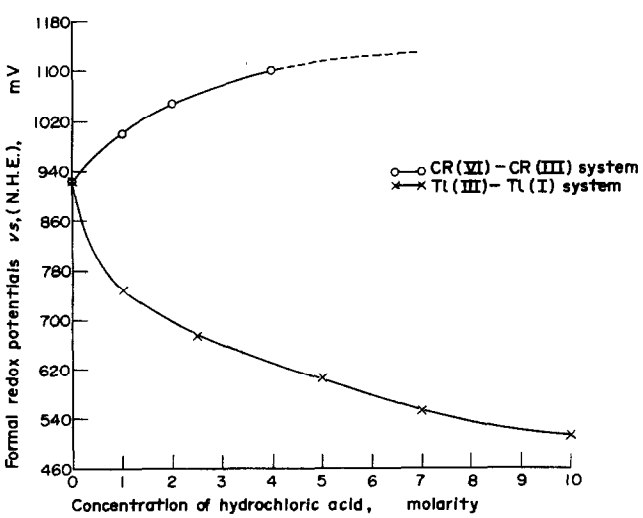

Fig. 1. Formal redox potentials of Tl(III)/Tl(I) and Cr(VI)/Cr(III) systems in hydrochloric acid media.

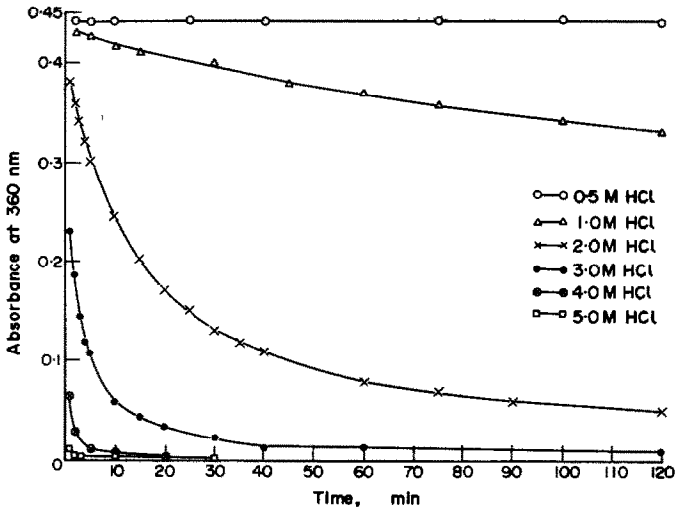

Fig. 2. Effect of hydrochloric acid concentration on the kinetics of the reaction between Tl(I) and Cr(VI).

hydrochloric acid concentration from 1 to 6*M*. Hence the reaction rate at room temperature (29°) was determined by measuring the absorbance (at 360 nm) of mixtures in various acid media, as shown in Fig. 2. The results show that (*i*) the speed of the reaction between thallium(I) and chromium(VI) increases with the concentration of the hydrochloric acid, (*ii*) the reaction does not appear to take place if the medium is 0·5*M* or less in hydrochloric acid, (*iii*) the reaction is quite rapid, complete and comes to equilibrium in less than 2 min if the hydrochloric acid concentration is > 5*M*.

Similar experiments were also carried out at 80°, the volume of the mixture being kept constant and the mixture not in contact with atmospheric oxygen. The reaction is then complete within 3 min, provided the hydrochloric acid concentration is ⩾ 3*M*. When the acid is only 2*M*, the reaction is not complete even after heating for more than an hour.

From these observations it is clear that the titration of thallium(I) with potassium dichromate should be feasible provided the medium is > 5*M* in hydrochloric acid. The results obtained by application of the procedure are given in Table 1.

That the effect of hydrochloric acid concentration on the potential of the thallium couple is due to the chloride ion was established by keeping the hydrogen ion concentration constant with perchloric acid and varying the chloride concentration, and by varying the acidity in the absence of chloride (Tables 2 and 3). However, according to the thermodynamics the titration should be feasible in 2*M* hydrochloric acid, and the necessity to use a much

Table 2. Formal redox potentials of Tl(III)/Tl(I) system in mineral acids (*vs.* N.H.E.), *mV*

Concentration of acid, *M*	$HClO_4$	HNO_3	H_2SO_4	*H_3PO_4 + 0·5*M* H_2SO_4	HCl
0·10	1236	1279	1215	1205	862
0·25	1255	1267	1212	1197	816
0·50	1249	1252	1210	1188	782
1·00	1249	1240	1216	1179	746
2·50	1272	1224	1225	1166	682
5·00	1330	1221	1230	1167	606
7·50	1433	1230	1273	1178	553
10·00	—	1248	1320	1195	513
11·85	—	—	—	1204	—
12·50	—	1270	1372	—	—
15·00	—	—	1427	—	—

* Since thallium(III) hydroxide does not dissolve easily in phosphoric acid it is dissolved in minimum amount of sulphuric acid before addition to phosphoric acid of the required strength.

Table 3. Effect of varying concentrations of hydrogen ion and chloride ion on the formal redox potentials of the Tl(III)/Tl(I) system (*vs.* N.H.E.), *mV*

$HClO_4$, *M*	Chloride, *M*	Formal redox potential of Tl(III)/Tl(I)	Chloride, *M*	$HClO_4$, *M*	Formal redox potential of Tl(III)/Tl(I)
1·00	0	1250	0·1	0·10	883
1·00	0·0025	1156	0·1	0·50	882
1·00	0·01	989	0·1	1·00	867
1·00	0·10	867	0·1	2·00	855
1·00	0·50	784	0·1	3·00	844
1·00	1·00	768	0·1	4·00	831
1·00	2·00	721	0·1	5·00	821
5·00	0	1330	1·0	0·10	785
5·00	0·0025	1266	1·0	0·50	774
5·00	0·01	967	1·0	1·00	768
5·00	0·10	820	1·0	2·00	753
5·00	0·50	743	1·0	3·00	738
5·00	1·00	721	1·0	4·00	726
			1·0	5·00	721
			0·10	1·90	854
			0·25	1·75	844
			0·75	1·25	794
			1·00	1·00	768
			1·25	0·75	766
			1·75	0·25	762

higher acidity implies that hydrogen ions play an important part in determining the kinetics (as would be expected from the equation for the reaction). As there is no excess of dichromate in the titration solution until after the end-point there will be no oxidation of chloride by the dichromate.

Department of Chemistry
Andhra University
Waltair, India

S. R. SAGI
G. S. PRAKASA RAJU
K. V. RAMANA

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Summary—The formal redox potentials of the thallium(III)–thallium(I) couple in different acids of varying strengths are reported. The minimum concentration of hydrochloric acid required for a direct titration of thallium(I) with potassium dichromate is 5*M*. Thallium(I) can be titrated directly with the primary standard oxidant, potassium dichromate, at room temperature, with ferroin as indicator, in 6*M* hydrochloric acid. Atmospheric oxygen must be excluded.

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PRELIMINARY COMMUNICATION

DETECTION OF HYDRAZINES AND AMINES WITH NITRO COMPOUNDS

H.E. Malone

1411, West Kerrick Street, Lancaster, California 93534, U.S.A.

The following work* was begun with the intention of developing a method for determining methylhydrazine in the presence of various amines. This work was never completed; proving or disproving the ideas proposed, by investigating the effects of reactant concentrations, selection of solvents, times of reactions, etc., remains to be done.

Hydrazines and amines are normally determined in small concentrations by their reactions with an aldehyde (dimethylaminobenzaldehyde) which forms the respective azine and hydrazone or, with amines, a Schiff base, all of which give yellow or yellow-orange compounds, depending on the aldehyde used (anisaldehyde white - yellow).

The author has demonstrated that some hydrazines, primary and secondary amines, diamines, triamines and tetramines form highly coloured compounds with nitro and dinitro compounds. By proper selection of solvents and concentration of hydrazines and amines, qualitative analysis of mixtures of hydrazines and amines or specific identification of individual hydrazines or amines is possible. Table 1 shows the colours obtained with specific amines (primary, secondary, tertiary, di-, tri- and tetra-) and hydrazines with various mononitro and dinitro compounds, containing a variety of functional groups. The reagents themselves are colourless.

For the tests shown, only pure compounds were used, hence the intensity of the colours and the sensitivity of those producing reddish-black and brownish-black compounds. It appears that hydrazines can be determined readily in the presence of most amines, although diamines, triamines and tetramines might offer some difficulty because of the deep blues and greens formed. Methylhydrazine and 1,1-dimethylhydrazine in the presence of the amine

*Part of the work submitted as a Ph.D. Thesis at the University of Edinburgh, 1974.

Table 1. Colour reactions of hydrazines and primary amines with nitro compounds

	I	II	III	IV	V	VI	VII	VIII	IX	X	XI	XII
2,4-Dinitrotoluene	P	B	YG	B	B	C	Y	R	R	BG	BG	DG
m-Dinitrobenzene	P	RP	O	R	R (Pi)	O	Y	RBr	RBR	P	P	P
2,6-Dinitrotoluene	P	Bur	RBr	RBr	RBr	Pi	Y	O	RBr	BG	DG	DG
2,4-Dinitrophenol	O	Y-O	Y	Y	Y	Y	Y	RBr	RBr	Y	Y	Y
o-Dinitrobenzene	BrG	BrG	Y	Y	Y	Y	C	RBr	RBr	RO	O	Y
o-Nitroaniline	C	YO	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y
p-Nitroaniline	YG	G	G	Y	Y	Y	C	Y	Y	G	G	G
1,4-Dinitrosopiperidine	C	C	C	C	C	C	C	C	C	C	C	C
1-Chloro-2,4-dinitrobenzene	RBr	GBl	DR	Y	YO	Y	Y	RBl	RBl	RBl	RBl	YO
4-Chloro-3,5-dinitrobenzonitrile	BrBl	Bl	BrBl	O	O	O	Y	RBr	RBl	RO	O	O
2,4-Dinitroanisole	Bl	GBl	YBr	Y	Y	O	C	O	O	DR	DR	O
4-Amino-2-chloro-5-nitropyrimidine	RBr	Y	Y	Y	Y	Y	C	Y	Y	RBr	Y	Y
2-Amino-3-nitropyridine	Bl	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y
4-Amino-3-nitrobenzotrifluoride	R	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y
1,5-Difluoro-2,4-dinitrobenzene	BrBr	RO	O	Y	Y	Y	YG	R	R	Y	R	Y
2,4,7-Trinitrobenzaldehyde	GBl	RBl	RBl	RBl	RBl	RBl	C	BrBl	BrBl	RBl	RBl	RBl
1,3-Dinitronaphthalene	RBl	RP	RBl	RBl	RBl	RBl	BrBl	RBr	RBr	RBl	RBl	RBl
1,Chloro-2,4,6-trinitrobenzene	RP	Bur	DR	DR	DR	R	Y	BrBl	BrBl	RP	RP	RP
2,4-Dintrofluorobenzene	PBl	Bl	BrBl	RO	RO	Y	Y	BrBl	BrBl	BrBl	RO	RO
2,4,7-Trinitro-9-fluoroenone	BrBl	BrBl	RBr	Y	Y	O	Y	DR	DR	RY	DR	R

I = hydrazine
II = methylhydrazine
III = 1,1-dimethylhydrazine
IV = n-butylamine
V = n-heptylamine
VI = dimethylamine
VII = tributylamine
VIII = N-ethylaniline
IX = dimethylaniline
X = ethylenediamine
XI = diethylenetriamine
XII = triethylenetetramine

P = purple
B = blue
Y = yellow
G = green
C = colourless
Br = brown
O = orange
Pi = pink
Bl = black
Bur = burgundy
D = dark

groups could be detected by using o-dinitrobenzene, p-nitroaniline, 1-chloro-2,4-dinitrobenzene, 4-chloro-3,-5-dinitrobenzonitrile, 2,4-dinitroanisole, and 2,4,7-trinitrofluorenone. Compounds containing the chloro and fluoro groups reacted readily. By proper selection of conditions, colorimetric methods for air pollution measurements of hydrazines and amines, diamines, etc., might be feasible; differentiation of primary from secondary and tertiary amines and secondary from tertiary amines may also be possible. Glass tubes containing a substrate impregnated with selective nitro, dinitro, trinitro, chloro or fluoro compounds could be prepared and known volumes of air containing amines drawn through the glass tubes. The colour produced would be indicative of the amine group as well as the concentration of the amine.

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NOTE

NOMENCLATURE IN THERMAL ANALYSIS - III

The recommendations in the First Report of the Nomenclature Committee of the International Confederation for Thermal Analysis (ICTA)[1] have now been approved by IUPAC[2] and ASTM[3] and the Second Report[4] has been submitted to both bodies. The interest engendered by these reports is evidenced by the fact that the Sub-Committees dealing with the French[5] and Japanese[6] languages have published definitive documents based on the First Report and versions of one or both have appeared in Czech,[7] Italian,[8] Japanese,[9] Polish[10] and Slovenian.[11]

The Council of ICTA have directed that this Third Report, approved in Business Session at the Fourth International Conference on Thermal Analysis at Budapest, Hungary, in July 1974, be published as a definitive document with the request that the recommendations therein be adhered to in all publications in the English language. The Committee are currently considering thermoanalytical techniques not so far examined in detail and hope to submit a report on these to the Fifth International Conference in Japan in 1977.

I. AMPLIFICATION OF FIRST REPORT

The definition of differential scanning calorimetry in the First Report applies only when power-compensation instruments are used and no definition has been proposed to cover the use of heat-flux instruments: in French the two have been clearly distinguished.[5] The Committee also recognize that there has over the past few years been increasing use of differential thermocouples for measurement under isothermal external conditions. It is therefore recommended that the following two terms and definitions be added to those in the First Report:

Quantitative differential thermal analysis (quantitative DTA). This term covers those uses of DTA where the equipment is designed to produce quantitative results in terms of energy and/or other physical parameters.

The record should be plotted in the same manner as a normal DTA curve.

Differential thermal analysis (DTA) in an isothermal environment.

A variant of DTA in which the temperature difference between a substance and a reference material is continuously recorded against time as the two specimens are maintained in a nominally isothermal environment.

The record should be plotted in the same manner as a normal DTA curve.

The term isothermal DTA is incorrect and the abbreviation QDTA is not considered to be warranted.

II. MULTIPLE TECHNIQUES

In view of recent developments, the brief comments on multiple techniques, simultaneous and combined, in the First Report[1] require clarification and the following names and definitions have been approved.

Simultaneous techniques. This term covers the application of two or more techniques to the same sample at the same time - e.g. simultaneous thermogravimetry and differential thermal analysis.*

Coupled simultaneous techniques. This term covers the application of two or more techniques to the same sample when the two instruments involved are connected through an interface† - e.g. simultaneous differential thermal analysis and mass spectrometry.

Discontinuous simultaneous techniques. This term covers the application of coupled techniques to the same sample when sampling for the second§ technique is discontinuous - e.g. discontinuous simultaneous differential thermal analysis and gas chromatography, when discrete portions of evolved volatile(s) are collected from the sample situated in the instrument used for the first§ technique.

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* In writing, the names of simultaneous techniques should be separated by "and" when used in full and by a hyphen when abbreviated acceptably - e.g. simultaneous TG-DTA. Unless contrary to established practice, all abbreviations should be written in capital letters without full-stops.

† A specific piece of equipment that enables two instruments to be joined together.

§ In coupled simultaneous and discontinuous techniques, the first technique to be mentioned is that in which the first, in time, measurement is made - e.g. when a DTA instrument and a mass spectrometer are connected through an interface, DTA-MS is the correct form, not MS-DTA.

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c/o Industrial and Laboratory Services*
P.O. Box 9
Lyme Regis
Dorset, U.K.

R.C. MACKENZIE (Chairman)
C.J. KEATTCH (Secretary)
T. DANIELS
D. DOLLIMORE
J.A. FORRESTER
J.P. REDFERN
J.H. SHARP

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* The address given is that of the Secretary.

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LETTER TO THE EDITOR

DETERMINATION OF VANADIUM(V), CHROMIUM(VI) AND CERIUM(IV) IN BINARY OR TERNARY MIXTURE

SIR,

Potentiometric titration with iron(II) differentiates vanadium(V) and cerium(IV) but not vanadium(V) and chromium(VI), or chromium(VI) and cerium(IV) when present together. The methods[1] available for the determination of these species in binary or ternary mixture are generally cumbersome and less accurate. I now propose a different scheme for this determination, based on the following considerations.

Vanadium(IV) can be titrated[2] with cerium(IV) sulphate at room temperature, using ferroin indicator, even in the presence of chromium(III). Chromium(VI) is reduced completely[3] by vanadium(IV) in a short time if the latter is used in excess. Although it seems that arsenic(III) selectively reduces chromium(VI) when added in excess to a solution containing chromium(VI) and cerium(IV) in dilute sulphuric acid, it is not possible to titrate the latter oxidant with iron(II) without interference from arsenic(III), when ferroin is used as indicator. At the concentrations used, arsenic(III) and cerium(IV) are *not* without reaction as is generally assumed,[1] and the reaction is catalysed by chromium(III) formed from the reaction of chromium(VI) and arsenic(III). It is even possible to determine arsenic(III) through a reaction between arsenic(III) and cerium(IV) catalysed by chromium(III) at room temperature and the results are correct to within $\pm 0{\cdot}2\%$. The procedure for this is as follows.

To 5–10 ml of 0·05*M* cerium(IV) sulphate add 2–6 ml of ~0·05*N* arsenic(III) (free from chloride) and 1 ml of 0·1*M* chromium(III) [prepared from potassium chromium(III) sulphate], stir the mixture well and allow it to stand for 5 min. Add 5 ml of 20*N* sulphuric acid and dilute to 45 ml, and titrate the excess of cerium(IV) with 0·05*M* iron(II), using a drop of 0·01*M* ferroin as indicator.

It is possible that the reaction occurs through the following steps:

$$\mathrm{Cr(III) + Ce(IV) \overset{\text{fast}}{\rightleftharpoons} Cr(IV) + Ce(III)} \quad (1)$$

$$\mathrm{Cr(IV) + Ce(IV) \xrightarrow{\text{slow}} Cr(V) + Ce(III)} \quad (2)$$

$$\mathrm{Cr(V) + As(III) \xrightarrow{\text{fast}} Cr(III) + As(V)} \quad (3)$$

Evidently step (2) is faster than the rate-determining step of the uncatalysed arsenic(III)–cerium(IV) reaction. It is also not possible to determine titrimetrically the total of vanadium(V) and cerium(IV) when chromium(VI) is present in the same solution, by using the selective reduction of the latter with arsenic(III), and for the same reason. It has been observed that chromium(VI)[4] and/or vanadium(V) do not interfere in the potentiometric titration of cerium(IV) in 0·5–1·0*M* nitric acid with oxalate. It seems that this is possible owing to the slow kinetics of the reactions of chromium(VI) and vanadium(V) with oxalate.

RECOMMENDED PROCEDURES

Vanadium(V) + chromium(VI) or vanadium(V) + cerium(IV)

(*i*) Titrate with 0·05*M* iron(II) a solution containing 2–5 ml of ~0·05*M* vanadium(V) and 2–5 ml of ~0·05*N* chromium(VI) [or 2–5 ml of ~0·05*M* cerium(IV) sulphate in 1*N* sulphuric acid] in 5–6*M* sulphuric acid medium, using a drop of 0·01*M* ferroin as indicator. Alternatively, treat the solution containing vanadium(V) and chromium(VI) [or cerium(IV)] with 20 ml of 0·05*M* iron(II) solution and titrate the unreacted iron(II) with 0·05*N* dichromate or cerium(IV) sulphate in 5–6*M* sulphuric acid medium, using ferroin as indicator. This gives the sum of vanadium(V) and chromium(VI) [or cerium(IV)].

(*ii*) Treat a similar solution of vanadium(V) and chromium(VI) [or cerium(IV)] as in (*i*) with 20 ml of 0·05*M* iron(II) or vanadium(IV) and titrate the unreacted reductant (after a lapse of 5 min in the latter case) with cerium(IV) sulphate in 7–8·5*M* acetic acid medium, using ferroin as indicator. Alternatively, for cerium(IV) use a procedure similar to (*iii*) below.

The value of chromium(VI) or cerium(IV) is calculated and the value of vanadium(V) obtained by difference.

Chromium(VI) + cerium(IV)

A procedure similar to (*i*) or (*ii*) above is used but the titrations in the former can be done in 2*N* sulphuric acid medium [cerium(IV) sulphate is used for the titration of excess of iron(II)]. The sum of chromium(VI) and cerium(IV) is then calculated. A procedure similar to (*iii*) below is used to determine the value of cerium(IV). The value of chromium(VI) is then obtained by difference.

Vanadium(V) + chromium(VI) + cerium(IV)

A procedure similar to (*i*) is used to determine the sum of vanadium(V), chromium(VI) and cerium(IV), then a procedure similar to (*ii*) is used to determine the sum of chromium(VI) and cerium(IV).

(*iii*) Titrate a solution containing 2–5 ml of each of 0·05*M* vanadium(V), 0·05*N* chromium(VI) and 0·05*M* cerium(IV) in 50 ml of 0·5–1·0*M* nitric acid, with 0·05*N* oxalic acid to a potentiometric end-point. The potential drop at the equivalence point is 150–200 mV per 0·04 ml of titrant as against 300–400 mV in the titration of cerium(IV) alone. The oxalic acid used corresponds to the cerium(IV) in the mixture. The values of the chromium(VI) and vanadium(V) are obtained by difference.

The relative errors of the visual procedures and potentiometric methods used are within ±0·2 and ±0·5% respectively.

Department of Chemistry K. SRIRAMAM
Andhra University
Post-Graduate Centre
Guntur-522005, India

25 July 1974

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EINFLÜSSE DRITTER PARTNER BEI DER LÖSUNGSSPEKTRALANALYSE NACH DEM ZERSTÄUBERVERFAHREN—I

EINFLÜSSE ANORGANISCHER FREMDIONEN

GERHARD ACKERMANN

Lehrstuhl für analytische Chemie, Sektion Chemie, Bergakademie Freiberg, 92 Freiberg (Sachsen), DDR

und

MANFRED MÜNX

VEB Mansfeld Kombinat Wilhelm Pieck, Forschungsinstitut für NE-Metalle Freiberg, 92 Freiberg (Sachsen), DDR

(*Eingegangen am* 22 *Juni* 1973. *Angenommen am* 17. *Januar* 1974)

Zusammenfassung—Es wird ein Zerstäuberverfahren für die spektrographische Bestimmung von Aluminium und Silicium in metallurgischen Produkten beschrieben. Die Methode gestattet es, Gehalte zwischen 0,1% und 10% mit Variationskoeffizienten $\leq 5\%$ zu erfassen. Untersuchungen zum Einfluß dritter Partner zeigen, daß Zusätze von Alkali- und Erdalkalisalzen das Nachweisvermögen des Verfahrens verbessern, ohne die Reproduzierbarkeit der Meßergebnisse nachteilig zu beeinflussen. Die Ursachen für dieses Verhalten liegen in einer Verschiebung der Ionisations- und Anregungsgleichgewichte der zu bestimmenden Elemente im Funkenplasma zugunsten der Atomkonzentrationen. Weiterhin kann festgestellt werden, daß hohe Säurekonzentrationen, besonders von Schwefelsäure, zu einer Abnahme der Linienintensitäten für Aluminium und Silicium führen. Die Hauptursache hierfür ist, daß die erhöhte Viskosität der Probelösung die Zerstäubungsgeschwindigkeit und damit den Aerosoltransport in die Funkenentladung stark beeinträchtigt.

Die Lösungsspektralanalyse bietet gegenüber der Analyse fester Proben den Vorteil, daß Standards beliebiger Zusammensetzung leicht hergestellt werden können. Leider sind auch Lösungsmethoden nicht frei von Interelementeffekten,[1,2] die sich sowohl steigernd wie verringernd auf die Linienintensitäten auswirken können.

Sind die Ursachen für erhöhte Intensitäten bekannt, so ist es möglich, die Empfindlichkeit des Bestimmungsverfahrens durch zielgerichtete Zusätze zu verbessern. Dies erscheint besonders wichtig, wenn die Methode eine gute Reproduzierbarkeit der Meßergebnisse liefert, aber unbefriedigende Nachweisgrenzen für die zu bestimmenden Elemente aufweist.

Da speziell für die Bestimmung von Aluminium und Silicium in metallurgischen Produkten mit einer stark wechselnden Probenzusammensetzung zu rechnen war, mußte den oben genannten Erscheinungen besondere Beachtung geschenkt werden. Neben der Entwicklung eines Bestimmungsverfahrens für Gehalte zwischen 0,1% und 10% ergab sich somit als Hauptaufgabe dieser Arbeit, grundlegende Untersuchungen über den Einfluß von Salzzusätzen auf die Linienintensitäten anzustellen.

VERSUCHSANORDNUNG UND ARBEITSWEISE

Nach einer kritischen Betrachtung der Literatur[1] und nach umfangreichen Vergleichsuntersuchungen[1] erschien es sinnvoll, für die Bestimmung von Aluminium- und Silicium-

gehalten in den Größenordnungen von 0,1% bis 10% ein Zerstäuberverfahren einzusetzen, da diese Arbeitsweise die geforderte hohe Reproduzierbarkeit der Meßergebnisse versprach. Solche Verfahren werden bereits in der Literatur beschrieben und für die Ermittlung der Aluminium- und Siliciumgehalte in silicatischen Gesteinen,[3] in Hochofen- und Martinschlacken,[4,5] in Titan- und Aluminiumlegierungen,[6–9] in Elektrolyten[10] und in anderen Salzlösungen[11] mit Erfolg eingesetzt. Dabei kommen recht unterschiedliche Elektrodenanordnungen und Zerstäubersysteme in Anwendung.

EXPERIMENTELLER TEIL

Nach der von uns gewählten Variante wird die gelöste Probe in einer Zerstäubereinrichtung des Zeiss'schen Flammenphotometers Modell III, die mit einem Fängergefäß nach Tarasevič und Troneva[12] gekoppelt ist, versprüht und über eine durchbohrte Elektrode in die Lichtquelle eingeblasen (Abb. 1). Als Elektrodenmaterial dient Graphit (VEB Elektrokohle Lichtenberg, Qualität T1), der vor der Aufnahme durch Glühen im Gleichstrombogen von seinen Oberflächenverunreinigungen befreit wird. Die Anregung erfolgt in einem Hochspannungsfunken (12 kV, 6000 pF, 0,3 mH). Als Aufnahmegerät dient ein Quarzspektrograph mittlerer Dispersion (Q 24, VEB Carl Zeiß, Jena). Die Lösung wird mit Preßluft (0,45 atü, 260 l/h) über eine Düse mit 0,4 mm Innendurchmesser zerstäubt. Die wichtigsten Daten der Arbeitsweise zeigt Tabelle 1.

Zur Erhöhung der Reproduzierbarkeit der Meßergebnisse wird jeder Probelösung 0,1 mg Cr/ml als innerer Standard zugesetzt. Die gewählten Bedingungen führen zu linearen Eichkurven für die Bestimmung des Aluminiums und des Siliciums in dem Konzentrationsbereich 0,01 bis 1,0 mg/ml. Die bei Konzentrationen von 0,1 mg/ml berechneten Variationskoeffizienten des Verfahrens betragen 3,1% für Silicium und 5,2% für Aluminium.

EINFLÜSSE VON FREMDIONEN AUF DIE BESTIMMUNG VON ALUMINIUM UND SILICIUM

Daß veränderte Säure- oder Salzkonzentrationen der Probelösung die Emission der Spektrallinien auch bei Zerstäuberverfahren beeinflussen können, ist wiederholt diskutiert worden. Über experimentelle Untersuchungen zu dieser Problematik berichten Kulcsar,[13–17] Gegus,[4,18,19] Tarasevič und Gusarskij[20] sowie Žuravlev und Ryzkova.[11] Die Ergebnisse dieser Arbeiten über die Matrixeffekte bei Zerstäubermethoden mit Funkenanregung

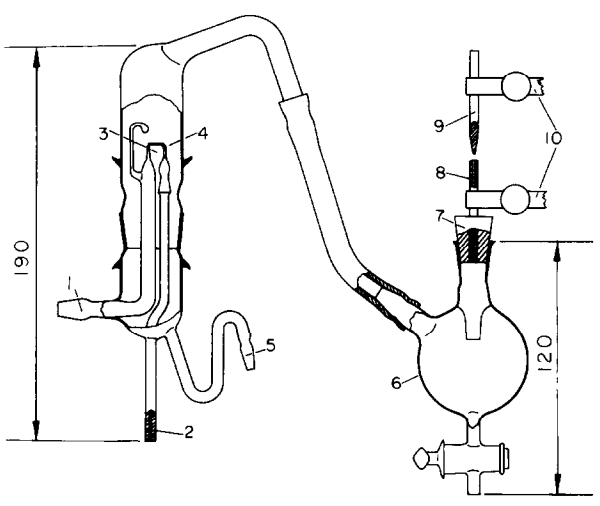

Abb. 1. Zerstäuber- und Elektrodenanordnung:

1. Gaszufuhr; 2. Ansaugrohr; 3. Gasdüse; 4. Flüssigkeitsdüse; 5. Lösungsrücklauf; 6. Fängergefäß; 7. durchbohrter Gummistopfen; 8. durchbohrte Elektrode; 9. Gegenelektrode, 10. Elektrodenhalter.

Tabelle 1. Bedingungen der spektrographischen Aufnahme und Auswertung

Gegenelektrode:	5 mm Durchmesser mit angedrehter Kegelspitze ($\sphericalangle 25°$)
Trägerelektrode:	durchbohrter Graphitstab mit einem Außendurchmesser von 5 mm, einem Innendurchmesser von 2 mm und einer Länge von 50 mm
Elektrodenabstand:	2 mm
Vorfunkzeit:	20 s
Belichtungszeit:	150 s
Zwischenblende:	5 mm
Spaltbreite:	0,020 mm
Kamerablende:	1:15
Zwischenabbildung:	auf 3000 Å
Plattenmaterial:	ORWO, blau extrahart, 9 × 24 cm
Analysenlinien:	Al 3082,16 Å/Cr 3132,06 Å Si 2516,12 Å/Cr 2677,16 Å

gestatten jedoch keine allgemeingültigen Schlußfolgerungen. Sie wurden teilweise an voneinander abweichenden Arbeitsweisen und für unterschiedliche analytische Problemstellungen erhalten. Der Möglichkeit, positive Matrixeffekte, bei denen bestimmte, im Überschuß vorliegende Fremdionen zu einer Intensitätssteigerung der Analysenlinie führen, für die Empfindlichkeitserhöhung eines Bestimmungsverfahrens mit hoher Reproduzierbarkeit der Meßergebnisse auszunutzen, wird leider wenig Beachtung geschenkt.

Aus diesen Gründen erschien es uns wichtig das oben beschriebene Bestimmungsverfahren für Aluminium und Silicium auf Störeinflüsse zu testen und gleichzeitig zu prüfen, welche Möglichkeiten sich bieten, durch zielgerichtete Zusätze ein erhöhtes Nachweisvermögen dieser Analysenmethode zu erreichen. Im Mittelpunkt unserer Untersuchungen standen Einflüsse von Elementen bzw. Ionen, die in metallurgischen Produkten häufig vorkommen (Ca^{2+}/Mg^{2+}) und von solchen, die bei alkalischen und sauren Aufschlüssen dieser Materialien im Überschuß auftreten (Na^+, K^+, Cl^-, NO_3^-, SO_4^{2-}, OH^-).

Einfluß von Salzzusätzen auf die Linienintensitäten

Es ist von spektrographischen Pulvermethoden hinreichend bekannt, daß Zusätze von Alkalisalzen zum Probematerial stabilisierend auf die Lichtquelle wirken und die Nachweisgrenze bestimmter Elemente verbessern. Es lag deshalb nahe, auch die Lösungsmethode auf derartige Effekte zu überprüfen.

Zu diesem Zweck wurden schwach salzsaure Aluminiumlösungen (0,02; 0,1 und 0,5 mg Al/ml) mit 0; 0,01; 0,1; 1,0 und 10,0 mg/ml Natrium bzw. Kalium in Form ihrer Carbonate, Chloride, Nitrate, Sulfate und Hydroxide versetzt und die dadurch hervorgerufenen Intensitätsänderungen der Linie Al I 3082,16 Å gemessen. Die ermittelten ΔY-Werte entsprechen dem Schwärzungsverhältnis von Linie und Untergrund.

Die Messungen ergeben bei Natriumzusätzen bis zu 10 mg/ml, unabhängig davon, ob sie als Chlorid, Sulfat, Nitrat, Carbonat oder Hydroxid zugegeben sind, einen kontinuierlichen Intensitätsanstieg der Aluminiumlinie d.h. eine Erhöhung des Nachweisvermögens (Abb. 2 bringt als Beispiel die Wirkung von NaCl-Zusätzen). Der ΔY-Wert steigt in günstigen Fällen um 0,5 bis 0,7 an. Das entspricht unter Zugrundelegung einer 45°-Eichgeraden, ausgedrückt in Konzentrationen, einem um eine halbe Zehnerpotenz verbesserten Nachweis.

Ein Einfluß der Anionen, der allerdings nicht Gegenstand unserer Untersuchungen war, liegt sicherlich vor, da die Anregung der gemessenen Linie über den atomaren Zustand des

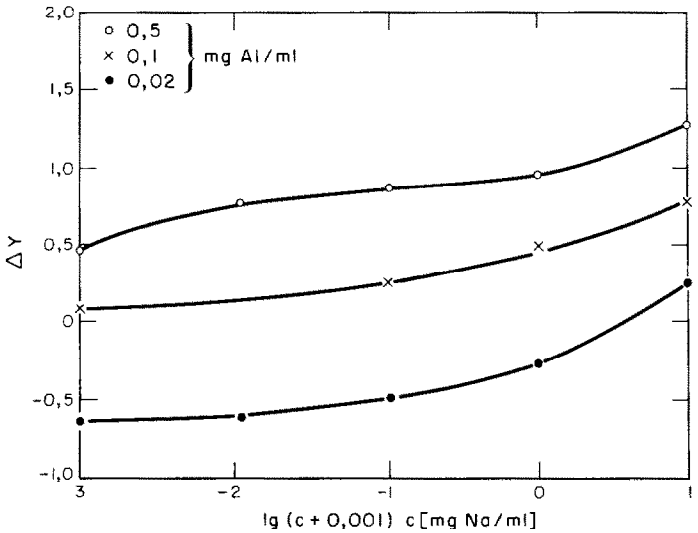

Abb. 2. Einfluß von Natriumzusätzen als NaCl auf die Intensität der Linie Al I 3082,16 Å.

Aluminiums geht. Die unterschiedlichen Dissoziationsenergien der chemischen Verbindungen können zu Änderungen der Anregung und damit der Linienintensität des Aluminiums führen, die jedoch bei unseren Untersuchungen offenbar durch den weit größeren Kationen- oder Salzeinfluß überdeckt werden. Der Grund für die gemessene Intensitätserhöhung ist demnach entweder in der Anwesenheit eines leicht ionisierbaren Kations (Kalium, Natrium) in der Entladungszone des Funkens oder in einer, durch die erhöhte Salzkonzentration bedingten, Veränderung des Zerstäubungsvorganges zu suchen.

Für die Untersuchung des Einflusses von Kaliumsalzen auf den Nachweis des Aluminiums wurden die beschriebenen Meßreihen wiederholt, wobei in den Probelösungen die Natriumsalze durch die entsprechenden Kaliumsalze ersetzt waren. Die erhaltenen Intensitätssteigerungen der Linie Al I 3082,16 Å kommen, wie zu erwarten war, den bei Natriumzusätzen gefundenen sehr nahe.

Auch für die Siliciumbestimmung sollte der Einfluß steigender Zusätze von Alkalisalzen auf das Nachweisvermögen untersucht werden. Zur Herstellung der dazu erforderlichen Siliciumstammlösung mit 5 mg Si/ml wurden 2,5 g metallisches Silicium in 80 ml 2,5*M* Natronlauge gelöst und auf 500 ml aufgefüllt. Verdünnungen dieser Lösung mit Wasser ergaben die für die Messungen nötigen Siliciumkonzentrationen. Für die spektrographischen Untersuchungen wurden Lösungen mit 0,05; 0,1 und 0,5 mg Si/ml hergestellt, denen Kalium in Mengen von 0,01 bis 10 mg/ml als Chlorid, Carbonat, Nitrat, Sulfat bzw. Hydroxid zugegeben war.

Die erhaltenen Ergebnisse zeigen übereinstimmend für alle Kaliumverbindungen, daß Zusätze von $<0{,}1$ mg K/ml zu Lösungen mit 0,05 und 0,1 mg Si/ml und solche von $<1{,}0$ mg K/ml zu Lösungen mit 0,5 mg Si/ml keine oder nur geringfügige Intensitätsänderungen der Linie Si I 2516,12 Å hervorrufen. Höhere Zusätze führen hingegen in beiden Fällen zu einem Anstieg des Linie-Untergrund-Verhältnisses, der bei gleichbleibender Untergrundschwärzung ($S_u = 0{,}05$) bis zu $\Delta Y = 0{,}5$ betragen kann. Berücksichtigt man, daß die Probelösungen ohne Zusatz mit 0,05; 0,1 und 0,5 mg Si/ml, bedingt durch ihre Herstellung bereits 0,09; 0,18 bzw. 0,92 mg Na/ml enthalten, so wird dieser Unterschied zu den für Aluminiumlösungen gefundenen Ergebnissen verständlich.

Auf die Untersuchungen des Einflusses von Natriumsalzen auf die Emission der Siliciumlinie wurde verzichtet, da die zu erwartenden Intensitätsänderungen sich von den bei Kaliumsalzen erhaltenen wenig unterscheiden dürften.

Da die Erdalkalien Calcium und Magnesium in nichtmetallischen Proben häufig neben Aluminium und Silicium auftreten, war es naheliegend auch ihren Einfluß auf die Intensität der Linien Al I 3082,16 Å und Si I 2516,12 Å zu untersuchen.

Steigende Zusätze an Calciumnitrat führen bis zu 1 mg Ca/ml für alle drei Aluminiumkonzentrationen zu einer Nachweisverbesserung, die bei 0,02 mg Al/ml entscheidend ist (Erhöhung des ΔY-Wertes um 0,4) während sie für hohe Aluminiumgehalte (0,5 mg/ml) geringfügig bleibt (Erhöhung des ΔY-Wertes um 0,1). Ein Überschuß von 10 mg Ca/ml führt jedoch wieder zu einer Intensitätsabnahme der Aluminiumlinie, die für 0,1 und 0,5 mg Al/ml größer ist als die vorher beschriebene Zunahme.

Magnesium, als Chlorid zu den Lösungen zugegeben, führt unter den gleichen Konzentrationsverhältnissen zu ähnlichen Ergebnissen. Die Nachweisverbesserung wird nur bei kleinen Aluminiumgehalten wirksam.

Die unter gleichen Meßbedingungen ermittelten Ergebnisse über den Einfluß von Erdalkalien auf die Intensität der Linie Si I 2516,12 Å sind den für das Aluminium gewonnenen ähnlich. Für die Konzentration 0,05 mg Si/ml führen steigende Zusätze bis zu 1 mg Ca/ml zu einer Nachweisverbesserung. Über 1 mg Ca/ml hinaus sinkt die Intensität der Siliciumlinie wieder ab. Bei den Konzentrationen 0,1 mg Si/ml und 0,5 mg Si/ml kann hingegen bis zu 1 mg Ca/ml kein Einfluß durch Calciumzusätze festgestellt werden; nur bei 10 mg Ca/ml ergeben sich verminderte Intensitätswerte. Lösungen, denen das Calcium als Chlorid zugegeben ist, führen zu ähnlichen Abhängigkeiten.

Die Unabhängigkeit der Linienintensität von der Menge der Erdalkalien bei hohen Siliciumkonzentrationen und niedrigen Zusätzen war nach den bei der Untersuchung des Alkalieinflusses auf die Siliciumemission erhaltenen Ergebnissen zu erwarten. Ihre Ursache ist auch hier in der relativ hohen Natriumgrundkonzentration der Probelösungen zu suchen.

Die Ergebnisse der bisherigen Untersuchungen führen zu der Aussage, daß Zusätze von Alkalien und Erdalkalien bei Anwendung des Zerstäuberverfahrens und der Funkenanregung den Nachweis des Aluminiums und des Siliciums bei Wahrung bestimmter Konzentrationsverhältnisse entscheidend verbessern. Untersuchungen zur Reproduzierbarkeit zeigen, daß sich die gemessenen Effekte eindeutig aus den Meßwertschwankungen hervorheben. Die aus 20 Aufnahmen an verschiedenen Lösungssystemen ermittelten Standardabweichungen der ΔY-Werte für Konzentrationen bei 0,1 mg/ml liegen zwischen 0,02 und 0.06. Berücksichtigt man, daß jeder Meßpunkt aus drei spektrographischen Aufnahment gewonnen wird, so reduzieren sich diese Werte nach[21] noch um den Faktor $1/\sqrt{3}$. Die dargestellten Abhängigkeiten können demnach als gesichert betrachtet werden, da die gemessenen Intensitätsänderungen wesentlich größer sind als die Streuung der ΔY-Werte. Dieses Ergebnis ist auf die nachfolgend beschriebenen Untersuchungen zum Einfluß erhöhter Säurekonzentrationen auf den Nachweis des Aluminiums und des Siliciums übertragbar.

Einfluß der Säurekonzentration auf die Linienintensität

Da viele metallurgische Produkte nur durch Anwendung von Säuren in Lösung zu bringen sind, war es wichtig, den Einfluß der Acidität auf die Intensität der Analysenlinien zu untersuchen.

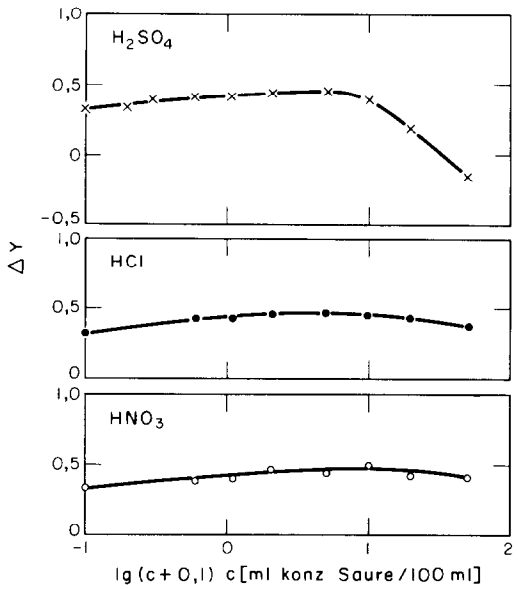

Abb. 3. Einfluß von Säurezusätzen auf die Intensität der Linie Al I 3082,16 Å (Al: 0,1 mg/ml).

Um die Abhängigkeit der Emission der Linien Al I 3082,16 Å und Si I 2516,12 Å von der Salz-, Salpeter- und Schwefelsäurekonzentration zu überprüfen, wurden salzsauren Aluminiumlösungen (pH 3–4) mit 0,1 mg Al/ml und Siliciumlösungen mit 0,1 mg Si/ml (pH 12) steigende Mengen (0 bis 50 ml pro 100 ml) der konzentrierten Säuren zugesetzt.

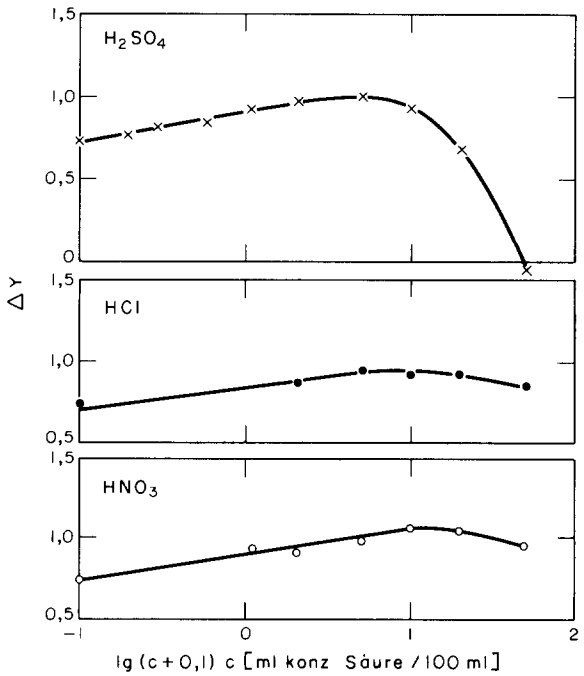

Abb. 4. Einfluß von Säurezusätzen auf die Intensität der Linie Si I 2516,12 Å (Si: 0,1 mg/ml).

Die an spektrographischen Dreifachaufnahmen dieser Lösungen gefundenen Meßergebnisse zeigen die Abb. 3 und 4.

UNTERSUCHUNGEN ZUR DEUTUNG DER MESSERGEBNISSE

Der Prozeß, den eine Probelösung vom Ansaugen durch den Zerstäuber bis zur Lichtemission der Elemente durchläuft, wird gewöhnlich in drei miteinander verknüpfte Vorgänge eingeteilt, nämlich: (1) Bildung des Aerosols und dessen Einbringung in die Entladungszone (Zerstäubung), (2) Bildung eines atomaren Dampfes einschließlich Dissoziation von Molekülen und Ionisation von Atomen (Verdampfung), (3) Lichtemission der Elemente (Anregung).

Diese drei Phasen finden bei der Verwendung indirekter Zerstäuber, also auch bei den von uns durchgeführten Untersuchungen, teilweise örtlich voneinander getrennt statt. Während die Zerstäubung, wenn man von dem Transportvorgang absieht, auf die Zerstäuberglocke beschränkt bleibt und die Anregung ausschließlich in der Entladungszone des Funkens stattfindet, beginnt die Verdampfung, zumindest die des Lösungsmittels, bereits bei der Entstehung des Aerosols und endet mit dem Eintritt bzw. mit dem Durchgang der Partikel in bzw. durch das Plasma. Alle drei Prozesse können einzeln oder in Kombination Ausgangspunkt für die von uns festgestellten Effekte sein.

Es ist bekannt, daß erhöhte Salz- oder Säurekonzentrationen die physikalischen Eigenschaften einer Lösung verändern können. Die Folge davon wäre ein verändertes Zerstäubungsverhalten der Flüssigkeit. Diese Erscheinung beeinflußt jedoch die Verdampfung der Probe und damit die Anregung des zu bestimmenden Elementes. Andererseits ist es möglich, daß die im Überschuß zugesetzten Elemente den Ionisations- und Anregungsmechanismus im Funkenplasma beeinflussen und damit zu veränderten Linienintensitäten für Aluminium und Silicium führen. Aus diesen Gründen war es zur Klärung des Sachverhaltes notwendig, die Wirkung der Zusätze auf die einzelnen Phasen des Verfahrensganges zu untersuchen.

Einflüsse von Salzzusätzen

Die Oberflächenspannung (α), die Dichte (d_f) und die Viskosität (η) der Lösung haben auf die Entstehung des Aerosols einen entscheidenden Einfluß. Um von ihrer Änderung mit dem Salzzusatz Kenntnis zu erhalten, wurde für die untersuchten Lösungen d_f durch Spindeln, α über die kapillare Steighöhe und η an einem Höppler-Viskosimeter gemessen. Die maximalen Fehler dieser Meßmethoden lagen unter $\pm 1\%$ des Sollwertes. Die ermittelten Werte zeigen, daß die Oberflächenspannung, die Dichte und die Viskosität der Lösungen von den gewählten Salzzusätzen praktisch nicht beeinflußt werden. Lediglich Zusätze von 10 mg/ml führen gelegentlich zu eindeutig meßbaren Erhöhungen der Werte, die jedoch 10% kaum übersteigen und, wie nachfolgende Untersuchungen bestätigen, zu gering sind, um Änderungen im Zerstäubungsvorgang hervorzurufen.

Die gewählte Sprüheinrichtung (Abb. 1) gestattet es, bei Vorgabe eines bestimmten Volumens über eine Zeitmessung die Zerstäubungsgeschwindigkeit (v) zu bestimmen. Dabei zeigt sich, daß für die von uns gewählten Salzarten und Konzentrationsbereiche v unabhängig vom Zusatz ist.

Dieses Ergebnis findet sich auch theoretisch bestätigt. Aus der Geometrie des Ansaugrohres und aus den für die Lösungen ermittelten physikalischen Größen lassen sich die

entsprechenden den Strömungsvorgang charakterisierenden Reynold'sschen Kennzahlen berechnen. Es ergeben sich für alle Lösungen Werte unter 500, die auf einen laminaren Strömungsvorgang und damit auf die Gültigkeit des Hagen–Poiseuill'eschen Gesetzes schließen lassen. In diesem Falle ist für die von uns gewählte Versuchsanordnung die Zerstäubungsgeschwindigkeit nur von der Viskosität abhängig, deren Konstanz die oben genannten Ergebnisse bestätigen.

Unabhängig von der Zerstäubungsgeschwindigkeit könnten erhöhte Salzkonzentrationen einen Einfluß auf die Ausbildung des Aerosols an der Zerstäuberdüse haben. Unter Annahme einer Gauß-Verteilung für die Tropfengröße ist der mittlere Tropfendurchmesser D_0 das entscheidende Charakteristikum für das entstandene Aerosol. Diese Größe ist mitbestimmend dafür, mit welcher Geschwindigkeit die Probelösung verdampft und im Funkenplasma angeregt wird. Sie steht somit in einer direkten Beziehung zur Intensität der Spektrallinien. Die theoretische Ableitung einer Beziehung zur exakten Berechnung des mittleren Tropfendurchmessers unter Berücksichtigung der Geräteparameter und der physikalischen Daten der Lösung ist auf Grund der vielen teilweise nur qualitativ bekannten Einflußfaktoren kaum möglich. Aus diesem Grunde bemüht man sich häufig,[22–26] die Tropfenverteilung des Aerosols auf experimentellem Wege zu bestimmen. Die sich hieraus ergebenden empirischen Beziehungen entsprechen einer Funktion

$$D_0 = f(\alpha, \eta, d_f, v, v_l, w_l)$$

in der außer den bereits bekannten Größen noch der Luftverbrauch $v_l(\mathrm{cm}^3/\mathrm{s})$ und die Geschwingigkeit der Luft in der Austrittsöffnung der Düse $w_l(\mathrm{cm/s})$ auftreten. Da bei unseren Untersuchungen w_l und v_l konstant gehalten werden und sich für α, η, d_f und v keine nennenswerten Änderungen ergeben, muß zwangsläufig auch der Tropfendurchmesser D_0 des an der Düse entstehenden Primäraerosols für die gewählten Konzentrationsbereiche unabhängig von der Art und der Höhe des Salzzusatzes bleiben. Da bei der gewählten indirekten Zerstäubung die Bedingungen der Tropfenselektion durch die Konstruktion des Zerstäubergefäßes festgelegt sind, gilt dies im gleichen Maße für die Lösungsmenge, die pro Zeiteinheit über die durchbohrte Elektrode als feiner Nebel in das Funkenplasma eintritt. Diese Größe wird in den nachfolgenden Betrachtungen als Durchsatz $v_d(\mathrm{cm}^3/\mathrm{s})$ bezeichnet. Konstant bleibt unter diesen Bedingungen auch der Wirkungsgrad (κ) des Zerstäubers, der durch die Beziehung

$$\kappa = \frac{v_d \cdot 100}{v} = \frac{v - v_r}{v} \cdot 100(\%) \tag{1}$$

definiert ist. Die hierzu nötige Konstanz der Rücklaufgeschwindigkeit $v_r(\mathrm{cm}^3/\mathrm{s})$ findet sich experimentell durch eine einfache Volumenmessung bestätigt.

Die Ergebnisse zeigen, daß die Ursachen für die bei Salzzusätzen festgestellten Intensitätserhöhungen der Atomlinien des Aluminiums und des Siliciums nicht im Zerstäubungsvorgang liegen, sondern vielmehr in Einflüssen der Zusätze auf den Entladungscharakter des Funkens zu suchen sind.

Elemente mit niedrigen Ionisationsenergien wie Kalium oder Natrium wirken in Plasmen als spektroskopische Puffer. Sie ändern den Charakter der Entladung und erhöhen die Intensität der Atomlinien von solchen Elementen, die höhere Ionisationsenergien erfordern.

Dieser Effekt ergibt sich aus den nach bestimmten Gleichgewichtsbeziehungen verlaufenden Elementarvorgängen im Plasma,[27] die auch von Boumans[28–30] zur Deutung von

Matrixeffekten im Gleichstrombogen herangezogen werden. Mandelstam[31] findet die Gültigkeit dieser Gleichgewichte auch für Funkenentladungen bestätigt.

Um die am System Aluminium–Natrium gefundenen spektrographischen Meßergebnisse zu erklären, genügt es, einige vereinfachende Voraussetzungen zu treffen.[1] Unter diesen Bedingungen werden die Ionisationsgleichgewichte für alle am Funkenplasma beteiligten Elemente durch die Saha-Gleichung in der Form

$$p_e \cdot \frac{x_j}{1 - x_j} = A \cdot T^{5/2} \cdot \frac{z_{ij}}{Z_{aj}} \cdot e^{-BU_{ij}/T} \qquad (2)$$

beschrieben. In dieser Gleichung sind A und B Konstanten, in die nur physikalische Elementargrößen eingehen.[27] U_{ij} bezeichnet das Ionisierungspotential und Z_{ij} und Z_{aj} stellen die Zustandssummen des ionisierten bzw. des atomaren Zustandes dar.

Bedient man sich der von Krempl[32] als Temperaturfunktion angegebenen und für Reinplasmen gültigen Elektronendrucke (p_e) und berücksichtigt die Temperaturabhängigkeit der Zustandssummen,[33] so lassen sich unter Anwendung der Saha-Gleichung die Änderungen des Ionisationsgrades (x_j) mit der Temperatur (T) für die am Plasma beteiligten Elemente ermitteln (Abb. 5).

Die Kurven zeigen, daß die Elemente in Reinplasmen entsprechend ihren Ionisierungspotentialen U_{ij} (Na: 5,09 V; Al: 5,98 V bzw. C: 11,24 V) bei recht unterschiedlichen Temperaturen ionisiert werden. Dieser Vorgang beginnt bei Natrium bereits unterhalb von 5000 K und ergibt bei 12000 K praktisch 100%ige Ionisierung. Entsprechend höhere Werte zeigt Aluminium mit 6000 K bzw. 15000 K. Kohlenstoff beginnt erst oberhalb 8000 K eine merkliche Ionisation zu zeigen.

Ein reines Aluminiumplasma hat[32] bei einer Temperatur von 12000 K einen Elektronendruck von 0,45 atm und einen Ionisationsgrad von 92,3% (Abb. 5). Setzt man der Probelösung unter sonst gleichen Bedingungen Natrium zu, so wird dieses Element auf Grund seines niedrigen Ionisierungspotentials entscheidend zum Elektronendruck beitragen. Bei einem Verhältnis Na:Al = 100:1 kann man von einem reinen Natriumplasma sprechen. In diesem Fall ergeben sich gleiche Plasmabedingungen, d.h. ein Elektronendruck von

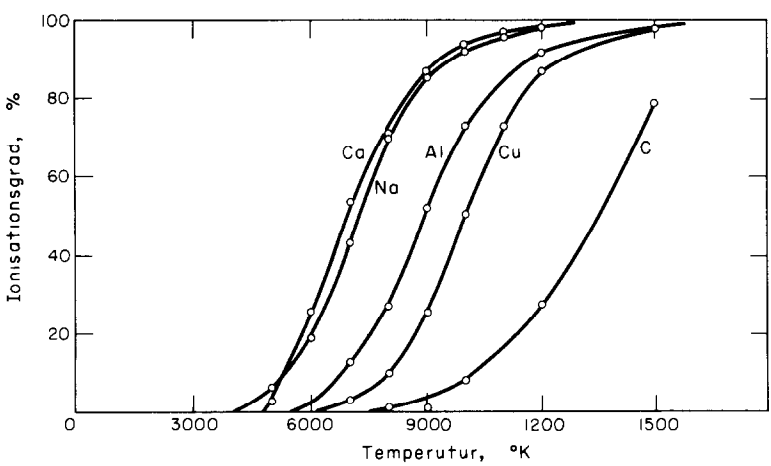

Abb. 5. Änderung des Ionisationsgrades der Elemente Aluminium, Natrium, Calcium, Kupfer und Kohlenstoff mit der Temperatur des Funkens.

0,45 atm, bereits für Temperaturen von 8000 K, bei denen 70,1% des Natriums ionisiert vorliegen. Dabei vermindert sich aber der Ionisationsgrad des Aluminiums auf 27,2%. Daraus geht hervor, daß der Anteil der für die Intensität der Atomlinie Al I 3082,16 Å maßgeblichen neutralen Aluminiumatome (n_0) von 7,7% auf 72,8% der insgesamt vorgelegten Aluminiumatome angestiegen ist. Da die Anzahl der angeregten Partikel (n_a) ein Maß für die Linienintensität ist, erklärt sich die experimentell festgestellte Nachweisverbesserung bereits aus der Boltzmann-Gleichung

$$n_a = n_0 \cdot \frac{g_a}{g_0} \cdot e^{-E_a/kT} \tag{3}$$

durch die direkte Proportionalität zwischen n_a und n_0. Eine Abschätzung an unserem Modellsystem Aluminium–Natrium nach (3) ergibt eine Erhöhung der Zahl der angeregten Teilchen um etwa 40%, obwohl die bei Natriumzusatz sinkenden Temperaturen diesem Effekt entgegen wirken.

Auf die gleiche Weise erklärt sich die nachweisverbessernde Wirkung, die Calcium-, Magnesium- oder Kaliumsalze auf das Aluminium haben. Dabei ist zu berücksichtigen, daß sich dieser spektroskopische Puffereffekt bei Erdalkalien nicht aus den Ionisierungspotentialen (6,11 V für Ca bzw. 7,64 V für Mg) sondern aus dem hohen Verhältnis der Zustandssummen ergibt, das nicht wie bei Aluminium unter 0,2 liegt sondern immer $> 1{,}0$ ist.

Auf völlig analoge Weise erklären sich die an Siliciumlösungen gemessenen Effekte. Auf Grund des hohen Ionisierungspotentials von 8,15 V müßte die Nachweisverbesserung für Silicium noch deutlicher hervortreten. Dieser Effekt wird jedoch durch die hohe Natriumgrundkonzentration der Siliciumlösungen verwischt.

Nach diesen Ergebnissen dürften Zusatzelemente mit Ionisierungspotentialen über 7,5 V bei Zustandssummenverhältnissen unter 1,0 keinen Einfluß auf die Intensität der Aluminiumlinie haben. Spektrographische Untersuchungen an Aluminiumlösungen, denen Bor, Selen, Kupfer, Eisen, Nickel und Gallium in steigenden Mengen zugesetzt sind, bestätigen diese Annahme. Eisen, Kupfer, Nickel, Bor und Selen ändern die Intensität der Linie Al I 3082,16 Å nicht. Die Ursache hierfür liegt in den entsprechenden Ionisationsgraden. Die Funktionen $x(T)$ dieser Elemente—Abb. 5 zeigt dies am Beispiel des Kupfers—sind gegenüber der entsprechenden Aluminiumkurve zu höheren Temperaturen verschoben. Das Aluminium bleibt bei solchen Zusätzen Hauptlieferant für die Elektronen des Plasmas, seine Atom- und Ionenkonzentrationen ändern sich nicht. Diese Elemente sind somit als spektroskopische Puffer nicht geeignet.

Geringfügige Erhöhungen der ΔY-Werte für Zusätze von 10 mg/ml, wie sie sich bei Kupfer, Nickel und Eisen andeuten, ergeben sich daraus, daß der große Überschuß eines Elementes mit niedrigem Ionisierungsgrad eine, wenn auch prozentual sehr niedrige, Anzahl von Elektronen abgibt, die bei einem kleinen Aluminiumgehalt (0,1 mg/ml) bereits intensitätssteigernd auf die gemessene Atomlinie wirken kann.

Auch Gallium führt bei Gehalten über 1 mg/ml zu einem Intensitätsanstieg der Linie Al I 3082,16 Å. Das Verhalten von Gallium im Funkenplasma wird bei einem Ionisierungspotential von 6,00 V und bei einem Verhältnis der Zustandssummen von 0,189 bei 6000 K nach (2) durch eine Funktion $x(T)$ charakterisiert, die mit der des Aluminiums weitgehend übereinstimmt. Demnach kann keine Pufferwirkung vorliegen; der Intensitätsanstieg erweist sich als ein Verdünnungseffekt. Die zur Aufrechterhaltung des Plasmas nötige Elektronenkonzentration wird bei steigender Galliumkonzentration in zunehmendem Maße

durch die Ionisation dieses Elementes geliefert. Damit erhöht sich zwangsläufig die Atomkonzentration des Aluminiums und als Folge davon die Intensität der Linie Al I 3082,16 Å.

Einflüsse der Säurekonzentrationen

Betrachtet man die in den Abb. 3 und 4 dargestellten Meßergebnisse hinsichtlich ihrer Ursachen, so kann nach den vorangegangenen Darlegungen eine spektroskopische Pufferwirkung von vornherein ausgeschlossen werden. Die säurebildenden Elemente Wasserstoff, Sauerstoff, Stickstoff und Chlor liegen bei der gewählten Versuchsanordnung bereits bei Lösungen ohne Zusatz in reichlichem Überschuß vor. Außerdem erfordern sie einschließlich des Schwefels Ionisationsenergien, die zwischen 10,36 eV und 14,54 eV liegen und nicht geeignet sind, die Ionisationsgleichgewichte für Aluminium und Silicium zu verschieben.

Es ist demnach naheliegend die Ursachen für die gemessenen Intensitätsänderungen im Zerstäubungsvorgang zu suchen. Im Gegensatz zu Salzzusätzen führt eine Zugabe von Säuren zu recht entscheidenden Änderungen der physikalischen Eigenschaften der Probelösungen. Dies gilt für Aluminium- und Siliciumlösungen im gleichen Maße und wird am Beispiel von Schwefelsäurezusätzen (Abb. 6) besonders deutlich. Die Dichte und die Viskosität zeigen einen steilen Anstieg. Bei einer Zugabe von 50 ml Säure/100 ml Lösung erhöhen sich die Werte um den Faktor 1,5 bzw. 5,5. Die Änderung der Oberflächenspannung ist demgegenüber gering. Schwefelsäurekonzentrationen über 2 ml Säure/100 ml führen zu einem leichten Anstieg.

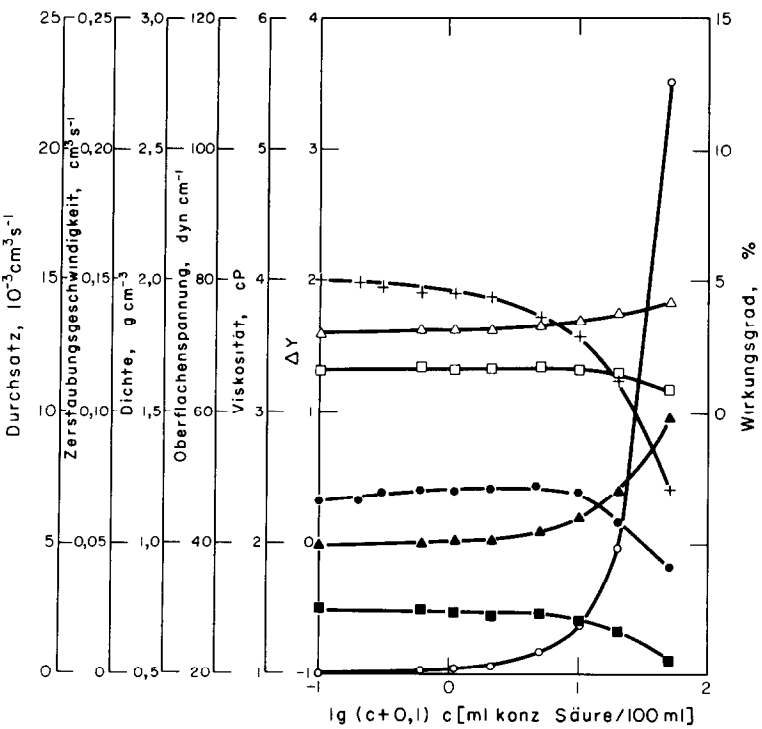

Abb. 6. Physikalische Eigenschaften, Zerstäuberdaten und Intensität der Linie Al I 3082,16 Å von Lösungen mit 0,1 mg Al/ml und mit steigenden Schwefelsäurekonzentrationen.

Um den Einfluß von Säurezusätzen auf den Zerstäubungsvorgang zu überprüfen, wurden an den Aluminiumlösungen mit Schwefelsäurezusatz die Durchsätze (v_d), die Zerstäubungsgeschwindigkeiten (v) und die Wirkungsgrade (κ) nach (1) bestimmt. Die Ergebnisse sind in Abb. 6 den zugehörigen ΔY-Werten gegenüber gestellt. Auch sie bestätigen die Gültigkeit des Hagen–Poiseuille'schen Gesetzes für den Lösungstransport, d.h. die pro Zeiteinheit angesaugte Lösungsmenge (v) sinkt mit der ansteigenden Viskosität steil ab, so daß bei einer Konzentration von 50 ml Schwefelsäure/100 ml die Zerstäubungsgeschwindigkeit nur noch weniger als 50%—verglichen mit der Lösung ohne Zusatz—beträgt.

Gleichzeitig führt die ansteigende Oberflächenspannung zu einer Vergrößerung des mittleren Tropfendurchmessers und damit zu einem Absinken des Wirkungsgrades. Eine Verstärkung dieses Effektes ergibt sich noch dadurch, daß die stets unmittelbar an der Zerstäuberdüse einsetzende Verdampfung der Tropfen bei hohen Schwefelsäurekonzentrationen eingeschränkt wird.

Diese Erscheinungen führen gemeinsam dazu, daß der Durchsatz und damit die Zahl der pro Zeiteinheit in die Funkenentladung gebrachten Aluminiumatome auf etwa 25% ihres ursprünglichen Wertes absinken. Diese Tatsache erklärt die verminderte Intensität der Linie Al I 3082,16 Å bei hohen Schwefelsäuregehalten in der Probelösung.

Da die physikalischen Eigenschaften der Lösungen durch die Art und die Höhe des Zusatzes bestimmt werden erklärt sich die Intensitätsabnahme der Linie Si I 2516,12 Å (Abb. 4) auf völlig analoge Weise. Das schwächere Absinken der ΔY-Werte bei Zusätzen von Salz- und Salpetersäure ergibt sich aus einem geringeren Viskositätsanstieg.

Ein Anstieg der Linienintensität, wie er für Säurezusätze bis zu 5 bzw. 10 ml/100 ml für Aluminium ebenso wie für Silicium auftritt (Abb. 3 und 4), kann seine Ursache nicht in den physikalischen Eigenschaften der Lösungen haben, da diese für geringe Zusätze konstant bleiben, und sich somit auch keine Änderungen im Zerstäubungsvorgang ergeben.

Der Grund für die auftretende Nachweisverbesserung ist offensichtlich in chemischen Vorgängen zu suchen, die in der Lösung stattfinden. So verschieben sich z.B. die chemischen Gleichgewichtsbedingungen in Siliciumlösungen, denen steigende Säuremengen zugesetzt werden, zugunsten des kolloidal gelösten Siliciumdioxids. Rechnet man die angewendeten Zusätze (Abb. 4) in Normalitäten um, so zeigt sich, daß bei 1,5–2,0N übereinstimmend für alle Säuren eine maximale Intensität der Linie Si I 2516,12 Å erreicht wird. Oberhalb dieser Konzentration werden die Intensitäten bereits durch die veränderten physikalischen Eigenschaften der Lösungen bestimmt.

Im spektroskopischen Sinne kann dieser Intensitätsanstieg demnach als Anioneneffekt gedeutet werden, d.h. Silicium als Siliciumdioxid in Gegenwart eines Natriumsalzes läßt sich in einem Hochspannungsfunken besser zur Lichtemission anregen als Silicium in silicatischer Bindung. Ein zwingender Beweis hierfür ist jedoch nur über einen quantitativen Vergleich der energetischen Bedingungen möglich.

Für die Intensitätserhöhungen, die bei Säurezusatz zu Aluminiumlösungen in einem geringeren Maße auftreten, ist die Erklärung in ähnlichen Ursachen zu suchen, daß nämlich Verschiebungen in den Ionenkonzentrationen zur Anreicherung von leicht verdampfbaren, leicht dissoziierbaren und damit anregungsgünstigen Aluminiumverbindungen führen.

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GAS-CHROMATOGRAPHIC SEPARATION OF AROMATIC AMINES, NITRILES AND HYDROCARBONS—I

SABRI M. FARROHA and SAMIR S. EMEISH

College of Science, University of Baghdad, Iraq

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Summary—A mixture of mono- and di-substituted nitriles was separated on six different liquid phases, but a mixture of mono- and di-substituted anilines was separated on only two liquid phases. The forces influencing the separation and elution order of these solutes are discussed. The absence of selective interactions between aromatic hydrocarbons and the various liquid phases was proved thermodynamically. An *ortho* methyl substituent increases the log of the specific retention volumes of the nitrile solutes by an approximately constant amount.

Gas-chromatographic separations of aliphatic nitriles have been reported by many workers.[1,2] The behaviour of tolunitriles was studied on different liquid phases.[3,4] A quantitative study of the dimerization of nitriles and the consequent effect on gas-chromatographic solute–solvent interactions have been reported.[5,6]

The behaviour of aromatic amines was studied by James,[7] and others have reported resolution of substituted aromatic amines on various liquid phases.[8,9] Aromatic hydrocarbons have been extensively studied and several liquid phases found to be selective (*e.g.*, the tetrahalophthalate esters).[10,11] Janák and Hřivnáč have explained several cases of aromatic selectivity in terms of π-interactions.[12]

In the present work, the factors influencing the elution characteristics and resolution of mixtures of aromatic hydrocarbon, aniline and aromatic nitriles are discussed.

EXPERIMENTAL

Apparatus

The bulk of the experimental work was performed with a Beckman GC-45 gas chromatograph equipped with a thermal-conductivity detector. An optimum nitrogen flow-rate of 25 ml/min at NTP was used. A current of 125 mA and an attenuation of 8 was found suitable for the best experimental peak shape and height. Columns, from Perkin-Elmer, were made in coils of stainless-steel tubing (2 m long and 3 mm o.d). The composition of the liquid phases and the packing specifications of the columns are shown in Table 1.

Materials

Table 2 summarizes some of the physical properties of the materials studied, which were obtained from Fluka AG (aromatic hydrocarbons and aromatic nitriles) and Hopkin and Williams Ltd. (aromatic amines).

Sampling

Mixtures of equal weights of each of the aromatic hydrocarbons, nitriles and amines were blended in 3-ml cylindrical Pyrex glass cells. Samples ranging from 0·5 to 0·7 μl for the aromatic amines and nitriles and 0·2 μl from the aromatic hydrocarbons were injected with a 1-μl Hamilton syringe.

Calculation of results

The specific retention volumes V_g^0 were calculated by the method of Littlewood *et al.*[13] and are given in Table 3. Plots of log V_g^0 vs. $1/T$ were generally linear. No difference was noticed in the retention time of the components whether they were injected individually or in a blend, and the results were reproducible.

Table 1. Specifications of liquid phases

Liquid phase	% w/w	Weight of phase g
1,2,3,-Tris(2-cyano-ethoxy)-propane on Chromosorb W AM-DMCS (TCEP)	8	0·2
Carbowax 6000 + sodium dodecylbenzene sulphonate on Chromosorb P (CDBS)	25	1·61
Benzidine on Chromosorb W	10	0·25
Poly(propylene glycol) (LB-550-x) on Chromosorb W (PPG)	15	0·37
Dinonyl phthalate on Chromosorb W (DNP)	10	0·25
Di-n-decyl phthalate on Chromosorb P (DPH)	15	0 72
Tritelyl phosphate on Chromosorb W (TTP)	10	0·25
Silicone oil MS 550 on Chromosorb W (SO)	10	0·25
Silicone gum rubber E_3O_1 on Chromosorb G AW-DMCS	2·5	0 107
Apiezon L + Bentone 34 on Chromosorb W (APL-34)	20	0·48

The activity coeffecient of the solute in the solvent at infinite dilution, γ^0, was calculated[18–20] from the equation

$$\gamma^0 = \frac{1{\cdot}7027 \times 10^7}{MP_2^0 V_g^0} \tag{1}$$

where M is the molecular weight of the liquid phase and P_2^0 is the vapour pressure of the solute

The excess partial molar free energy $\Delta\bar{G}_e^0$, enthalpy $\Delta\bar{H}_e^0$, and entropy $\Delta\bar{S}_e^0$, of mixing at infinite dilution were calculated from the equations.

$$\Delta G^0 = RT \ln \gamma^0 \tag{2}$$

$$\ln \gamma_1 - \ln \gamma_2 = \frac{\Delta H^0}{R}\left(\frac{T_2 - T_1}{T_1 T_2}\right) \tag{3}$$

and

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \tag{4}$$

Table 2. Physical properties*

Compound	B.p., C	Dipole moment calc., Debrye	n_D^{40}	Electron polarizability, $cm^3 \times 10^{25}$
Benzene	80·1	0·00	$1{\cdot}50112^{20}$	1 5265
Toluene	110·6	0·37	$1{\cdot}49693^{20}$	1·5170
m-Xylene	139 1	0·37	$1{\cdot}49772^{20}$	1·5186
Mesitylene	164·7	0 00	$1{\cdot}49937^{20}$	1·5222
Benzonitrile	190·7	4·39	1·5189	1·5657
o-Tolunitrile	204·0	4·22	1·5191	1 5665
m-Tolunitrile	214 0	4·59	1 5196	1·5674
p-Tolunitrile	217·0	4 76	1·5212	1 5709
2,5-Dimethylbenzonitrile	104/18 mmHg	4·39	1·5255	1·5804
2,4-Dimethylbenzonitrile	112/12 mmHg	4 41	1·5211	1 5705
2,3-Dimethylbenzonitrile	112/25 mmHg	4 43	1·5178	1·5634
Aniline	184·4	1·48	1 5863	1 7084
o-Toluidine	199·8	1·34	1 5776	1 6787
o-Chloroaniline	209·0	1·71	1·5895	1 7151
m-Chloroaniline	230·0	2·75	1 5942	1 7246
p-Chloroaniline	231·0	3·17		
6-Chloro-2-methylaniline	215·0	1·77	1·5679	1 6707
5-Chloro-2-methylaniline	237 0	3·24	1·5759	1·6874
4-Chloro-2-methylaniline	241 0	3 37	1·5755	1·6866

* The physical properties were collected from different sources.[13,14,15] The dipole moments were calculated according to Smyth[16] and n_D^{40} values were measured at this laboratory

Table 3. Specific retention volume V_g^0 (ml/g) of solutes on the liquid phases studied

Solutes	TCEP				PPG			DNP			APL + 34				TTP		
	(80)	(90)	(100)	(110)	(80)	(90)	(100)	(80)	(90)	(100)	(80)	(90)	(100)	(110)	(90)	(100)	(110)
Benzene	48	43	40	32	51	39	34	57	47	40	32	28	23	19	77	63	50
Toluene	74	58	54	42	103	73	61	119	91	76	67	52	41	30	115	101	75
m-Xylene	111	87	76	56	210	146	114	256	190	150	147	110	81	59	204	176	124
Mesitylene	155	130	108	78	438	290	220	572	407	309	341	242	173	116	396	365	211
	(110)	(120)	(130)	(140)	(100)	(110)	(120)	(100)	(110)	(120)	(130)	(100)	(110)	(120)	(100)	(110)	(120)
Benzonitrile	652	439	2998	142	476	332	223	657	425	294	205	265	1713	114	403	261	184
o-Tolunitrile	775	508	348	163	726	499	325	1100	692	461	314	434	274	181	629	386	270
m-Tolunitrile	960	628	431	195	897	608	396	1410	880	572	390	484	303	195	868	535	356
p-Tolunitrile	1171	758	506	226	1012	676	436	1580	981	636	429	564	348	288	868	535	356
2,5-Dimethyl-benzonitrile	1171	758	506	226	1388	420	583	2348	1420	902	595	834	509	318	1359	808	503
2,4-Dimethyl-benzonitrile	1356	869	581	252	1577	1034	649	2629	1586	1007	656	1209	705	437	1359	808	504
2,3-Dimethyl-benzonitrile	1592	1016	672	294	1799	1169	735	2983	1781	1125	704	1084	651	409	1635	945	602
	(120)	(130)	(140)		(110)	(120)	(130)	(100)	(120)	(130)		(140)	(150)	(160)		(100)	(110)	(120)
Aniline	835	531	237		624	398	275	451	301	208		118	82	62		453	311	209
o-Toluidine	1042	655	289		906	597	396	823	524	362		175	119	85		792	510	332
o-Chloroaniline	1317	838	257		1619	989	645	1295	818	538		241	165	117		1409	858	540
6-Chloro-2-methylaniline	1472	929	399		2384	1828	841	2247	1307	861		283	206	148		2126	1244	774
m-Chloroaniline	3675	2223	920		3703	2155	1342	2884	1713	1100		561	348	238		3799	2139	1253
p-Chloroaniline	3675	2223	920		3921	2274	1411	2884	1713	1100		632	384	255		3799	2139	1253
5-Chloro-2-methylaniline	4657	2787	1135		5288	3043	1903	5124	2978	1866		966	480	319		6239	3320	1732
4-Chloro-2-methylaniline	4657	2787	1135		5573	3225	1977	5124	2978	1866		920	572	377		6239	3320	1732

DISCUSSION

Resolution of the mixture of aromatic nitriles was achieved on six out of the ten liquid phases used; these phases were Benzidine, TCEP, CDES, PPG, DNP and APL-34, and the order of the peaks was benzonitrile, *o*-, *m*-, *p*-tolunitriles, 2,5-, 2,4- and 2,3-dimethylbenzonitriles (except that 2,3-DBN emerges before 2,4-DBN from APL-34). The elution order

Table 3. *continued*

Solutes	Benzidine			SO			SGR			CDBS			DPH		
	(110)	(120)	(80)	(90)	(100)	(80)	(90)	(100)	(90)	(100)	(110)	(80)	(90)	(100)
Benzene	20	18	45	35	26	48	44	40	14	11	9	49	44	35
Toluene	27	22	63	53	44	69	61	54	22	18	14	89	74	56
m-Xylene	35	29	118	88	79	124	102	80	40	31	23	182	144	104
Mesitylene	51	40	235	158	132	231	163	134	72	56	39	385	280	194
	(110)	(120)	(130)	(100)	(110)	(80)	(90)	(100)	(120)	(130)	(140)	(100)	(110)	
Benzonitrile	592	396	278	220	141	244	187	135	127	93	67	232	156	
o-Tolunitrile	803	534	366	351	208	435	306	219	163	116	83	385	246	
m-Tolunitrile	1078	701	475	439	274	557	391	270	195	140	98	529	328	
p-Tolunitrile	1268	888	550	457	274	557	391	270	220	155	110	529	328	
2,5-Dimethyl-benzonitrile	1423	916	604	703	405	904	628	438	250	177	124	927	579	
2,4-Dimethyl benzonitrile	1754	1110	726	755	423	991	662	455	285	201	139	927	579	
2,3-Dimethyl-benzonitrile	2022	1277	828	869	498	1096	730	522	322	230	159	927	579	
		(110)		(90)	(100)	(110)	(80)	(90)	(100)					
Aniline		618		255	202	125	244	187	135					
o-Toluidine		867		448	351	208	435	306	236					
o-Chloroaniline		1058		650	509	290	609	408	303					
6-Chloro-2-methylaniline		1413		1142	852	506	1044	696	489					
m-Chloroaniline		2896		1212	940	506	1044	696	489					
p-Chloroaniline		3038		1212	940	506	1113	764	522					
5-Chloro-2-methylaniline		4642		1774	1669	871	1948	1257	859					
4-Chloro-2-methylaniline		4642		2239	1686	871	1948	1257	859					

of these solutes is in accord with the order of their increasing dipole moments. While the elution order of the tolunitriles agrees with the increasing order of their vapour pressure and electron polarizability, the elution order of the dimethylbenzonitriles is the reverse of their order of both volatility and electron polarizability.

The mixture of anilines was separated on only two liquid phases (PPG and APL-34), in the elution order: aniline, *o*-toluidine, *o*-chloroaniline, 6-chloro-2-methylaniline, *m*-chloroaniline, *p*-chloroaniline, 5-chloro-2-methylaniline and 4-chloro-2-methylaniline. The components are eluted in order of decreasing vapour pressure and increasing dipole moment.

Theoretically, nitriles would be expected to have longer retention times than anilines,[21–23] but the results obtained showed the contrary. The anilines have higher V_g^0 values than nitriles or any liquid phase, and the difference in V_g^0 values between anilines and nitriles is greatest on PPG and lowest on SGR. The vapour pressure of the anilines and the nitriles cannot be considered as contributing to the observed results, because benzonitrile (b.p. 190·7°) was eluted before aniline (b.p. 184·4°) and *o*-tolunitrile (b.p. 204°) emerged before *o*-toluidine (b.p. 199·8°). However, the results are explicable in terms of hydrogen-bonding between the aromatic amines and nitriles and the liquid phases. The effect of hydrogen-bonding is predominent on PPG but is unimportant on SGR, so the difference in V_g^0 values for amines and nitriles is large on PPG and small on SGR. Thus, the aniline and benzonitrile have the same V_g^0 value on SGR; *o*-toluidine and *o*-tolunitrile also have identical V_g^0 values.

The factor dominating the order of elution of the aromatic hydrocarbons is the vapour pressure. These solutes are preferentially retarded on TTP and DNP but this is not due to π-interactions for the following reasons. The liquid phases CDBS, benzidine and DPH contain aromatic rings but the specific retention volumes on CDBS are lower than those obtained on any other liquid phase and lower on benzidine than on APL-34. If π-interactions were involved, the excess partial molar enthalpies of solution would be negative, but on TTP or DNP (see Table 5) positive enthalpies of solution were obtained. It has been pointed out by Littlewood[24] that π-interactions are not involved in the solution of atomatic hydrocarbons in DNP, TTP, TCEP or BDP. Furthermore, Maczek and Phillips[25] have shown that the order of elution of benzene and n-octene is the same on all these liquid phases.

Thermodynamics of solution

The excess partial molar thermodynamic quantities for the aromatic hydrocarbons and some anilines (*o*-toluidine and *o*-, *m*- and *p*-chloroanilines) have been calculated. It is to be noted that these quantities are susceptible to many uncertainties[26–29] but they are useful for purposes of comparison.

The vapour pressures of the solutes were calculated by using the Antoine equation and are listed in Table 4. The activity coefficients for the solute at infinite dilution in DNP, PPG and TTP were calculated by using equation (3) and are tabulated in Table 5. The activity coefficient in different solvents and at any temperature increases as the number of methyl groups increases, thus: mesitylene > *m*-xylene > toluene > benzene.

o-Toluidine has a higher γ^0 value than the chloroanilines in all solvents and at all temperatures. The higher γ^0 and $\Delta\bar{G}_s^0$ values of the anilines in TTP and DNP compared with those in PPG are due to the increased π-electron density in the ring systems in the first two liquid phases.[26]

Table 4. Vapour pressures and activity coefficients at various temperatures

	Temp., °C	Aromatic hydrocarbon				Temp., °C	Monosubstituted anilines			
		Benzene	Toluene	*m*-Xylene	Mesitylene		*o*-Toluidine	*o*-Chloroaniline	*m*-Chloroaniline	*p*-Chloroaniline
Vapour pressure, *mmHg*	80	757·7	291·2	114·2	45·1	110	42·2	33·3	14·8	12·2
	90	1021·0	407·7	164·6	68·4	120	63·1	50·1	23·8	19·6
	100	1350·5	556·3	223·6	101·0	130	91·5	76·2	36·2	31·5
Activity coefficient γ_2^0 (on DNP)	80	0·948	1·173	1·391	1·578	110	1·171	0·943	0·953	1·156
	90	0·849	1·101	1·212	1·461	120	1·229	0·993	0·998	1·211
	100	0·746	0·975	1·212	1·305	130	1·229	0·988	1·027	1·173
Activity coefficient γ_2^0 (on PPG)	80	0·796	1·037	1·288	1·567	110	0·810	0·574	0·565	0·647
	90	0·784	1·041	1·286	1·559	120	0·822	0·625	0·604	0·694
	100	0·678	0·908	1·212	1·394	130	0·861	0·630	0·637	0·696
Activity coefficient γ_2^0 (on TTP)	80	0·592	0·990	1·376	1·743	110	2·146	1·617	1·549	1·790
	90	0·543	0·824	1·172	1·253	120	2·208	1·707	1·550	1·882

Table 5. Thermodynamic data for aromatic hydrocarbons, and monosubstituted anilines on different phases

	ΔG_c^{-0}, cal/mole						$\Delta \bar{H}_c^{-0}$, kcal/mole		$\Delta \bar{S}_c^{-0}$ cal . mole^{-1} deg^{-1}	
	80°	90°	100°	110°	120°	130°	90°	120	90°	120
					on DNP					
Benzene	−37	−118	−217				2·81		8 15	
Toluene	112	69	−19				1·61		4 3	
m-Xylene	221	188	142				1 76		4·3	
Mesitylene	320	273	197				1·96		4 7	
o-Toluidine				120	161	165		−1 45		−4·1
o-Chloroaniline				−45	−6	−10		−1·54		−3 9
m-Chloroaniline				−37	−2	3		−1·38		−3 5
p-Chloroaniline				110	140	128		−1·39		−3 9
					on PPG					
Benzene	−160	−175	−288				0·39		1·5	
Toluene	26	29	−72				−0·10		−0 3	
m-Xylene	177	182	142				0·03		0 6	
Mesitylene	315	320	246				0·13		0·6	
o-Toluidine				−160	−153	−120		−0·44		−0 7
o-Chloroaniline				−422	−367	−370		−2·56		−5·6
m-Chloroaniline				−434	−393	−361		−2·00		−4 1
p-Chloroaniline				−331	−284	−290		−2·14		−4·7
					on TTP					
Benzene		−378	−452				2·10		7·0	
Toluene		−7	−143				4·67		12 9	
m-Xylene		230	118				4·08		10 6	
Mesitylene		400	167				8·40		22 0	
o-Toluidine				591	618			−0·85		−3·7
o-Chloroaniline				365	417			−1·62		−5 2
m-Chloroaniline				287	342			−1 81		−5 5
p-Chloroaniline				423	493			−1·50		−5 0

The excess partial molar free energies, enthalpies and entropies of mixing are given in Table 5. The enthalpy of mixing of the aromatic hydrocarbons in any solvent is always positive, implying the absence of selective interactions, while it is always negative when anilines are involved, which results from the strong specific solute–solvent interaction.

The effect of an o- or m-methyl substituent on retention volume

The effect of a substituent in an aromatic ring on the specific retention volume is a reflection of the solution properties involved in gas chromatography. The effect of a methyl group *ortho* to a nitrile or an amine group is demonstrated by comparing the logarithms of the specific retention volumes of the nitriles and anilines. The pairs used were:

Benzonitrile	*o*-Tolunitrile
m-Tolunitrile	2,5-Dimethylbenzonitrile
p-Tolunitrile	2,4-Dimethylbenzonitrile
Aniline	*o*-Toluidine
o-Chloroaniline	6-Chloro-2-methylaniline
m-Chloroaniline	5-Chloro-2-methylaniline
p-Chloroaniline	4-Chloro-2-methylaniline

The results show that there is always an increase in the specific retention volume of the component with an *o*-methyl group. The differences in the logarithms of the specific retention volumes of the pairs of solutes are listed in Table 6.

Table 6.

Liquid phase	T. °C	a	b	c	d	e	f	g
DNP	100	0·224	0·221	0·221				
	110	0·211	0·208	0·208	0·269	0·239	0·150	0·150
	120	0·196	0·197	0·199	0·242	0·204	0·240	0·240
	130	0·186	0·184	0 190	0·240	0·204	0·269	0·269
PPG	100	0·185	0·189	0·193				
	110	0 176	0·177	0·185	0·162	0·168	0·155	0·153
	120	0·163	0·169	0·173	0·176	0·267	0·150	0·152
	130				0·159	0 293	0·152	0·146
SGR	80	0·252	0·211	0·251	0·252	0·234	0·271	0·243
	90	0·214	0·206	0·229	0·204	0·233	0·256	0·216
	100	0·211	0·211	0·227	0·243	0·207	0·245	0·216
SO	90				0·245	0·245	0·265	0·267
	100	0 204	0·204	0·219	0·240	0·223	0·249	0·254
	110	0·167	0·170	0·189	0·222	0·251	0·236	0·236
TTP	100	0·194	0·195	0·195	0·243	0·179	0·215	0·215
	110	0·169	0·179	0·179	0·215	0·161	0·191	0·191
	120	0·166	0·150	0·228	0·201	0·156	0·142	0 142
TCEP	100	0·075	0·086	0·064				
	120	0·063	0·081	0·060	0·096	0·048	0·103	0·103
	130	0·070	0·069	0·060	0·091	0·045	0·098	0·098
	140	0·060	0·065	0·048	0·088	0·048	0·091	0·091
	150				0·081	0·048	0·087	0·087
Apiezon L + B	100	0·215	0·236	0·330				
	110	0·204	0·225	0·307				
	120	0·199	0·213	0·181				
	130	0·176	0·201	0·159				
	140				0·170	0·071	0·135	0·163
	150				0·160	0·096	0·140	0·173
	160				0·133	0·103	0·127	0·168
Benzidine	110	0·133	0·121	0·141				
	120	0·131	0·116	0·097				
	130	0·120	0·104	0·121				
CDBS	120	0·106	0·109	0·113				
	130	0·098	0·104	0·111				
	140	0·089	0·102	0 102				

(*a*) = log V_g^0 (*o*-tolunitrile) − log V_g^0 (benzonitrile).
(*b*) = log V_g^0 (2,5-DBN) − log V_g^0 (*m*-tolunitrile).
(*c*) = log V_g^0 (2,4-DBN) − log V_g^0 (*p*-tolunitrile).
(*d*) = log V_g^0 (*o*-tolunitrile) − log V_g^0 (aniline).
(*e*) = log V_g^0 (6-chloro-2-methylaniline) − log V_g^0 (*o*-chloroaniline)
(*f*) = log V_g^0 (5-chloro-2-methylaniline) − log V_g^0 (*m*-chloroaniline).
(*g*) = log V_g^0 (4-chloro-2-methylaniline) − log V_g^0 (*p*-chloroaniline).

The increase in the logarithm of the specific retention volume of a solute containing a cyano group when a methyl group is substituted in the *ortho* position is approximately constant. It has been suggested that the nitrile group does not suffer from steric interferences because of its cylindrical shape, and the same constancy is not shown by the differences in the specific retention volumes of the analogous aniline pairs.

In Table 7, the minimum and maximum difference values of columns *a*, *b* and *c* at the temperatures of experiment on each liquid phase are quoted. The lowest minimum differ-

Table 7.

Liquid phase	Temp. range, °C	Minimum difference value	Maximum difference value
DNP	100–130	0·184	0·224
PPG	100–120	0·163	0 193
SGR	80–100	0 206	0·252
SO	90–110	0·167	0·219
Apiezon L + B	100–130	0·159	0·330
TTP	100–120	0·150	0·228
CDBS	120–140	0·089	0·109
Benzidine	110–130	0·097	0·141
TCEP	110–140	0·048	0·086

ence value is 0·048 obtained on TCEP in the temperature range 110–140° and the highest maximum difference value is 0·330 obtained on Apiezon L + Bentone 34 in the temperature range 100–130°.

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CHROMATOGRAPHIC BEHAVIOUR OF 48 CATIONS ON STANNIC AND TITANIUM ARSENATE PAPERS IN AQUEOUS NITRIC ACID SYSTEMS

MOHSIN QURESHI and S. D. SHARMA

Chemistry Section, Z. H. College of Engineering & Technology, Aligarh Muslim University, Aligarh, U.P., India

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Summary—The chromatographic behaviour of 48 metal ions on titanium arsenate, stannic arsenate and Whatman No. 1 papers in 10^{-5} 3*M* nitric acid has been studied along with the effect of pH on R_M.

An outstanding feature of chromatography on papers impregnated with inorganic ion-exchangers is the possibility of interesting separations with the help of simple aqueous solvents. Of these, nitric and perchloric acid are especially attractive because their complex-forming ability is very slight and hence they can be used to study the mechanism of separations. However, few studies with such systems have been reported.[1–5] A systematic study on titanium arsenate papers was reported recently by Qureshi and co-workers. They found that the selectivity sequence for cations on titanium arsenate papers is not the same as that on titanium arsenate columns and they defined a new quantity R_i ($R_i = R_f$ on untreated papers minus R_f on treated papers) which they proposed as a measure of the ion-exchange effect.

The present study is a continuation of the work by Qureshi, Rawat and Sharma,[6] and covers the chromatographic behaviour of 48 metal ions on papers impregnated with stannic arsenate. Results for titanium arsenate and Whatman No. 1 papers are included for comparison, and a number of interesting separations have been developed.

EXPERIMENTAL

Apparatus

Chromatography was performed on 15 × 3·5 cm Whatman No. 1 paper strips in 20 × 5 cm glass jars.

Preparation of ion-exchange papers

Whatman No 1 paper strips were impregnated in 0·1*M* stannic chloride for 3–5 sec, the excess of reagent being removed by placing the strips on filter-paper sheets, and were then allowed to dry for 15 min at room temperature The strips were then dipped in 0·25*M* sodium arsenate solution for 15 sec. The excess of solution was drained off and the strips were placed on a filter sheet. These strips were dried at room temperature and then washed with distilled water thrice in order to remove the excess of reagents. Finally they were dried at room temperature and used for chromatography

Procedure

Test solution (1 or 2 spots) prepared as described previously,[6–8] was placed on the paper with a thin glass capillary. The paper was then conditioned for 15 min and then dipped in solvent until the solvent ascent was 11 cm. The front (R_L) and rear (R_T) R_f values of the spots were measured. Sn^{2+} was detected with phosphomolybdic acid solution and the other ions as reported previously.[6]

Table 1 Separation of cations on stannic arsenate papers, as predicted by R_f values (all take 30 min)

Metal ion separated (R_T–R_L)	Solvent	Ions that interfere
Sn^{2+} (0·00–0·20)	0·1*M* HNO_3	Al^{3+}, Cr^{3+}, Ni^{2+}, Cu^{2+}, Y^{3+}, Zr^{4+}, Nb^{5+}, Ru^{3+}, In^{3+}, Sb^{3+}, Ce^{3+}, Hf^{4+}, Pb^{2+}, Th^{4+}, UO_2^{2+}, Ti^{4+}, Sm^{3+}, Nd^{3+}, Bi^{3+}
Bi^{3+}(0·00–0·20)	0·1*M* HNO_3	Al^{3+}, Cr^{3+}, Fe^{3+}, Ni^{2+}, Cu^{2+}, Y^{3+}, Zr^{4+}, Nb^{5+}, Ru^{3+}, Ag^{+}, In^{3+}, Sb^{3+}, Ce^{3+}, Ce^{4+}, Hf^{4+}, Pb^{2+}, Th^{4+}, UO_2^{2+}, Ti^{4+}, Sm^{3+}, Nd^{3+}, Sn^{2+}
Ti^{4+}(0·00–0·16)	0·1*M* HNO_3	Al^{3+}, Cr^{3+}, Fe^{3+}, Cu^{2+}, Zr^{4+}, Nb^{5+}, Ru^{3+}, Ag^{+}, Sb^{3+}, In^{3+}, Sn^{2+}, Ce^{3+}, Ce^{4+}, Hf^{4+}, Pb^{2+}, Bi^{3+}, Th^{4+}, UO_2^{2+}
Mo^{6+}(0·82–0·98)	0·01*M* HNO_3	Mg^{2+}, Ga^{3+}, Se^{4+}, Nb^{5+}, Cs^{+}, Pt^{4+}, W^{6+}, Au^{3+}
Ga^{3+}(0·66–0·98)	0·001*M* HNO_3	K^{+}, Nb^{5+}, Mo^{6+}, Se^{4+}, Cs^{+}, Rb^{+}, Ir^{3+}, Pt^{4+}, Hg^{2+}, W^{6+}, Au^{3+}
Se^{4+}(0·80–1·00)	0·001*M* HNO_3	K^{+}, Ga^{3+}, Nb^{5+}, Mo^{6+}, Cs^{+}, Ir^{3+}, W^{6+}, Pt^{4+}
Pt^{4+}(0·72–0·98)	0·01*M* HNO_3	K^{+}, Mg^{2+}, Ga^{3+}, Se^{4+}, Rb^{+}, Nb^{5+}, Mo^{6+}, Cs^{+}, Ir^{3+}, W^{6+}, Au^{3+}
W^{6+}(0·88–1·00)	0·001*M* HNO_3	K^{+}, Se^{4+}, Nb^{5+}, Mo^{6+}, Cs^{+}, Ir^{3+}, Pt^{4+}, Ga^{3+}
Sb^{3+}, Zr^{4+} or Hf^{4+} (0·00–0·18)	3*M* HNO_3	Fe^{3+}, Nb^{5+}, Mo^{6+}, Ag^{+}, Ce^{4+}, Th^{4+}, W^{6+}, Ti^{4+}

Table 2. Separations achieved experimentally on stannic arsenate papers (30 min)

Solvent	Separations achieved (R_T R_L)
0·00001*M* HNO_3	UO_2^{2+}(0·00–0·24)– Mo^{6+}(0·60–0·96)
0·001*M* HNO_3	Tl^{+}(0·06–0·26)—Ga^{3+}(0·66–0·90) Ir^{3+}(0·00–0·20)– Ga^{3+}(0·66–0·90) Fe^{3+}(0·00–0·22)—Mo^{6+}(0·81 1·00) VO^{2+}(0·00–0·22) Mo^{6+}(0·82–1·00)
0·01*M* HNO_3	Cr^{3+}(0·00–0·24)– Mo^{6+}(0·78·1·00) Y^{3+}(0·00–0·28)—Ga^{3+}(0·72 0·97) Al^{3+}(0·00–0·22)–Ga^{3+}(0·74 1·00)
0·1*M* HNO_3	UO_2^{2+}(0·00–0·48)– VO^{2+}(0·60–0·78) Bi^{3+}(0·00 0·16)—Tl^{+}(0·56–0·78) Sn^{2+}(0·00–0·22)—Cd^{2+}(0·66–0·88) Th^{4+}(0·00–0·40) La^{3+}(0·70–0·88) Zr^{4+}(0·00–0·08)–W^{6+}(0·81–1·00) Th^{4+}(0·00–0·40)—W^{6+}(0·80 0·98) Ag^{+}(0·00 0·22)—Pt^{4+}(0·80 0·98)
1·0*M* HNO_3	Fe^{3+}(0·00–0·58)– Cr^{3+}(0·88–1·00)
2*M* HNO_3	Ag^{+}(0·00–0·30)– Cu^{2+}(0·70–0·94)
3*M* HNO_3	Sb^{3+}(0·00–0·16)– Pb^{2+}(0·68–0·94) Sb^{3+}(0·00–0·14)– Sn^{2+}(0·67–0·85)

RESULTS

In many cases it was found possible to separate one cation from numerous metal ions. These separations are summarized in Table 1. The ions investigated were Ag^{+}, Al^{3+}, Au^{3+}, Ba^{2+}, Be^{2+}, Bi^{3+}, Cs^{+}, Ca^{2+}, Cd^{2+}, Co^{2+}, Cu^{2+}, Ce^{3+}, Cr^{3+}, Ce^{4+}, Fe^{2+}, Fe^{3+}, Ga^{3+}, Hg^{2+}, Hf^{4+}, In^{3+}, Ir^{3+}, K^{+}, La^{3+}, Mg^{2+}, Mn^{2+}, Mo^{6+}, Ni^{2+}, Nd^{3+}, Nb^{5+}, Pb^{2+}, Pr^{3+}, Pt^{4+}, Rb^{+}, Ru^{3+}, Sn^{2+}, Sr^{2+}, Sb^{3+}, Sm^{3+}, Se^{4+}, Tl^{+}, Th^{4+}, Ti^{4+}, UO_2^{2+}, VO^{2+}, W^{6+}, Y^{3+}, Zn^{2+} and Zr^{4+}.

DISCUSSION

The results reveal certain interesting points. Thus for almost all cations the R_f values are lower on treated than untreated papers. This may be due to (1) ion-exchange (2) precipitation (3) adsorption. As shown in Fig. 1 the difference in R_f values on untreated and treated papers (R_i) generally increases with increase in pH and becomes maximum at pH 2, the steep rise being between pH 1 and 2. This shows that pH 2 is the most favourable acidity for ion-exchange. However, R_i is maximum at pH 0 for Zr^{4+}, Hf^{4+}, Sb^{3+} and Bi^{3+}, and at pH 1 for Th^{4+}. Excessive hydrolysis of Sb^{3+} and Bi^{3+} in acidic solution or the formation of insoluble arsenates of Zr^{4+}, Hf^{4+} or Th^{4+} may be the reason for this abnormal behaviour.

Exceptions are Au^{3+}, Sb^{3+}, Ce^{3+}, Ce^{4+}, Pb^{2+}, Pt^{4+}, Pr^{3+}, Nd^{3+} and Sm^{3+}, for which the R_f values are nearly the same on both papers, but at pH > 2 Ce^{3+} and Ce^{4+} tail extensively, and Pr^{3+}, Nd^{3+} and Sm^{3+} are almost completely adsorbed on titanium arsenate papers. The similar behaviour of Au^{3+} and Pt^{4+} on all three papers is probably because they are present as anionic complexes which are not sorbed significantly. Ag^{+} has a low

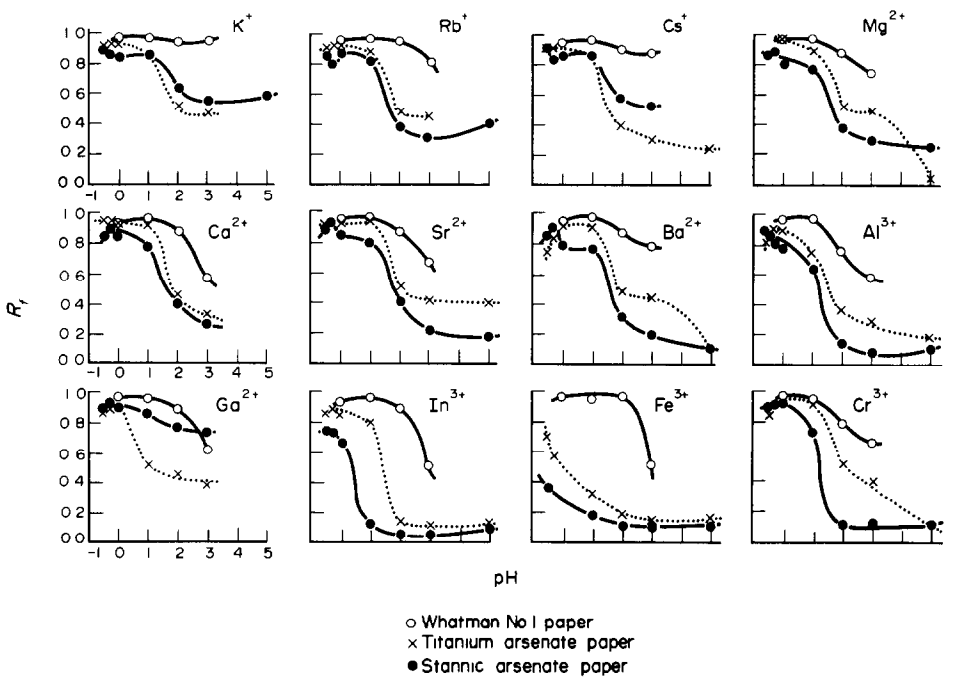

Fig. 1a Plots of R_f *vs.* pH —○— Whatman No. 1 paper; -- × -- titanium arsenate paper; —●— stannic arsenate paper.

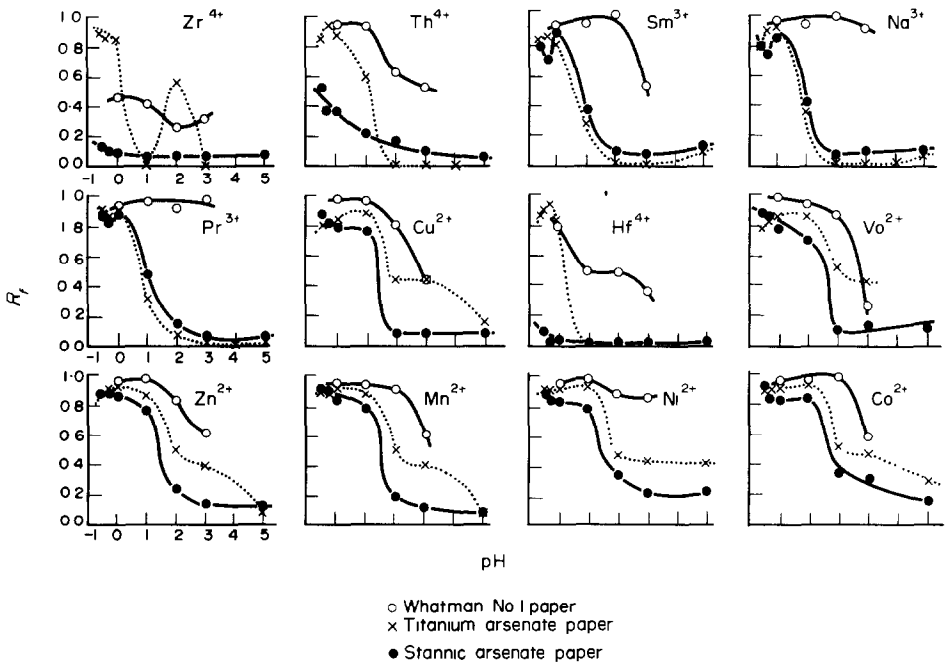

Fig. 1b. Plots of R_f *vs.* pH —○— Whatman No. 1 paper, -- × -- titanium arsenate paper; —●— stannic arsenate paper

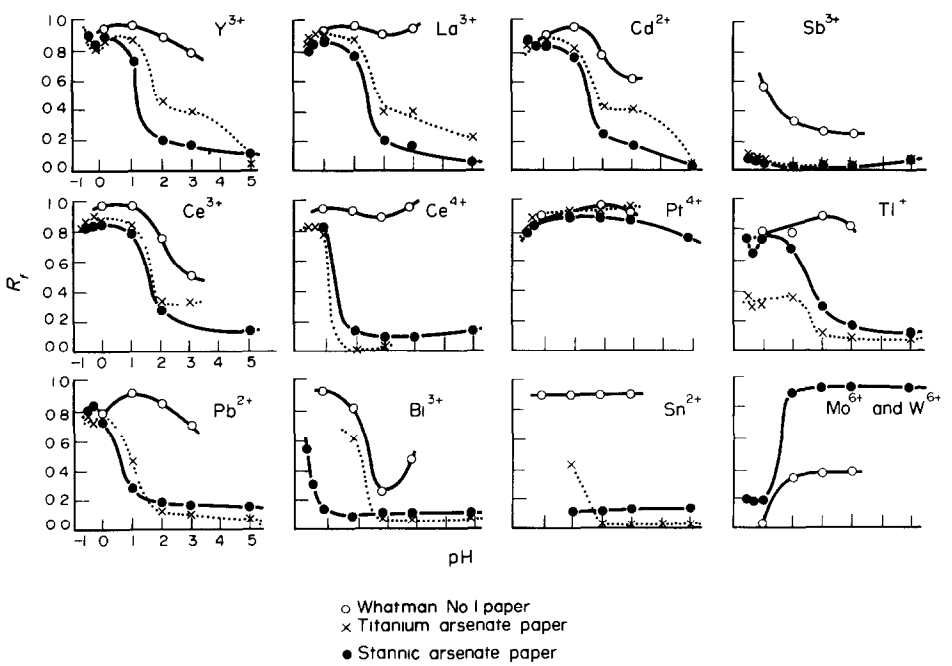

Fig. 1c. Plots of R_f *vs* pH. —○— Whatman No. 1 paper, -- × -- titanium arsenate paper, —●— stannic arsenate paper.

R_f value owing to its interaction with the exchanger. It has been shown by Murray *et al.*[9] that cations are preferably exchanged when the gel has a negative surface charge, but Ag^+ is considerably exchanged even when the gel has a positive charge. This has been explained by them on the assumption that the adsorption of Ag^+ is due to Ag^+–matrix interaction. Stannic arsenate is highly selective for Fe^{3+} and even at low pH the R_f of Fe^{3+} is not very high. Therefore Fe^{3+} can easily be separated from Al^{3+}, Cr^{3+} and Cu^{2+}. Sb^{3+} is known to be strongly adsorbed by cellulose and therefore it has very low R_f values on both the treated papers. Sn^{2+} has a high R_f value at pH 1 but at higher pH it is completely adsorbed on titanium arsenate papers, probably because of formation of a more stable tin arsenate. On stannic arsenate papers the R_f value of Sn^{2+} is the same over the whole pH range.

The plots for Mo^{6+} and W^{6+} are almost identical. For both the R_f value is low at pH 0, increasing rapidly at pH 1 and becoming constant for the pH range 1–5. In both cases, the R_f value on untreated paper is lower than on stannic arsenate paper.

At pH 0 the ion-exchange effect should be negligible and therefore the difference in R_f values on treated and untreated papers (R_i) at this pH should reflect the uptake of cations by a mechanism other than ion-exchange, *e.g.*, adsorption, precipitation *etc.* Because stannic arsenate is a weak ion-exchanger it will be only slightly ionized in the presence of 1*M* nitric acid. If we take the average R_i at pH 0 then some general conclusions can be drawn. For univalent cations it is 0·06, for bivalent 0·10, for tervalent 0·24 and for quadrivalent 0·48. It increases with charge and is approximately $= 0{\cdot}06 \times 2^{n-1}$ where n is the charge on the cation. Subtraction of R_i at pH 0 from R_i at any other pH will give a fair idea of the ion-exchange behaviour of the cation concerned on impregnated papers. Plots of ΔR_i *vs.* pH, almost all give a maximum at pH 2, confirming thereby that maximum ion-exchange occurs at this pH. Ions which hydrolyse extensively or form very insoluble arsenates show a negative ΔR_i, *e.g.*, Sb^{3+}, Bi^{3+}, Zr^{4+}, Hf^{4+} and Th^{4+}.

A plot of R_M *vs.* pH, where $R_M = \log (1/R_f - 1)$, gives straight lines for those ions which are sorbed by an ion-exchange mechanism. When the sorption is not by this mechanism a break results in the curves as in the case of Ag^+, Tl^+, VO^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Mn^{2+}, Pb^{2+}, Cr^{3+}, In^{3+}, Fe^{3+}, Al^{3+}, Sm^{3+}, Nd^{3+}, Pr^{3+}, Hf^{4+}, Zr^{4+}, Pt^{4+}, Mo^{6+}, W^{6+} and Ti^{4+}. For the initial straight lines obtained, the curves obey the equation $n\text{pH} = 6R_M +$ constant, where n is the charge on the cation.

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ZERO-CURRENT BIPOTENTIOMETRIC END-POINT INDICATION WITH PRETREATED ELECTRODES—II

OXIDIMETRIC TITRATION OF Fe(II) WITH USE OF GOLD ELECTRODES

L. KÉKEDY

Department of Analytical Chemistry, "Babeş-Bolyai" University, Str. Arany J.nr.11, Cluj, Romania

A. POPESCU

Faculty of Chemistry, University of Craiova, Calea Bucureşti nr 165, Craiova, Romania

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Summary—Experimental data are presented for zero-current bipotentiometric indication of the end-point in titration of Fe(II) with Ce(IV), Cr(VI) and/or Mn(VII), based on the use of two differently pretreated gold indicator electrodes.

Zero-current bipotentiometry is based on the measurement, during the course of a titration, of the potential difference between two indicator electrodes having different values for one or more of the following potential-controlling parameters: C (concentrations of the electroactive species at the electrode surface), i (current), a (electrode area), δ (thickness of the Nernst diffusion layer), α (electrochemical transfer coefficient) and k_s (heterogeneous rate constant of the electrochemical reaction). Techniques based on differences in C, i, A and δ are well known.[1] The possibility of exploiting differences in kinetic parameters (α, k_s), based on the use of a pair of differently pretreated electrodes, has been reported.[1] This new principle has been applied with good results to end-point indication in oxidimetric Fe(II) titrations, by use of two differently pretreated platinum electrodes (Part I of this series).[2] A qualitative interpretation of the different forms of titration curves has been also advanced.[1] A quantitative simulation is to be published.[3] The present paper deals with the same titration with the use of two differently pretreated gold electrodes. Although gold is the first in the thermodynamic nobility scale of the metals and the fourth in the practical one,[4] its electrochemical properties, similarly to those of platinum, depend to a great extent on its pretreatment and prehistory. No systematic studies on the analytical applications of pretreatment effects on gold have been reported.

EXPERIMENTAL

A conventional potentiometric titration assembly was used, consisting of a 50-ml tall-form beaker, a 10-ml semimicro burette, and a magnetic stirrer. Two identical rectangular gold foil electrodes were used, each 1 cm square. Before use the electrodes were treated according to one of the procedures indicated in Table 1. After each pretreatment the electrodes were thoroughly washed with doubly distilled water, placed directly in the titration vessel and connected to an MV 84 Type pH-meter (input impedance $> 10^{12}$ Ω). The potential difference between the electrodes was read directly. An auxiliary electrode (SCE) enabled us to follow separately the potential of each indicating electrode during the titration. The equivalence volumes were read from the bipotentiometric titration curves and for comparison, they were calculated from the potentiometric ones according to Hostetter and Roberts.[7] Unless otherwise stated a mixture of 5·00 ml of $10^{-2}M$ ferrous sulphate and 25·00 ml of $1N$

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Table 1. Pretreatment procedures used

	Pretreatment	Nature of the surface
1	Anodization in 1*N* H_2SO_4 at different potentials *vs.* SCE (indicated in text)	Oxidized
2	1*N* $K_2Cr_2O_7$ (in 1*N* H_2SO_4)*	Oxidized
3	1*N* $KMnO_4$ (in 1*N* H_2SO_4)*	Oxidized
4	30% H_2O_2*	Oxidized
5	Concentrated HNO_3*	Oxidized
6	*Aqua regia**	Bare
7	Cathodization in 1*N* H_2SO_4 at different potentials *vs.* SCE (indicated in text)	Reduced
8	1*N* $FeSO_4$ (in 1*N* H_2SO_4)*	Reduced
9	1*M* KCN*	Bare
10	1*M* Phenol*	Poisoned†
11	Oxidation with concentrated HNO_3 then dipping in concentrated HCl for a few sec	Bare
12	Ignition in the oxidative zone of a Teclu flame for a few sec	Mixed (*i.e.*, both oxidized and reduced sites)

* Dipping in for 2 min.

† Different modes of poisoning or inhibiting electrode processes are known.[5] Quantitative data concerning the effect of phenol (interface inhibitor) on Br_2 and I_2 evolution have been reported.[6]

sulphuric acid was titrated with $10^{-2}N$ Ce(IV), Cr(VI) or Mn(VII). Some experiments were run with more dilute Fe(II) solutions (10^{-3}, $10^{-4}M$). Analytical grade chemicals and doubly distilled water were used throughout.

RESULTS AND DISCUSSION

The 74 bipotentiometric titration curves obtained during this investigation could be classified according to their shape, in the following four categories.

Type I: conventional sigmoidal curves characterized by the existence of an inflexion point which coincided with the end-point (Fig. 1, curves *a–c*).

Analysis of the individual electrode potential data reveals that these forms appear when the potential variation of one of the electrodes during the titration is small, this electrode serving as a kind of reference electrode. Depending on the polarity of the electrodes the titration curves of this type have a normal (curve *a*, Fig. 1) or an inverse *S*-shape (curves *b* and *c*, Fig. 1).

Type II: some distorted forms (Z-form) of an S-shaped curve, usually composed of nearly linear parts (curves *d–f*, Fig. 1), without inflexion point. The equivalence point could be identified (known solutions being titrated) with one intersection point of the linear parts (see Fig. 1).

Type III: forms similar to the first derivative of a normal S-shaped potentiometric titration curve (Fig. 2, curves *a–c*), characterized by the maximum (or minimum) value of the potential difference between the indicator electrodes at the equivalence point. These forms appear when both electrodes exhibit approximately the same basic titration curve, but one curve (the potential of one electrode) lags behind the other. Depending on the sign of the lag the peak is oriented upwards (maximum) or downwards (minimum) respectively.

Type IV: forms similar to the second derivative of a normal S-shaped curve (curves *d–f*, Fig. 2) characterized by an approximately zero potential difference at the equivalence point. Nevertheless, it was sometimes observed that some peak values on the titration curves agreed better with the known equivalence volume than did the zero value of the

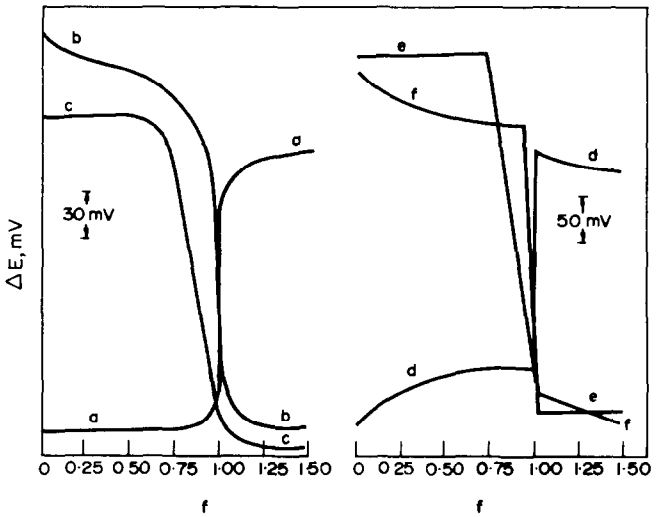

Fig. 1. Type I and II titration curves. The pretreatment procedures applied to the electrodes (electrode 1 and electrode 2 respectively) are indicated by the numbers in Table 1, and the titrant is given in parenthesis.
Type I: *a*—11 and 5 (Ce^{4+}); *b*—5 and 8 (MnO_4^-); *c*—8 and 2 ($Cr_2O_7^{2-}$). Type II: *d*—1 (+2000 mV) and 7 (−600 mV) (Ce^{4+}); *e*—5 and 11 (MnO_4^-); *f*—1 (+2000 mV) and 12 (MnO_4^-).

titration signal. From this point of view these type IV curves can be considered as distorted forms of type III curves. Type IV appears when one curve differs from the other with respect to both shape and lag,[3] including the possibility that the lag between the individual curves changes sign at the end-point.

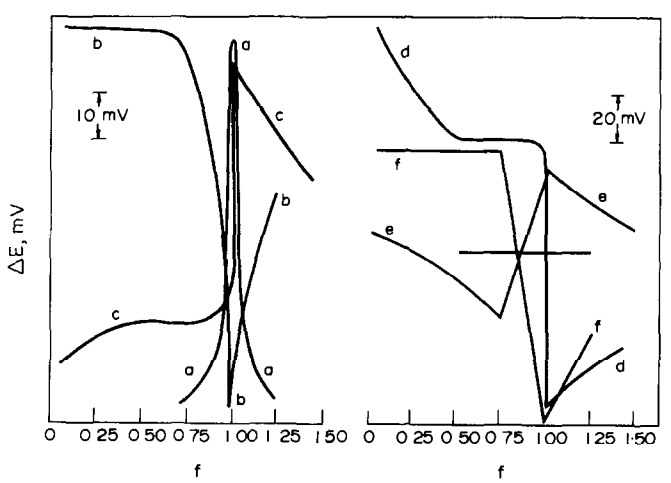

Fig. 2. Type III and IV titration curves. See legend to Fig. 1.
Type III: *a*—7 (−600 mV) and 1 (+1500 mV) ($Cr_2O_7^{2-}$); *b*—1 (+1500) and 7 (−600 mV) ($Cr_2O_7^{2-}$); *c*—11 and 1 (+1500 mV) (Ce^{4+}). Type IV: *d*—9 and 2 (Ce^{4+}); *e*—8 and 2 (MnO_4^-), *f*—10 and 12 ($Cr_2O_7^{2-}$).

The great variety of intermediate forms obtained is attributed to the fact that to some extent all the parameters which determine the shape of the individual potentiometric curves are operative. Bipotentiometric curves similar to types II and III have been obtained in constant-current bipotentiometry[8] (d.c. differential electrolytic potentiometry) as well as in a.c. bipotentiometry[9] (differential electrolytic potentiometry with periodic polarization). All these forms (types I–IV) reflect the effect of the surface state on electrode kinetics, being influenced not only by the oxidation state of the electrode metal but also by the nature and the amount of substances adsorbed. Therefore similar pretreatments (oxidative or reducing) yielded different titration curves depending on whether the pretreatment was chemical or electrochemical. Similarly, electrodes given the same pretreatment yielded different curves with different titrants. For instance an oxidized and a reduced electrode pair in most cases exhibited a type III curve when Fe(II) was being titrated with Ce(IV), but always a type I curve with permanganate or dichromate. When one electrode was poisoned, type II curves were always obtained when titrating with permanganate. In cerimetric titrations the curves were of type III (one electrode poisoned with phenol) or of type IV (one electrode treated with cyanide). In permanganate titrations no such selectivity could be observed. When one electrode was ignited type III curves were always obtained in titrations with dichromate, but when the electrode was bare, *i.e.*, free from both oxidized and reduced sites, second-derivative forms appeared. Also in these titrations a pair of chemically oxidized or reduced electrodes always exhibited S-shaped titration curves, but when the same oxidative or reductive pretreatments were performed electrochemically, well-formed type IV curves were obtained. All these results illustrate the effect of the adsorbed species on the form of the titration curves. At the same time this phenomenon is considered responsible for the poor reproducibility of the curve shapes. The details of this effect are still not well understood.

The potential break near the equivalence point was evaluated as ΔE between $f = 0{\cdot}90$ and $1{\cdot}10$ in the case of potentiometric curves and as ΔE between $f = 0{\cdot}75$ and $1{\cdot}00$ (f = de-

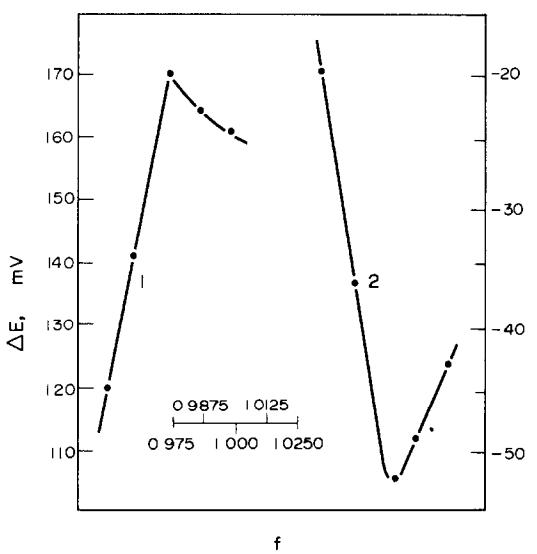

Fig 3. Expanded titration curves near the end-point. *1*—11 and 7 (+300 mV) (Ce^{4+}). *2*—1 (+1700 mV) and 7 (+600 mV) ($Cr_2O_7^{2-}$)

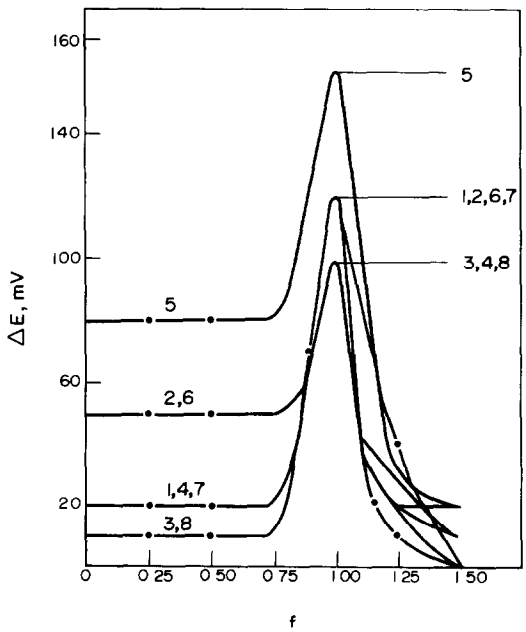

Fig. 4. Zero-current bipotentiometric titration curves of Fe(II) with Ce(IV). 8 replicate titrations (sequence indicated on the curves). The pretreatments (2 and 10, Table 1) repeated after each titration.

gree of titration) in the case of bipotentiometric ones. In the former case values between 530 and 100 mV were obtained, whereas in the latter the break showed variations between 20 and 490 mV. These data enable us to choose the most efficient pretreatment procedure. Details of the end-point region for two recommended titrations are shown in Fig. 3. The observed individual redox potential values, as well as the redox potential changes corresponding to a given degree of titration sometimes showed accentuated pretreatment effects. Taking only the redox potentials observed at $f = 0{\cdot}5$ (the system is well poised, the ratio $[Fe^{3+}]:[Fe^{2+}]$ is 1:1), values between 330 and 1020 mV (*vs.* SCE) were observed, depending on pretreatment and the titrant used. Nevertheless, the mean values observed during a great many titrations (different pretreatments, randomly taken) showed no significant differences dependant on the titrant used. For instance the mean value of the redox potentials at $f = 0{\cdot}5$ of 54 cerimetric titrations was 432·2 mV, whereas the same for 44 dichromate titrations was 431·2 mV. A similar effect was observed in other stages of the titrations. For example, for titration from $f = 0{\cdot}25$ to 0·50, one would predict a potential increase of 30 mV. Experimental values between 0 and 30 mV were observed. Sometimes, mainly when excessively oxidized electrodes were used, at the beginning of the titration a potential decrease could be observed, which was evidently due to the interaction between the reducing medium and the electrode surface. On this occasion it was observed that gold electrodes oxidized electrochemically at lower anodic potentials ($< 1{\cdot}36$ V *vs.* SCE) showed smaller potential fluctuations than those anodized at higher ones. All these phenomena need further investigation.

The reproducibility of the method and also the durability of the pretreatments have been investigated. The mean of all the potentiometric equivalence volumes obtained was 5·01 ml

(standard deviation $s = 0{\cdot}04_5$ ml, $n = 53$), that of the bipotentiometric ones (all pretreatment combinations used) being 5·00 ml ($s = 0{\cdot}02_8$ ml, $n = 27$). The corresponding values for titrations with permanganate were 5·02 ml potentiometric ($s = 0{\cdot}03_9$, $n = 46$); 4·99 ml bipotentiometric ($s = 0{\cdot}02_2$, $n = 25$); and with dichromate 5·01 ml potentiometric ($s = 0{\cdot}05_5$, $n = 25$); 4·98 bipotentiometric ($s = 0{\cdot}02_4$, $n = 22$). As expected, the bipotentiometric indication yielded a higher precision, the potential fluctuations being partially cancelled. It has already been mentioned that in some cases the equivalence points agreed better with some well-defined points on the titration curves other than those characteristic for the respective curve-form (see Figs. 1 and 2). In such cases these values were taken in the calculations. In order to test the reproducibility and the duration of a single pretreatment combination, an electrode oxidized with dichromate and one poisoned with phenol were used to follow the cerimetric Fe(II) titration. This combination in this case yielded type III titration curves, easy to interpret. At first the pretreatment was repeated after each titration (Fig. 4).

Inspection of the curves reveals that with repeated pretreatment the reproducibility is excellent as far as the form and the equivalence volumes are concerned. Only the height of the peaks showed some fluctuation. The same result was obtained with permanganate titrations (one electrode ignited, the other bare) as well as with titrations with dichromate (one electrode cathodized at −600 mV, the other anodized at +1500 mV, *vs.* SCE). When the same titration was repeated without renewing the pretreatment (the electrodes were only washed after each titration) the activity of the electrodes fell gradually, manifested in the decrease of the height of the peaks (Fig. 5). Nevetheless, the shape of the titration curves remained unchanged and so did the end-point. Consequently the pretreatment must be renewed every 2 or 3 titrations.

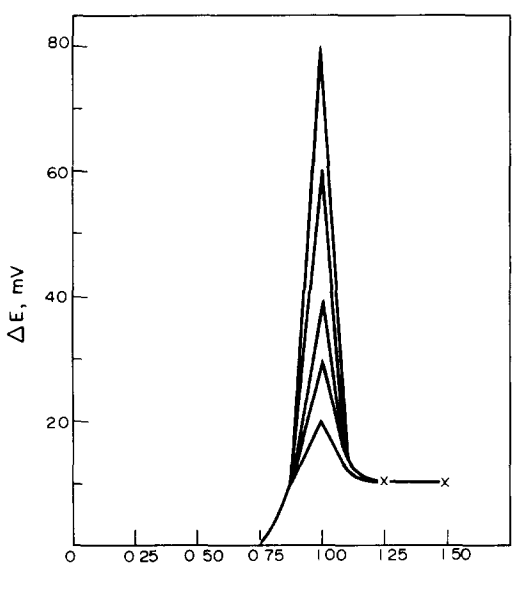

Fig. 5. Zero-current bipotentiometric titration curves of Fe(II) titration with dichromate. Replicate titrations without repeating the pretreatments (+1500 mV and −600 mV). Decreasing peak heights correspond to the succession of titrations.

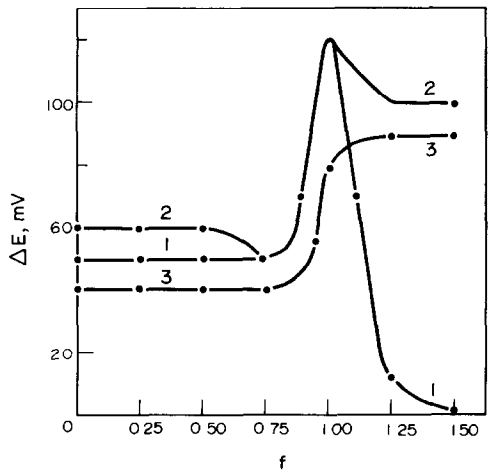

Fig. 6. Zero-current bipotentiometric titration curves of Fe(II) titrations with Ce(IV). Decreasing titrand concentrations: *1*—$10^{-2}M$, *2*—$10^{-3}M$; *3*—$10^{-4}M$. Conditions as in the case of Fig. 4.

Ferrous solutions of lower concentration were also titrated (Fig. 6). In this case also the shape of the titration curve varies markedly with dilution, especially the portion after the equivalence point. This is attributed to decrease in the charge-transfer rate and increase of the effects of adsorption conditions on the electrode process.

The variation of the shape of the titration curves with dilution was also observed in a.c. bipotentiometry.[9]

CONCLUSIONS

Zero-current bipotentiometry based on pretreatment effects can be performed with gold electrodes, and the end-point indication compares favourably with classical potentiometry in terms of accuracy and precision. Simplicity in realization and measurement (no reference electrode is needed) are the special advantages of the method. As little information is available on the effect of pretreatment on the response of the electrodes, the most suitable pretreatment combination at the present time must be found by trial and error. Solid electrodes being used, reproducibility is assured only by repeating the pretreatment procedure before each titration. Even in this case the memory effect sometimes causes fluctuations in response.

Criteria for selection are: appearance of well-formed titration curves with characteristic points making possible the unambiguous and exact location of the end-point, and easy practical realization and reproducibility. In the case of the present titrations only the peak-shaped first-derivative type curves gave acceptable results, the point of maximum (or minimum) potential indicating undoubtedly the end-point. S- or Z-shaped curves often yielded erroneous results. The favourable pretreatment procedure which should be applied to the electrodes differs depending on the titrant to be used. For titrations with Ce(IV), which is a reversible system, ignited electrodes proved useless in any electrode combination. Combination of an oxidized and a reduced, or a bare-metal and a reduced electrode is recommended. Other pretreatments were not suitable. For titrations with permanganate

or dichromate, where both systems are irreversible, the combination of one ignited electrode with one treated in some other way proved useful. If one of the electrodes was not ignited, no well-formed titration curve could be obtained.

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THE USE OF 5-(4-PYRIDYL)NONANE FOR THE SEPARATION OF CHROMIUM(VI) FROM FISSION PRODUCTS IN HYDROCHLORIC ACID MEDIA

M. IQBAL and M. EJAZ®

Nuclear Chemistry Division, Pakistan Institute of Nuclear Science & Technology, P.O. Nilore, Rawalpindi, Pakistan

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Summary—The distribution of chromium(VI) between 5-(4-pyridyl)nonane in benzene and hydrochloric acid media has been studied as a function of the concentration of the acid, extractant, chromium(VI), chloride and a few other ions. The extraction mechanism and the composition of the extracted complexes of Cr(VI) have been proposed. The separation of Cr(VI) from uranium, thorium and fission products in 3*M* hydrochloric acid has been achieved.

Stainless steel is commonly used in the construction of nuclear reactors as well as for the cladding of reactor fuel elements. A commonly encountered neutron-induced activity in stainless-steel corrosion products is that of chromium-51, the solvent extraction separation of which from reactor cooling-water or from fission products is generally desired. The solvent extraction of Cr(VI) with liquid anion-exchangers has been described by several authors.[1–5] This communication deals with the extraction of chromium(VI) with a new liquid anion-exchanger, a high molecular-weight substituted pyridine, 5-(4-pyridyl)nonane, from hydrochloric acid solutions. 5-(4-Pyridyl)nonane is a high-boiling liquid miscible with water-immiscible organic solvents and is suitable for solvent extraction application.

EXPERIMENTAL

Reagents

5-(4-Pyridyl)nonane (PyN) (K & K Labs. Inc., Plainview, N.Y.) was purified by vacuum distillation before use. It is a pale yellow oily liquid, b.p. 94°/0·8 mmHg, n_D^{20} 1·485, d^{20} 0·9208 g/cm^3. Its solubility in water is 1·2 g/l The purity of the reagent was checked by GLC on a 10% Carbowax 20M column at 220°, a single peak being obtained.

Mineral acid solutions were generally prepared from BDH volumetric solution ampoules and all other chemicals used were of analytical-reagent grade.

^{51}Cr tracer (as chromate) and the other tracers except where stated were obtained from Radiochemical Centre, Amersham. Sodium chromate was used in the experiments where the total concentration of Cr(VI) was raised to 0·05*M*. ^{233}U was purified by solvent extraction[6] before use (the concentration of uranium in the initial aqueous phases was $\sim 10^{-3}M$). ^{234}Th was isolated[7] from natural uranium. ^{99m}Tc was separated from its parent 66·6-hr ^{99}Mo by solvent extraction according to the method of Faddeeva *et al.*[8] ^{54}Cu, ^{198}Au and ^{99}Mo were obtained by neutron activation of the respective reagent grade salts, CuO, $AuCl_3$ and MoO_3 in the research reactor of the Pakistan Institute of Nuclear Science and Technology. The radioisotopes ^{60}Co, ^{59}Fe(III), ^{54}Mn, ^{63}Ni and ^{144}Ce in chloride form; ^{95}Nb and ^{95}Zr (freed from its daughter ^{95}Nb before use) in the form of oxalate complexes and ^{110m}Ag in nitric acid solution were pure enough to meet the catalogue specifications.

Radiochemical assay and instrumentation

For alpha assay an argon gas-flow proportional counter, Harwell type 3-7/11558, in conjunction with an EKCO fast scaler, type N530F, was used and also a Nuclear Chicago Corporation alpha scintillation counter Model DS-S Serial 1709 Solid beta-emitting samples were assayed with an end-window Geiger assembly

equipped with a G.E.C. tube type EHM 2/S. Gamma-ray count-rates were determined with a Nuclear Chicago single-channel analyser, model 872, coupled with a 3 × 3 in. NaI(Tl) well-type scintillation counter. Gamma spectra were taken with a Nuclear Data ND-4410 computer system 512-1024 multichannel analyser model 2560. The detector used with this analyser was a 4 × 3 in. NaI(Tl) crystal.

Measurement of distribution coefficients

Equal volumes of the aqueous and the organic phase (equilibrated previously with an aqueous solution of the same matrix composition as the solution from which chromium was to be extracted) were shaken together for 5 min, sufficient time for equilibration. To avoid errors due to loss of radioactive material, the material balance was checked, those experiments having a balance of less than 90% being repeated.

RESULTS AND DISCUSSION

Results obtained for extraction of trace and macro amounts of chromium(VI) from hydrochloric acid with 0·1*M* PyN in benzene are shown in Fig. 1. The higher extraction of macroamounts of Cr(VI) may be due to the preferential formation and extraction of condensed chromate ions.[9]

The influence of PyN concentration on the extraction of trace quantities of Cr(VI) from 0·25, 0·5 and 1*M* hydrochloric acid was investigated with benzene as diluent (Fig. 2). A linear relation between log $D_{Cr(VI)}$ and log [PyN] with slope of unity holds for 0·25*M* hydrochloric acid medium, which suggests that for traces of chromium the reaction sequence is

$$PyN + HCl \rightleftharpoons (PyNH)^+Cl^-$$

$$(PyNH)^+Cl^- + HCrO_4^- \rightleftharpoons (PyNH)^+HCrO_4^-$$

In the more concentrated acid systems (0·5 and 1*M*), the extraction coefficients for trace Cr(VI) are not readily interpretable. The *D* value starts decreasing at reagent concentration

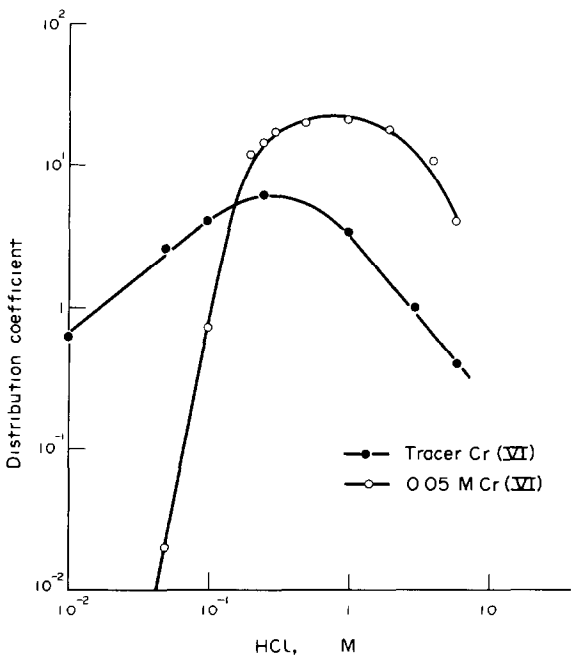

Fig. 1. Distribution of Cr(VI) between HCl and 0·1*M* PyN in benzene as a function of hydrochloric acid concentration.

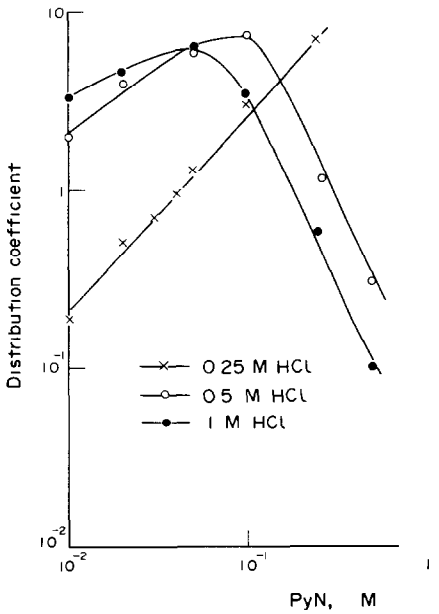

Fig. 2. Dependence of the trace Cr(VI) distribution ratio on the PyN concentration in the organic phase.

greater than 0·1*M*. This could be caused by aggregation of amine hydrochlorides, resulting in the monomer–micelle equilibrium involving intermediate stages (dimers, trimers and higher polymers)

$$PyNH^+ + Cl^- \rightleftharpoons PyNH^+.Cl^- \rightleftharpoons (PyNH^+.Cl^-)_2 \rightleftharpoons$$
$$(PyNH^+.Cl^-)_n \rightleftharpoons (PyNH^+Cl^-)_{micelle}$$

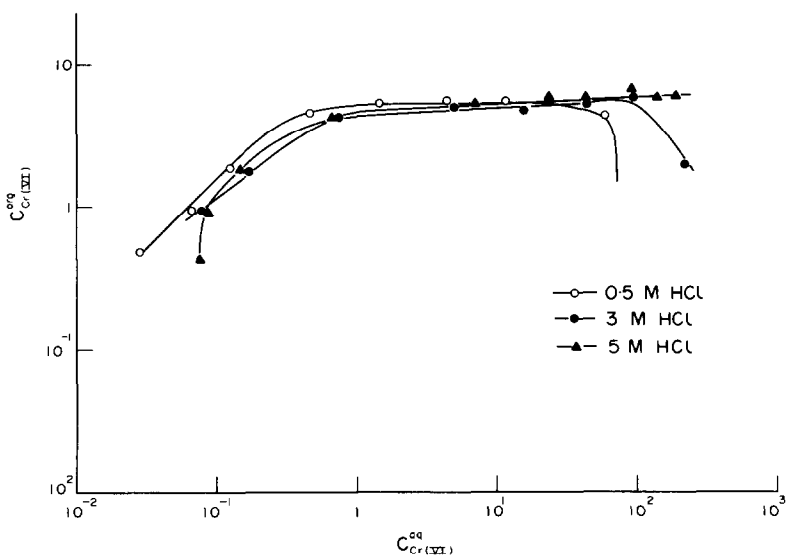

Fig. 3. Extraction isotherms in the systems 0·1*M* PyN in benzene/0·5, 3, 5*M* HCl + variable Cr(VI).

The extraction curves for the systems 0·10*M* PyN in benzene plus 0·5, 3 and 5*M* hydrochloric acid plus variable [Cr(VI)] are shown in Fig. 3 (extraction equilibrium curves). The maximum loading of the organic phase is about 6 g of chromium per litre irrespective of the acidity of the aqueous phase. Maximum uptake of the extracted compound by the organic phase from 0·5*M* hydrochloric acid is obtained when the original aqueous solutions contain 5–20 g of Cr(VI) per litre. The uptake by the organic phase decreases sharply when the original aqueous concentration of Cr(VI) is increased above 20 g/l. A possible reason is that condensation polymerization of the large amounts of Cr(VI) in the aqueous phase decreases the hydrogen-ion concentration to such an extent that the stability of the amine salt of the type $(PyNH)^+$ is considerably decreased.

With 3*M* hydrochloric acid medium the loading of 0·1*M* PyN/benzene decreases at chromium concentration above about 100 g/l. in the aqueous phase, but with 5*M* hydrochloric acid no fall in loading was observed even up to 220 g of Cr(VI) per litre in the initial aqueous phase.

The effect of various salts on the distribution coefficient of Cr(VI) between hydrochloric acid media and 0·1*M* PyN/benzene is seen in Fig. 4. In the case of 0·5*M* hydrochloric acid, sodium chloride and sodium sulphate in concentrations up to 1*M* are without effect. The effect of fluoride and nitrate is probably due to competition for the amine or to the formation of inextractable fluoride and nitrate complexes of Cr(VI).

Figure 5 shows the Cr(VI) distribution as a function of potassium oxalate, ammonium acetate, sodium citrate and potassium tartrate concentration in the aqueous phase of 0·5*M* hydrochloric acid. In the case of potassium oxalate, precipitation took place after addition

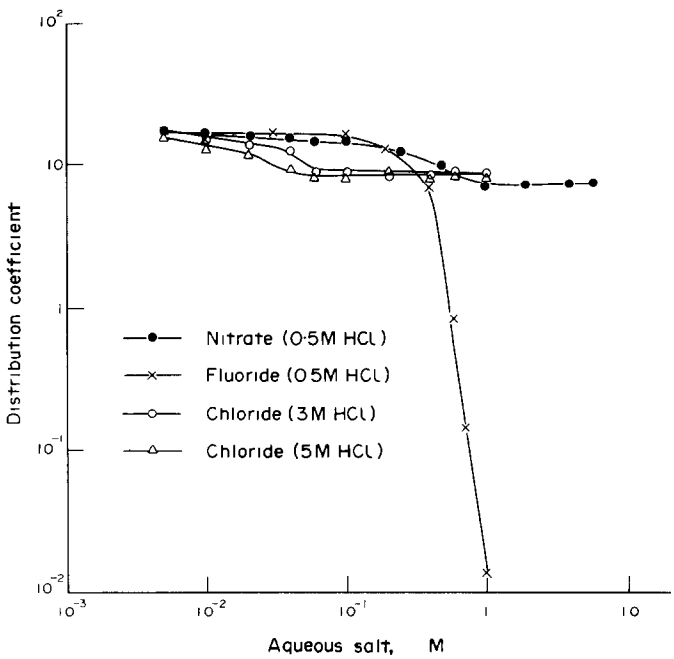

Fig. 4. Variation of distribution coefficient of Cr(VI) with concentration of different salts for extraction by 0·1*M* PyN/benzene.

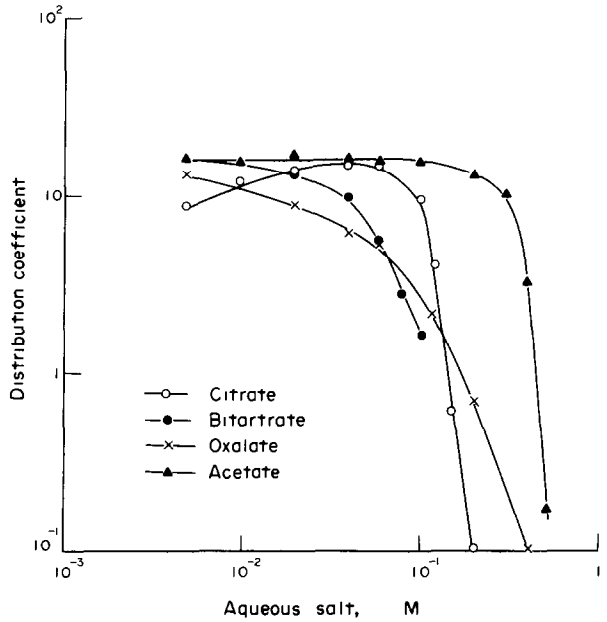

Fig. 5. Distribution of Cr(VI) as a function of the concentration of oxalate, citrate, tartrate and acetate ions from 0·5*M* HCl by 0·1*M* PyN/benzene.

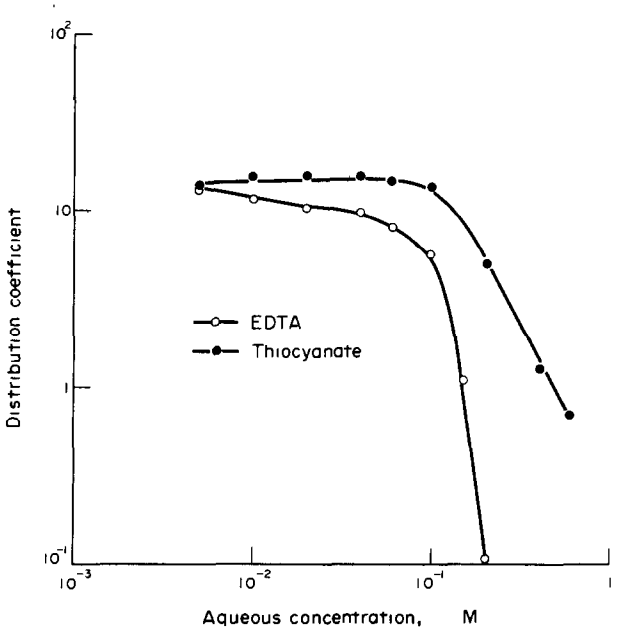

Fig. 6. Variation of the distribution coefficient of Cr(VI) with the concentration of EDTA and sodium thiosulphate from 0·5*M* HCl for extraction by 0·1*M* PyN/benzene.

Table 1. Distribution coefficient of various metal ions between 0·1*M* 5-(4-pyridyl)nonane/benzene and 3*M* hydrochloric acid

Metal ion	Concentration in the initial aqueous phase, *M*	*D* values
^{99m}Tc(VII)	C.F.	~0·25
^{99}Mo(VI)	10^{-5}	~0·015
^{233}U(VI)	10^{-3}	$<10^{-1}$
^{95}Nb(V)	C.F	$<10^{-2}$
^{95}Zr(IV)	10^{-9}	$<10^{-3}$
^{234}Th(IV)	C.F.	$<10^{-3}$
^{106}Ru	10^{-5}	~5·5
^{144}Ce(III)	10^{-9}	$<10^{-3}$
^{90}Y(III)	C.F.	$<10^{-3}$
^{198}Au(III)	10^{-8}	>10
^{60}Co	10^{-8}	<10−3
^{90}Sr(II)	10^{-9}	<10−3
^{54}Cu(II)	10^{-7}	<10−3
^{63}Ni(II)	10^{-6}	<10−3
^{137}Cs	10^{-9}	$<10^{-3}$

C.F. = carrier-free

of the extractant to initial aqueous phases which were 0·005–0·02*M* with respect to potassium oxalate. No precipitation occurred at higher concentrations. Part of the precipitate remained in the organic phase after centrifugation, the rest remaining in the aqueous phase and partially settling. Tartrate gave similar behaviour.

The effect of EDTA and potassium thiocyanate on the extraction of 0·05*M* Cr(VI) from 0·5*M* hydrochloric acid is shown in Fig. 6. In both cases the extraction decreases with increase of their concentration in the aqueous phase. Precipitation in the aqueous phases was observed at concentration greater than 0·06*M* in the case of EDTA.

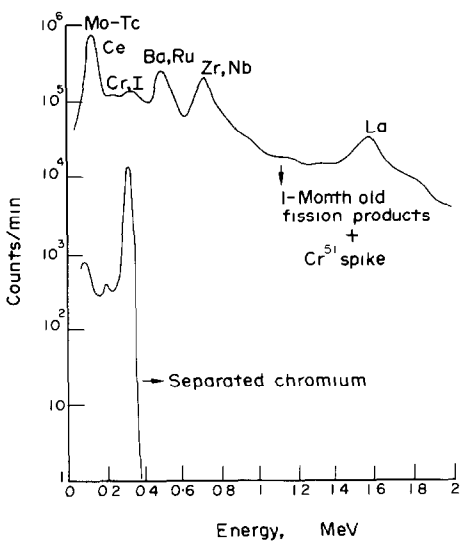

Fig. 7. Separation of spiked chromium(VI) from one-month cooled fission products and their gamma spectra.

Reducing agents, *e.g.*, thiosulphate, hydrazine hydrochloride and ascorbic acid prevent the extraction in whole or in part (depending on their concentration) by reducing Cr(VI) to inextractable Cr(III).

From Fig. 1 it is evident that chromium(VI) can be stripped from the organic phase by using very dilute hydrochloric acid. It is also possible to strip the chromium by stirring the solvent phase with a reducing agent to convert Cr(VI) into Cr(III).

The selectivity of the extraction separation of chromium(VI) with 0·1*M* PyN/benzene from 3*M* hydrochloric acid was studied. The behaviour of uranium, thorium and important fission products was examined. The results are presented in Table 1. A ^{51}Cr(VI) spike was separated from fission products (cooled for 1 month) by extraction with 0·1*M* PyN/benzene from 3*M* hydrochloric acid. The 3*M* acid was used in order to reduce co-extraction of Tc and Mo. The interference of iodine was prevented by preliminary extraction with carbon tetrachloride. The organic phase was stripped with 3*M* hydrochloric acid–0·1*M* ascorbic acid. The co-extracted ruthenium [perhaps ruthenium(IV)] did not accompany chromium in the stripping step. The gamma spectra (Fig. 7) showed the clean separation of chromium(VI).

Acknowledgements—Dr. Mukhtar Ahmad checked the purity of the reagent by GLC. Messrs M. Saeed and Riaz Joseph gave valuable assistance with the measurement/counting of radioactive samples and the calculations on *D* values.

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ANALYTICAL APPLICATIONS OF HYDRAZONES

MOHAN KATYAL
St. Stephen's College, Delhi 110007, India
YAG DUTT
Chemistry Department, Delhi University, Delhi 110007, India

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Summary—A review of the analytical applications of hydrazones is presented.

Hydrazones are azomethines characterized by the presence of the triatomic grouping >C=N—N<. Many of the physiologically active compounds find application[1] in the treatment of several diseases such as tuberculosis, leprosy and mental disorder. On the other hand, aroylhydrazones (I) are reported to possess tuberculostatic activity.[2,3] This is attributed to the formation of stable chelates with transition metals present in the cell.

$$R-CH=N-NH-CO-R'$$

(I)

Thus many vital enzymatic reactions catalysed by these transition metals cannot take place.[4–6] Hydrazones act as herbicides, insecticides, nematocides, rodenticides and plant growth regulators. They show spasmolytic activity, hypotensive action and activity against leukaemia, sarcomas and other malignant neoplasms. Hydrazones are used as plasticizers and stabilizers for polymers, polymerization initiators, antioxidants, *etc.* They act as intermediates in preparative chemistry. The structural aspects of the compounds have been recently reviewed.[1]

In analytical chemistry, hydrazones find application in detection, determination and isolation of compounds containing the carbonyl group. More recently, they have been extensively used in detection and determination of several metals. Many other analytical potentialities of these compounds have also been explored. The aim of this review is to summarize the analytical aspects of the hydrazones.

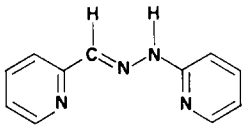
Hydrazones act as multidentate ligands with metals (usually from the transition group), forming coloured chelates. These chelates are then used in selective and sensitive determination of the metals. The ligands may be co-ordinated to the metal through the nitrogen atoms either alone or in combination with some other electronegative atom such as oxygen or sulphur. In the following survey, the hydrazones which have been more extensively studied from the analytical point of view are usually taken first, followed by similar types or those comparatively less used.

Hydrazones, in general, are prepared by refluxing the stoichiometric amounts of the appropriate hydrazine and aldehyde or ketone dissolved in a suitable solvent. The compound, which usually crystallizes out on cooling the solution, is recrystallized from a suitable solvent. Many hydrazones are now commercially available.

TAL 22/2—D

Pyridine-2-aldehyde-2-pyridylhydrazone (PAPH)

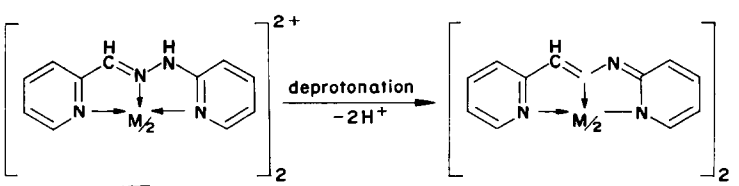
The compound PAPH (**II**) was introduced by Lions and Martin[7] in 1958. Its pale yellow crystals (m.p. 179–180°) are obtained by reacting 2-pyridinealdehyde with 2-pyridylhydrazine. Lions and co-workers[8–13] carried out detailed physicochemical investigations of the



(II)

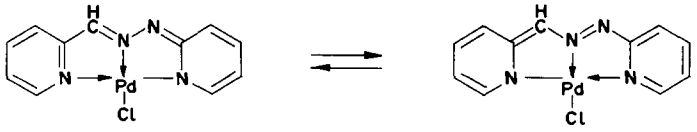
metal complexes formed with the hydrazone. The complexes[8–10] of Zn, Cd, Hg, Fe, Co and Ni with PAPH contained the metal and ligand in 1:2 ratio. The complexes were of two types—(*i*) charged and water-soluble and (*ii*) uncharged, which were obtained by replacement of the imino protons by a bivalent metal ion in mildly alkaline medium. However, in the case of Co, the isolated complex was charged because of oxidation of Co to the tervalent state. The stability constants of the complexes formed with Cu, Zn, Cd, Mn, Fe and Ni have also been reported. The nature of complexation with Co was thoroughly investigated.[11] Complexes of Cu, Zn, Cd, Hg, Sn, Cr, Mn, Co(II) and Ni with PAPH in 1:1 ratio were isolated[12,13] and characterized as charged species. Copper also formed an uncharged complex with PAPH.

The study on analytical applications of PAPH began in 1963 when Gibson and co-workers[14] published a survey of the visible spectra of aqueous solutions containing metal ions in presence of the hydrazone. They stated that PAPH should be a useful colorimetric reagent and an acid–base indicator. The spectrophotometric determination of Pd with PAPH in a basic ethanol–water medium (pH 11·6) was reported by Bell and Rose;[15] the method had low tolerance for some metals. The determination was also accomplished in acidic medium. Quddus and Bell[17] improved the values of the molar absorptivities by extracting the deprotonated complexes (**IV**) of the bivalent metal ions of Cu, Zn, Cd, Mn,



(III) (IV)

Fe, Ni and Pd with PAPH in chloroform and suggested spectrophotometry in conjunction with extraction for determination of Fe (λ_{max}405 nm) and Pd (λ_{max}560 nm). From the study of the infrared and mass spectra it was concluded[18] that Pd forms a square-planar complex (**V**, *a* and *b*) with terdentate PAPH in mildly acidic medium (pH 3·1), the complex being extractable into *o*-dichlorobenzene. The complexation is used to determine 10–100 μg of Pd colorimetrically. Appreciable amounts of many metals including those belonging to the iron-group (group VIII of the periodic table) could be tolerated and the method compares favourably with other methods.

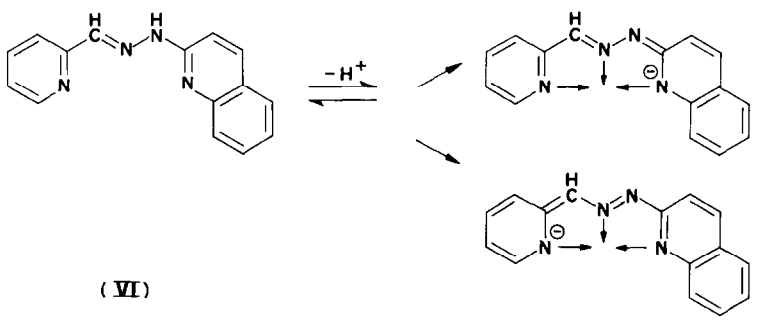


(V,a) (V,b)

The complexes of bivalent Cu, Zn, Cd, Fe and Ni with PAPH were successfully employed[19] as visual acid–base indicators in titrations of weak and strong acids and bases. Based on the extraction of the intensely coloured deprotonated forms of the Cu, Ni and Fe complexes into organic solvents, they were used as extraction indicators[20] in titrations involving strong alkali *vs.* strong acid. Another use of the bis-complex of tervalent cobalt with PAPH was in the nephelometric determination[21] of Ag(I) and Hg(II). The procedure is based on adduct formation by these ions with $[Co(PAP)_2]^+$. In the complex $[Co(PAP)_2]^+$, the two unco-ordinated nitrogen (imino) atoms are peripheral and they interact with Ag(I) or Hg(II). The adduct formed corresponds to the molar composition $[Co(PAP)_2]ClO_4 . AgNO_3$ or $[Co(PAP)_2]ClO_4 . Hg(NO_3)_2$. The method is used to determine 0·2–2·2 μg/ml of Ag or 0·1–0·54 μg/ml of Hg. The uses of various PAPH analogues have been summarized.[22]

Pyridine-2-aldehyde-2-quinolylhydrazone (PAQH)

Slightly different from PAPH, another compound PAQH (VI) was studied by Heit and Ryan[23] in 1965. This weakly acidic reagent can lose the acidic hydrogen atom in the hydrazone group and incorporate the resulting electron pair into a new stable resonating system irrespective of the type of chelated metal: PAQH formed stable square-planar 1:1 chelates with Cu(II) and Pd(II) while bis-chelates were formed with Fe(II), Co(II), Ni(II) and also Cu(II). The stability constants of the metal complexes were determined potentiometrically in 1:1 dioxan–water media. The high values of the molar absorptivities of the complexes suggested their possible use for spectrophotometric analysis.



(VI)

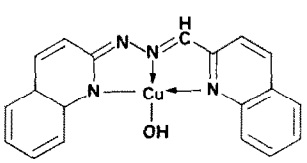
Based on the extractability of the purple Pd(II) complex with PAQH (λ_{max} 594 nm) into chloroform, a method was proposed[24–26] for determining micro amounts of Pd(II) in the pH range 1·5–2·3. The method is sensitive ($\epsilon_{594} = 1{\cdot}2 \times 10^4$ l. mole^{-1} . cm^{-1}) and selective; the determination can be accomplished even in the presence of other platinum group metals. The solid palladium complex isolated from chloroform contains the metal and ligand in 1:1 molecular proportion. However, Jensen and Pflaum[27] determined Pd(II) with PAQH in slightly alkaline medium (pH 8·0) after extracting the purple complex (λ_{max} 589 nm) into chloroform.

Cobalt and nickel have been selectively determined[28] spectrophotometrically. The cobalt complex, once formed at high pH, remains stable when the pH is lowered to 3·0, while other complexes are destroyed. The complex has maximum absorption at 510 nm, obeys Beer's law in the range 0·2–2·0 μg/ml of cobalt and has a molar absorptivity of $3{\cdot}0 \times 10^4$. In the presence of thioglycollic acid only the nickel complex ($\epsilon = 5{\cdot}1 \times 10^4$) is extractable into chloroform, permitting determination of the metal in the range 0·1 1·0 μg/ml at 492 nm. The reagent is used[29] for the determination of nickel in sea-water. Prior concentration of the metal is not necessary. The interference due to transition metals is avoided by the application of masking agents. The absorbance of the benzene extract of the nickel complex is measured at 515 nm.

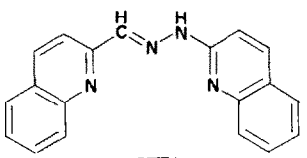
The fluorescence of the zinc complex with PAQH in chloroform at pH 8·0 is measured at 535 nm with excitation at 485 nm, to determine 0·026–0·31 ppm of zinc.[30] The main interfering ions are Co(II), Cd(II), Cu(II), Fe(II), Hg(II), Ni(II), CN^- and SCN^-: in their absence the accuracy is high.

The chromatographic properties of Cu, Fe, Co and Ni complexes with PAQH have been investigated.[31] After the extraction of the complexes into a mixture of chloroform and amyl alcohol the four elements are separated directly by thin-layer chromatography, their concentration being determined semi-quantitatively from the diffuse-reflectance spectra of the spots. Further, a method[32] comprising the ring-oven technique and circular chromatography has been developed for the separation and subsequent determination of these transition metals with an error between 5 and 12%. The procedure takes less than 30 min and is suitable for determining trace metals in water and algae.

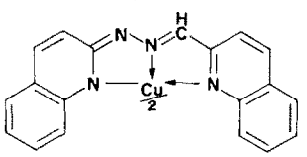
Extraction characteristics of Cu(II), Zn(II), Cd(II), Fe(II), Co(III) and Ni(II) chelates with PAQH have been studied[33] by means of transmission and atomic-absorption spectroscopy. The organic solvents used were benzene, isoamyl alcohol and methyl isobutyl alcohol—the last two are suitable for direct aspiration into the flame after addition of equal volumes of ethanol. The complexes extracted in the organic phase are of the MA_2 type. With cobalt, however, a $Co(III)A_2X$ ion-pair complex (where X is a suitable organic or inorganic anion) is probably extracted.



Proposed structure of the analytical species of interest



(VII)



Proposed structure of the isolated deprotonated complex

Quinoline-2-aldehyde-2-quinolylhydrazone (QAQH)

When satisfactory analytical results were obtained with PAPH and PAQH the next choice was to synthesize QAQH (**VII**) with extended π-bonding in the system. The compound finds application in selective and sensitive determination of copper[34,35] and compares favourably with its precursors. The stability of the copper complex with PAQH is

greater than that of the copper complex with QAQH, but the correspondingly lower stability of other metal complexes with QAQH permits a highly selective determination of copper with QAQH. The metal is determined after extraction of the complex into nitrobenzene[34] ($\epsilon = 4{\cdot}7 \times 10^4$ at 536 nm) or benzene[35] ($\epsilon = 5{\cdot}8 \times 10^4$ at 540 nm). The method has been applied[36] in direct determination of copper at the ppM (parts per milliard) level in sea-water.

Table 1. λ_{max} and ϵ values of the metal chelates extracted into chloroform

Metal ion	QAPH λ_{max}, nm	QAPH ϵ, $10^4\,l.mole^{-1}.cm^{-1}$	PDAPH λ_{max}, nm	PDAPH ϵ, $10^4\,l.mole^{-1}.cm^{-1}$	PDAQH λ_{max}, nm	PDAQH ϵ, $10^4\,l.mole^{-1}.cm^{-1}$
Cu(II)	512	5·8	522	7·1	536	6·6
Ni(II)	524	6·2	530	5·3	—	—
Zn(II)	512	5·1	525	7·0	530	5·7
Cd(II)	517	4·1	525	7·3	—	—
Pd(II)	615	1·6	625	1·8	640	1·2

Quinoline-2-aldehyde-2-pyridylhydrazone (QAPH) and related compounds

With a view to investigation of the effect of substitution of a more extended π-system on the aldehyde moiety of nitrogen-containing heterocyclic hydrazones, three new compounds were prepared,[37,38] *viz.* the pyridylhydrazones of quinoline-2-carboxaldehyde (QAPH) and of phenanthridine-6-carboxaldehyde (PDAPH) and the 2-quinolylhydrazone of phenanthridine aldehyde (PDAQH). Results of spectroscopic measurements on the metal chelates extracted into non-polar solvents such as chloroform (Table 1) from borate-buffered solutions (pH 9) show that the reactions with the higher molecular-weight hydrazones are very sensitive and make them attractive for analytical applications. The values of λ_{max} for the red chelates, however, do not differ significantly. The reagents show no selectivity toward the metal ions with which they chelate, except for Pd(II); the blue to greenish-blue palladium chelates absorb at much longer wavelengths and other platinum metals do not interfere.

The dissociable imino hydrogen atom in the hydrazone molecule is remote from the coordination sites and is therefore not directly involved in the chelation. The loss of this weakly acidic hydrogen from the molecule and redistribution of the electron pair previously shared by it results in a stable resonating system irrespective of the kind of metal ion chelated. This explains the spectroscopic similarity of the metal chelates.

PDAPH is used[38] to determine a fraction of a ppm of zinc but cadmium interferes. Other bivalent metal ions can be masked with thiourea, dimethylglyoxime and citrate. With the exception of cyanide and EDTA, which form strong complexes with zinc, common anions do not interfere. PDAPH can also be used[37,38] for spectrophotometric determination of zinc though the method is less sensitive, and, of the less polar solvents only chloroform is useful as extractant. PDAPH, on the other hand, forms a chelate which can be extracted into hexane or benzene and has a much greater stability to light.

Besides these terdentate hydrazones, many more (Table 2) were prepared[39,40] by condensation of equimolar proportions of the particular aldehyde or ketone with hydrazine. The fluorescence intensity of the zinc chelates of these compounds depends on the preference of the chelates for the >C=N— structural form. Benzimidazole-2-aldehyde-2-quinolylhydrazone has high fluorescence intensity because only one structural form, with

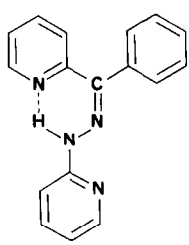
Table 2.

N-Heterocyclic hydrazone	$\lambda_{excitation}$, nm	$\lambda_{emission}$, nm	Relative fluorescence
PAPH	455	515	1
QAPH	490	540	2
PDAPH	490	545	7
Phenyl-2-pyridylketone-2-pyridylhydrazone	420	470	8
PDAQH	525	610	16
QAQH	495	595	20
Pyridine-2-aldehyde-2-phenanthridylhydrazone	450	540	100
Benzimidazole-2-aldehyde-2-pyridylhydrazone	510	600	110
Benzimidazole-2-aldehyde-2-pyridylhydrazone	440	510	140
Phenanthridine-2-aldehyde-2-phenanthridylhydrazone	580	620	230
Benzimidazole-2-aldehyde-2-phenanthridylhydrazone	480	530	440
Phenyl-2-pyridylketone-2-quinolylhydrazone	470	550	450
PAQH	470	535	660
Phenyl-2-pyridylketone-2-phenanthridylhydrazone	490	575	1520
Benzimidazole-2-aldehyde-2-quinolylhydrazone	470	520	2000

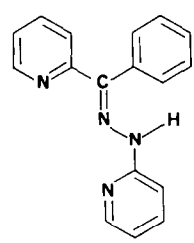
>C=N—, would maintain the conjugation of the aromatic rings. This reagent is therefore most sensitive for the spectrofluorimetric determination of zinc (<1 ppM can be determined).

2-Benzoylpyridine-2-pyridylhydrazone (BPPH)

The ligand 2-benzoylpyridine-2-pyridylhydrazone (BPPH) has been studied in detail.[41,42] Its *syn* (**VIII** *a*) and *anti* (**VIII** *b*) isomers were separated and identified on the basis of ultraviolet, NMR and infrared spectra. The *syn* form was characterized by intramolecular hydrogen bonding. In this configuration, the ligand could not function as ter-

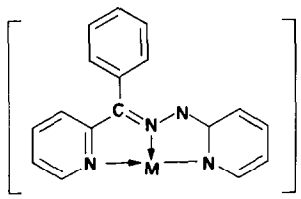


(**VIIIa**)



(**VIIIb**)

dentate and formed complexes of low molar absorptivity. The *anti* isomer, acting as terdentate, formed the expected intensely coloured chelates. The ligand is used in spectrophotometric determination of iron, cobalt, nickel, copper and zinc. The metal ions are easily determined at the following levels: Fe, 0·3 ppm; Co, 0·2 ppm; Ni, 0·13 ppm; Cu,



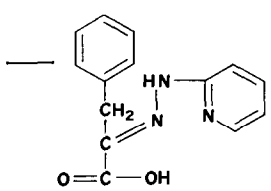
(where M = Fe, Ni, Cu, Zn)

(IX)

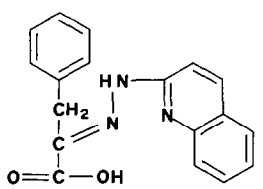
0·14 ppm; Zn, 0·13 ppm. The deprotonated complexes (**IX**) which were obtained in alkaline medium contain metal and the ligand in 1:2 ratio. With cobalt, however, cationic species [$Co(BPPH)(BPP)^{2+}$ and $Co(PP)_2^+$] result from oxidation of the metal ion by dissolved oxygen in the system. Besides the formation of these analytically important deprotonated complexes, iron and cobalt also form stable water-soluble cationic species in acidic solution. The effect of diverse ions in determination of the metals with BPPH in basic conditions was studied. The method was successfully applied to determination of zinc in phosphor bronze and in presence of large amounts of aluminium.

Heterocyclic hydrazones of phenylpyruvic acid (PPA-PH and PPA-QH)

With the hydrazones described above, chelation takes place through nitrogen atoms. It was thought[43,44] worthwhile to replace one of the nitrogen atoms of the hydrazones with the more electronegative oxygen atom and thereby to improve the chelating characteristics of the compounds. With this in view, stoichiometric amounts of a heterocyclic hydrazine (pyridyl or quinolyl) and phenylpyruvic acid were condensed and the following compounds synthesized:



Phenylpyruvic acid
2-pyridyl hydrazone (PPA-QH)



Phenylpyruvic acid
2-quinolyl hydrazone (PPA-QH)

It is found that they are sensitive reagents (Cu 0·002 $\mu g/cm^2$ for 0·001 absorbance) for spectrophotometric determination of copper. The complexation takes place in the alkaline range (between pH 9 and 12) where most foreign ions are precipitated, and hence any precipitate must be removed and the absorbance of the solution measured. The complex contains the metal and ligand in 1:2 ratio.

Heterocyclic hydrazones of 8-quinolinols

2-Pyridyl- or 2-quinolyl-hydrazine was condensed with several carbonyl-substituted 8-quinolinols (Table 3) in order to prepare hydrazones of analytical interest and possibly use them as anti-tumour compounds.[45] With most metals they formed yellow, orange or brown chelates, a result to be attributed to the colour of the hydrazone function masking that of the chelate group. One mole of a bivalent metal ion reacted with two moles of most

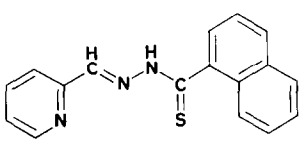
Table 3

8-Quinolinol substituent	Hydrazine
5-CHO	2-Pyridyl-
5-CHO-2-CH_3	2-Pyridyl-
5-$COCH_3$	2-Pyridyl-
5-$COCH_3$-2-CH_3	2-Pyridyl-
5-CHO	2-Quinolyl-
5-CHO-2-CH_3	2-Quinolyl-
2-CHO	2-Quinolyl-
5-$COCH_3$	2-Quinolyl-
7-CHO-5-CH_3	2-Quinolyl-

of the hydrazones to form a chelate. From the study it is apparent that none of the compounds possesses any significant activity either as anti-tumour agent or as an analytically useful chelating agent.

Salicyl-2-aldehyde-2-quinolylhydrazone (SAQH)

A method is discussed[46] for the determination of organothiophosphorus pesticides by *in situ* fluorimetry after separation on silica-gel layers. The process involves bromination and spraying with a mixture of manganese and SAQH. A direct relationship exists between the number and oxidation state of sulphur atoms in the pesticide and the sensitivity. The method is applied to the analysis of natural water samples spiked with Guthion. Recoveries ranging from 80% at 0·5 ppM to 92% at 100 ppM are possible and the results agree well with chromatographic data.



(X)

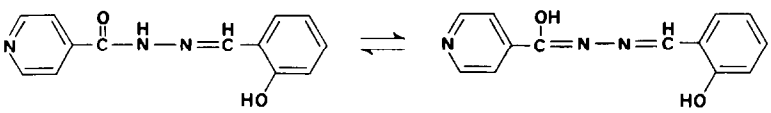
Pyridine-2-aldehyde-1-thionaphthylhydrazone (PATNH)

In order to replace one of the co-ordinating nitrogen atoms (in terdentate hydrazones) by sulphur, the compound PATNH was prepared[47] by condensation of equimolar amounts of α-thionaphthoic hydrazide[48] with pyridine-2-aldehyde. The compound pyridine-2-aldehyde-1-thionaphthylhydrazone (**X**) was isolated in the form of its lead salt. The reagent reacts with copper(II) in 1*M* hydrochloric acid to give a complex extractable into non-polar solvents such as benzene (λ_{max} = 480 nm, $\epsilon = 6{\cdot}35 \times 10^3$) and containing the metal and ligand in 1:2 ratio. It is used for absorptiometric determination of copper[47] in non-ferrous alloys and in salts. The method, however, lacks sensitivity (Sandell's sensitivity 0·01 $\mu g/cm^2$).

Isonicotinoyl hydrazones

o-Hydroxybenzaldehyde isonicotinoyl hydrazone (BIH) also called 1-isonicotinoyl-2-salicylidenehydrazine (INSH), shown in structure (**XI**), was prepared[49] by refluxing about

equimolar amounts of isonicotinic acid hydrazide and salicylaldehyde in water–ethanol solution. It was examined[50] for its chelatometric properties with a number of cations. It precipitates Cu(II), Ni(II), Zn(II), Pd(II) and Ce(IV), and forms soluble complexes with Pb(II), Fe(II), Co(II), Sn(II), TiO(II), VO(II), UO_2(II), Sb(III), Al(III), Fe(III), Th(IV) and Zr(IV). The precipitation of Cu(II) is quantitative and is used for gravimetric determination of the metal.



(XI)

Al(III) reacts with BIH, forming a yellow 1:1 complex (λ_{max} 375 nm; ϵ 12·7 × 10^3). A spectrophotometric method was developed[51] for microdetermination of 0·5–3·5 ppm of aluminium at pH 5·0. The Sandell sensitivity of the method is 0·0021 $\mu g/cm^2$. Besides many other ions which do not interfere, beryllium in 100-fold amount does not interfere in the determination of aluminium

Two moles of BIH react with one mole of the metal ions Co(II), Ni(II), Zn(II), Mn(II) or Cd(II), forming complexes[52–54] having λ_{max} between 380 and 420 nm with molar absorptivities between 1·5 × 10^4 and 2·5 × 10^4 (except the cadmium complex which does not show an absorption maximum). The complexes are soluble in 50% v/v aqueous dioxan and in organic solvents such as chloroform, pentan-1-ol and octan-1-ol. Spectrophotometric and extraction studies of the complexes have been reported. A comparative study has also been made on the complexing ability of the comparatively less polar ligand *o*-hydroxybenzaldehyde benzoyl hydrazone (BBH). The absence of heterocyclic nitrogen in the BBH molecule renders it less polar, and consequently its cobalt complex is soluble in the lower-polarity solvent chloroform while that of BIH remains insoluble. In 50% aqueous dioxan, the Zn–BBH and Mn–BBH complexes show absorption maxima at 380 (ϵ 2·4 × 10^4) and 400 nm (ϵ 1·35 × 10^4), respectively.

p-Dimethylaminobenzaldehyde isonicotinoyl hydrazone (DAIH) forms an intensely orange-yellow gelatinous precipitate with Hg(I) or Hg(II) in slightly acidic, neutral or slightly alkaline medium. Based on this reaction, selective detection of Hg(I) or Hg(II) is reported.[55] The values for the limit of identification and concentration limit are 40 μg of mercury(I or II) and 1:1250, respectively. A similar condensation product *p*-diethylaminobenzaldehyde isonicotinoyl hydrazone was also synthesized and tested in the same way. It gives identical results but its sensitivity towards Hg(II) is lower.

The fluorescence of the isonicotinic acid hydrazones of a number of carbonyl compounds (2-hydroxy-1-naphthaldehyde, salicylaldehyde, 2-hydroxy-*m*-tolualdehyde, 3-hydroxy-*p*-tolualdehyde, 4-hydroxy-*m*-tolualdehyde, 3-chloro-2-hydroxybenzaldehyde, 5-chloro-2-hydroxybenzaldehyde and 2-hydroxyacetophenone) has been examined.[56] In the presence of aluminium, these hydrazones give yellowish green fluorescence in an acetate buffer while under similar conditions the parent carbonyls exhibit only feeble fluorescence. The fluorescence intensity of the hydrazone of 2-hydroxy-1-naphthaldehyde (in presence of Al) is particularly strong, and the aldehyde is found to be a good reagent for the fluorimetric determination of 0·1–1·0 μg/ml of isonicotinic acid hydrazide.

The nature, properties and physical constants of the two complexes formed by vanadium(V) in acidic aqueous medium with acetone isonicotinoylhydrazone, and those of the

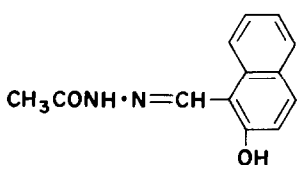
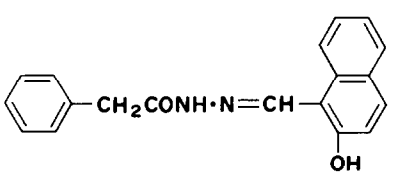
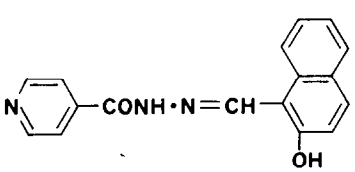
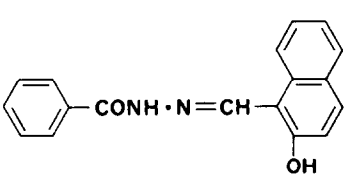
complex formed with 4-hydroxybenzaldehyde isonicotinoylhydrazone in 50% aqueous ethanol have been determined.[57] Use of the complexation is suggested for spectrophotometric determination of vanadium.

2-Hydroxy-1-naphthaldehyde hydrazones

Four derivatives of 2-hydroxy-1-naphthaldehyde hydrazones (Table 4) have been synthesized, and the fluorescence due to the reaction between these hydrazones and various metal ions indicates[58] that they are useful for the detection of aluminium. 2-Hydroxy-1-naphthaldehyde benzoic acid hydrazone (HNBH) gives the strongest fluorescence. A fluorimetric method for the determination of 0·1–1·0 ppm of aluminium with HNBH at pH 4·6 (acetate buffer) and in a mixed solvent medium of methanol and dimethylformamide (DMF) has been established.

Copper(II) reacts with 2-hydroxy-1-naphthaldehyde-2-benzothiazolylhydrazone[59] to form a 1:1 complex which can be extracted into chloroform from solution at pH 5·3–9·5 (acetate buffer). Up to 24 μg of copper can be determined by measuring the absorbance at 426 nm (ϵ 2·2 × 10^4). The sensitivity of the reaction is 0·0029 μg/cm^2. Several ions such as Ag(I), Hg(II), Ti(IV), Co(II), SCN^-, citrate and tartrate interfere.

Table 4. Identification of aluminium

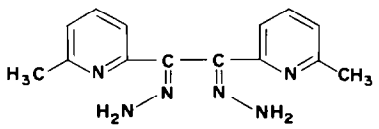
Reagent	Fluorescence colour	Limit of identification, *μg/drop*
	Violet	0·015
	Violet	0·015
	Greenish yellow	0·010
	Blue	0·005

8-Hydroxyquinaldehyde-8-quinolylhydrazone

In alkaline medium (preferably 0·1*M* potassium hydroxide), calcium forms a fluorescent 1:1 complex with this hydrazone.[60] The various constants of the reagent and of the complex have been determined, and a method is described for the determination of down to 0·1 ppm of calcium in potassium chloride and methyl trichlorosilane. The fluorescence is measured at about 510 nm (with excitation at around 420 nm). Alkali metal salts, 10-fold amounts of strontium and 100-fold amounts of barium or magnesium do not interfere.

Ferroin-type hydrazones

The synthesis, characteristics and analytical applications of bis(6-methyl-2-pyridyl)-glyoxal dihydrazone (**XII**) have been investigated.[61] The reaction of the reagent with thirty cations at various pH values was studied; it reacts only with copper(I) and palladium(II).



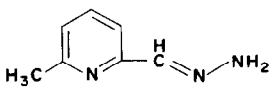
(**XII**)

In the reagent molecule, the methyl groups adjacent to the heterocyclic nitrogen atoms produce the well-known blocking effect. The 1:1 orange-yellow copper(I) complex (λ_{max} = 440 nm; $\epsilon = 8{\cdot}7 \times 10^3$) formed completely over the pH range 4·5–11·2, can be extracted into various organic solvents such as pentanol, chloroform and methyl isobutyl ketone. A method was developed for the spectrophotometric determination of trace amounts of copper in saturated brine, alkalis and milk. The most important advantage of using this reagent is the total recovery of copper that is possible from ammoniacal solutions.

The product which results from the interaction of diacetyl and hydrazine has been applied to the colorometric estimation of iron(II).[62,63] The stable red complex formed has maximum absorption at 490 nm and obeys Beer's law over the range 0·5–4·0 ppm of iron. In the procedure,[62] the reagent hydrazone is prepared *in situ* by mixing a 1% ethanol solution of diacetyl, a 0·5% aqueous solution of hydrazine sulphate and the buffered (acetate) solution of the ferrous salt, and incubating the whole reaction mixture at 60° for 10 min. The interferences are the same as in the colorimetric estimation of Fe(II) with 1,10-phenanthroline and 2,2′-bipyridyl, but the method has the advantages of economy, ease of preparation of the reagent and simplicity of the technique. In another procedure,[63] 1 g of sodium bicarbonate (to raise the pH to 9·4) was used instead of acetate buffer. Mohr's salt gave different results from ferrous sulphate owing to the reaction of the ammonium ion (in Mohr's salt) and diacetyl. Zn(II) does not interfere up to a ratio of 1000:1, and Cd(II) and Al(III) do not interfere up to a ratio of 500:1. Addition of 5 ml of 0·05*M* EDTA and 5 ml of 0·05*M* citrate masked possible interferences. Fe(III) can be determined by the same procedure after reduction to Fe(II). The coloured complex can also be extracted into nitrobenzene and the absorbance measured at 498 nm. After extraction, VO_3^-, Mn^{2+}, Ni^{2+} and Cu^{2+} do not interfere. The molar absorptivity is $1{\cdot}15 \times 10^4 \pm 1{\cdot}5\%$ in aqueous medium and $1{\cdot}38 \times 10^4 \pm 4{\cdot}7\%$ in nitrobenzene. The spectroscopic characteristics and composition of the solid Fe(II) complex[62,63] have also been studied.[64]

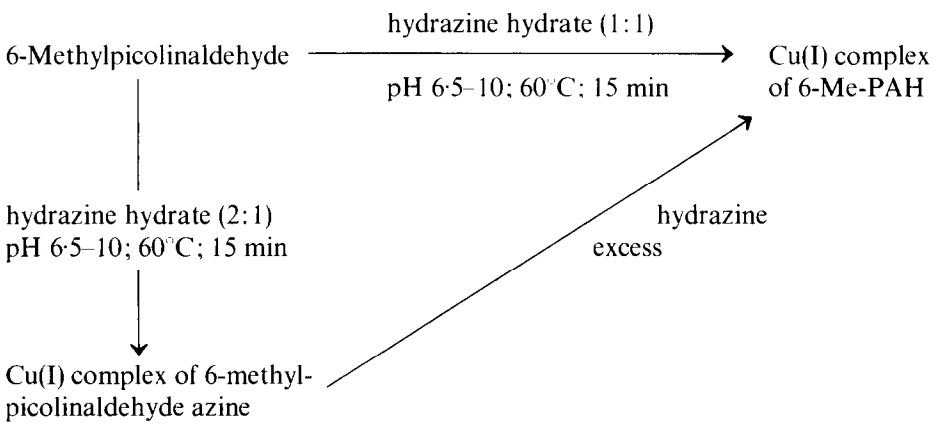
The synthesis, characteristics and analytical applications of 6-methylpicolinaldehyde hydrazone (6-Me-PAH) have been studied.[65] The compound (**XIII**) gives coloured solu-

tions with Cu(I) (λ_{max} = 425 nm; ϵ = 7·00 × 10^3) and with Pd(II). It has been used for the photometric determination of copper, in homogeneous medium, and by using an extraction technique with nitrobenzene. Beer's law is followed between 1 and 7 ppm of copper. With the extraction technique, Pd(II) and EDTA interfere when at the same concentration as copper, and Au(III) and Ni(II) from 100 ppm. The method is very accurate.



(XIII)

The Cu(I) complex of 6-Me-PAH can easily be obtained[66] by *in situ* synthesis, from solutions of Cu(II), hydrazine hydrate and 6-methyl picolinaldehyde either directly or *via* the azine-complex, depending on the amount of hydrazine used:



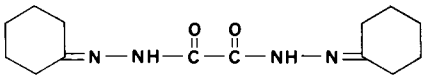
The molar absorptivity found in this *in situ* reaction is slightly lower than that for the complex produced by direct mixing of a copper solution with the hydrazone.[65]

The photometric applications of the coloured complex that results in the reaction between Fe(II) and α-pyridyldihydrazone used as such or synthesized *in situ*, have been investigated.[67] The complex was extracted into nitrobenzene and its absorbance measured at 486 nm. Mn^{3+}, Al^{3+} and Cd^{2+} do not interfere, but ions which complex Fe(II) interfere seriously. Beer's law is obeyed for 0·5–5·0 μg of iron per ml. The other ferroin-type reagents used for the spectrophotometric determination[68] of traces of iron are 2,2-bipyridylglyoxal dihydrazone, diacetyl dihydrazone and phenyl 2-pyridyl ketone hydrazone.

Bicyclohexanoneoxalyldihydrazone

Condensation of oxalylhydrazide with aldehydes or ketones results in hydrazones which react with traces of copper salts to give a blue colour. Nilsson[69] found that the hydrazone (**XIV**) formed by the reaction of 1 mole of oxalylhydrazide with 2 moles of cyclohexanone gives an intense blue colour with microgram amounts of copper. The reagent is used for the spectrophotometric determination of copper in paper pulp products[70] and in human serum.[71] The copper complex of the compound has a molar absorptivity of 1·6 × 10^4 at

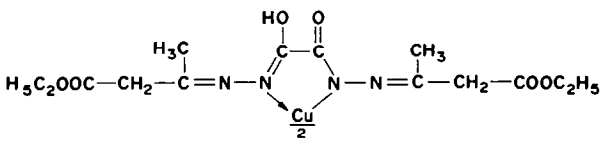
600 nm. The blue solution is clear, stable and shows constancy in absorbance in the pH range 7·0–9·0. The reagent does not give any colour with other ions usually present in biological materials.



(XIV)

Bis-(ethylacetoacetate)oxalyldihydrazone

In the course of critical investigations[72] on the derivatives of oxalic acid dihydrazide the compound bis-(ethylacetoacetate)oxalylhydrazone was found to be a sensitive and selective reagent for copper. At pH 9·0, copper forms a blue water-soluble 1:2 complex (**XV**) with the reagent. The molar absorptivity of the complex is $1{\cdot}39 \times 10^4$ for $\lambda_{max} =$ 585 nm. Out of the many foreign ions examined, Pt, Co and Ni are found to interfere.



(XV)

β-Resorcylaldehyde acetylhydrazone

The acid dissociation constants of the reagent in 40% aqueous ethanol were measured[73] potentiometrically and spectrophotometrically. Fe(III), U(VI), and Ti(IV) reacted chromogenically with the hydrazone, and Zn, Al, Sc and Ga formed complexes exhibiting blue fluorescence. The fluorescence intensity of the Sc-complex was appreciable with excitation at 406 nm. The reaction is used for determination of Sc (1–18 μg) in acetate buffer medium (pH 6·0). Cr, Ni, Co and Fe(III) interfere by decreasing the fluorescence intensity and Zn and Al by increasing it; Mn, Cd, Be and Mg are without effect. The stability constant of the 1:1 scandium complex has been determined.

Phenylhydrazones of phenolic aldehydes and ketones

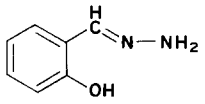
Eight phenylhydrazone derivatives of phenolic aldehydes and ketones were investigated[74] as gravimetric reagents for copper. Of these, salicylaldehyde phenylhydrazone was found to be the best; 25–60 mg of Cu(II) can be determined with an error of ~0·04%, or 0·08% in the presence of not more than 100 mg of Cd. A 10% ethanolic solution of the reagent was used and the precipitate was ignited to the oxide before weighing.

The possibility of using[75] the phenylhydrazones of salicylaldehyde, resacetophenone, *o*-hydroxyvanillin, *o*-hydroxyacetophenone and 2-hydroxy-1-naphthaldehyde as gravimetric reagents for the estimation of Pd was examined. *o*-Hydroxyacetophenone phenylhydrazone was found to be the most useful for the estimation of 15–47 mg of Pd in ammoniacal medium. The complex was finally ignited to the metal and weighed as such.

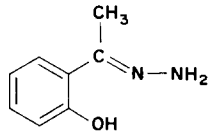
Salicylaldehyde hydrazone (SH) and o-hydroxyacetophenone hydrazone (AH)

The hydrazones SH and AH have been studied[76–78] analytically. Stability constants of the bivalent metal complexes with SH, determined potentiometrically in 75% aqueous

dioxan, follow the order UO_2 > Pb > Co > Zn; and for those with AH, in 50% aqueous dioxan, the order is UO_2 > Cu > Co > Ni. There is no significant complexation of SH with Mg(II), Mn(II) and Ni(II) ions, but Cu(II) and Fe(III) give precipitates even at low pH. AH does not form complexes with Mg(II), Mn(II), Zn(II) and Pb(II), while with Fe(III) it gives a precipitate at low pH.



(SH)



(AH)

Out of the six platinum-group metals, SH reacts with Pd and Os(VIII), giving coloured solutions suitable for their spectrophotometric determination. Besides these two metals, SH is used[76] for the determination of copper, iron and cobalt. The characteristics of the complexes are summarized in Table 5. On the basis of the differences in characteristics of the complexes with Pd and Os, the two metals are determined simultaneously. The yellow Ni(II)-complex with SH [which is $Ni(C_7H_7N_2O)_2 \cdot 2H_2O$] is paramagnetic and octahedral while the Pd(II)-complex [$Pd(C_7H_7N_2O)_2$] is diamagnetic and square-planar. Relevant ligand-field parameters for the Ni(II)-complex have been calculated.[76,78]

The yellow complex of Ni(II) with AH, having λ_{max} at 425 nm ($\epsilon = 7{\cdot}25 \times 10^2$) has been studied[76,77] at pH 10–10·5, in acetone–water (3:1) medium. The complex contains the metal and ligand in 1:2 ratio and obeys Beer's law up to 11·6 ppm of nickel. The Sandell sensitivity of the reaction is 0·08 $\mu g/cm^2$.

Some other hydrazones as analytical reagents

At pH 1·8, Pd(II) reacts with diacetylmonoxime-2-benzothiazolyl hydrazone[79] (DMBH) in 1:2 ratio, forming a complex ($\lambda_{max} = 560$ nm, $\epsilon = 5{\cdot}11 \times 10^3$) extractable into chloroform. The complex obeys Beer's law up to 15 ppm of Pd(II). In determination of 1 ppm of palladium, 41 cations [including Au(III), Ru(III), Rh(III), Ir(III) and Pt(II)—1000 ppm each; Sn(II) and Ce(III)—100 ppm each; V(V) 10 ppm] do not interfere.

Table 5. Characteristics of metal complexes with SH

Characteristic	Metal ion				
	Pd(II)	Os(VIII)	Cu(II)	Fe(III)	Co(II)
Colour	Yellow	Yellowish-green	Yellow	Yellowish-brown	Yellow
λ_{max}, *nm*	425	430	400	510	450
ϵ, $l.mole^{-1}.cm^{-1}$	$5{\cdot}3 \times 10^3$	$3{\cdot}2 \times 10^3$	$7{\cdot}8 \times 10^3$	$4{\cdot}1 \times 10^3$	$7{\cdot}9 \times 10^3$
pH for complex formation	4·0–5·0	4·0–10·0	7·5–8·7	3·0–5·0	6·2–7·0
Solvent	$CHCl_3$	20% DMF	75% acetone	CCl_4	$CHCl_3$
Composition (Metal·SH)	1:2	1:1	1:1	1:3	1:2
Beer's law range, *ppm*	Up to 21	Up to 19·7	Up to 5·6	Up to 3·6	Up to 5·8
Sensitivity, $\mu g/cm^2$	0·02	0·06	0·008	0·014	0·0074

In ammoniacal medium, cobalt forms complexes with the *p*-nitro- and 2,4-dinitrophenylhydrazones of 4-methylpentane-2,3-dione-2-oxime. Both these compounds find use[80] in sensitive detection of cobalt. Many ions do not interfere; the interference of Cu(II) and Ni(II) is prevented by the addition of cyanide.

The complex formed between UO_2(II) and gossypol isonicotinoyl hydrazone (molar composition 1:2, λ_{max} = 440 nm) is extractable into chloroform, at pH 3, and is used[81] in the colorimetric determination of 3–12 μg of uranyl per ml.

The bis(phenylhydrazone) of oxamide is oxidized by Cu(II), Hg(II), Fe(III), $[Fe(CN)_6]^{3-}$ or aqueous chlorine solution to give violet or blue species extractable into chloroform. Based on this phenomenon, photometric methods have been developed[82] for microdetermination of these ions or chlorine and also determination of the hydrazones by means of ferricyanide.

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MASSENSPEKTROMETRISCHE UNTERSUCHUNGEN ZUR ELEMENTARANALYSE ORGANISCHER VERBINDUNGEN—III*

VERBRENNUNGSVORGÄNGE IM LEEREN ROHR†

WALTER WALISCH® und OTTOKAR JAENICKE

Organische und Instrumentelle Analytik, Universität des Saarlandes, 66 Saarbrücken, B.R.D.

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Zusammenfassung—Es wird eine Meßanordnung beschrieben, die es gestattet, alle Phasen von Verbrennungsprozessen in Abhängigkeit von Trägergas, Temperatur, Verweilzeit und Rohrfüllung zu untersuchen. Die organische Probe wird hierzu mit konstanter Geschwindigkeit einem Trägergasstrom zugeführt und mit diesem in wenigen Millisekunden durch eine Überbrückungskapillare dem Verbrennungsraum zugeleitet. Die dort entstehenden Reaktionsprodukte werden mittels einer viskosen Einlaßsonde abgeschnüffelt und einem Massenspektrometer zugeführt. Reaktionszeit und Reaktionstemperatur sind in weiten Grenzen einstellbar oder stetig veränderlich. Trägt man, bei vorgegebener Reaktionszeit, den Reaktionsgrad der verschiedenen Verbrennungsprodukte in Abhängigkeit von der Temperatur auf, so erhält man in den Oxidations-Thermogrammen eine übersichtliche Darstellung des Verbrennungsprozesses. Aus den Thermogrammen repräsentativer Verbindungen wird deutlich, daß in Anwesenheit von Sauerstoff der Zerfall der Proben bei erheblich tieferer Temperatur erfolgt, als dies in Inertgas der Fall ist. Als Primärschritt der Zersetzung wird die "oxidative Pyrolyse" erkannt, die häufig zu völlig anderen Produkten führt, als die Inertpyrolyse. Die gefundenen Zwischenprodukte sind teilweise strukturspezifisch und insbesondere bei stickstoffhaltigen Proben sehr zahlreich und langlebig (bspw. Kohlenmonoxid, Stickstoffmonoxid, Dicyan, Cyanwasserstoff, Cyansäure und Methylcyanat). Die oft zitierte "Schwerverbrennbarkeit" ist im wesentlichen darauf zurückzuführen, daß Kohlenmonoxid, Cyansäure und Cyanwasserstoff erst bei sehr hoher Temperatur vollständig verbrannt werden. Die Verbrennungseigenschaften des "leeren Rohres" können durch eine Füllung mit Quarzwolle merklich und durch teilweise Füllung mit Platinwolle erheblich verbessert werden.

In Teil I[1] dieser Reihe wurde ein massenspektrometrisches Detektionssystem beschrieben, das es gestattet, alle Komponenten in einem ruhenden oder strömenden Gasgemisch auch unter extremen Bedingungen von Druck und Temperatur verhältnismäßig genau zu bestimmen. In Teil II[2] dieser Reihe wurde dieses System erfolgreich zur massenspektrometrischen Bestimmung von Verbrennungsprodukten durch Peakintegration eingesetzt. Dabei zeigte sich, daß diese Methode besonders geeignet ist, den Ablauf des Verbrennungsvorgangs im "leeren Rohr" messend zu verfolgen.

Wie vielfach gezeigt wurde,[3–6] liefert, unter geeigneten Bedingungen und bei Verwendung von Sauerstoff als Trägergas, die Verbrennung im leeren Rohr in sehr kurzer Zeit für viele Elemente charakteristische Endprodukte und kann daher bei der Elementaranalyse eingesetzt werden. Die manchmal ungenügende quantitative Ausbeute wird durch hohe Temperaturen und Bafflesysteme,[7] lange Verbrennungszonen[8] oder Düsen[9] verbessert.

* Teil II—W. Walisch und O. Jaenicke, *Talanta*, 1971, **18**, 175.

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Die Kontrolle der "Qualität der Verbrennung" geschieht in den genannten Fällen ausschließlich durch Messung der Gesamtmenge des entstandenen, charakteristischen Endproduktes. Der Verbrennungsprozeß selbst bleibt unbeobachtet. Dies gilt auch für die Beiträge von Kainz *et al.*[10,11] sowie Klimova *et al.*,[12] die versuchten, "Verbrennungsfehler" zu lokalisieren. Die von diesen Autoren eingesetzte gravimetrische Bestimmung der Verbrennungsprodukte erlaubt allenfalls die Beobachtung eines Teils der interessierenden Reaktionen.

Unter dem vagen Begriff "Verbrennung" werden im allgemeinen eine Vielzahl von physikalischen und chemischen Vorgängen, die parallel oder konsekutiv ablaufen, zusammengefaßt. Dazu gehören beispielsweise:

Verdampfung der Probe, Pyrolyse der Probe zu Bruchstücken während oder nach dem Verdampfen, Primäroxidation, Verbrennung zu stabilen Endprodukten.

Eine aussageträchtige Untersuchung des Verbrennungsprozesses darf deshalb nicht nur die Umsatzoptimierung der Endprodukte betrachten, sondern muß eine Aufgliederung des Verbrennungsprozesses erreichen, um die Ursachen einer unvollständigen Oxidation eindeutig zuzuordnen. Erst dadurch ist ein gezieltes Eingreifen in den Verbrennungsprozeß möglich. Ferner ist hierbei auf ein strukturspezifisches Verbrennungsverhalten, wie es in Teil II erwähnt wurde, zu achten. Die Kenntnis der Strukturspezifität erlaubt die Charakterisierung der schwerverbrennbaren Stoffklassen und bietet darüber hinaus die Möglichkeit, aus dem Verbrennungsablauf Aussagen zur Struktur zu machen.

Aus Gründen der Normierbarkeit und der Reproduzierbarkeit ist es sinnvoll, vorerst den Verbrennungsvorgang unter idealen Bedingungen zu betrachten, die sich dadurch auszeichnen, daß die dampfförmige Probe im Sauerstoffüberschuß fortlaufend und gleichmäßig in das geheizte, leere Reaktionsrohr eingeleitet wird. Damit reduzieren sich alle stofflichen Vorgänge auf Gasphasenreaktionen, deren Beeinflussung mittels heterogener Wandkatalyse durch die Rohrdimension genau festgelegt ist. Die hierbei erhaltenen Ergebnisse werden sich weitgehend auf die realen Bedingungen übertragen lassen, denn in der Mikroelementaranalyse kann der Verdampfungsvorgang bei der stationären Verbrennung meistens so gesteuert werden, daß immer eine ausreichende Sauerstoffmenge vorhanden ist.[13] Tritt eine Pyrolyse schon während der Verdampfung ein, so entstehen thermisch stabile Bruchstücke, deren Verbrennung unter den oben angegebenen idealen Bedingungen verläuft.

Schwierigkeiten bereiten bei dieser stationären Verbrennung allerdings die zur Explosion neigenden Stoffklassen. Deshalb verwendet die Ultramikroelementaranalyse die unkontrolliert verlaufende Schnellverbrennung[14,15] (Puls-Verbrennung), bei der, aufgrund der kleinen Mengen, der großen Gasmengeströme und der sofort wirksam werdenden Durchmischung mit Sauerstoff durch Diffusion, die Idealbedingungen mindestens für die Sekundärverbrennung wieder einigermaßen erfüllt sind. Insoweit sind die mittels der stationären Verbrennung gewonnenen Erkenntnisse auch für explosive Stoffklassen bedeutsam.

Die Aufklärung der Verbrennungsvorgänge im leeren Rohr erfolgt zweckmäßigerweise in folgenden Schritten.

(*a*) Bestandsaufnahme aller Zwischenprodukte, die im Ablauf der Verbrennung wichtiger Stoffklassen auftreten.

(*b*) Untersuchung der Verbrennung thermisch stabiler Gase.

(*c*) Beobachtung des Entstehens und Verschwindens der Zwischenprodukte der Verbrennung in Abhängigkeit von Struktur, Verbrennungstemperatur und Verbrennungszeit.

(*d*) Messung des Einflusses von Sauerstoffpartialdruck, Wandgegebenheiten und Katalysatoren.

(*e*) Aufklärung des Reaktionstypes und Messung der Geschwindigkeitskonstanten wichtiger Verbrennungsreaktionen.

(*f*) Studium der Strukturabhängigkeit der Pyrolyse in inertem Trägergas.

Im vorliegenden Teil dieser Reihe werden wir uns ausschließlich mit den Aufgaben (*a*) bis (*d*) befassen. Die Ergebnisse unserer kinetischen Untersuchungen werden unmittelbar folgen. Die Unberührtheit des ganzen Fragenkomplexes läßt erwarten, daß keine der genannten Aufgaben abschließend gelöst werden kann. Wir gehen vielmehr davon aus, daß es sich bei unserem Beitrag allenfalls um einen ersten Schritt in das unerschlossene Gebiet der "Verbrennungsreaktionen organischer Verbindungen" handeln kann.

MESSANORDNUNG

In Abb. 1 sind die wichtigsten Elemente der Meßapparatur schematisch dargestellt. Das Trägergas—Sauerstoff oder Sauerstoff–Helium—wird aus der Druckflasche DF über die Kapillarschläuche DK und VK sowie ein Absorptionsrohr AR dem Reaktionssystem zugeführt. Das Druckausgleichsrohr DR, über das ein kleiner Teil der Trägergase abströmt, gewährleistet genau einstellbare, konstante Drucke und—in Verbindung mit der Kapillare VK—konstante Trägergasströme durch das System.

Das Trägergas tritt am hinteren Ende in den Verdampfer VD ein, der durch Schliff mit dem Probenverdampfungsraum VR verbunden ist. Am Ende des Verdampfers sitzt ein kleiner Schliffkern, in dem sich eine Innenheizung IH befindet und auf den die Verdampfungshülse VH gesteckt wird. In die Verdampfungshülse wird vor Beginn einer Messung die Probensubstanz eingefüllt. Bei richtiger Betriebsspannung von IH tritt aus einer Bohrung OH, deren Durchmesser etwa 1 mm beträgt, eine ausreichende Probendampfmenge mit konstanter Geschwindigkeit in VR ein und wird dort unverzüglich vom Trägergas durch die Überbrückungskapillare in den Reaktionsraum RR transportiert. Der austretende Substanzstrom v^0 [mMol/s] hängt ausschließlich von der Größe der Bohrung OH und dem Probenpartialdruck in VH ab. Dieser Partialdruck wird von der Temperatur T_V der Verdampferhülse bestimmt. T_V wird mittels des Thermoelementes TH gemessen und dadurch ausreichend konstant gehalten, daß einerseits der Innenheizer IH mit einer elektronisch stabilisierten Spannung betrieben wird und andererseits ein Isolations-Glasrohr GR eine reproduzierbare Wärmeabgabe bedingt.

Mit diesem Verdampfersystem gelingt es, Probenpartialdrucke p^0 bis zu 20 mb im Trägergasstrom von bis zu 1 Nml/s* über Stunden auf $\pm$ 5% konstant zu halten. Das ganze Verdampfersystem ist, ebenso wie das Reaktionsrohr, aus Quarz angefertigt, so daß Verdampfertemperaturen bis 800 K möglich sind, und auch Verbindungen mit sehr hohem Schmelzpunkt (bspw. Fumarsäure) erfolgreich untersucht werden können, solange die Verdampfung der geschmolzenen Probe oder die Sublimation ohne Zersetzung erfolgt.

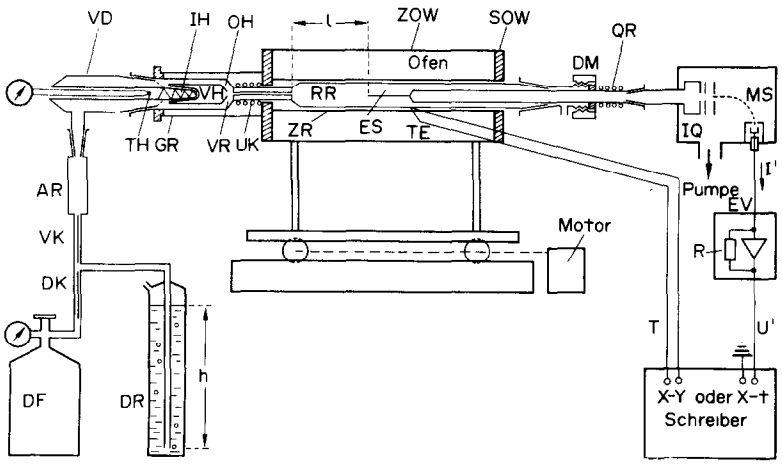

Abb. 1. Schema der Messanordnung.

* [Nml/s] = Normalmilliliter pro Sekunde.

Verdampfungsraum und Reaktionsrohr sind mittels eines dickwandigen Quarzrohres (Innendurchmesser 0,6 mm, Länge 70 mm) miteinander verschmolzen. In dieser Überbrückungskapillare ÜK erfolgt der Temperatursprung von der Verdampfertemperatur T_V zur Reaktionstemperatur T in wenigen Millisekunden. Gleichzeitig verhindert diese Kapillare ein "Zurückschlagen der Verbrennung" in den Verdampferraum. Durch eine zusätzliche Heizwicklung wird die aus dem Ofen herausragende Hälfte der Überbrückungskapillare immer auf einer Temperatur gehalten, die leicht über T_V liegt. Kurz vor der seitlichen Ofenwand SOW und in dieser Wand, die aus Hartasbest besteht, erfolgt dann auf einer Strecke von 20 mm der Sprung auf die Reaktionstemperatur Da bei kleinen Rohrquerschnitten der Temperaturausgleich in Gasen extrem schnell erfolgt,[16] reicht der innerhalb des Ofens befindliche Teil von ÜK auch unter extremen Umständen zur Temperaturanpassung.

Der nach dem Reflektionsprinzip[17] gebaute Ofen (Innen- und Außenhaut der zylindrischen Ofenwand ZOW besitzen einen sehr hohen Reflektionsgrad; die Innenwandung absorbiert wenig Strahlung, und die Außenwandung emittiert wenig Strahlung) enthält ein Zentralrohr ZR, auf dem ein Kanthal-Widerstandsband so gewendelt ist, daß die größeren Wärmeverluste an den Enden kompensiert werden. Bei einer Gesamtlänge des Ofens von 380 mm entsteht so eine isotherme Zone von 300 mm. Im Bereich von 500–1200 K sind die Abweichungen vom Mittelwert $< \pm 5$ K. Die Betriebsspannung für den Ofen ist über einen Drehtransformator einem Stabilisationstrafo entnommen, der neben einer kurzen Einstellzeit eine sehr gute Langzeitkonstanz ($\pm 0{,}3\%$) garantiert Mittels des Drehtransformators kann die an der Ofenwicklung anliegende Spannung entsprechend der gewünschten Reaktionstemperatur T eingestellt oder (durch Motor gesteuert) stetig verändert werden. Die Temperature T wird mit dem Thermoelement TE gemessen und gegebenenfalls mit einem X–t- bzw. einem X–Y-Schreiber registriert.

Das im Zentralrohr liegende Reaktionsrohr hat einen Innendurchmesser von 8 mm, was in etwa den Dimensionen der Verbrennungsrohre der Elementaranalyse entspricht. Das Reaktionsrohr endet außerhalb des Ofens in einem Schliffkern, auf den die Durchführungsdichtungsmanschette DM aufgesetzt ist. Durch diese Manschette führt ein Quarzrohr (4,5 mm Innen- und 6 mm Außendurchmesser) in das Reaktionsrohr hinein. Dieses Quarzrohr ist einerseits über einen Schliff mit der Ionenquelle IQ des Massenspektrometers MS verbunden und endet andererseits innerhalb des Reaktionsrohres in der viskosen Einlaßsonde ES. Durch diese Kapillare wird entsprechend der in Teil I gegebenen Begründung ein repräsentativer Gasmengenstrom von etwa 0,001 Nml/s in die Ionenquelle gesaugt, und es entstehen dort—gemäß Gleichung (6) in Teil I—repräsentative Partialdrucke, die die Messung der Partialdrucke p^i aller Reaktionsprodukte am Ort der Probenahme in RR ermöglichen. Ofen mit Reaktionsrohr und Verdampfer sind auf einen kleinen Wagen montiert und gegenüber der Einlaßsonde von Hand oder mittels Motorantrieb verschiebbar. Dadurch kann die Probenahme an jedem Punkt des Reaktionsrohres erfolgen und damit die Abhängigkeit der Zusammensetzung vom Ort der Probenahme unstetig oder stetig untersucht werden. Die aus dem Ofen herausragenden Teile des Sondenrohres sind mittels einer verschiebbaren Spiralwicklung geheizt, so daß im Hochvakuumteil der Sonde die Temperatur immer > 450 K bleibt, wodurch eine Kondensation der zu messenden Reaktionsprodukte vermieden und eine Adsorption weitgehend eingeschränkt wird. Die Einstellzeit dieser Sonde (90% des Endwertes bei sprunghafter Änderung eines Partialdruckes am Ort der Probenahme) beträgt 0,5 s

Als Massenspektrometer MS wurden bei unseren bisherigen Untersuchungen das Kleingerät THN 205 E der Firma Thomson-Houston, Paris (Permanentmagnet, Hochspannungsscan, bei einer Auflösung von etwa 60), sowie des Universalgerät CH-5 der Firma VARIAN-MAT, Bremen (Magnetfeldscan, mit einer eingestellten Auflösung von etwa 600) eingesetzt. In beiden Fällen wurden Faradayfänger zur Messung der Ionenströme verwendet. Die bei $R = 10^{11}\ \Omega$ relativ große Zeitkonstante des Elektrometerverstärkers EV (etwa 0,3 s) läßt die an sich mögliche Verkürzung der Einstellzeit der sonstigen Meßanordnung (Einlaßsonde und Vakuumsystem) momentan wenig sinnvoll erscheinen. Es sind vorerst also nur die Zwischenprodukte faßbar, die unter den genannten Bedingungen in genügender Konzentration und mit einer Lebensdauer von mindestens 0,2 s auftreten. Selbstverständlich könnte hier, allerdings unter Verzicht auf Genauigkeit, die Verwendung eines Fängers mit Sekundärelektronenvervielfacher und einer schnelleren Einlaßsonde das zugängliche Zwischenproduktenspektrum erheblich vergrößern.

ARBEITSTECHNIK UND AUSWERTUNG

Durch Einstellen der Höhe h der Wassersäule im Druckausgleichsrohr DR wird der Trägergasstrom auf den gewünschten Wert v [mMol/s] eingestellt. Die Reaktionszeit t ergibt sich dann aus dem Abstand l [mm] zwischen dem im Ofen liegenden Ende der Überbrückungskapillare und der Spitze der Einlaßsonde, dem Durchmesser d [mm] des Reaktionsrohres, der Temperatur T des Reaktionsrohres und dem eingestellten Trägerstrom. Solange $v^0 \ll v$ kann die durch die Verbrennung zusätzlich entstehende Gasmenge vernachlässigt werden

Zur Einstellung von v^0 werden l und T so hoch gewählt, daß vollständige Verbrennung des Kohlenstoffs zu Kohlendioxid gewährleistet ist. Dann wird das Massenspektrometer auf Masse 44 eingestellt und die Heizleistung des Verdampfers so lange gesteigert, bis die resultierende Peakintensität U^{44}_{max} den gewünschten Probenstrom v^0 anzeigt. Unabhängig von l kann bei genügend hohem T der Probenstrom auch dadurch gemessen werden, daß der Trägerstrom und damit die Probenzufuhr plötzlich gestoppt werden. Nach genügend langer Zeit ist die Verbrennung der in RR vorhandenen Probe vollständig, und U^{44}_{max} wird angezeigt. Durch Messung der absoluten CO_2-Empfindlichkeit des Meßsystems (dynamische Zugabe eines bekannten CO_2-Stromes zum

Trägergas) und bei Kenntnis der Kohlenstoffzahl c der Probe, läßt sich der Probenstrom v^0 aus U^{44}_{max} genau bestimmen. Dies ist jedoch für unsere Messungen gar nicht erforderlich, denn der Verbrennungsgrad des eingesetzten Kohlenstoffs ergibt sich in erster Näherung unmittelbar aus $U^{44}_{i,T}$ und U^{44}_{max}. Wie Rupp *et al.*[18,19] zeigten, sind nämlich für die von uns gefundenen Zwischen- und Endprodukte annähernd gleiche Partialdruckempfindlichkeiten für den jeweiligen 100%-Peak zu erwarten. Diese Erwartung wurde durch Kontrolluntersuchungen[15] in ausreichendem Maße bestätigt ($\pm 20\%$), und wir können deshalb, bei nicht zu großem Anspruch an die Genauigkeit, alle Zwischen- und Endprodukte auf U^{44}_{max} beziehen. Damit vereinfacht sich die Auswertung erheblich, und die sonst sehr mühseligen Eichmessungen entfallen ganz. Allerdings muß die Massendiskriminierung als Folge der molekularen Strömung innerhalb des Massenspektrometers berücksichtigt werden. Da der Gesamtdruck im Reaktionsrohr gleich dem Außendruck und damit ausreichend konstant ist, und das Trägergas in Verbindung mit der Temperatur der Einlaßkapillaren ES die Viskosität nahezu ausschließlich bestimmt, vereinfacht sich die in Teil I abgeleitete Gleichung (7) für eine vorgegebene Temperatur T zu*

$$U^i = K_T p^i (M^i)^{1/2}. \tag{1}$$

Zur Auswertung der Meßergebnisse zum Zwecke der Elementaranalyse bietet sich der schon erwähnte Verbrennungsgrad an, der unter Bezugnahme auf den Zustand nach vollständiger Verbrennung angibt, wie weit die Verbrennung fortgeschritten ist. Da aber die meisten Zwischenprodukte nicht als Endprodukte auftreten, wäre eine solche Bezugnahme nicht praktikabel. Deshalb berechnen wir aus den Meßergebnissen den Reaktionsgrad $\alpha^i = p^i/p^0 = v^i/v^0$.

Aus $$p^0 = \frac{U^{44}_{max}(44)^{-1/2}}{K_T \cdot c} \quad \text{und} \quad p^i = \frac{U^i (M^i)^{-1/2}}{K_T}$$

läßt sich der gesuchte Reaktionsgrad in einfacher Weise nach Gleichung (2) bestimmen.

$$\alpha^i_{i,T} = c \cdot \frac{U^i}{U^{44}_{max}} (44/M^i)^{1/2} \tag{2}$$

Handelt es sich bei dem beobachteten Reaktionsprodukt i um ein Endprodukt, so kann der Verbrennungsgrad leicht aus α^i berechnet werden.

Die Auswertung wird schwieriger, wenn der 100%-Peak des Reaktionsproduktes i noch von anderen Massen belegt wird. Dann müssen die Fragmentierungsspektren der sich störenden Gaskomponenten ausgewertet und der gesuchte Intensitätsanteil U^i aus dem mehrfach belegten Massenpeak in bekannter Weise mit Hilfe der Subtraktionsmethode ermittelt werden. Zur vollständigen Zuordnung der beobachteten Massenpeaks ist es dabei in manchen Fällen unvermeidbar, ausführliche Identifizierungsuntersuchungen anzustellen. Dabei ist es eine große Hilfe, daß alle Ionenbruchstücke des gleichen Ausgangsmoleküls i im $U^i(t)$-Diagramm gleiches Verhalten zeigen

Zur Aufnahme von Oxidations-Thermogrammen wird—bei feststehender Sonde—die Ofentemperatur mit etwa 0,3 K/s variiert. Das Massenspektrometer bleibt dabei auf einem für die Komponente i repräsentativen Peak eingestellt. Bei konstantem l und v ändert sich t entsprechend der Gasgleichung. Eine Korrektur dieser Abhängigkeit könnte experimentell durch entsprechend gesteuerte Veränderung von l erhalten werden. Der Aufwand für eine derartig synchrone Veränderung von l und T erscheint für unsere orientierenden Messungen noch nicht gerechtfertigt. Vielmehr wird die Sonde bei $l = 100$ mm—das entspricht einem Reaktionsvolumen von 5 ml—fest eingestellt Bei dem üblicherweise für die Aufnahme von Oxidations-Thermogrammen eingestellten Trägerstrom von 0,8 Nml/s ergibt sich für die niedrigste vorkommende Reaktionstemperatur von 700 K eine Reaktionszeit von 2,35 s und für die maximale Reaktionstemperatur von 1100 K, 1,49 s. Im Bereich von 800 K bis 1000 K, in dem die wesentlichen Vorgänge zu beobachten sind, kann mit ausreichender Näherung von einer Reaktionszeit von etwa 1,8 s ausgegangen werden.

Wie in Teil I gezeigt, beeinflußt die Temperatur der Einlaßsonde das Ausgangssignal gemäß der dort abgeleiteten Gleichung (7), und die gemessenen Massenintensitäten U^i_T sind deshalb ensprechend zu korrigieren (vgl Tab. IV in Teil I) und auf die Temperatur umzurechnen, bei der die Eichung mit Kohlendioxid vorgenommen wurde

Zur Messung der Reaktionstemperatur mittels TE ist ein NiCr–Ni-Mantelthermoelement mit Ausgleichsleitung eingesetzt Die Thermospannung liegt am Y-Eingang eines X–Y-Schreibers. Da im betrachteten Temperaturbereich die Thermospannungskurve ausreichend linear verläuft, erhält man, wenn man die jeweilige Peakintensität an den X-Eingang legt, sofort ein Thermogramm $U^i(T)$, aus dem das gesuchte Thermogramm $\alpha^i(T)$ auf

* Bei Gleichung (7) in Teil I ist vorausgesetzt, daß die interne Partialdruckempfindlichkeit E^i bei der jeweiligen Temperatur T_w des Stromungswiderstandes W_{5-6} gemessen wird. Ist dagegen die Empfindlichkeit E^i_0 bei der Bezugstemperatur T_0 bestimmt, so ergibt sich die Empfindlichkeit für eine andere Betriebstemperatur T_w zu:

$$E^i_{Tw} = E^i_{T0} \cdot T_0/T_w$$

und entsprechend:

$$C^i = C^i_0 \; T_0/T_w.$$

die gezeigte Weise berechnet wird. Zur Aufklärung der bei organischen Verbindungen gefundenen Ergebnisse erwies es sich als vorteilhaft, das Reaktionsverhalten einiger Gase, die häufig als Zwischenprodukte entstehen, ausführlich unter Verbrennungsbedingungen im leeren Rohr zu untersuchen. Hierzu werden diese Gase mit der in Teil I beschriebenen dynamischen Technik dem Trägergas stetig zugemischt und dann über die Überbrükkungskapillare dem Reaktionsraum zugeleitet. Alle anderen Bedingungen bleiben unverändert. Stehen die gewünschten Gase nicht in Druckflaschen zur Verfügung, so werden sie durch Pyrolyse geeigneter Verbindungen im Verdampfersystem erzeugt.

ERGEBNISSE UND DISKUSSION

Primäre Verbrennungsprodukte

Bisher gibt es keine Angaben über die tatsächlich bei den Verbrennungsvorgängen der Elemetaranalyse enstehenden Zwischenprodukte. Vielmehr wird—auf Grund der ausschließlich beobachteten "Vollständigkeit der Verbrennung" durch Messung der Endprodukte—die Schwerverbrennbarkeit auf das Entstehen von Bruchstücken wie Methan, Kohlenmonoxid, Essigsäure u.ä. zurückgeführt.[20] Wir konnten dagegen in ersten orientierenden Messungen im leeren Rohr feststellen, daß bspw. Methan nach einer Reaktionszeit von 1,8 s bei 1000 K bereits vollständig verschwunden ist, daß aber gleichzeitig erst die Hälfte des erwarteten Kohlendioxids entstanden ist. Es entstehen demnach auch bei einfachen Verbindungen wie Methan noch Zwischenprodukte, die eigentlich erst die Schwerverbrennbarkeit bedingen. Diese unbekannten Zwischenprodukte müssen also erst einmal aufgefunden werden. Dabei bleibt vorerst der Bereich der kurzlebigen Reaktionsprodukte noch unerschlossen, da, wegen der Zeitkonstanten von Einlaß-, Vakuum-, Verstärker- und Registriersystem, allenfalls noch Spezies mit einer Lebensdauer von einigen Zehntelsekunden erfaßt werden können.

In Tabelle 1 sind die Ergebnisse solcher orientierenden Untersuchungen zusammengestellt. Die Reaktionstemperatur T betrug in allen Fällen 970 K, die Reaktionszeit t war auf 0,6 s eingestellt ($l = 10$ mm, Sauerstoff = 0,3 ml/s) und die Verdampfertemperatur so gewählt, daß sich ein Partialdruck der Probe von wenigen mb ergab. Damit war ein ausreichender Sauerstoffüberschuß gewährleistet. In allen Fällen erfolgt die Verdampfung der eingesetzten Verbindung M gleichmäßig. Lediglich bei Melamin zeigt sich, in Übereinstimmung mit den Beobachtungen von May,[21] eine Zersetzung der Probe, und die Zusammensetzung des Probendampfes ist nicht mit der Zusammensetzung der Probe identisch, weil bei der Thermolyse Ammoniak abgegeben wird.

In Tabelle I sind bei den üblicherweise zur Elementaranalyse benutzten Verbrennungsprodukten—Wasser, Kohlendioxid und Stickstoff—die α_u^i-Werte in Klammern angeführt, die man nach vollständiger Verbrennung finden würde. Erwartungsgemäß wird unter den gegebenen Umständen eine vollständige Verbrennung in keinem Fall erreicht, und die gemessenen Reaktionsgrade bestätigen unsere Ausgangshypothese, daß die Verbrennung organischer Verbindungen in mindestens zwei Schritten erfolgt:

1. Oxidative Pyrolyse zu verhältnismäßig stabilen Zwischenprodukten.
2. Verbrennung dieser stabilen Zwischenprodukte zu den bekannten Endprodukten.

Die Reaktionsprodukte der Primärverbrennung zeigen eindeutige Zusammenhänge mit der Struktur der Ausgangsverbindung. Dabei sind CHO-Verbindungen artenarm, und die strukturellen Unterschiede werden vor allem an der Größe der α^i-Werte sichtbar. Dagegen liefern stickstoffhaltige Verbindungen zahlreiche Primärprodukte, und die Existenz einiger Zwischenprodukte scheint an sich schon strukturspezifisch zu sein.

Wider Erwarten sind—Benzol ausgenommen—die Ausgangsverbindungen trotz der milden Bedingungen (970 K, 0,6 s Reaktionszeit) schon weitgehend zerstört. Die oxidative

Tabelle 1. Reaktionsgrad α^i; $T = 973$ K, $t = 0{,}6$ s

Eingesetzte Verbindung M	gefundene α^i-Werte für i gleich							
	M	H_2O	HCHO	CO	CO_2	HCN	N_2	NO
Benzol	0,4	1,6 (3,0)	0,2	1,4	2,0 (6,0)	—	—	
Anthracen	—	4,4 (5,0)	—	11,8	5,5 (14,0)	—	—	—
Durol*	—	6,1 (7,0)	-	7,1	3,4 (10,0)	-		
Durochinon	-	4,3 (6,0)	—	4,8	4,9 (10,0)	—	—	—
Brenzkatechin	0,07	3,1 (3,0)	—	1,8	3,2 (6,0)	-	—	—
Azobenzol	—	4,6 (5,0)	0,04	8,2	4,1 (12,0)	—	1,0 (1,0)	—
Anilin	0,09	3,0 (3,5)	—	1,8	4,3 (6,0)	0,4	0,2 (0,5)	0,3
Melamin*	—	2,7 (3,0)	—	—	1,8 (3,0)	0,5	3,3 (3,0)	0,5
Tetramethylharnstoff*	0,02	4,5 (6,0)	—	0,8	2,5 (5,0)	0,6	0,5 (1,0)	0,2

* Zusätzlich werden noch folgende Zwischenprodukte gefunden (jeweiliger α-Wert in [ ]).
Durol: C_2H_6 [0,3].
Melamin: NH_3 [2,0]; HOCN [1,1]; $(CN)_2$ [0,05].
Tetramethylharnstoff: HOCN [0,2]; $(CN)_2$ [0,02].

Pyrolyse scheint also in der Regel sehr schnell zu verlaufen, und die sogenannte Schwerverbrennbarkeit mancher Stoffklassen muß mit der langsamen Verbrennung einiger stabiler Zwischenprodukte begründet werden.

Besonders überraschend sind die sehr hohen CO-Gehalte auch bei Verbindungen, in denen keine CO-Gruppierung enthalten ist. Sauerstoff ist in allen Fällen in grossem Überschuß vohanden, und Sauerstoffmangel kann nicht hierfür verantwortlich gemacht werden. Offensichtlich ensteht Kohlenmonoxid als Folge einer häufig vorkommenden Primärreaktion. Andererseits wird Methan, das angeblich in vielen Fällen entstehen soll und dem die Schuld an der Schwerverbrennbarkeit gegeben wird, in keinem Falle beobachtet.

Eine ausführliche Diskussion, welche die Ergebnisse weiterer Messungen mit einbezieht, erfolgt.[15] Sicher reicht jedoch die bei dem geschilderten Verfahren entstehende "analytische Momentaufnahme" nicht aus, um das vielfältige Verbrennungsgeschehen aufzuklären. Vielmehr müssen grundlegende Untersuchungen über die Verbrennung einfacher Gase und die Bildung dieser Gase bei der oxidativen Pyrolyse vorangestellt werden.

Verbrennung thermisch stabiler Gase

Aus Abb. 2 ist ersichtlich, welchen Einfluß die Temperatur auf der "Verbrennung" der eingesetzten Gase hat. Zur besseren Vergleichbarkeit der gefundenen Werte ist nicht der jeweilige Reaktionsgrad α^i, sondern der entsprechende Verbrennungs-Umsatz $V_u[\%] = 100 \cdot \alpha^i/\alpha_u^i$ dargestellt. Die Verbrennungsdiagramme wurden, wie eingangs für den Fall von Gasen beschrieben, aufgenommen. Cyansäure und Cyanwasserstoff wurden durch Feststoffpyrolyse von Harnstoff bzw. Thioharnstoff im Verdampfer erzeugt. Wasserstoff wurde in die Untersuchung mit einbezogen, weil das Auftreten dieses Gases als Zwischenprodukt

nicht ausgeschlossen ist. Mit dem von uns meistens benutzten "kleinen Massenspektrometer" kann jedoch Wasserstoff nicht gemessen werden. Die Frage des zwischenzeitlichen Auftretens von Wasserstoff bleibt vorerst also noch offen. Die Eingangsdampfdrucke p^0 lagen zwischen 3 mb (Cyansäure) und 20 mb (Wasserstoff), und die Reaktionswärme hat demnach die Reaktionstemperatur am Reaktionsort allenfalls geringfügig über die gemessene Temperatur T angehoben.

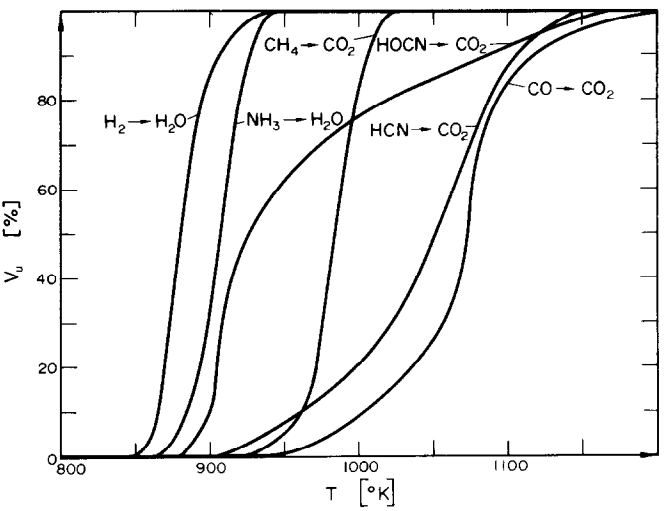

Abb. 2. Verbrennung thermisch stabiler Gase: Reaktionszeit $t = 1.8$ s.

Im Falle von Wasserstoff und Ammoniak wurde das Endprodukt Wasser gemessen; bei Methan und Kohlenmonoxid wurde Kohlendioxid registriert; der Umsatz von Cyanwasserstoff und Cyansäure wurde aus dem Verschwinden der Ausgangsverbindung berechnet, dabei war sichergestellt, daß in diesen beiden Fällen des Verschwinden der Ausgangsverbindung mit dem Auftreten der Verbrennungsendprodukte völlig synchron verläuft und demnach keine Zwischenprodukte auftreten. Die mittlere Reaktionszeit t (bei 973 K) betrug 1,8 s.

Läge der Verbrennung eine Molekularreaktion zweiter Ordnung mit entsprechend hoher Aktivierungsenthalpie zugrunde, so wäre die maximale Steilheit der Verbrennungsdiagramme erheblich geringer, als es bei den untersuchten Beispielen mit 3%/K der Fall ist. Nach der "transition state" Theorie ist, wenn die Aktivierungsentropie keine außergewöhnlichen Werte besitzt, die maximale Steilheit einer Umsatz-Temperaturkurve nämlich umgekehrt proportional der Temperaur und erreicht etwa 1%/K bei 1000 K. Wir nehmen deshalb an, daß in den steilen Bereichen ein Kettenmechanismus vorliegt. Für einen solchen Reaktionsmechanismus sprechen auch die Ergebnisse unserer kinetischen Untersuchungen, über die wir in Teil IV[22] dieser Reihe berichten werden, sowie die Beobachtungen anderer Autoren.[23–25]

Alle Verbrennungsdiagramme der Abb. 2 zeigen mindestens teilweise den für Kettenreaktionen typischen Verlauf. Unterhalb einer Mindesttemperatur T_{min} tritt das Endprodukt nicht in merklichem Umfange auf; die beobachtete Reaktion läuft praktsich *nicht* ab. Nach Überschreiten von T_{min} steigt, nach Durchlaufen einer mehr oder weniger langen

Anlaufphase, der Verbrennungs-Umsatz plötzlich steil an. Oberhalb dieser "Zündung" zeigt der Umsatz in der "Zündregion" einen nahezu konstanten großen Anstieg dV_u/dT und läuft dann, wieder flacher werdend, in die 100% Linie ein. Die Temperatur im Wendepunkt eines Verbrennungsdiagramms ist genauer bestimmbar als der Beginn der Zündung und wird zukünftig als Zündtemperatur T_Z *von* Wasserstoff, Methan usw. (steile negative Kennlinie) oder *zu* Wasser, Kohlendioxid usw. (steile positive Kennlinie) bezeichnet.

Während bei Wasserstoff, Ammoniak und Methan offensichtlich der Kettenmechanismus das ganze Reaktionsgeschehen beherrscht, sind in den Verbrennungsdiagrammen von Cyansäure, Cyanwasserstoff und Kohlenmonoxid flache Abschnitte enthalten, die einen anderen Reaktionstyp andeuten. Wir vermuten, daß hierbei Wandreaktionen mit Radikalcharakter eine erhebliche Rolle spielen. Dafür sprechen auch die in diesen Fällen von uns beobachtete beträchtliche Erniedrigung der Zündtemperatur bei Verwendung einer Rohrfüllung aus Quarzwolle (Tab. II) und der zeitliche Ablauf der betreffenden Reaktionen.[22]

Verbrennungsablauf bei organischen Verbindungen

In den Abb. 3–10 ist dargestellt, wie bei einigen einfachen organischen Verbindungen der Verbrennungsvorgang unter "Oxidations-Thermogramm-Bedingungen" im einzelnen abläuft. Bei der Verbrennung von Methan (Abb. 3) tritt Kohlendioxid früher auf, als auf Grund von Abb. 2 hätte erwartet werden können, wodurch der Anschein erweckt wird, daß ein Teil des Kohlenstoffs unmittelbar zu Dioxid verbrennt. Dem widerspricht jedoch der synchrone Verlauf von Wasser- und Monoxid-Diagramm. Wir neigen daher zu der Ansicht, daß in diesem Fall die Primärverbrennung des Kohlenstoffs—abgesehen vom oxidativen Pyrolyseprodukt Formaldehyd—ausschließlich zum Kohlenmonoxid führt. Dieses Monoxid wird dann in einer weiteren Kettenreaktion zum Dioxid verbrannt. Diese Annahme wird durch die Beobachtung gestützt, daß die Zündtemperatur von CO zu CO_2 mit zunehmender Wasserkonzentration im Trägergas stark abnimmt. Setzt man z.B. dem Trägergas Sauerstoff etwa 1% Wasser zu, so fällt die Zündtemperatur von Monoxid von 1070 K auf 970 K (vgl. Abb. 22 und Tab. 15 in [15]). Offenbar findet eine Kettenkatalyse statt, bei der Hydroxylradikale die Funktion der Kettenträger übernehmen.[26]

Auch die Entstehung des Kohlenmonoxids wird durch die sonstigen Bedingungen wesentlich mitbestimmt. So bewirkt eine Verkleinerung der Methankonzentration ein Ansteigen des Monoxid-Maximums von 970 K (p^0 = 15 mb) auf 1085 K (p^0 = 3 mb). Damit wird die Abhängigkeit des Verbrennungsverlaufs von Zufälligkeiten bereits an den einfachsten Verbindungen—Kohlenmonoxid und Methan—deutlich demonstriert. Gleichzeitig ergibt sich aus diesen Beobachtungen die Erkenntnis, daß bei der Elementaranalyse der Verbrennung von CO zu CO_2 ausschlaggebende Bedeutung zukommt, da es offenbar nicht möglich ist, die Bildung von Kohlenmonoxid zu verhindern.

Am Thermogramm von Benzol (Abb. 4) fällt die extreme Stabilität der Ausgangsverbindung ins Auge. Die oxidative Pyrolyse beginnt erst bei 930 K und zwar mit dem gleichzeitigen Auftreten von Kohlendioxid, Wasser, Kohlenmonoxid, Formaldehyd und Acetylen. Die beiden zuletzt genannten treten allerdings nur geringfügig in Erscheinung.

Eine Verkürzung der Reaktionszeit erhöht den Anteil von Acetylen nicht wesentlich und es darf angenommen werden, daß die Verbrennung zu Kohlendioxide, Kohlenmonoxid und Wasser *nicht* über primär gebildetes Acetylen abläuft. Der Sauerstoff scheint vielmehr direkt am Benzol anzugreifen. Diese Hypothese wird durch die Ergebnisse unserer Untersuchungen zur Inertpyrolyse[27] gestützt. In Helium bleibt nämlich einerseits Benzol bis zu

1300 K stabil und andererseits entsteht aus Acetylen bei sehr hohen Temperaturen Benzol. Wahrscheinlich verläuft die Verbrennung von Benzol über hydroxylierte und andere sauerstoffhaltige Zwischenverbindungen.[28]

Im Falle der Methanolverbrennung (Abb. 5) sind drei Phasen feststellbar. Bereits bei 800 K treten Formaldehyd und Wasser in Erscheinung, und Formaldehyd erreicht bei 880 K einen Maximalwert von 20%. Bei dieser Temperatur setzt dann die Zündung von Methanol ein, der Formaldehyd verschwindet, und es entsteht mit einer extrem steilen Zündkennlinie nahezu 100% Kohlenmonoxid. In der dritten Phase verbrennt dann Kohlenmonoxid bei flacher Kennlinie und relativ niedriger Zündtemperatur, die auf die Anwesenheit von Wasser zurückzuführen sind, zu Kohlendioxid.

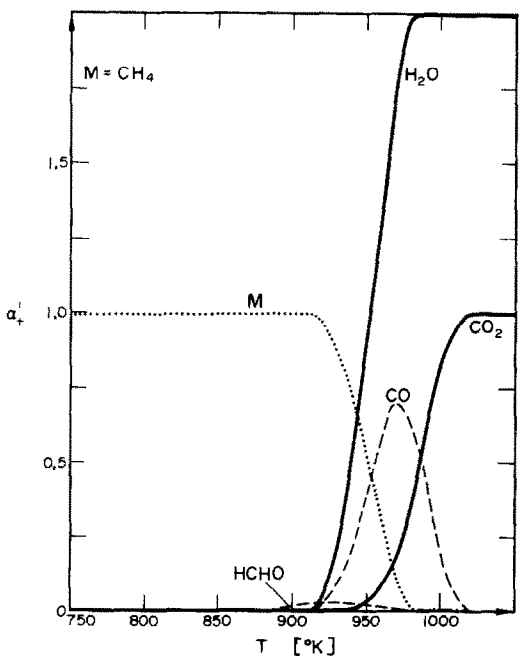

Abb. 3. Thermogramm von Methan

Setzt man dem Sauerstoff 2% Methan zu, so ändert sich am Verbrennungsverhalten von Methanol nichts. Andererseits beginnt die Verbrennung von Methan bereits bei 880 K; also erheblich früher als in Abwesenheit von Methanol (vgl. Abb. 3) und gleichzeitig mit diesem. Dies kann nur damit erklärt werden, daß eine Kettenübertragung bei gleichartigen Radikalen möglich ist, und so wird verständlich, daß Methan in keinem der untersuchten Fälle als Zwischenprodukt auftritt.

Aceton (Abb. 6) ist, im Vergleich zu den bisher besprochenen Beispielen, nicht besonders stabil. Bereits bei 750 K tritt Kohlendioxid in Erscheinung. Kohlenmonoxid und Formaldehyd tauchen erst bei höheren Temperaturen auf. Die Thermogramme dieser drei primären Verbrennungsprodukte steigen dann bis etwa 900 K langsam an, während das Aceton nahezu linear verschwindet. Der erste Kettenreaktionsmechanismus wird bei 910 K an der Zunahme der Steilheit des CO-Thermogramms deutlich. Dieses schnellere

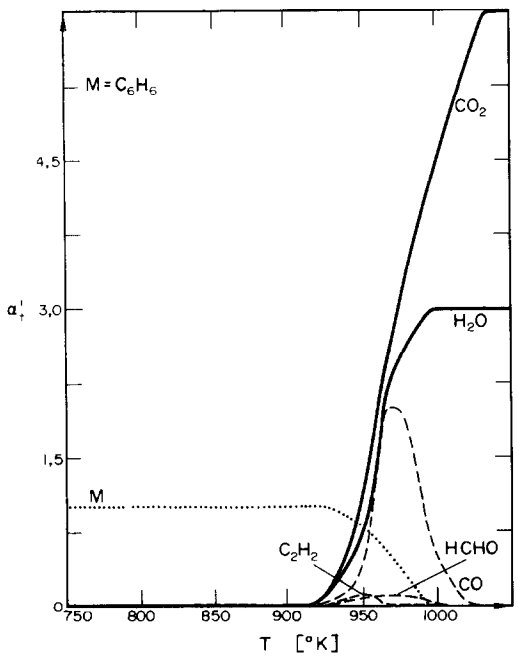

Abb. 4. Thermogramm von Benzol.

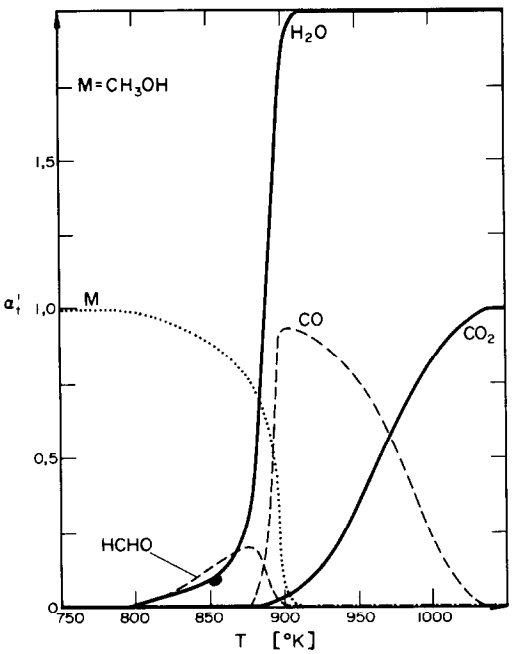

Abb. 5. Thermogramm von Methanol.

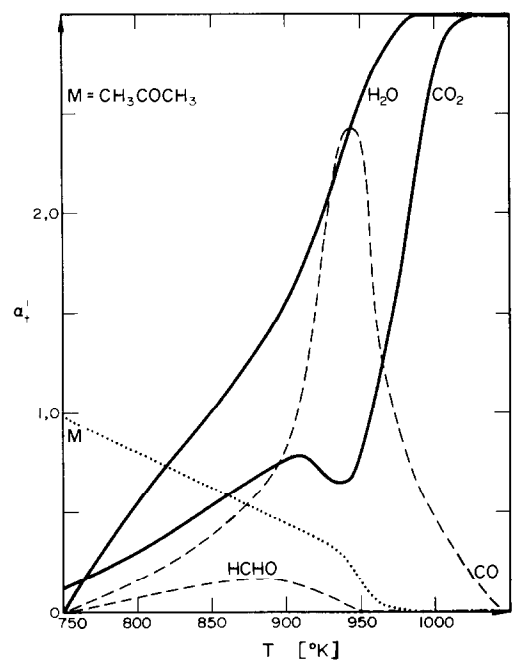

Abb. 6. Thermogramm von Aceton.

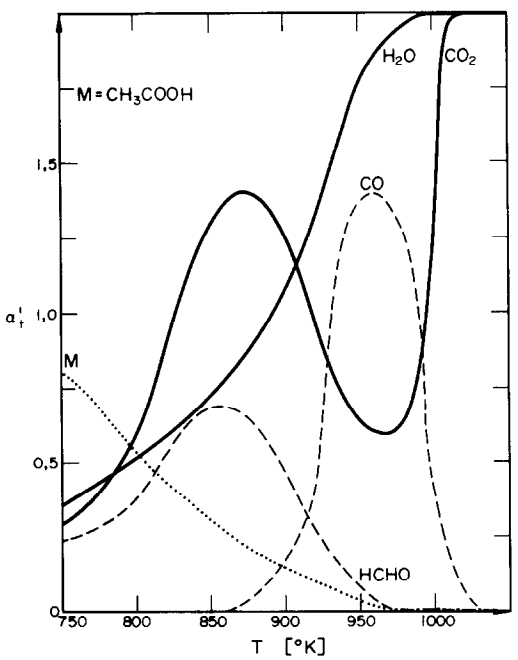

Abb. 7. Thermogramm von Essigsäure.

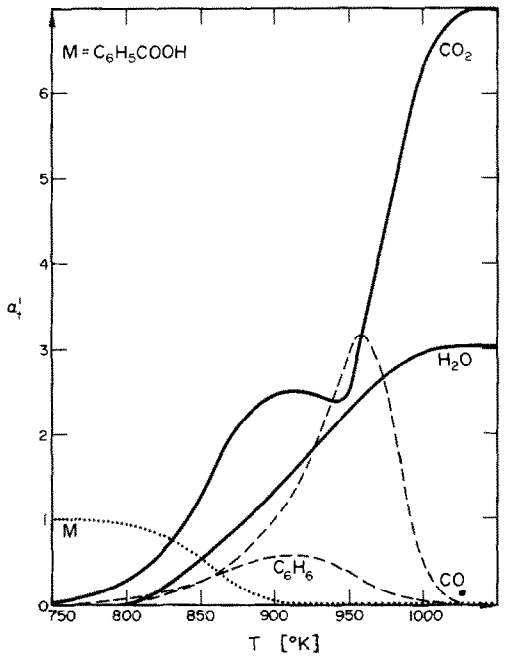

Abb. 8. Thermogramm von Benzoesäure.

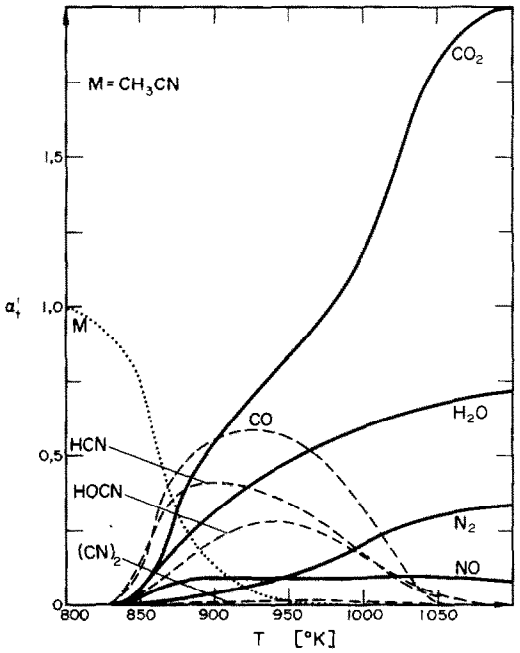

Abb. 9. Thermogramm von Acetonitril.

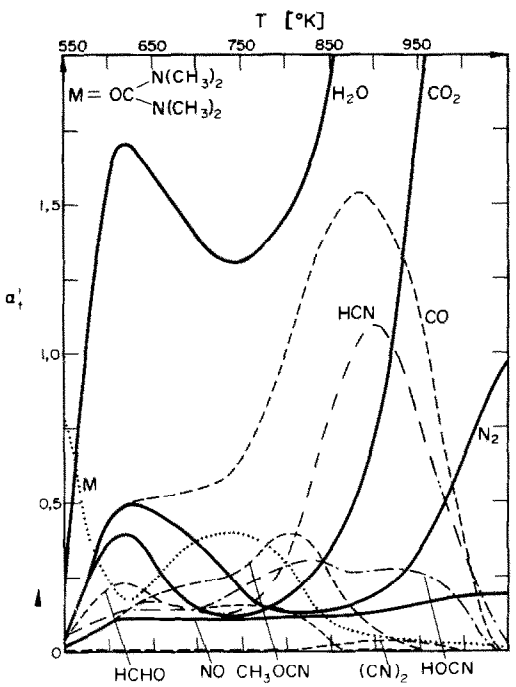

Abb. 10. Thermogramm von Tetramethylharnstoff.

Ansteigen des α^{CO}-Wertes ist aber nicht auf einen entsprechenden Acetonverlust zurückzuführen, sondern eher auf ein gleichzeitiges Absinken von Kohlendioxid und Formaldehyd. Offenbar wird das frühzeitig aus der Carbonylgruppe entstandene Kohlendioxid durch Formaldehyd wieder reduziert. Die letzte Verbrennungsstufe setzt bei 950 K mit der Zündung von CO und dem steilen Ansteigen der CO_2-Kennlinie ein. Auch jetzt ist noch immer ein Teil des Acetons intakt, und erst bei 970 K ist die Ausgangsverbindung völlig umgesetzt.

Auch bei der Verbrennung von Essigsäure (Abb. 7) tritt Kohlendioxid bereits bei sehr niedrigen Temperaturen in Erscheinung. Aus dem gleichzeitigen und gleich intensiven Auftreten von Wasser und Formaldehyd muß geschlossen werden, daß Essigsäure in dieser Phase Kohlendioxid abspaltet und der Methylrest zu Wasser und Formaldehyd verbrennt. Erst bei 880 K beginnt ein neuer Prozeß; das Kohlendioxid wird unter Bildung von Wasser durch den Aldehyd zu Kohlenmonoxid reduziert. Bei 950 K ist das übliche CO-Maximum zu beobachten, und die Endphase der Verbrennung beginnt mit dem steilen Anstieg des CO_2-Thermogramms.

Offenbar spalten alle organischen Säuren Kohlendioxid sehr früh ab, denn auch bei Benzoesäure (Abb. 8) ensteht CO_2 bereits unterhalb 750 K. In diesem Falle tritt allerdings als zweites Pyrolyseprodukt Benzol auf, das dann, wie in Abb. 4 gezeigt, verbrennt. Erstaunlicherweise entsteht in dieser Phase eindeutig mehr Kohlendioxid, als in der Ausgangsverbindung vorgebildet ist. Eine Abnahme dieser Konzentration erfolgt allerdings nicht, da kein Reduktionsmittel vorhanden ist. Statt dessen bleibt α^{CO_2} zwischen 900 und 960 K konstant bei 2,5; während Wasser und Kohlenmonoxid wie bei den früheren Beispielen zunehmen und bei hohen Temperaturen das typische Verhalten zeigen.

In Abb. 9 ist mit Acetonitril erstmals das Thermogramm einer stickstoffhaltigen Verbindung dargestellt. Obwohl die Ausgangsverbindung sehr einfach strukturiert ist, gestaltet sich die Verbrennung einigermaßen komplex. Die Nitrilgruppe reagiert offenbar nicht unmittelbar mit Sauerstoff, sondern bildet erst einmal Cyanwasserstoff, während gleichzeitig aus der Methylgruppe CO, CO_2 und H_2O enstehen. Die zeitweise Anwesenheit von Hydroxylradikalen kann daraus abgeleitet werden, daß die Cyansäurekonzentration noch ansteigt, während der Cyanwasserstoffanteil abfällt. Dicyan tritt ab 900 K in Spuren auf und kann bis 1050 K nachgewiesen werden. Daneben entstehen auch bei niedriger Temperatur bereits NO und N_2, und eine strukturspezifische Primärprodukt-Stöchiometrie kann deshalb nicht beobachtet werden. Die nachträgliche Verbrennung von HCN und HOCN liefert nur Stickstoff, und es entsteht kein weiteres Stickstoffmonoxid.

Die außerordentliche Stabilität von Acetonitril—Spuren sind noch bis 1000 K nachweisbar—wird durch eigene Pyrolyse-Untersuchungen[27] und Messungen anderer Autoren[29] bestätigt. In inertem Trägergas beginnt der Zerfall von Acetonitril erst bei 1140 K und das Pyrolysethermogramm verläuft anschließend so flach, daß bei 1260 K erst 25% der Ausgangsverbindung zerfallen sind. Die Anwesenheit von Sauerstoff bewirkt auch hier über den Mechanismus der oxidativen Pyrolyse ein schnelleres Auseinanderbrechen der Verbindung.

Bei Tetramethylharnstoff beginnt die oxidative Pyrolyse bereits bei sehr niedriger Temperatur. Deshalb wurde zur Untersuchung eine engere Einlaßsonde eingesetzt, die den in Abb. 10 gewählten Meßbereich von 550 bis 1000 K zugänglich macht. Das Geschehen auf der Tieftemperaturseite ist außerordentlich vielfältig. Bereits bei 600 K liegen mit Wasser, Kohlenmonoxid, Stickstoff, Kohlendioxid, Formaldehyd, Cyanwasserstoff, Cyansäure, Methylcyanat und Stickstoffmonoxid neun primäre Oxidationsprodukte in beträchtlichem Umfange neben dem Ausgangsmolekül M vor. Bei 620 K erreicht M ein Minimum

von etwa 20%. Bei der gleichen Temperatur bilden Kohlenmonoxid, Cyansäure und Stickstoffmonoxid ein Plateau, und Formaldehyd, Stickstoff und Kohlendioxid durchlaufen ausgeprägte Maxima. Anschließend steigt die Konzentration der Ausgangsverbindung bis 750 K wieder an, und die Primärprodukte, die ein Maximum gebildet hatten, sinken entsprechend ab.

Es ist sehr unwahrscheinlich, daß Tetramethylharnstoff durch Rekombination von primären Verbrennungsprodukten erneut entsteht, wie bspw. CO durch Reduktion von CO_2 bei der Verbrennung von Essigsäure (Abb. 7). Wir neigen vielmehr zu der Auffassung, daß das Maximum im Thermogramm der Ausgangsverbindung bei 750 K darauf zurückzuführen ist, daß Reaktionsmechanismen, die bei niedrigerer Temperatur zu einem schnellen Abbau von Tetramethylharnstoff beitragen, bei höheren Temperaturen nicht mehr ausschlaggebend sind und durch andere Reaktionstypen abgelöst werden.[30] Eine vollständige Aufklärung des sehr komplexen Tieftemperatur-Geschehens ist wohl nur durch Aufnahme der wesentlichen $\alpha_T^i(t)$-Diagramme zu erhalten. Bis 740 K scheint jedenfalls der Einfluß von Pyrolysevorgängen, die ohne Beteiligung von Sauerstoff ablaufen, zu überwiegen, denn die Sauerstoffbilanz bei dieser Temperatur ergibt erst einen Verbrauch von 1/2 Mol Sauerstoff pro Mol M.

Ab 850 K verläuft die Verbrennung in etwa analog zur Verbrennung von Acetonitril. Lediglich Stickstoffmonoxid steigt gegenüber dem Anfangswert noch etwas an. Das Geschehen oberhalb 1000 K entspricht in vollem Umfange dem Thermogramm der Abb. 9 und ist—zur Vergrößerung des Maßstabes im interessanten Bereich—in Abb. 10 nicht wiedergegeben. Bei 1120 K ist mit $\alpha^{CO_2} = 5$, $\alpha^{H_2O} = 6$, $\alpha^{N_2} = 0{,}9$ und $\alpha^{NO} = 0{,}2$ die Verbrennung abgeschlossen.

Allen Oxidations-Thermogrammen ist auf der Hochtemperaturseite gemeinsam, daß Kohlenmonoxid bei etwa 950 K ein Maximum durchläuft und dann als letztes aller Zwischenprodukte verbrennt. Die bei stickstoffhaltigen Verbindungen häufig entstehenden Zwischenprodukte Cyansäure und Cyanwasserstoff sind ebenfalls sehr stabil und sicher mit dafür verantwortlich zu machen, daß bei der klassischen Elementaranalyse einige stickstoffhaltige Stoffklassen systematisch Fehler zeigen.[31]

Die Tieftemperaturseite der Thermogramme wird dagegen von den strukturabhängigen Primärprodukten beherrscht, deren Zu- und Abnahme—auch in ihrer gegenseitigen Abhängigkeit—noch einer eingehenden Untersuchung bedarf. Schon jetzt ist jedoch ein Zusammenhang zwischen den in der Ausgangsverbindung enthaltenen funktionellen Gruppen und den entstehenden Zwischenprodukten eindeutig nachgewiesen. So bildet sich, wie weitere Messungen zeigen, Cyanwasserstoff immer aus Cyano- und Imino-Funktionen. Dagegen entsteht Stickstoffmonoxid primär ausschließlich aus Nitro- und Nitroso-Funktionen und erst sekundär aus der Verbrennung von anderen stickstoffhaltigen Gruppen wie Ammoniak oder Cyansäure. Offenbar ist der Tieftemperaturbereich der Verbrennungs-Thermogramme grundsätzlich zur Feststellung funktioneller Gruppen geeignet; jedoch müssen weitere Experimente erst zeigen, inwieweit durch Wahl der Reaktionsbedingungen die unspezifische Verbrennung gegenüber der strukturspezifischen oxidativen Pyrolyse zurückgedrängt werden kann.

Einfluß der Verbrennungsbedingungen

Für die Elementaranalyse ist eine vollständige Verbrennung zu den erwählten Endprodukten erforderlich und das eben geschilderte strukturspezifische Verhalten eher hinderlich. Andererseits beruht die häufig zur Erklärung von systematischen Fehlanalysen heran-

gezogene "Schwerverbrennbarkeit" nahezu ausschließlich auf der thermischen Stabilität weniger Zwischenprodukte und nicht wie bisher vielfach angenommen, auf der Stabilität der Ausgangsverbindungen. Die am schwersten verbrennbaren Gase—Kohlenmonoxid, Cyansäure und Cyanwasserstoff—sind deshalb so schwer verbrennbar, weil Teile ihrer Thermogramme verhältnismäßig flach verlaufen und dementsprechend eine hohe Temperatur und eine lange Verbrennzeit zur vollständigen Oxidation benötigt werden.

Das Fehlen einer schmalen und vollständigen Zündregion, wie sie als Folge einer ungehemmten Kettenreaktion beispielsweise bei Wasserstoff beobachtet wird, ist also bei den genannten Zwischenprodukten für die Schwerverbrennbarkeit verantwortlich, und es liegt nahe, nach Rohrfüllungen zu suchen, die den Mechanismus der Verbrennung derart beeinflussen, daß diese Reaktionshemmung beseitigt wird. Eine solche Rohrfüllung muß andererseits weitgehend inert sein und darf keinesfalls mit einem der Zwischenprodukte längerlebige Bindungen eingehen, da hierdurch eine störende Retention der Verbrennungsprodukte verursacht würde.

Als einfachste Rohrfüllung bietet sich die Quarzwolle an, die vielfach bei der Elementaranalyse eingesetzt wird. Durch eine solche Füllung werden die Oberfläche und die Zahl der Wandstöße vervielfacht. Eine katalytische Wirkung ist dagegen nicht zu erwarten. Trotzdem ändert sich, wie Tab. 2 zeigt, das Verbrennungsverhalten der untersuchten Gase nicht unerheblich. Die Quarzwolle (Fadendurchmesser etwa 0,01 mm) war bei den angeführten Messungen mit einer Packungsdichte von etwa 0,1 g/ml auf 100 mm Länge zwischen der Überbrückungskapillare und der Einlaßsonde eingesetzt. Damit können die gefundenen Umsatztemperaturen $T_{5\%}$, $T_{50\%}$ und $T_{95\%}$ unmittelbar mit den ensprechenden Werten des leeren Rohres verglichen werden, denn die Reaktionszeit bleibt mit 1,8 s bei 978 K die gleiche wie im leeren Rohr, und es wurden die gleichen Spezies wie bei Abb. 2 gemessen.

Die Quarzwolle ergibt eine wesentliche Verbesserung der Verbrennung nur bei den Zwischenprodukten Cyansäure und Cyanwasserstoff. Daneben erhöht diese Füllung allerdings die Qualität des Verbrennungsrohres für explosionsartig ablaufende Vorgänge (Pulsverbrennung) erheblich dadurch, daß einerseits eine innige Durchmischung mit dem Trägergas Sauerstoff auch unter diesen Umständen gewährleistet wird, und andererseits das Durchschlagen unverbrannter fester oder flüssiger Primärprodukte oder Explosionsrückstände (Ruß u. ä.) verhindert wird. Insbesondere die zuletzt genannte physikalische Wirkung der Quarzwolle rechtfertigt ihren Einsatz in der Elementaranalyse. Dabei darf aber nicht übersehen werden, daß zumindest bei der Schwefelbestimmung lästige Retentionszeiten und Memoryeffekte[14] durch die Quarzwolle bedingt sind.

Tabelle 2. Vergleich der Verbrennungseigenschaften von leerem Rohr, Quarzwolle und Platinwolle

Verbindung	Umsatztemperaturen, K, für V_u = 5; 50; 95%						
	leeres Rohr			Quarzwolle			Pt-Wolle
	5%	50%	95%	5%	50%	95%	95%
Wasserstoff	864	880	917	830	930	990	<720
Ammoniak	882	907	930	<670	760	830	760
Methan	958	985	1010	930	1090	1100	1030
Cyansäure	895	952	1120	<670	680	735	<720
Cyanwasserstoff	940	1055	1116	<670	760	1000	<720
Kohlenmonoxid	990	1070	1140	800	990	1150	<670

Im Gegensatz zur Quarzwolle greift eine Füllung mit Platinwolle offensichtlich tief in den Verbrennungsprozeß ein. Obwohl in diesem Falle die aus Platindraht von 0,05 mm Durchmesser gebildete Wolle nur über eine Länge von 10 mm unmittelbar hinter der Überbrückungskapillaren locker gestopft war (die Packungsdichte mit 2 g/ml ergibt einen Füllfaktor von etwa 10%), liegen fast alle Umsatztemperaturen bei sonst gleichen Meßbedingungen erheblich tiefer. Lediglich die Methanverbrennung verläuft wie im leeren Rohr. Dagegen ist Kohlenmonoxid bei 650 K bereits vollständig verbrannt (eine niedrigere Temperatur konnte bei der verwendeten Einlaßsonde nicht eingestellt werden, da mit abnehmender Temperatur der Druck in der Ionenquelle unzulässig hohe Werte erreicht).

Erstaunlicherweise erfolgt die Verbrennung von Wasserstoff ohne steile Zündkennlinie; sie ist aber ebenfalls in erheblich tiefere Temperaturregionen verlagert und bereits bei 730 K praktisch vollendet. Auch Cyansäure und Cyanwasserstoff verbrennen in Anwesenheit von Platin bei relative niedrigen Temperaturen und die Ammoniakoxidation wird durch die Platinkatalyse ebenfalls begünstigt. Im letzteren Falle ist aber—wie bei Wasserstoff—die Zündregion breiter geworden und ΔT_Z beträgt etwa 150 K (gegenüber 50 K im leeren Rohr bei allerdings 900 K).

Wahrscheinlich verläuft die Verbrennung an Platin nach einem LH-Mechanismus,[32] bei dem die Reaktion in der chemisorbierten Schicht geschwindigkeitsbestimmend ist, und bei dem Adsorptions- und Desorptionsvorgänge schnell ablaufen. Als chemisorbierte Schicht ist eine Belegung mit Sauerstoffatomen anzunehmen. Dadurch wird die zur Kettenfortpflanzung erforderliche Sauerstoffatom-Konzentration bereits bei wesentlich tieferen Temperaturen erreicht, als dies im Rohr ohne Katalysator der Fall ist.

Da der Verbrennungsmechanismus von Methan offenbar keine Sauerstoffatome benötigt,[33] kann die Platinwolle auch keine Änderung bewirken. Imgekehrt wird die oxidative Pyrolyse vieler thermisch stabiler Verbindungen durch Sauerstoffatome eingeleitet, und es ist in diesen Fällen auch für den ersten Teil des Verbrennungsprozesses eine erhebliche Verbesserung durch Platinwolle zu erwarten.

Wir konnten beispielsweise beobachten, daß Durol bei Verwendung von Platinwolle bereits bei 720 K völlig verschwunden ist, während im leeren Rohr bei 1000 K noch 5% der Ausgangsverbindung vorhanden sind. Auch die Zersetzung von Benzol beginnt an Platin bereits bei 600 K (leeres Rohr 900 K). Allerdings ist die Zersetzungskennlinie äußerst flach, und erst bei 1010 K ist Benzol völlig verschwunden. Damit besteht gegenüber dem leeren Rohr kein Unterschied hinsichtlich der benötigten Verbrennungstemperatur, denn diese wird ausschließlich durch die vollständige Verbrennung und nicht durch den Verbrennungsbeginn bestimmt.

Im Gegensatz zum leeren Rohr werden nach Platinwolle die thermisch stabilen Zwischenprodukte CO, HCHO, HCN und HOCN nicht beobachtet. Es erfolgt vielmehr ein direkter Übergang zu den Endprodukten. Die strukturspezifische oxidative Pyrolyse tritt z.B. bei Tetramethylharnstoff nicht auf. Hier werden ausschließlich die Endprodukte CO_2, N_2, H_2O und NO gefunden. Damit erweist sich Platinwolle als sehr geeignet, in Verbrennungsrohren eingesetzt zu werden. Dies gilt auch für den Platinwollepfropfen, der die Kupferoxidfüllung bei unserem Pulsverbrennungsverfahren[17,34] vom Verdampfungsraum trennt.

Zur Untersuchung des Einflusses des Sauerstoffpartialdruckes auf die Verbrennung wählten wir das Trägergasgemisch (96,5% Helium und 3,5% Sauerstoff), das in unserem CHN-Automaten[34] verwendet wird. Im übrigen blieben die Meßbedingungen gegenüber den Versuchen im leeren Rohr unverändert (keine Quarzwolle und keine Platinwolle). Un-

ter diesen Bedingungen beginnt die Oxidation von Kohlenmonoxid in etwa bei der gleichen Temperatur wie in reinem Sauerstoff, verläuft danach aber ohne ausgeprägte Zündung und erreicht bei 1200 K erst einen Verbrennungsumsatz von 40%. Dagegen zeigt die Wasserstoffoxidation in jeder Hinsicht das gleiche Verhalten wie in reinem Sauerstoff. Methan wiederum zündet erst bei wesentlich höherer Temperatur, verbrennt dann allerdings bei 1150 K mit extrem steiler Kennlinie, ohne daß Kohlenmonoxid in bemerkenswertem Umfang in Erscheinung tritt.

Im leeren Rohr kann also allenfalls mit Sauerstoff als Trägergas erfolgreich verbrannt werden. Ist der Sauerstoff durch Inertgase stark verdünnt, so müssen unbedingt Oxidationshilfen wie Platinwolle oder Kupferoxid eingesetzt werden. Bei genügendem Sauerstoffanteil (bspw. 50% Sauerstoff, 50% Helium) und Verwendung des Verbrennungskatalysators Platin, garantiert eine Reaktionszeit von 2 s bei einer Temperatur von nur 1100 K eine vollständige Verbrennung. Da eine derartige Rohrfüllung kaum Retentionszeiten bedingt, ergibt sich, in Verbindung mit massenspektrometrischer Detektion der Verbrennungsprodukte, eine zur Bestimmung vieler Elemente geeignete Schnellmethode.

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Summary—A measuring system is described which permits study of all stages of combustion processes as functions of carrier gas, temperature, residence time and tube filling. The organic sample is fed at constant speed into a stream of carrier gas. The mixture reaches the combustion chamber within a few milliseconds *via* a transfer capillary. With the help of a viscous inlet system, a sample of the resulting reaction products is taken and fed into a mass spectrometer. Reaction time and temperature can be adjusted within wide ranges or varied continuously. A plot of the extent of reaction of the various combustion products against temperature at a chosen reaction time yields an oxidation-thermogram which gives a clear picture of the combustion process. It is evident from thermograms of selected compounds that the samples decompose in the presence of oxygen at appreciably lower temperatures than in inert gas. The primary step of the decomposition is "oxidative pyrolysis" which often leads to other products than "inert pyrolysis" The intermediate products found are partly structurally specific and, especially with nitrogen-containing samples, are numerous and long-lived (for example, carbon monoxide, nitric oxide, cyanogen, hydrocyanic acid, cyanic acid and methyl cyanate). The notorious "difficult combustibility" is largely due to the fact that carbon monoxide, cyanic and hydrocyanic acids undergo complete combustion only at very high temperature. The combustion properties of the "empty tube" can be improved noticeably by a filling of quartz wool and markedly by partly filling with platinum wool.

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SHORT COMMUNICATIONS

TITRIMETRIC DETERMINATION OF GOLD BY PRECIPITATION WITH HYDROQUINONE

(*Received* 19 *February* 1974 *Revised* 18 *June* 1974. *Accepted* 25 *August* 1974)

Hydroquinone, first introduced by Beamish and co-workers,[1] is one of the best reagents for the gravimetric determination of gold. The metallic gold separates out as large particles and the reagent affords a good separation of gold from associated metals, but in general the method is slow because the precipitated gold has a marked tendency to stick to the walls of the beaker, thus offering difficulties in the transfer of the metal into the filter Volumetric methods possess a distinct advantage since this tedious operation can be dispensed with.

Several volumetric procedures are recorded in the literature and Beamish[2,3] has given a critical account of the various reagents. Iodometric,[4–6] ascorbic acid[7–9] and hydroquinone[10] methods are amongst the most prominent. Iodometric methods give accurate values but require careful control of pH and the amounts of iodide added when copper and iron are also present. Ascorbic acid suffers from the disadvantage of instability and both the visual indicator methods[7,9] need prior separation of the associated metals before gold is determined. Pollard's direct titrimetric determination of gold with hydroquinone,[10] using a visual indicator, does not suffer from these disadvantages but the method is best suited for determining gold only in amounts of 2 mg or less. With the exception of ferrous salts, none of the transition metal salts have been recommended as titrants by Beamish.[11] Tin(II) was also not considered suitable by the same author. Iron(II) salts are considered to be valuable for the determination of gold by back-titration procedures but their application for the determination of gold in presence of foreign metals has not been extensively studied. The procedure described in this communication is simpler and more rapid than most of the existing procedures and gold in the range 1·3–97·7 mg can be conveniently estimated without any rigid control over conditions Moreover, many associated metals do not interfere with the determination.

EXPERIMENTAL

Reagents

Gold chloride solution. Commercial gold, obtained from the local market, was purified by the procedure developed by Drawe.[12] The purified gold was dissolved in *aqua regia*, the solution evaporated thrice with concentrated hydrochloric acid and the residue dissolved and diluted to volume with 0·1 *M* hydrochloric acid. The solutions prepared contained 1–2 mg of gold per ml and were standardized gravimetrically.[1,13] A separate gold solution of the same strength was also prepared from chloroauric acid (Johnson Matthey), and was similarly standardized

Ceric sulphate solution, 0·05*M* Prepared from ceric ammonium nitrate according to the procedure given by Vogel[14] and standardized against sodium oxalate.[15,16]

Hydroquinone solution. About 1·35 g of pure hydroquinone was dissolved in 500 ml of 1–3% v/v sulphuric acid and standardized with ceric sulphate.[17] The solution remained stable for several weeks though its equivalence was found to decrease by about 0·5% within the first 24 hr from its preparation.[18]

Diphenylamine indicator solution, 1%. In concentrated sulphuric acid.

Table 1. Volumetric determination of gold by precipitation with hydroquinone

Gold taken, *mg*	Gold found, *mg*	Gold taken, *mg*	Gold found, *mg*
1·30	1·30	28·69	28·58
2·60	2·60	31·82	31·79
5·20	5·21	37·13	36 98
13·00	13·00	87·92	88·30
17 37	17·33	97·70	97·30
26·77	26·77		

Procedure

An aliquot of the gold solution was diluted to *ca.* 100 ml in a conical flask and the acid concentration adjusted to 0·05–0·1 *M* with 2*M* hydrochloric acid. A known and excessive volume of standard hydroquinone solution was added at a rate of 5–6 ml/min with swirling of the mixture. A drop of indicator was added and the excess of hydroquinone titrated with ceric sulphate to the violet end-point. The whole procedure could be completed within about 15 min. When the initial acid concentration of the gold solution was too high, the solution was evaporated on a hot water-bath to remove excess of acid[19] and the determination was carried out as described above. The results in Table 1 show clearly that the method can be used for the determination of gold in amounts ranging from 1·3 to 97·7 mg.

Determination of the error of the method

Six determinations of 8·90 mg of gold gave 8·96, 8·93, 8·93, 8·90, 8·93 and 8·90 mg, a mean value 8·925 mg, standard deviation 0·022 mg.

Table 2. Determination of gold in presence of foreign metal ions

Gold taken, *mg*	Added, *mg*				Gold found, *mg*
	Copper	Iron	Zinc	Nickel	
19·52	60	—	—	—	19·45
19·52	—	—	60	—	19·52
19·52	—	60	—	—	19·45
19·52	—	—	—	60	19·60
19·52	30	—	30	—	19·52
19·52	—	25	25	25	19·60
39·04	20	20	20	20	38·92
39·04	40	30	30	40	39·00
	Platinum		Palladium		
19·52	30		—		19·52
19·52	60		—		19·60
19·52	—		45		19·45
19·52	—		60		19·60
19·52	25		25		19·52
19·52	40		25		19·60
19·52	50		30		19·67
	Tellurium				
5·20	10				5·21
5·20	20				5·21
6·50	25				6·51
6·50	30				6·51
6·50	50				6·51
13·00	50				13·04
13·00	60				13·06

Effect of foreign metal ions

Gold is associated with base metals such as copper, zinc, nickel and iron in its alloys. It is also collected (by lead *etc.*) along with other noble metals such as platinum and palladium in its metallurgy. Gold is associated with tellurium in its ores. Hence the various metals, as the chlorides, were added in varying proportion to the gold solution and gold was determined by the procedure described above. The results in Table 2 show that these metals did not interfere in the estimation of gold when present in threefold w/w ratio to the gold, but when iron was present, the addition of 5 ml of phosphoric acid was necessary before the titration because of the reduction of Fe(III) to Fe(II) by hydroquinone, and the similarity of E° for this system and the indicator

Effect of chloride ion

Beamish *et al.*[1] state that reduction of gold(III) in cold 1·2*M* hydrochloric acid is complete in 2 hr. We have found that the gold(III) can be completely reduced to metal with hydroquinone at room temperature within a few minutes if the chloride ion concentration is maintained at 0·1*M* or less. We have also observed that reduction of gold(III) to metal with oxalic acid was quicker when the chloride ion concentration was kept low [20] In order to elucidate the effect of chloride ion on the reducibility of Au(III) to Au, the following experiment was conducted.

Ten ml of the gold solution (19·52 mg of gold) in 0·1*M* hydrochloric acid were taken in a 150-ml beaker and evaporated on a hot water-bath nearly to dryness to remove excess of acid.[19] The residue was dissolved in about 20 ml of water and the pH adjusted to nearly 1·5 with 2*N* sulphuric acid during dilution to 100 ml. Gold solutions become unstable if the pH is greater than 2.[21] The potential of the system was then measured with a platinum indicator electrode coated with a fine film of gold (this was obtained when a large number of potentiometric titrations of gold chloride were carried out with oxalic acid, using a platinum indicator electrode) and a saturated calomel reference electrode. To this solution 1*M* sodium chloride was added stepwise (1–25 ml) to give various chloride ion concentrations. This procedure was necessary because the separate aliquots of the same gold solution, after evaporation and subsequent dilution to the same volume, gave different starting potentials. This was due to trace amounts of hydrochloric acid being present with the residue even after evaporation. Complete removal of hydrochloric acid is not possible since it leads to the partial decomposition of the gold salt itself. After each addition, the contents were well stirred and the potential noted after a time pause of 1–2 min. To obtain chloride ion concentrations greater than 0·2*M*, the requisite quantity of solid sodium chloride was added to the solution. For practical purposes, the initial free chloride ion concentration was taken as zero. The experiments were repeated with concentrated hydrochloric acid in place of sodium chloride and the potentials obtained were noted. The values are represented graphically in Fig. 1. Erdey[8] carried out a similar type of experiment but did not take into account the need to keep the initial chloride ion concentration to a minimum. Therefore the maximum potential he obtained was around 855 mV *vs.* SCE, whereas our experiment gave 955 mV *vs.* SCE. Further, Erdey observed a fall of about 100 mV for an addition of nearly 20 ml of 6*M* potassium chloride, but we observed the same fall on the addition of only 1 ml of 1*M* sodium chloride. This indicates that a small increase in the chloride ion concentration will considerably reduce the potential of the system.

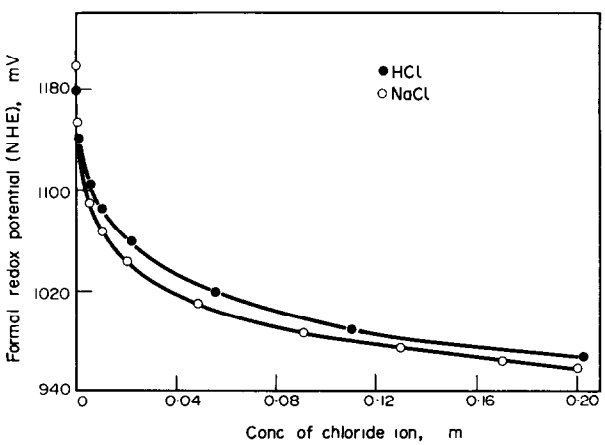

Fig. 1. Effect of chloride ion concentration on the formal redox potential of the gold(III)/gold system.

Experiments were also carried out to find the effect of sulphate ion concentration on the potential of the system containing chloride ion. The sized aliquot of the same gold solution was taken, diluted to 100 ml without prior evaporation and 1*M* sodium sulphate (or 9*N* sulphuric acid) was added stepwise to obtain different sulphate ion concentrations. The results recorded indicate that sulphate ions do not alter the potential of the system (Table 3).

The effect of chloride ion on our procedure was also studied. In these experiments, the same aliquots of the gold solutions were taken and varying amounts of hydrochloric acid or sodium chloride were added and the solutions diluted to 100 ml. To each of these solutions, 20 ml of hydroquinone solution were rapidly added and the excess was determined immediately with ceric sulphate. The results recorded in Table 4 lend further support to the fact that the reduction of gold is influenced by the chloride ion concentration.[20] Experiments 8 and 9 in the Table indicate clearly that sodium and hydrogen ions do not have any effective influence on the reduction of gold(III) by hydroquinone.

Determination of gold in a commercial sample

A commercially available gold alloy containing gold, copper and small amounts of silver was analysed as follows. The sample was dissolved in a minimum volume of *aqua regia*, and evaporated on a steam-bath, care being

Table 3. Formal redox potential of $AuCl_4^-/Au$ system in a medium of varying sulphate ion concentration

Sodium sulphate added		Sulphuric acid added	
Sulphate ion concentration, *M*	Formal redox potential *vs.* NHE, *V*	Sulphate ion concentration, *M*	Formal redox potential *vs.* NHE, *V*
—	1·052	—	1·168
0·005	1·058	0·009	1·169
0·01	1·059	0·018	1·172
0·0476	1·062	0·09	1·173
0·1	1·064	0·18	1·172
0·5	1·070	0·52	1·169
1·0	1·079	1·02	1·163

taken to avoid baking. The evaporation was repeated thrice with small volumes (2–3 ml) of concentrated hydrochloric acid. The residue was extracted with about 10 ml of 0·1*M* hydrochloric acid and the solution filtered through a Whatman No. 42 filter paper (9 cm) into a 250-ml flask. The filter paper was washed with about 100 ml of 0·1*M* hydrochloric acid. The filter paper was then ashed and treated with a few drops of *aqua regia*, and the evaporation was repeated. The residue was dissolved in 0·1*M* hydrochloric acid and the solution filtered into the original flask, and the combined solution was made up to volume with 0·1*M* hydrochloric acid. Various aliquots of the solution were analysed for gold by our procedure. It was also simultaneously analysed gravimetrically with hydroquinone. The gravimetric procedure gave the gold content of the alloy as 79·07%, whereas our procedure showed it to be 78·94 ± 0·06%.

Table 4. Values of gold obtained at different chloride ion concentrations

No.	Gold taken, *mg*	Medium	Gold found, *mg*
1	19·52	1*M* HCl	16·92
2.	19·52	0·5*M* HCl	19·31
3	19·52	0·1*M* HCl	19·60
4	19·52	0·05*M* HCl	19·60
5.	19·52	0·01*M* HCl + 1*M* NaCl	16·33
6	19·52	0·01*M* HCl + 0·5*M* NaCl	19·00
7	19·52	0·01*M* HCl + 0·1*M* NaCl	19·60
8.	19·52	0·01*M* HCl + 1·0*M* H_2SO_4	19·60
9.	19·52	0·01*M* HCl + 1*M* Na_2SO_4	19·60

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Department of Chemistry
Sri Venkateswara University
Tirupati-517502, *India*

S. C. Soundar Rajan
N. Appala Raju

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Summary—A rapid method for the volumetric determination of gold is described. Gold(III) is reduced to metal with excess of hydroquinone at room temperature and the excess is titrated with ceric sulphate. The effect of chloride ion on the reducibility of gold(III) to the metal is discussed. This method can be successfully employed for the determination of gold in presence of certain base and noble metals. The method was successfully adopted for the determination of gold in a commercial sample.

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EXTRACTIVE PHOTOMETRIC SIMULTANEOUS DETERMINATION OF IRON(II) AND COPPER(II) WITH *syn*-PHENYL-α-PYRIDYL KETOXIME AND ANALYSIS OF FERRITES

(*Received* 29 *May* 1974. *Accepted* 27 *August* 1974)

Simultaneous determination of iron and copper is often a problem in analysis of catalysts, metals and alloys, mixed oxides used as ferrites, biological materials and minerals and ores.

For the simultaneous determination of copper and iron a polarographic method was suggested by Cathro and Walkley[1] and Hetman.[2] Usatenko and Suprunovich[3] developed a differential amperometric method for the simultaneous determination of iridium, palladium, iron and copper. Amongst the extractive photometric methods for the determination of iron and copper those of Wilkins and Smith[4] and of Karvanek[5] use the technique of estimation of the two elements in different phases. The complexes of Fe(II) and Cu(II) with 1,10-phenanthroline are estimated at pH 8·3 at 510 nm and 435 nm in the aqueous and organic phases (n-octanol) respectively. Brasted[6] developed a titrimetric procedure for iodometric determination of both metals. Kitson[7] developed a spectrophotometric method using ammonium thiocyanate. Successive photometric end-point detection in an EDTA titration is recommended by Underwood.[8] Banerjea and Tripathi[9] developed a method of simultaneous spectrophotometric determination of Cu(II) and Fe(II) with methyl-2-pyridyl ketoxime. A sequential titrimetric procedure—with a potentiometric end-point followed by a spectrophotometric one—was suggested by Takeuchi.[10] Simultaneous use of two ligands for the determination of Cu(II) and Fe(II) in a mixture is recommended by Zak and Ressler.[11] The same method was extended to determination of serum iron and copper and of iron-binding capacity by Joossens and Claes[12] and Lander and Zak.[13]

A method due to Schilt and Taylor[14] consists of measuring photometrically the complexes of Cu and Fe with 3-(2-pyridyl)-5,6-diphenyl-1,2,4-triazine and then measuring only the Fe complex by converting Cu quantitatively into its cyanide complex. A method using a single extraction with *N*-phenylbenzohydroxamic acid is reported by Parkov and Nhi.[15] We present in this paper an extractive method for simultaneous spectrophotometric determination in which both elements are extracted into the organic phase with *syn*-phenyl-α-pyridyl ketoxime (HPPK). The method is quicker than those suggested in the literature and the reagent is easily synthesized. Copper was estimated with HPPK in slightly acidic medium and at 370 nm by Deguchi and Yamamoto.[16] Sen[17] has reported the spectrum of the copper–HPPK complex in alkaline medium with an absorption maximum at 475 nm. Iron was estimated in alkaline medium at 550 nm with HPPK by Trusell and Diehl[18] The present method is based on their findings The synthesis and the colour reactions of HPPK with several metals were reported by Sen.[19,20] The method is further applied to ferrites.

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EXPERIMENTAL

Reagents

The reagent *syn*-phenyl-α-pyridyl ketoxime was prepared from 2-benzoylpyridine according to Trusell and Diehl.[18] The product was crystallized several times from ethyl alcohol to give the pure *syn*-form as colourless prisms, m.p. 151–152° (literature value 151–152°).[21] The reagent was used as a 1% solution in 95% ethanol. The stock solutions of copper and iron containing 1 mg of metal per ml were prepared by dissolving analytical-grade cupric sulphate and ferrous ammonium sulphate in doubly distilled conductivity water containing a few drops of analytical-grade sulphuric acid, standardized spectrophotometrically,[23] and further diluted as required. Chloroform was distilled before use. Doubly distilled conductivity water was used throughout. Aqueous sodium carbonate solution was prepared from analytical-grade material.

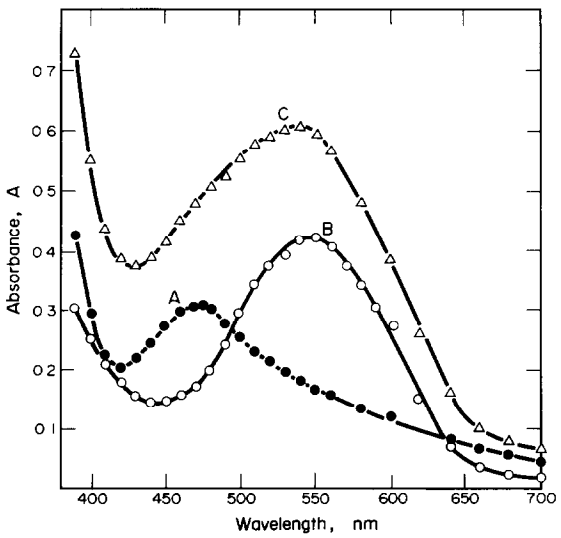

Fig. 1. Absorption spectra of (*A*) –●–●–●– Copper complex ($7.87 \times 10^{-5} M$); (*B*) –○–○–○– iron complex ($3.58 \times 10^{-5} M$) and (*C*) –△–△–△– mixture of both.

Table 1. Properties of the complexes

Complex	λ_{max}, nm	ϵ_1 *l.mole*$^{-1}$*.cm*$^{-1}$ 475 nm	550 nm	Colour
Cu(II)	475	3.94×10^3	2.16×10^3	Brown
Fe(II)	550	5.17×10^3	1.19×10^4	Red

Table 2. Analysis of samples

Sample	Fe(II), $10^{-5}M$ Taken	Found	Cu(II), $10^{-5}M$ Taken	Found	Relative standard deviation, % Fe	Cu
I	3·578	3·52	1·575	1·57	0·1	1·1
II	1·789	1·75	7·874	7·99	0·7	0·9
III	1·789	1·77	4·724	4·75	0·6	0·1
IV	2·683	2·64	3·149	3·14	0·1	0·9
V	3·578·	3·50	7·874	8·01	0·5	1·1

Table 3. Analysis of ferrites

Sample	Weight, *mg*	Iron(III) oxide						Copper(II) oxide					
		Expected			Found			Expected			Found		
		Fe, *mg*	Fe_2O_3, *mg*	Fe_2O_3, %	Fe, *mg*	Fe_2O_3, *mg*	Fe_2O_3, %	Cu, *mg*	CuO, *mg*	CuO, %	Cu, *mg*	CuO, *mg*	CuO, %
A	14·70	5·14	7·35	50·0	5·08	7·26	49·4	5·87	7·35	50·0	5·83	7·31	49·7
B	12·21	2·85	4·07	33·3	2·79	3·99	32·7	6·50	8·14	66·7	6·40	8·02	65·7
C	9·03	0·63	0·90	10·0	0·63	0·90	10·0	6·49	8·13	90·0	6·45	8·09	89·5

Procedure

An aliquot of sample containing up to 0·04 mg of Fe(II) and 0·2 mg of Cu(II) was diluted to about 10 ml, 1 ml of 1% ascorbic acid solution and 1 ml of reagent solution were added and the pH was adjusted to 10·0 with sodium carbonate solution The solution was transferred to a 100-ml separatory-funnel and was shaken with 3 ml of chloroform for 2 min. It was allowed to stand for 5 min and then the chloroform layer was transferred to a 10-ml flask through a small dry cotton plug in the stem of the separatory-funnel. The extraction was repeated and the combined extracts were diluted to the mark. The absorbance was measured in triplicate at 475 and 550 nm. The concentrations of the two elements were then determined by solving the appropriate simultaneous equations.

Analysis of ferrites

Ferrites are sintered mixed oxides and are extensively used in electronic devices. When the material is mixed oxides of iron(III) and copper(II) the present method can be successfully applied.

About 10 mg of accurately weighed powdered sample is dissolved in 2·0 ml of concentrated nitric acid by boiling. Concentrated sulphuric acid is then added and heating continued till white fumes appear and the volume is about 1 ml. The mixture is then cooled and made up to the mark with distilled water in a 50-ml standard flask. An aliquot containing up to 30 μg of Cu and 15 μg of Fe is taken in a separatory-funnel, and the procedure is applied.

RESULTS AND DISCUSSION

The absorption spectra of the Fe(II) and Cu(II) complexes and of a mixture of the two are given in Fig. 1. The reagent does not show absorption within the region 400–700 nm. When the pH range 9·0–11·0 is used the absorption is constant for several hours. Hence a pH of 10·0 was used for determinations. If iron is present as Fe(III), ascorbic acid acts as a suitable reducing agent. The entire amount of Fe(II) and Cu(II) is extracted in two extractions. For iron(II), copper(II) and mixtures of the two, Beer's law is obeyed up to 0·004 mg/ml for Fe(II) and 0·02 mg/ml for Cu(II) in the chloroform layer, and the absorbances are additive over these ranges.

The absorption maxima for the Fe(II) and Cu(II) complexes are at 550 and 475 nm respectively. The molar absorptivities at these wavelengths are summarized in Table 1.

The equations

$$A_{475} = \epsilon^{Fe}_{475} \times [Fe] + \epsilon^{Cu}_{475} \times [Cu]$$
$$A_{550} = \epsilon^{Fe}_{550} \times [Fe] + \epsilon^{Cu}_{550} \times [Cu]$$

are used to develop the simultaneous equations

$$[Cu] \times 10^4 = 3\,337 \times A_{475} - 1{\cdot}452 \times A_{550}$$
$$[Fe] \times 10^4 = 1\,106 \times A_{550} - 0{\cdot}606 \times A_{475}$$

where A_{550} is the absorbance of the mixture at 550 nm and A_{475} that at 475 nm; [Fe] and [Cu] are the molar concentrations of iron and copper. An accurate set of equations should be derived for the particular spectrophotometer to be used for the determinations.

Several synthetic mixtures were prepared and analysed in triplicate The results are summarized in Table 2. Table 3 gives the results of analyses of three ferrite materials; each measurement was made in quadruplicate.

The relative standard deviations are 0·7% for Fe(II) and 1·1% for Cu(II).

Nickel and cobalt interfere strongly, and this method is applicable only in the absence of these ions.

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Department of Chemistry
Shivaji University
Kolhapur-416004
Maharashtra State, India

C. K. BHASKARE®
S. G. KAWATKAR

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Summary—A rapid method of simultaneous spectrophotometric determination of up to 4 ppm of iron(II) and 20 ppm of copper(II) in a mixture by chloroform extraction of the *syn*-phenyl-α-pyridyl ketoxime complexes at pH 10·0, is developed. Measurements are made at 550 and 475 nm. Two simultaneous equations are solved to obtain the concentrations of the two ions. Analysis of five synthetic mixtures in triplicate gave relative standard deviations of 0·7% for Fe(II) and 1·1% for Cu(II).

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SEPARATION AND GRAVIMETRIC DETERMINATION OF CERIUM AND LANTHANUM WITH *N*-*m*-TOLYL-*m*-NITROBENZOHYDROXAMIC ACID

(*Received* 16 *January* 1974. *Revised* 1 *August* 1974. *Accepted* 29 *August* 1974)

The hydroxamic acids have found wide analytical application. *N*-Phenylbenzohydroxamic acid (PBHA) is widely used as a gravimetric reagent for determination of various metal ions.[1–6] Introduction of a bulky group into PBHA gives a larger molecular weight and hence better conversion factor and may improve the selectivity of the reagent. With this in view a new reagent, *N*-*m*-tolyl-*m*-nitrobenzohydroxamic acid (TNBHA), has been developed for the gravimetric determination and separation of cerium and lanthanum from several commonly occurring metals and from other rare earths.

EXPERIMENTAL

Reagents

The *N*-*m*-tolyl-*m*-nitrobenzohydroxamic acid was synthesized by the procedure of Agrawal and Tandon,[7] m.p. 118° (literature value 118°). Its purity was checked by thin-layer chromatography and infrared and ultraviolet spectroscopy. A 0·01*M* solution in ethanol was used.

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EXPERIMENTAL

Reagents

The *N*-*m*-tolyl-*m*-nitrobenzohydroxamic acid was synthesized by the procedure of Agrawal and Tandon,[7] m.p. 118° (literature value 118°). Its purity was checked by thin-layer chromatography and infrared and ultraviolet spectroscopy. A 0·01*M* solution in ethanol was used.

Aqueous 0·001*M* stock solutions of cerium and lanthanum were prepared by dissolving 0·4042 g of ceric sulphate and 0·4330 g of lanthanum nitrate in a litre of doubly distilled water, and standardized titrimetrically [8]

Solution of the masking agents (1% w/v) were prepared in doubly distilled water.

Procedure

In a 1-litre beaker, 20 ml of 0·001*M* cerium or lanthanum and about 500 ml of water were heated to 60° on a steam-bath. Then 20 ml of 0·01*M* TNBHA in ethanol was added dropwise with constant stirring, followed by 0·1*M* ammonia until precipitation was complete The pH (3,8–4·1 for cerium and 7·5–8·5 for lanthanum) was adjusted with 0·1*M* ammonium chloride. The granular complex thus obtained was digested for 2–3 hr on a steam-bath, filtered off on a sintered-glass crucible of porosity 4 and washed thoroughly with hot water and finally with ten 10-ml portions of 20% aqueous ethanol. The complex was dried at 110° and weighed directly as $(C_{14}H_{11}N_2O_4)_nM$.

Separation of cerium and lanthanum from foreign ions. A 20-ml portion of 0·001*M* cerium or lanthanum was mixed with a known amount of the foreign metal ion and diluted to 500 ml. The pH was adjusted to 3·8–4·1 or 7·5–8·5 with 0·1*M* ammonia and nitric acid. A 10-ml portion of 1% potassium cyanide solution was added and the mixture heated to 60° on a steam-bath and the precipitation *etc*, completed as before, except that only a 1-hr digestion was used. The cerium or lanthanum could be separated from and determined in presence of Ag^+, Mn^{2+}, Zn^{2+}, Ca^{2+}, Hg^{2+}, Cu^{2+} Ga^{3+} and Ni^{2+}

Cerium or lanthanum could be separated from Pd^{2+}, Pb^{2+}, Be^{2+}, Sb^{3+}, Sn^{4+}, Bi^{3+}, Zr^{4+} and Ti^{4+} if 10 ml of 1% citrate and oxalate solution were used instead of the cyanide solution.

Cerium and lanthanum could also be separated from Al^{3+}, V^{5+}, Mo^{6+} by using Mg–EDTA as masking agent.

Separation of lanthanum from cerium, uranium, thorium and rare earths. Lanthanum was separated from thorium, uranium and cerium by precipitating these at pH 3·8–4·8 with TNBHA and then precipitating lanthanum at pH 7·5–8·5 in the filtrate.

Praseodymium and neodymium form soluble complexes with NTBHA at pH 8·5, which have no effect on the determination of cerium and lanthanum.

RESULTS AND DISCUSSION

The experimental results are given in Tables 1 and 2. The cerium and lanthanum precipitates are fairly soluble in dioxan, ethanol, chloroform and benzene, and sparingly soluble in carbon tetrachloride, ethyl acetate, ether and glacial acetic acid. They are decomposed when treated with concentrated sulphuric, perchloric, nitric or hydrochloric acid. The analytical results indicate the compositions to be $(C_{14}H_{11}N_2O_4)_4$ Ce and $(C_{14}H_{11}N_2O_4)_3$La.

Precipitation is complete over the pH ranges 3·8–4·1 for cerium and 7·5–8·5 for lanthanum. The maximum error is 13 ± 0·02 mg for 2–28 mg of cerium and ±0·01 mg for 2–14 mg of lanthanum.

Masking agents

The presence of excess of cyanide and magnesium–EDTA did not interfere with the precipitation of cerium or lanthanum However, excess of citrate and oxalate inhibited the precipitation.

Infrared spectra

The infrared spectrum of a mull of TNBHA showed peaks at 3279, 1600 and 917 cm^{-1}, due to stretching vibrations of O–H, C=O and N–O respectively The spectra of the precipitates show no peak for the O–H stretching vibration (3279 cm^{-1}). The peak due to the carbonyl (C=O), stretching vibration in the spectra of the precipitates is located at 1560 or 1555 cm^{-1}, but the peak due to the N–O stretching vibration is almost unaffected.

Table 1 Gravimetric determination of cerium(IV) and lanthanum(III) with *N*-*m*-toly-*m*-nitrobenzohydroxamic acid

Cerium taken, *mg*	Cerium found, *mg*	Lanthanum taken, *mg*	Lanthanum found, *mg*
2·80	2·82	2 78	2·77
5·60	5·61	5·56	5·56
5·60	5 58	5·56	5·57
14·00	13·99	11·12	11·12
14·00	14 02	13·90	13·90
28·00	28·01	13·90	13·90

Table 2. Separation and determination of cerium(IV) and lanthanum(III) from other metals

Ce taken, *mg*	La taken, *mg*	Foreign ions, *mg*	Masking	Ce found, *mg*	La found, *mg*
8·40	5·56	Ag^{+} 60	Cyanide	8·40	5·57
14·00	11·12	Mn^{2+} 100	Cyanide	14·00	11·13
14·00	—	Ni^{2+} 100	Cyanide	14·01	—
8·40	11·12	Cu^{2+} 80	Cyanide	8·42	11·14
8·40	11·12	Zn^{2+} 80	Cyanide	8·38	11·11
8·40	11·12	Cd^{2+} 80	Cyanide	8·38	11·12
14·00	11·12	Hg^{2+} 100	Cyanide	14·03	11·11
14·00	11·12	Pd^{2+} 80	Citrate + oxalate	14·01	11 12
8·40	5·56	Be^{2+} 100	Citrate + oxalate	8·42	5·57
8·40	5·56	Ga^{3+} 80	Cyanide	8·37	5·56
19·60	13·90	Sb^{3+} 80	Citrate + oxalate	19·58	13·92
19·60	13·90	Bi^{3+} 80	Citrate + oxalate	19·64	13·89
14·00	13·90	Ti^{4+} 60	Citrate + oxalate	14 02	13·90
14·00	11·12	Zr^{4+} 60	Citrate + oxalate	14·02	11·12
14·00	—	As^{3+} 80	Citrate + oxalate	14·00	—
—	5·56	Pd^{2+} 80	Citrate + oxalate	—	5·56
14·00	11·12	Al^{3+} 80	Mg–EDTA	14·02	11·12
—	13·90	Sn^{4+} 100	Citrate + oxalate	—	13·91
—	13·90	Ce^{3+} 100	*	—	13·91
14·00	13·90	Pr^{3+} 100	*	14·00	13·88
14·00	13·90	Nd^{3+} 100	*	14·00	13·88
—	11·12	Th^{4+} 100	*	—	11·14
14·00	13·90	V(*V*) 100	Mg–EDTA	14·02	13·92
14·00	11·12	Mo(*VI*) 100	Mg–EDTA	13·98	11·12
—	11·12	U(*VI*) 100	*	—	11 11

* Adjusting the pH.

Therefore it may be concluded that the O–H group loses a proton and the residual oxygen atom and the oxygen atom of the carbonyl group are co-ordinated with the cerium or lanthanum.

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Department of Chemistry
Maulana Azad College of Technology
Bhopal (M.P.), India

H. L. KAPOOR

Department of Chemistry
Govt. Polytechnic
Ujjain (M.P.), India

Y. K. AGRAWAL®*
P. C. VERMA

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* Present address: Health Physics Division, Bhabha Atomic Research Centre, Trombay, Bombay-400085, India.

Summary—Cerium and lanthanum were determined gravimetrically by selective precipitation with *N*-*m*-tolyl-*m*-nitrobenzohydroxamic acid and separated from several metal ions such as Ag^{+}, Be^{2+}, Pb^{2+}, Mn^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Hg^{2+}, Pd^{2+}, Ga^{3+}, Al^{3+}, Bi^{3+}, Sb^{3+}, Sn^{4+}, Ce^{3+}, Pr^{3+}, Nd^{3+}, Ti^{4+}, Zr^{4+}, Th^{4+}, V^{5+}, Mo^{6+} and U^{6+}. The precipitates were weighted directly after drying at 110°. The analytical results indicated the composition of the complexes to be $(C_{14}H_{11}N_2O_4)_nM$.

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ANALYTICAL DATA

FORMATION OF FERROCYANIDES—IV*

Th(IV), Nd(III), UO_2(II) AND Hg(II)

(*Received* 23 *November* 1973, *Revised* 4 *September* 1974, *Accepted* 11 *September* 1974)

In earlier studies the possibility was pointed out of obtaining complexes of the types M–$Fe(CN)_6$ and M′–M″–$Fe(CN)_6$, depending on the characteristics of the two cations[1–5] in the reaction between a metal ion and potassium ferrocyanide. For these complexes thermodynamic parameters and stability ranges were also evaluated.[6,7]

The present investigation similarly studied the systems formed by potassium hexacyanoferrate(II) and Th(IV), Nd(III), UO_2(II) and Hg(II).

EXPERIMENTAL

Potentiometric titrations were done with the cell described earlier.[2] For the system Hg(II)–$K_4Fe(CN)_6$ potentiometric titrations were also done with a membrane selective electrode for mercury.

The $K_4Fe(CN)_6$ solution was standardized potentiometrically[1] with zinc under the analytical conditions for formation of $K_2Zn_3[Fe(CN)_6]_2$ and kept in dark bottles.

The solutions of the nitrates of Th(IV), Nd(III) and UO_2(II) were standardized gravimetrically by means of urea,[8] ammonium oxalate[9] and ammonia[9] respectively; that of Hg(II) was standardized by oscillometric titration with potassium chloride.[10]

RESULTS AND DISCUSSION

System $Th(NO_3)_4$–$K_4Fe(CN)_6$–H_2O

The results obtained indicate the formation of only the white $ThFe(CN)_6$ irrespective of the direction of titration over the ranges studied: pTh = 1–3 and $pFe(CN)_6^{4-}$ = 1–2·92. The same compound was also obtained in 0·5 *M* potassium nitrate medium. The potential drop at the equivalence point was 80–100 mV

System $Nd(NO_3)_3$–$K_4Fe(CN)_6$–H_2O

Nd(III) reacts very slowly at room temperature, so the titrations were carried out at 70°. The direction of the titration and the presence of 0·5 *M* potassium nitrate have no influence on the stoichiometry of the compound formed; only the white $KNdFe(CN)_6$ was obtained. The concentration ranges investigated were pNd = 1·42–2·96 and $pFe(CN)_6^{4-}$ = 1·42–3·2.

The potential drop at the equivalence point was 100–120 mV.

System $UO_2(NO_3)_2$–$K_4Fe(CN)_6$–H_2O

In order to avoid the hydrolysis of UO_2(II) this reaction was studied in 10^{-2} *M* nitric acid medium.[11] Only the reddish-brown $K_4(UO_2)_4[Fe(CN)_6]_3$ is obtained (also in presence of 0·5 *M* potassium nitrate). The potential drop at the equivalence point was about 80 mV. The concentration ranges studied were pUO_2 = 1·1–2·92 and $pFe(CN)_6^{4-}$ = 1·4–3·2.

System $Hg(NO_3)_2$–$K_4Fe(CN)_6$–H_2O

The results obtained by both the methods utilized are similar; the white precipitate obtained changes rapidly into a blue substance. Titration of $Fe(CN)_6^{4-}$ with Hg(II) gave a product $Hg_2Fe(CN)_6$, but in the reverse titration it was impossible to obtain a compound of definite stoichiometry, and this is attributed to the decomposition of $Fe(CN)_6^{4-}$ by Hg(II) at a rate proportional to the Hg(II) concentration.[12] Hence it may be assumed that different cyanide complexes are formed, depending on the amount of Hg(II).

Table 1 summarizes the results of a number of titrations and indicates the analytical possibilities.

* Presented at the "Convegno Nazionale di Chimica Analitica" Ferrara (Italy), 16–18 October, 1973. Supported by the Consiglio Nazionale delle Ricerche—Roma.

Table 1 Stoichiometry of the reaction between $K_4Fe(CN)_6$ and Th(IV), Nd(III), UO_2(II) and Hg(II)

Titrand (50 ml) *mmole*	Titrant, *mmole*	Formula	Found, *mmole*	Error, %
Th(IV)	$Fe(CN)_6^{4-}$			
0·530	0·531	$ThFe(CN)_6$	0·531	+0·2
1·060	1·062		1·062	+0·2
1·590	1·600		1·600	+0·6
0·318*	0·313		0·313	−1·6
1·590*	1·585		1·585	−0·3
$Fe(CN)_6^{4-}$	Th(IV)			
0·375	0·372		0·372	−0·8
0·625	0·615		0·615	−1·6
1·875	1·860		1·860	−0·8
0·125*	0·122		0·122	−2·4
1·250*	1·260		1·260	+0·8
Nd(III)	$Fe(CN)_6^{4-}$			
0·235	0·232	$KNdFe(CN)_6$	0·232	−1·3
0·705	0·698		0·698	−1·0
1·881	1·864		1·864	−0·9
0·470*	0·465		0·465	−1·0
1·880*	1·874		1·874	−0·3
$Fe(CN)_6^{4-}$	Nd(III)			
0·375	0·375		0·375	0
1·000	1·021		1·021	+2·1
1·875	1·910		1·910	+1·8
0·625*	0·638		0·638	+2·1
1·000*	1·001		1·001	+0·1
UO_2(II)	$Fe(CN)_6^{4-}$			
0·712	0·536	$K_4[(UO_2)]_4[Fe(CN)_6]_3$	0·714	+0·3
1·424	1·095		1·460	+2·5
2·136	1·628		2·168	+1·8
0·498*	0·375		0·500	+0·4
1·068*	0·840		1·088	+1·9
$Fe(CN)_6^{4-}$	UO_2(II)			
0·500	0·672		0·505	+2·5
0·750	0·982		0·736	−1·8
1·250	1·580		1·220	−2·4
0·250*	0·328		0·246	−1·6
1·250*	1·595		1·200	−4·1
$Fe(CN)_6^{4-}$	Hg(II)			
0·125	0·256	$Hg_2Fe(CN)_6$	0·128	+2·4
0·250	0·508		0·254	+1·6
0·500	1·008		0·504	+0·8
0·175*	0·348		0·174	−0·6
0·500*	1·003		0·501	+0·2

* In 0·5 *M* KNO_3 medium.

Table 2. pK_{sp} values of $ThFe(CN)_6$, $KNdFe(CN)_6$ and $K_4(UO_2)_4[Fe(CN)_6]_3$ at different temperatures and ionic strengths

Formula	KNO_3, M	μ	25°C	35°C	45°C	55°C	65°C
$ThFe(CN)_6$	1·0	1·04	8·17	8·39	8·57	8·81	9 55
	0·75	0·79	9·19	8·90	9·39	9·68	10·13
	0·50	0·54	8·79	9·06	9·32	9·54	10·13
	0·25	0·29	9·35	9·70	10·04	10·34	11·16
	0·10	0·14	10·06	10·39	10 63	10·99	11·52
$KNdFe(CN)_6$	1·0	1·06	7·31	7·03	7·30	7·07	6·75
	0·75	0·81	7·86	7·65	7·87	7·89	7·72
	0·50	0 56	7·34	7·64	7 67	7·56	7·47
	0·25	0 31	8·25	8·31	8·33	8·33	8·30
	0·10	0 16	8·78	8·86	8 91	8·91	8·99
			20 °C	30°C	40°C	50°C	
$K_4(UO_2)_4[Fe(CN)_6]_3$*	1·0	1·03	29·67	29·88	29·95	30·80	
	0·75	0·78	30·59	30·79	30·79	31·35	
	0 50	0·53	30·41	30·94	31·11	31·90	
	0·25	0·28	31·77	32·00	32·07	32·88	
	0·10	0·13	33·52	33·54	33·71	34·24	

* In $30·8 \times 10^{-3}$ M HNO_3.

Solubility products

K_{sp} values of the compounds $ThFe(CN)_6$, $KNdFe(CN)_6$ and $K_4(UO_2)_4[Fe(CN)_6]_3$ were obtained by means of measurements at different temperatures of the potential of a Pt electrode in a redox system of the type:

$$10^{-6}\ M\ Fe(CN)_6^{3-} \;\Big|\; \begin{matrix} Fe(CN)_6^{4-} \\ KNO_3 \text{ satd.} \end{matrix}$$

in presence of an excess of the precipitating ion.

Table 2 shows the results; those for $K_4(UO_2)_4[Fe(CN)_6]_3$ were obtained in nitric acid medium ($3·08 \times 10^{-2}$ M).

Institute of Analytical Chemistry
University of Messina
98100 *Messina, Italy*

ATHOS BELLOMO
DOMENICO DE MARCO
AGATINO CASALE

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Summary—The stoichiometry of the reaction between ferrocyanide and thorium, neodymium, uranyl ion and mercury(II) has been investigated. The first three give single products irrespective of the order of addition of the reagents, but the last does not. If mercury(II) is added to ferrocyanide $Hg_2Fe(CN)_6$ is obtained, but if ferrocyanide is added to mercury(II) various cyanide complexes of mercury are formed The K_{sp} values for the precipitates are reported.

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PRELIMINARY COMMUNICATION

REMOVAL OF TRACE METALS FROM SEAWATER BY A CHELATING RESIN

T.M. Florence* and G.E. Batley

Australian Atomic Energy Commission Research Establishment,
Lucas Heights, N.S.W. (Australia)

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Because of the very low concentrations of heavy metals in seawater, their determination by atomic absorption spectrophotometry requires a preliminary concentration step. Concentration is usually achieved by solvent extraction[1], but recently the application of chelating resins has rapidly gained in popularity[2-4]. Chelating resins are simpler to use and less time-consuming than solvent extraction, and allow much higher concentration factors to be attained. Most laboratories use a chelating resin column in the manner originally described by Riley and Taylor[2], *i.e.*, the seawater at natural pH (pH 8.1) is passed through a 6 cm x 1.2 cm diameter column of 50-100 mesh, hydrogen form Chelex-100 resin (Bio Rad Laboratories) at a flow rate of 3 mℓ min^{-1}. After passage of a sufficient volume of seawater (4 ℓ), the absorbed metals are eluted with a suitable solvent, usually 2 M HNO_3.

We studied the retention of Zn, Cd, Pb and Cu from seawater on a column of Chelex-100 by analysing the original seawater and the column effluent for these metals, using direct anodic stripping voltammetry (ASV). Cadmium, lead and copper were determined simultaneously using a rotating glassy carbon electrode[5], while zinc was measured at a hanging mercury drop electrode[6]. Labile metal was determined by adding 0.1 mℓ of 2 M HNO_3 per 25 mℓ of seawater (pH 2.3), while total metal was determined after adding 2 mℓ of 2 M HNO_3 per 25 mℓ seawater, and heating to boiling for 10 min (pH 0.7). In the case of zinc, sodium acetate was added before measurement to bring the pH to 4.5. The data shown in Table 1 and Figure 1 were typical of those obtained from a near-shore surface seawater sample. Similar results were found for several other Pacific samples analysed, including one taken 10 miles from the coast.

*To whom requests for reprints should be addressed.

TABLE 1. Removal of trace metals from seawater by Chelex-100 chelating resin*

Volume of effluent mℓ ψ	Total metal, µg ℓ$^{-1}$				Labile metal, µg ℓ$^{-1}$				Labile removed, %				Bound† removed, %			
	Zn	Cd	Pb	Cu	Zn	Cd	Pb	Cu	Zn	Cd	Pb	Cu	Zn	Cd	Pb	Cu
initial	3.9	0.45	0.84	0.65	1.77	0.22	0.30	0.40		-				-		
100	3.3	0.51	0.87	0.43	1.19	0.27	0.27	0.23	33	nil	10	43	0.9	nil	nil	20
250	2.9	0.40	0.80	0.30	0.75	0.15	0.25	0.13	58	32	17	68	nil	nil	nil	32
750	2.12	0.34	0.76	0.19	0.11	0.12	0.23	0.05	94	46	23	88	5.6	4.3	1.9	44
1,000	1.94	0.33	0.71	0.20	0.05	0.09	0.18	0.06	97	59	40	85	13	nil	1.9	44
2,000	-	0.25	0.69	0.17	-	0.05	0.18	0.03	-	77	40	93	-	13	5.6	44

*Seawater at pH 8.1 through a 6 x 1.2 cm column of Chelex-100.

†Bound metal = total metal - labile metal.

ψSamples were collected from the column and analysed after passage of the stated volume of effluent.

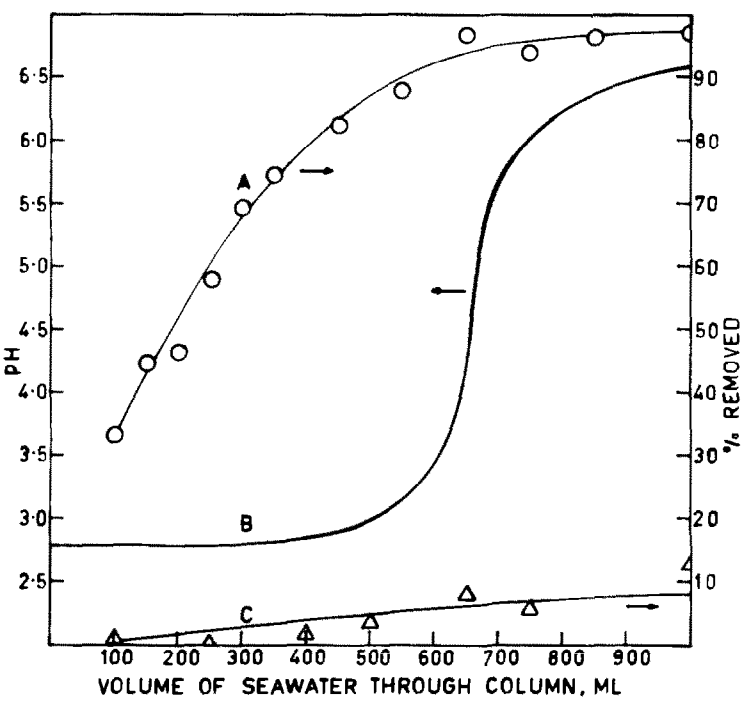

Fig. 1. Effect of volume of seawater through column of Chelex-100 chelating resin on pH of effluent and removal of zinc. A removal of labile zinc, B pH of effluent, C removal of bound zinc.

In agreement with Riley and Taylor[2], we found complete retention (>98%) of ionic spikes of all four metals when added to seawater. However, retention of the metals *naturally present* in seawater was considerably less (Table 1, Figure 1). The hydrogen form of Chelex-100 is gradually neutralised by the bicarbonate and metals present in seawater, and a plot of pH *vs.* volume of effluent has the shape of a typical acid-base titration curve (Figure 1), with the pH of the effluent finally rising to 7.4 after 4 ℓ of seawater. As expected[4,7,8], the retention of trace metals from seawater increased with increasing pH. With the exception of copper, bound metals (*i.e.* total - labile) are very poorly extracted by the chelating resin, even at a high pH. Labile zinc and copper are almost quantitatively retained after the passage of 1 ℓ of sample, but labile lead and cadmium are not completely removed. On the other hand, when synthetic seawater[9] (prepared from salts which had been ignited to 600° to remove organic matter) was passed through a column of H^+-form Chelex-100, Zn, Cd, Pb and Cu impurities were removed quantitatively even when the effluent pH was as low as 2.8. In the case of synthetic seawater, values for labile and total metal are almost identical.

It is apparent that Chelex-100 chelating resin cannot be used in the manner described by Riley and Taylor[2] for the quantitative concentration of Zn, Cd, Pb and Cu from seawater. Use of the resin in the sodium or ammonium, rather than the hydrogen form improved the retention of Zn, Cd and Pb, but absorption was still not complete. A computer study (described in a subsequent paper) of a synthetic seawater containing typical concentrations of known organic chelating agents showed that at low pH values Zn, Cd, Pb and Cu would exist entirely as free metal ion or as chloro and sulphato complexes. Even at higher pH values a powerful chelating agent similar to EDTA would be bound by the relatively high concentrations of Mg, Ca, Fe and Cr present in seawater. It is likely then that the results for 'bound' metal shown in Table 1 are due to metals adsorbed on or occluded in colloidal organic or inorganic particles, and not to the presence of soluble organic chelating agents.

There has been considerable dispute in the literature about the correct value for the concentration of lead in seawater. Patterson has suggested[10] that most of the published results for lead are erroneously high due to contamination during sampling and analysis. Patterson and co-workers, using stable isotope dilution mass spectrometry[11], found that all four of the surface coastal seawaters that they examined contained less than 0.08 μg ℓ^{-1} of

total lead. Their samples were taken from an industrialised, polluted area.

We found labile lead in the range 0.2-0.8 μg ℓ^{-1}, and total lead in the range 0.3-1.0 μg ℓ^{-1}, for surface Pacific Ocean samples taken off Sydney. Great care was taken in the collection and filtering of these samples, and in the pre-treatment of the plastic sampling bottles. Direct anodic stripping is a simple method of analysis which requires minimum manipulation of the sample, and consequently provides little opportunity for contamination. In any case, contamination can be detected by the 'doubling' of each operation, and measuring any increase in the lead value. Blanks are extremely low, because ultra-pure HNO_3 is the only chemical added to the sample. We believe, therefore, that the values we found represent the true lead content of the samples collected. A full discussion of this point will be given in a subsequent paper.

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TALANTA REVIEW*

DETERMINATION OF SMALL AMOUNTS OF MERCURY

S. CHILOV

Research Laboratory, Kodak (Australasia) Pty. Ltd.,
P.O. Box 90, Coburg, Victoria 3058, Australia

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Summary – A number of methods for the determination of trace amounts of mercury are reviewed with emphasis on sensitivity and ease of application.

Accompanying the growing awareness of the dangers of pollution by mercury, is the need for more accurate and reliable methods of analysis of the wide variety of materials which may contain traces of mercury, present in both organic and inorganic combination. Although many methods for the trace determination of mercury have been published in the last fifty years, most date from less than ten years ago. A recent overall review of methods for trace mercury determination is lacking though some bibliographies and specialized reviews are available[1–5]. An attempt is made here to compare the more commonly used methods in terms of sensitivity, equipment and sample manipulation required, and suitability for automation or for screening large numbers of samples, as is required in many food analysis and environmental monitoring applications.

Because of the large number of publications on the subject, this review is confined to discussion of methods for the determination of concentration at the ppm level or quantities less than 1 μg. Upper limits for mercury levels in foodstuffs have been set at 0·05 ppm (World Health Organization) and 0·5 ppm (U.S. Food and Drug Administration) and it is of greater importance to be able to determine mercury accurately in this range than at higher levels.

Although inorganic and phenyl mercury are the usual forms of mercury released in wastes, much of the mercury assimilated into plant and animal tissue is present as methylmercury. Organomercury compounds have been extensively used in the past in agricultural applications and as fungicides in the paint and paper manufacturing industries. These sources and the mercury compounds, organic and inorganic, from industrial processes account for a large part of the mercury released into the biosphere by human activity. Analytical methods must be able to determine either one or both of these forms.

SAMPLING AND SAMPLE STORAGE

Important in any environmental trace analysis is the method of sampling and, if there is a delay before an analysis can be made, the conditions of storage of the sample.

Of a number of mercury compounds tested, Jenne[6] found that methylmercury chloride was the most volatile. The vapour pressures of methyl and ethyl forms of organomercury compounds are greater than those for the corresponding phenyl compounds. Methyl and ethyl forms, other than methylmercury chloride, have vapour pressures similar to that of metallic mercury at room temperature, while the rate of vaporization of inorganic mercury compounds decreases in the order Hg, Hg_2Cl_2, HgS, HgO. Prevention of mercury loss by volatilization is thus important not only during but also before the analysis.

In the case of dilute aqueous solutions of mercury exposed to the air it has been established that major loss of inorganic mercury occurs by disproportionation of Hg(I) to Hg(II) and Hg(0),

*For reprints of this Review see Publisher's announcement near end of this issue.

followed by loss of Hg(0) to the air.[7] The addition of oxidants which will keep mercury in the Hg(II) form reduces this loss. A further study,[8,9] using ^{203}Hg showed that in very dilute aqueous basic solution, mercury is lost at a rate increasing with pH of the solution and, in solutions containing chloride ion, independent of the chloride concentration. For storage of dilute mercury solutions it appears best to acidify the solution[10] and have sufficient oxidant present (*e.g.*, $KMnO_4$) to keep mercury in the bivalent form.[7,11] Radiotracer and flameless atomic-absorption studies, however, have shown that 80% of the mercury in natural water samples that is initially associated with particulate matter will enter the solution phase if it is acidified, although loss to the container is not significant. Seldman has recently questioned the earlier findings, however, especially with regard to very dilute solutions.[11a]

In addition to volatilization, mercury may be lost from the solution by adsorption on the walls of the container.[12-17] Mercury is adsorbed strongly on glass[15] and heating to 500–550° is necessary for its removal. Polythene containers will also adsorb mercury quite strongly.[10,17] Pyrex glass, polycarbonate and Teflon make the most suitable sample containers[17] and, if samples are acidified to pH 1 for storage, adsorption losses become negligible.[12] In samples containing suspended matter, there is often a higher concentration of mercury in the particulate matter than in solution. Non-homogeneous samples containing suspended matter should be filtered for storing, especially if the content of suspended matter is high. The importance of specifying the condition of samples used in mercury analysis should be stressed, *e.g.*, the moisture content of fish and other biological materials, which may vary considerably.

METHODS OF ANALYSIS

For samples where it is of interest to establish whether organomercurials are present, solvent extraction[18-20] and the rate of reduction in acid cysteine reagent[21,22] have been used to differentiate between organically and inorganically bound mercury. Chromatography may subsequently allow identification of organomercurials.[18-20,23] Organically bound mercury may also be determined from the difference between total and ionic mercury present. Most procedures for the determination of mercury require its conversion into the metallic or the ionic form, although the standard procedure for determination of mercury in air has long been direct ultraviolet photometry.[24] If mercury in a sample can be concentrated as a compound which is then thermally decomposed to yield mercury vapour, a photometric determination is again possible.[25-27] Absorption of ultraviolet light by mercury is the basis of the atomic-absorption procedures which have now generally replaced the standard dithizone (diphenylthiocarbazone) colorimetric procedure.[28] Non-destructive analysis is possible by neutron activation.

Determination as metal

Stock[29-33] was one of the first involved in trace analysis for mercury. His technique of heating the sample in a closed tube to distil mercury and of collecting the liberated mercury in a cooled part of the tube requires some practical skill. The metallic mercury, in the form of a drop, was placed on a microscope slide and its diameter measured under magnification. For a small drop, the diameter was proportional to the amount of mercury present in the sample. A variation of this technique was to collect the mercury by amalgamation on a copper wire. The mercury could then be collected as a drop by heating the wire sufficiently to release it from the amalgam.

A gravimetric determination of mercury as the metal has been described.[34] The mercury evolved from the sample on heating in an alkali metal carbonate–peroxide melt is condensed and weighed.

Colorimetric methods

A digestion step is generally applied before colour development but is sometimes omitted with air and natural water samples. It is incorporated in the procedure to bring all the mercury into the ionic form (Hg^{2+}) for complexing. The most commonly used digestion media are acid oxidizing mixtures.

Sample digestion and preparation. For determination of mercury in air, the sample is drawn

through a permanganate solution;[35,36] water samples are also generally treated with permanganate to oxidize mercury to Hg^{2+}. The Analytical Methods Committee of the Society for Analytical Chemistry[28] has compared a number of digestion media and recommends an H_2SO_4 – HNO_3 digestion procedure using an apparatus devised by Gorsuch.[28b] Combining the distillate and the residue from the digestion should minimize loss of mercury. Loss as chloro-compounds is not significant below 140°.[28b] For routine analysis a permanganate digestion may be more convenient.

This has been used in conjunction with the dithizone colorimetric method for mercury determination in biological materials,[37-40] coal[41,42] and soils.[43] A combined H_2SO_4 – HNO_3 – $KMnO_4$ digestion was used for analysis of organs and blood.[44] Oxidizing acid digestion with perchloric, nitric and sulphuric acids has been used for plants[45] and vegetable and animal tissues.[46,47] Provided that care is taken to avoid loss of mercury as chloride in the perchloric acid digestion, these procedures should be satisfactory. Hydrogen peroxide in a mixture with nitric and sulphuric acids has also been used.[48]

A novel approach is the use of enzymatic digestion.[49] The digestion is followed by oxidation of mercury with permanaganate. This digestion medium, though slow in action, may be attractive for particular sample types and eliminates the possible loss of mercury by volatilization when oxidation is extremely vigorous.

Vasilevskaya and Shcherbakov[43] destroyed the sample matrix by heating with lead dioxide and distilling the metallic mercury formed. This mercury was subsequently dissolved in concentrated nitric acid and extracted into dithizone solution. The method was applied to the analysis of soils.

When care is taken, there should be no difference between the results of using various digestion media, the sample type governing the choice between a vigorous and milder oxidant. Schöniger-flask combustion of vegetable, grain and fish samples[50-55] has led to acceptable recoveries of mercury. Gutenmann and Lisk[50] were able to use up to 10 g of sample for combustion.

A further method has been used to extract mercury from coal.[56] Inorganic mercury compounds are extracted individually from the sample. Ethanol–water mixtures extract HgO and $HgCl_2$, and ethanolic sodium sulphide solutions of different concentrations/extract HgS and elemental mercury.

Colour development. Dithizone (diphenylthiocarbazone) is the most widely used reagent for colorimetric determination of mercury. The reagent is extremely sensitive (it can be used to measure 0·01 ppm of mercury)[57] but because both the reagent and the mercury complex are extremely susceptible to variation in laboratory conditions, the method becomes less reliable.[28] Addition of acetic acid eliminates the light-sensitivity shown by mercuric dithizonate. Dithizone also forms coloured complexes with a large number of other metals and this leads to a greater likelihood of interferences in analysis. A number of modifications to reduce interference from other metals which are complexed by dithizone and from organic materials which could be extracted together with the mercury complex have been tested, and include the following.

(*a*) Back-extraction of mercury into aqueous acid after destruction of the dithizonate complex with nitrous acid or other reducing agent. The mercury is then re-extracted with dithizone solution. A thiosulphate reversion has also been reported.[58]

(*b*) Addition of complexing agents such as EDTA, CN^-, SCN^- to minimize formation of the dithizonate complexes of other metals present.[28,35,41,47]

(*c*) Precipitation of interfering ions with bromide, iodide or thiosulphate.[36,37]

(*d*) Use of a different organic solvent and different wavelength for measurement of the absorbance of mercuric dithizonate complex. For example, in the presence of copper, dithizone in the less effective solvent chloroform is used and the measurement is made at 492 nm.[59] In the absence of copper, extraction with carbon tetrachloride and measurement of absorbance at 485 nm is recommended. Toluene may also be used as a solvent for dithizone.[60]

(*e*) Distillation of mercury from the digestion mixture into dithizone solution. Other methods for lessening interference by removing mercury from the digestion mixture have also been successful. Mercury can be reduced to the metal, the solution aerated and the vapour transported into permanganate solution. Excess of permanganate is destroyed with

hydroxylammonium chloride and the mercury can then be extracted into dithizone solution.[61] Mercury has been carried from the digest by a stream of dry hydrogen chloride gas, into a dithizone–CCl_4 solution.[62] This procedure, though a simple method of removing interference, is unsuited to the analysis of large numbers of samples.

(*f*) Ion-exchange. Kuroda *et al.*[63] used ion-exchange to isolate mercury from the solution of the sample. Mercury was collected as the thiocyanate complex on the anion-exchange resin and was determined with dithizone after elution. Special glass microbeads have been used to adsorb the Hg^{2+}–ethylenediamine complex from aqueous solution.[64] A solution of dithizone in carbon tetrachloride was used to elute the mercury.

The dithizone determination can be adapted to a wide variety of samples. Although it is inherently very sensitive, the drawbacks of comparatively low sensitivity in practice (0·1 ppm for food and biological samples[65]) and the instability of the reagent and the mercury–reagent complex have encouraged the search for alternative procedures.

In general, colorimetric methods are ideal for the analysis of large numbers of samples and a variety of colorimetric methods have been published. Usually, the mercury complexes formed in these methods have lower molar absorptivities than the dithizonate and are thus less dependent on reaction conditions for accurate results. To date, no other colorimetric reagent has shown itself to be superior to dithizone.

Diphenylcarbazone is extremely sensitive to changes in pH, making its use difficult.[66] The 2-naphthol analogue of dithizone, di-2-naphthylthiocarbazone, has been used for the determination of mercury in air and in selenium.[67] These applications are expected to have known and limited interferences. In the latter case 0·04 ppm mercury could be measured. Oxamide bis-(phenylhydrazone) has been used for the determination of microgram amounts of mercury.[68] Use of 1-(2-pyridylazo)-2-naphthol in chloroform[68] appears less sensitive than the dithizone procedure. 4,4′-Dinitrodiazoaminobenzene may be used for determination of about 1 ppm of mercury.[70] *N*-Phenylbenzohydroxamic acid in chloroform allows determination of 0·4 ppm of mercury.[71] The complex formed is apparently of lower stability than mercuric dithizonate, being susceptible to interference from chloride as well as cyanide and EDTA.

Nitrofurazone is subject to much interference from reductants,[72,73] while furacilin (5-nitro-2-furaldehyde semicarbazone) has also been found to be subject to interference. The sensitivity is similar to that found with dithizone. Sulpharsazen has been used to determine mercury at concentrations of the order of 0·04 ppm.[74] Thiothenoyltrifluoroacetone has been used to detect 0·05 ppm of mercury in waste water.[75] Bindschedler's Green [4,4′-bis(dimethylamino)diphenylamine] has been recommended as a colorimetric reagent for mercury,[76] and claimed to be less sensitive than dithizone to the reaction conditions. A sensitivity as low as 0·1 ppm has been obtained. 4-(2-Pyridylazo)-resorcinol lacks the advantages of increased sensitivity and is susceptible to considerable interference.[77] Metalphthalein allowed determination of mercury down to 0·1 ppm.[78] Kawase[79] discussed the extractability and formation constants of complexes of 1-(2-pyridylazo)-phenanthrene-9-ol, 1-(2-pyridylazo)-acenaphthylene-8-ol and 1-(benzothiazol-2-yl-azo)-phenanthrene-9-ol with mercuric ion. The phenanthrenol complexes are more suitable at lower concentrations.

Several authors have used dyes to extract mercury into another phase for measurement, either by directly complexing the mercuric ion or by forming an ion-association complex which can be extracted into organic media. For mercury determination in the ranges 0·1 – 6 ppm, antipyrine dyes in benzene or toluene have been used.[80] Complexes formed are of the type dye–Hg–halide (bromide or chloride).

Crystal Violet (C.I. Basic Violet 3) has been used to determine 0·1 μg of mercury.[81] Rhodamine B[82] is a less sensitive reagent, having been used to measure mercury down to 1 ppm. Brilliant Green[83] (C.I. Basic Green I) forms an ion-association complex with mercuric chloride or bromide, which is soluble in benzene. No interference was encountered from a number of metal ions, though nitrate interfered. Chloride and sulphate were tolerated. Xylenol Orange[84] is also liable to interferences. It is sensitive to Hg(II) ions in the range 15 – 20 μM and appears to have no advantage over dithizone. Methylene Blue has been used to extract HgI_4^{2-} into chloroform.[85] For application in analysis the chloroform extract should contain 0·2 – 2 ppm of mercury. If the mercury in the sample is at too low a concentration to achieve this, it may be precipitated as the sulphide on a filter impregnated with cadmium sulphide, and the

precipitate dissolved before proceeding with the determination.

The metal chelate cation, tris(2,2′-bipyridyl) iron (II), has been used to extract HgI_4^{2-} from aqueous solution,[86] and $HgBr_4^{2-}$ into 1,2-dichloroethane, the background absorbance then being less intense than that obtained with HgI_4^{2-}.[87] The sensitivity is poorer than that with dithizone (being applicable in the range 1 – 10 ppm), though masking with nitrilotriacetic acid enables a number of heavy metals to be tolerated.

Although the bromide complex was found most suitable for extraction of ion-pairs, a pyrazolene dye, α-(4-chloro-1,3-diphenyl-5-pyrazolon-4-yl)-4,4′-bis(dimethylamino)benzhydrol, has been successful in extracting other anionic halide and thiocyanate complexes for the determination of 0·1 – 2 ppm of mercury.[88] Organomercurials will complex with Ruhemann's Purple [2-(1,3-dioxoindan-2-yl)iminoindane-1,3-dione].[89] Extraction of the complex into ether and spectrophotometric measurement allows determination of 2 – 20 μg of mercury.

The nickel complex with antipyrinyldithioformic acid[90] has been used in the direct determination of about 1 ppm of mercury. The Ni(II) is displaced by Hg(II) and the decrease in the absorbance of the nickel complex is dependent on the amount of mercury present.

Preparation of the dithizone complex of mercury has also served as a purification procedure before measurement of the mercury concentration by techniques other than colorimetry.[91-94]

The oxidation of thiamine by mercury(II) gives rise to a high fluorescence which can be used for the determination of mercury in the range 0·01 – 0·5 ppm.[95] The fluorescence is strongly affected by salt concentration in the sample, which should be kept below 0·2*M*. This factor may make the method unsuitable for samples requiring digestion.

Neutron-activation analysis (NAA)

In the majority of published methods, the comparative NAA technique is used, wherein a standard is irradiated at the same time as the sample. Such a procedure is much simpler than the absolute technique where the neutron flux must be accurately known and a quantitative radiometric assay carried out after the irradiation.

Irradiation converts organically bound mercury into Hg_1^0, Hg_2^{2+} or Hg^{2+} and it has been found[96] that the form of mercury in the standard need not be the same as that in the sample, provided that the mercury levels are comparable. This work was carried out on fish samples but the results can probably be extended to other biological materials.

Selection of optimum nuclear reaction. The most commonly used reactions are $^{196}Hg(n,\gamma)^{197}Hg$ and $^{202}Hg(n,\gamma)^{203}Hg$. Activation by $^{196}Hg(n,\gamma)^{197}Hg$ suffers no apparent interference from primary or secondary reactions, though there is possible interference from self-shielding in comparison samples. This reaction permits detection of lower levels of mercury than does the $^{202}Hg(n,\gamma)^{203}Hg$ reaction where interference from $^{206}Pb(n,\alpha)^{203}Hg$ and $^{203}Tl(n,p)^{203}Hg$ is possible.

Preparation of samples for irradiation. Samples are normally sealed in quartz ampoules or in aluminium foil, though Pillay[97] and Filby *et al.*,[98] among others, have sealed samples in heavy grade polythene film for irradiation.[99]

Many biological samples contain a large proportion of water, which is best removed before irradiation, allowing the sample to be better compacted. Freeze-drying of samples before irradiation may lead to considerable losses of organically bound mercury. This is particularly important with water samples, where large volumes cannot be used. Low-temperature ashing may also lead to mercury losses.[97] Since irradiation converts organically bound mercury into Hg^0, Hg_2^{2+} and Hg^{2+}, which are less volatile, high-flux γ- irradiation before ashing may prevent these losses.

Removal of water concentrates the mercury in the sample, a result which may also be achieved by the removal of the mercury as a compound or its transfer into another phase. The mercury dithizonate complex has been found to be involatile at room temperature even if held for long periods at low pressure. This property is the basis of a method for extracting the mercury from the sample before irradiation and depositing it on a plastic matrix as the dithizonate complex.[100] Seiler[101] separated mercury from other ions by thin-layer chromatography before irradiation.

Irradiation. Irradiation may cause a rise in temperature to 100°, leading to possible loss of mercury. Brune[102,117] has developed a system for low-temperature irradiation of samples,

which should minimize loss. The method has been applied to the analysis of fish and whole blood samples. A water-cooled irradiation system[98] for determination of mercury in human blood has been described. After irradiation, it may be necessary to reduce surface contamination of the sample such as that arising from cutting.

Post-irradiation assays. Post-irradiation assays can involve either separation of the mercury from the matrix, followed by measurement of its characteristic radiation, or, where the radiation from mercury is sufficiently different from that of the matrix, direct measurement of its radioactivity.[89,103]

If the matrix is not grossly activated, direct counting of radiation or γ-spectrometry of the sample may be satisfactory. The introduction of the high-resolution Ge(Li) spectrometers makes this feasible.[98,104-108] The Ge(Li) detectors, although having higher resolution, have generally lower sensitivity than the NaI(Tl) detectors. Guinn *et al.*[108] have used the two types of detector in conjunction in determination of mercury in flour.

Non-destructive methods,[98,104,107] though unsuitable for routine analyses because of their lower sensitivity and the long irradiation times required, are important when the sample must be preserved or when only a small sample is available and multi-element analyses are required. In the latter case, only one irradiation is necessary and, though long in both irradiation time and calculations required to correct for interfering elements, will allow simultaneous determination of a number of elements.

In contrast to the long times required (up to 30 days) for non-destructive analysis, destructive procedures require irradiation for only a matter of hours and the subsequent analysis time is correspondingly reduced.

Measurement of the activity of mercury present in the sample is easier if the mercury can be concentrated and isolated from possible interference in the matrix. Isolation has generally been carried out after irradiation, although Becknell *et al.*[109] concentrated the mercury in water samples on an ion-exchange resin as $HgCl_4^{2-}$, before irradiation and counting of radiation from the decay of ^{197}Hg. Weiss and Crozier[110] converted all the mercury into Hg^0 before irradiation. Ljunggren *et al.*[111] also carried out separation before irradiation. They dissolved inorganic samples in hydrofluoric acid, added mercury carrier and precipitated mercury as the sulphide. The precipitate was redissolved in a mixture of nitric and sulphuric acids. Van de Sloot and Das[111a] collected trace mercury from natural waters on activated charcoal, irradiated the charcoal and distilled the mercury into a second charcoal trap, passing the products over heated silver-coated glass wool to remove bromine.

Isolation and extraction of the mercury after the irradiation has been accomplished by several means, the sample matrix often determining the most suitable procedure. Digestion with an acid oxidizing mixture is used in almost all cases before the isolation. At the digestion stage, mercury carrier is usually added to compensate for loss of mercury (which may be considerable) and to permit a more accurate determination. Inactive mercury carrier is usually added as a mercury salt but a droplet of metallic mercury may also be used.[112,113] After exchange with the active mercury is complete, the droplet is removed and dissolved in nitric acid for counting of γ-activity. The rapid exchange between Hg_2^{2+}, Hg^{2+} and the mercury in certain organomercury compounds has been utilized for the mercury determination.[114] The following isolation techniques have been applied after the digestion: ion-exchange, precipitation, solvent extraction, distillation or volatilization, and deposition. Combinations of some of these techniques have also been used: distillation and precipitation,[115,116] ion-exchange and volatilization,[108,117] volatilization and deposition,[99,118,119] precipitation and ion-exchange,[120] solvent extraction, ion-exchange and precipitation.[122]

Ion-exchange. The method of Ehmann and Huizenga,[123] adapted by Bowen and Gibbons,[124] collects mercury as $HgCl_4^{2-}$ on an anion-exchange resin, whence it is subsequently eluted for precipitation as HgS for counting. This has been simplified and improved[96,125] by direct measurement of the activity of the $HgCl_4^{2-}$ retained on the resin. This eliminates the uncertainty in eluting $HgCl_4^{2-}$ from the resin and shortens the procedure. It has been used for the determination of mercury in the range from 200 ppm down to 10 ppM (parts per milliard). Gillette[107] and Marowsky[120] also made use of $HgCl_4^{2-}$ formation for an anion-exchange separation of mercury.

Ishida *et al.*[126] dissolved the sample after irradiation and, after the addition of inactive

carrier and thiocyanate, passed the solution through an anion-exchange resin, eluted with hydrochloric acid and counted the activities of ^{197m}Hg, ^{197}Hg and ^{203}Hg. The method was found suitable for a wide range of materials such as rice, cuttlefish and rock. A combination of ion-exchange and distillation of mercury with counting of ^{203}Hg allowed determination of 0·003 ppm of mercury in blood.[117]

Marowsky[120] eluted mercury from an ion-exchange resin with thiourea and subsequently precipitated the mercury with sulphide. The activity of the precipitate was measured. Mercury separation by ion-exchange and precipitation as HgS has been used for the determination of mercury in a wide variety of foods.[122]

In a simultaneous determination of copper, zinc, cadmium and mercury in biological material,[127] anion-exchange allowed isolation of mercury and its determination at levels as low as 0·5 ng.

Paper loaded with anion-exchange resin may be used as a filter to preconcentrate the mercury in a sample of water.[109] The mercury can be collected on the paper as $HgCl_4^{2-}$ and subsequently irradiated and counted as ^{197}Hg. Chlorine treatment has been used to convert organomercury compounds into $HgCl_4^{2-}$ for collection on the resin. Mercury concentrations of 0·03 – 66 ppM have been measured by this method. As a further isolation step mercury may be distilled from the digestion flask before the anion-exchange step. Samples containing water may be freeze-dried to reduce the volume and increase the sensitivity, but losses of organomercury during this process are high, and the method of Becknell *et al.*[109] offers an alternative to this method and to low-temperature irradiation[102,117,128,129] as a means of increasing the sensitivity of analysis of water samples.

Precipitation. Direct precipitation, without prior separation of mercury from the digest is, in many cases, insufficient to isolate the mercury adequately from possible interferences. Although most separations are carried out after irradiation, Weiss and Crozier[110] reduced mercury in sea-water samples to Hg^0 with a stannous chloride solution, isolating the mercury before irradiation. Where mercury is precipitated directly, further manipulations are generally required to purify the precipitate for measurement of activity. However, after addition of mercury carrier to the digested irradiated biological sample, mercury can be precipitated as HgS for direct counting of γ-activity.[130] Interference was found negligible above 0·01 ppm of mercury.

Mercury has been precipitated as mercury iodide–copper ethylenediamine from the digestion mixture.[131] Das *et al.*[116] isolated mercury from HgS, precipitated after digestion of the irradiated sample, by heating the precipitate. The mercury mirror deposited in a cooler part of the system is measured for the γ-emission from ^{197}Hg.

Mercury has also isolated before the precipitation.[138] The irradiated sample is heated to 1200° in a closed system, volatilized mercury being collected in cold traps. The mercury is recovered as $HgCl_2$ and its activity counted. Thatcher and Johnson,[133] after irradiation of the sample and precipitation of mercury with carrier mercury and stannous chloride, counted the ^{197}Hg γ-activity.

Mercury may also be precipitated as the sulphide. In the analysis of soils,[115] addition of mercury carrier to the digestion mixture was followed by distillation of mercury and precipitation of HgS from the distillate. Down to 0·03 μg could be determined by counting the activity of the precipitate. Fusion of soil and rock samples with sodium peroxide after irradiation enabled mercury to be distilled from the sample and precipitated as the sulphide for counting.[134]

As mentioned in the previous section, mercury has been precipitated as HgS after purification by ion-exchange and again subjected to ion-exchange before measurement of the activity of ^{203}Hg.[120] Mercury can be precipitated as the oxide[97] only if adequate precautions are taken to ensure that the sample is pure before precipitation. A solution for precipitation of HgO may be prepared from precipitated HgS.

Solvent extraction. The most favoured solvent extraction procedure is based on the formation of the mercury–dithizone complex after irradiation and digestion of the sample.[135,136] The solvent is either chloroform or carbon tetrachloride. This procedure has been used on a wide variety of samples from biological[136] to water.[137] Extraction of mercury from the digestion mixture after irradiation, as a preliminary to reversion to $HgCl_4^{2-}$ and

adsorption on an anion-exchanger for counting, has led to a detection limit of 0·1 ppM for samples of laboratory reagents and materials.[121] Anion-exchange of $HgCl_4^{2-}$ followed by extraction with tri-iso-octyl thiophosphate separated mercury from a copper matrix.[107]

Distillation or volatilization. In many cases, distillation has been used as a preliminary step for the isolation of mercury. $HgCl_2$ or $HgBr_2$ have been distilled from the post-irradiation digestion mixture into absorbent solutions, for the precipitation of mercury (for example as HgS) for counting.

Alternatively, a destructive distillation to volatilize HgO has been used as the final step before counting. The mercury-containing material, *e.g.*, HgS[116] or irradiated sample[121] is heated to high temperature and the metallic mercury collected in a cool part of the system. The activity of the mercury distilled can then be measured. Rook *et al.*[138] quantitatively separated mercury by combustion of the irradiated sample. The mercury was condensed and then dissolved for activity measurement. The method is applicable to a wide variety of matrices. Flour and coal samples with mercury between 0·015 and 5 ppm have been analysed. Mercury volatilized on ignition of irradiated sample has been collected on filter paper impregnated with Se and the activity of the paper then measured.[99] The activity of mercury electro-deposited from a solution of $HgCl_2$ distilled from the digestion mixture after irradiation, was measured to determine mercury in coals.[118] The activity of mercury (oxide or bromide) in the distillate from the digestion of biological material has also been measured directly.[139]

Deposition. Mercury can be isolated from the sample matrix after irradiation, by electro-deposition or by amalgamation. The sample must first be digested to ensure that all the mercury is in solution. Häsänen[140] added copper powder to the digested sample, this copper being collected by filtration and its activity measured for the photo peak of ^{197}Hg. Electro-deposition from a solution of $HgCl_2$[118,119,141] was mentioned in the previous section. In a specialized case, the determination of mercury in gallium, mercury was reduced to the metal and subsequently determined as a chelate compound.[142]

The volatilization and deposition methods have the advantage of being simple and applicable to a wide variety of sample matrices.

Other radiometric methods

Isotope dilution. These methods generally involve destruction of the sample (by combustion or digestion) followed by addition of the active isotope of mercury and (solvent) extraction of mercury to isolate it from other species in the solution. The activity of the extract is measured. Since no carrier is added, the amount of mercury present is very low and care must be taken to avoid contamination. The reagents added are in the form of very dilute solutions. In contrast to activation analysis, the activity of the sample is low and irradiation is not required, simplifying handling of the sample.

This type of analysis lends itself to automation.[143,144] A procedure developed by Briscoe *et al.*[143] for the Technicon "AutoAnalyzer" involves solvent extraction with zinc dithizonate in carbon tetrachloride of a solution of the sample to which ^{203}Hg has been added. The method is claimed to be very sensitive but has been applied only to determination of mercury in low-grade ore deposits. Other sample types may necessitate the introduction of further purification steps.

Růžička and Lamm[144] used oxygen-flask combustion of the sample to release mercury in the inorganic form. This was followed by oxidation of mercury and addition of ^{203}Hg isotope. Mercury was extracted with dithizone–carbon tetrachloride solution. A further purification step, *viz.* re-extraction of mercury into the aqueous phase and final extraction into zinc dithizonate, permits measure of the γ- activity for determination of mercury present.

Fish samples were prepared for extraction of mercury, by digestion in a nitric–sulphuric acid mixture.[141,145] Instead of dithizone as the complexing agent for extraction and isolation of mercury, ammonium pyrrolidinedithiocarbamate (APDC) in methyl isobutyl ketone (MIBK) was the extraction system used.

Isotope exchange. Mercuric di-n-butylphosphorothioate containing some ^{203}Hg and dissolved in carbon tetrachloride will exchange with mercury in an aqueous sample solution. A proportional relationship exists between the distribution of ^{203}Hg between the aqueous and organic phases and the mercury concentration. The amount of the complex added must be

known accurately and there must be between 0·1 and 10 times as much mercury in the carbon tetrachloride phase as is expected to be present in the sample. This method works best when the distribution coefficient is about unity. Anions which complex mercury and prevent interchange between the phases will interfere.[146] Davis and Arnold[147] used a method based on that of Handley[148] for determination of trace amounts of organomercurial. This method was tested only on a standard solution and difficulties may arise with other types of sample.

Mercury in urine and tissue samples has been determined by isotope exchange.[149] After dissolution of the sample, mercury was complexed, in this case with EDTA, and a trace of ^{203}Hg was added which equilibrated with a vapour containing inactive mercury. The ^{203}Hg content of the vapour was determined. Magos and Clarkson[150] used a simplified version of this method in the determination of mercury in air. The sample was passed through a ^{203}Hg-containing chelate solution. The ^{203}Hg equilibrated with mercury in the gas stream and was subsequently absorbed in permanganate solution for measurement. The procedure was satisfactory for 0·016 – 1·2 ppM of mercury.

In a specific method for determination of mercury, Bankovskis *et al.*[151] extracted the 8-mercaptoquinoline complexes of mercury halides.

Radiorelease. These methods are based on the replacement of a radioactive ion in a compound by mercury. The activity released is measured.

For determination of both organic and inorganic mercury, the sample was dissolved (Hg being converted into the Hg^{2+} form) and reacted with a complex of ^{60}Co. Mercury replaced ^{60}Co in the complex, and after a cation-exchange, the ^{60}Co held in the resin could be measured. Mercury down to 0·02 ppm could be determined in this way.[152]

The activity of the isotope ^{110}Ag was measured after displacement from $^{110}Ag_2S$ by mercury. The ^{110}Ag in solution or the decrease in activity of ^{110}Ag in the precipitate was a measure of the mercury initially present.[153] Displacement of silver from silver dibutylphosphorothioate has also been successful for determination of mercury.[148]

Interference may arise in isotopic exchange if the sample contains ions of the element that is being released from combination by mercury.

Chromatographic methods

Chromatography has been used both as a purification technique for subsequent determination of mercury by other methods, and as an analytical technique for direct analysis.

Thin-layer chromatography (TLC). The TLC methods are usually only semi-quantitative, emphasizing detection of mercury in trace amounts in the presence of other metal ions.

Starch has been used as the substrate in separation of cations of elements of group II of the periodic table and Pb^{2+}, Ag^{+} and Hg^{2+}.[150,154]

A quantitative method has been described by Wysocka.[155] After digestion of the sample to bring mercury into the Hg^{2+} form, this is extracted with dithizone in chloroform. After reduction of the volume, the chloroform extract is chromatographed on silica gel with propanol. The mercury is determined by comparison with a standard. Silica gel[156] has also been used in the control of mercuric oxide ointments, an application where the total mercury contents are much higher than in environmental samples. Planimetry and photo-densitometry are commonly used to measure the amount of mercury present, planimetry giving only a semi-quantitative measure.

TLC has been reported as a separation method for isolating mercury for neutron-activation analysis.[102] A number of inorganic nitrates were separated on Kieselgel, with butanol–HNO_3–H_2O. The mercury zone, detected with diphenylcarbazide, was removed and irradiated in a neutron flux and the activity measured by spectrometry. This method, however, has been used only for a mixture of inorganic salts and would require some modification for analysis of other samples.

Paper chromatography. Paper chromatographic separations have been described for biological samples,[157] 1 ng of mercury being detectable. Mercury has been separated from a number of other metal ions by paper chromatography[158] but such separations have often been confined to almost ideal conditions and have not been applied to actual samples. Barbiroli and Lipparini[159] extracted the mercuric dithizonate spot from the paper chromatogram for quantitative spectrophotometric determination of the mercury present.

Liquid ion-exchangers in benzene or chloroform solution have been used as developing solvents in the separation of metal ions on thiocyanate-impregnated paper.[160] Ion-exchange paper has been used to separate mercury from other ions.[161] In contrast to most other methods which require that mercury be in the inorganic form, this procedure permits detection of inorganic, alkyl and aryl mercury with dithizone spray reagent.

Ion-exchange chromatography. Ion-exchange resins, both cationic and anionic, have also been successfully applied to the separation of mercury from other ions.[162–164] Mercury can be eluted and detected colorimetrically, for example by the reaction with iodide and sulphite.[162]

Gas chromatography. Gas chromatographic methods can be used for the determination of organomercury compounds. Westöö[18–20] used a solvent extraction technique for the preliminary isolation of methylmercury compounds (the form of mercury predominant in animal tissue) which could then be determined by gas chromatography. TLC was used separately for identification. Methylmercury compounds attached to the sulphur atom of non-volatile compounds could not be determined initially[18] but a modified procedure allowed this.[19,20] However, Hartung[165] claims that under the acid conditions of the extraction, dimethylmercury dissociates to monomethylmercury and the total of mono and dimethylmercury is determined. Hartung[165] finds that at pH 8·2 this hydrolysis does not occur and both mono and dimethylmercury may be determined. Monomethylmercury forms a water-soluble cysteine adduct and leaves the dimethylmercury to be extracted by toluene. To increase the sensitivity of the determination of dimethylmercury, it is converted into monomethylmercury bromide which gives greater response with an electron-capture detector. This method is useful when it is necessary to differentiate between various forms of organically bound mercury, but if total organically bound mercury is required, the Westöö procedure has been much used and found satisfactory.

Kamps and McMahon[166] have utilized the Westöö procedure for determination of monomethylmercury in fish, a cysteine back-extraction procedure being used to provide clean-up. In another modification, the methylmercury from fish samples was extracted into toluene rather than benzene.[163,167] The methylmercury was extracted as the bromide, partitioned as the thiosulphate complex into aqueous ethanol and finally re-extracted as the iodide into benzene. It was subjected to gas chromatography in this form.

Newsome[168] used a similar procedure, extending it to the determination of methylmercury in cereal and grain products. The methods are sensitive to about 0·01 ppm of methylmercury.

A procedure for the isolation of methylmercury from biological tissues, in which methylmercury is converted into the cyanide in a diffusion cell and is then trapped on cysteine-impregnated filter paper has been described.[169] After this isolation, the mercury is extracted from the paper into benzene and determined by gas chromatography. The method has been applied to a wide variety of samples and because of the enrichment achieved in preparation as little as 1 ng per g of sample can be measured.

A number of alkyl mercury halides have been separated by gas chromatography,[170] the retention volume being dependent on the length of the alkyl chain rather than on the identity of the halide. The electron-capture detector has been used for detection of methylmercury chloride salts[18,20,168,169] as well as other alkyl and aryl mercury salts[171–172a] and their dithizonate derivatives.[173] An emission spectrometer[174] has been used for detection of organomercurials and construction of a simple mercury-specific gas-chromatographic detector has been described.[175] In the latter detector, mercury compounds are converted into free metallic mercury by combustion, and the concentration is measured by monitoring the absorbance at 254 nm.

Although solvent extraction and differential reduction[21,22,176] can be used to distinguish between organically and inorganically bound mercury, the chromatographic procedures may provide more specific identification of the form in which mercury is present and may thus find considerable use in environment and control studies.

Atomic fluorescence

As with atomic-absorption spectrophotometry (see below), atomic-fluorescence determination of mercury has been carried out with both flame and non-flame vaporization techniques. Atomic-fluorescence determination has certain advantages over atomic-absorption

methods. No closed cell is required, hence fogging of cell windows (as encountered in non-flame or cold-vapour atomic absorption) is eliminated, no drying agent need be used, no spurious signal from broad band absorption by organic contaminants is encountered, sensitivity can be high and the calibration graph is linear over a wide range of concentration.

A number of improvements in the instrumentation and technique which have led to increased sensitivity have been described in the literature. Among these are numbered the use of electrodeless discharge tubes as sources[177] and the use of pulsed selective vaporization of mercury into an inert (argon) atmosphere for the determination of mercury in graphite.[178] The latter technique resembles the use of the carbon-rod atomizer now increasingly used in atomic-absorption determinations. Increased sensitivity has also been obtained with the use of an elliptical aluminium cylinder which reflects radiation into the flame.[179] The increase in sensitivity was aided by use of a hydrogen flame and a total-consumption nebulizer. The previous detection limit of the order of 0·1 ppm[180] compares with 0·3 ppm by this method. This also improves on the sensitivity attainable by use of emission with low thermal-flame background in an instrument for non-dispersive atomic-fluorescence determination, where the detection limit was 1 ppm.[181] Concentration of the sample by solvent extraction and vaporization of the organic phase has also been successful in lowering the limits of detection. The mercuric dithizonate complex has been extracted into chloroform or MIBK for nebulization into an oxygen–hydrogen flame.[182] By this method 2 ppM were detectable, compared with only ppm levels without the extraction.

Use of a low-temperature butane–propane–air flame and addition of stannous chloride to the solution for atomization increased the conversion into atomic mercury and enabled 2 ppM of mercury to be determined.[183] An increase in sensitivity of the same order was obtained by Muscat *et al.*[184] when they used a reduction–aeration step to bring mercury into the atomic form in the analysis of rocks and sediments. The procedure is similar to that used to increase the sensitivity in the atomic-absorption determination of mercury. Detection limits of 3 ng (0·06 ppM) were possible.

A further increase in signal is obtained by using silver to collect the mercury before the fluorescence measurement. The mercury is released for measurement by heating. The signal is increased because all the mercury is present at one time. Signal noise is also reduced.[185] Its performance and operation have been discussed in connection with a monitoring method that gave a detection limit of 2 ppM.[186]

Direct determination of mercury in air was found unsatisfactory, the fluorescence signals being too weak owing to quenching by carbon monoxide and nitrogen.[187] Induction-heated carbon rods were used in the cell.

Since mercury lamps of intense and stable output are readily available, and the width of the line is not important provided that the source intensity is high, such sources are well suited to fluorescence determination. On the other hand, for atomic absorption, a narrow-line source is required to achieve high sensitivity. Hollow-cathode discharge tubes are far less intense than the simple mercury lamp, permitting the use of much simpler instrumentation for fluorescence determination.

Atomic-absorption spectrophotometry (AAS)

Mercury vapour meters (ultraviolet photometers) utilizing the special properties of mercury, namely its high vapour pressure and the relatively low stability of the oxide, have long been used for the determination of metallic mercury in air.[21]

Following the introduction of AAS and its application to the determination of mercury in solution, a number of modifications to increase the sensitivity of the procedure have emerged. The two major developments have been "flameless atomic absorption" and the "cold vapour" techniques, each capable of detecting around 0·1 ng.

Conventional AAS. Conventional flame atomic-absorption determination of mercury has been applied to both aqueous and organic extracts of the sample.[188–198] The usual measuring wavelength for the atomic-absorption methods is 253·7 nm but the principal mercury resonance line at 184·9 nm has been used with a nitrogen-purged optical path and a nitrogen-separated, premixed, nitrous oxide–acetylene flame.[191] Detection limits for aqueous solutions were 0·02 ppm for Hg_2^{2+} and 0·05 ppm for Hg^{2+} at the shorter wavelength. The sensitivities of the two

resonance lines have been compared.[199]

Before the atomic-absorption measurement, the sample is usually digested to bring mercury present into solution, this being required for nebulization. The common pretreatments involve acid oxidizing digestion or Schöniger-flask combustion, mercury being brought into solution as Hg^{2+}. Detection limits are of the order of 0·5 ppm.

The sensitivity of the atomic-absorption procedure was increased by extracting mercury into an organic solvent before introduction into the flame. As little as 0·05 mg of mercury per gram of sample could be determined when the acid digest was extracted with MIBK[190] or ammonium pyrrolidinedithiocarbamate in methyl n-amyl ketone[188] and the extract used for AAS, and 0·01 mg per g when the mercury was extracted with ammonium pyrrolidinedithiocarbamate in MIBK.[189,192,193] Dithizone in MIBK has been successfully applied to the chelation and extraction of mercury in digested rock samples before AAS.[194,195] The effect of iodide concentration on the extraction of mercuric iodide has been investigated although the system has been applied only to the determination of more than 5 ppm of mercury.[196]

The ion-association complex formed between the zinc 2,2′-bipyridyl cation and the bromomercurate anion enables mercury to be extracted into 1,2-dichloroethane. Indirect analysis for mercury has been achieved through AAS of the zinc extracted into the organic phase.[197] Trioctylamine has been used for extraction of HgI_4^{2-} before AAS determination.[199a]

Poluektov and Vitkun[200] observed that mercury solutions containing tin(II) gave a greatly enhanced signal when aspirated into the flame. It was shown that this enhancement was due to the more efficient reduction of mercury to the elemental state by stannous chloride than by the flame.[201–203] Further, Hingle *et al.*,[204] using an air–acetylene flame,[201–203] found that the sensitivity of the AAS procedure was increased when the mercury was present as Hg_2^{2+} rather than Hg^{2+} and when complexing agents such as EDTA, which form strong complexes with the mercuric ion, were added to the solution containing mercury as Hg_2^{2+}. The enhancement is due to the disproportionation of Hg_2^{2+} into Hg^{2+} and Hg^0. It was also confirmed that if reducing agents such as ascorbic acid or stannous chloride were added just before aspiration of the sample into the flame, the absorption signal was increased even further.

It was found[201,202] that a flame was not necessary and that the nebulizer could be replaced by a system which passed air through the sample after the addition of stannous chloride. The metallic mercury was carried by the air-stream into an absorption cell in the light path of a spectrophotometer. For the readings to be stable the mercury-carrying air-stream had to be dried. Earlier, Lindstrom[205] had used an air–hydrogen flame to convert mercury into the elemental state but, instead of measurement of the absorption due to mercury in the flame, the combustion gases and mercury vapour were led through scrubbers and condensers to remove interferences, before the absorption due to mercury was measured. This may be considered the forerunner of the flameless atomic-absorption technique, while the reduction – aeration procedure has developed into the cold vapour technique.

The boat technique, where mercury is extracted from the sample and the extract dried before the boat is heated in the flame to release mercury,[206] and the Delves sampling cup method, where the boat is made of nickel instead of tantalum,[207] are very dependent on the position of the sample and its rate of vaporization.

Cold-vapour techniques. The "cold vapour" method requires that the mercury first be brought into solution as Hg^{2+}, and then reduced to the metal and carried into a spectrophotometric cell by a stream of air or inert gas passing through the solution.

Following the observation of the enhancement of the absorption signal when mercury was reduced in solution,[202,203] Hatch and Ott[208] reduced mercury in the sample solution with stannous sulphate and recirculated the mercury vapour in a closed system to permit an equilibrium atomic-absorbance measurement. Samples of rocks and soils with mercury as low as 1 ppM could be analysed, but only acid-soluble mercury would be extracted. The procedure has since been widely applied. Sample types include water,[11,204–209] biological fluids and tissue,[215–220] rocks and sediments,[208,221,222] soils and related materials.[222a]

It is important that recoveries of added organomercury compounds should be checked since the digestion before the reduction should give quantitative conversion of all mercury into Hg^{2+}. It is now customary to use an acid permanganate digestion medium for most sample types. Alternatives are *aqua regia*[223] used on pulp and paper-board samples, and nitric acid for biological,[223] atmospheric and aquatic samples,[208–210,224] and food.[225] However, the nitric

acid procedure was reported to be unsatisfactory for blood samples,[216] for which $HClO_4-HNO_3$ is recommended.[226] The efficiencies of a number of digestion media for biological and other samples have been compared.[226,226a] A mixture of perchloric, nitric and sulphuric acids has been used in the preparation of fish samples for analysis.[219] Vanadium pentoxide acts as catalyst in the digestion of biological materials.[227] Persulphate has been used to oxidise organomercurials in natural waters.[227a] Loss of mercury during digestion must be guarded against (see section on colorimetric methods, above). A decompsotion bomb for break-down of rock and soil samples has been described.[221] After decomposition, the contents of the bomb are dissolved and the solution analysed for mercury by the cold vapour method.

The determination of mercury present as other than organomercurials in blood, urine and tissue does not require a preliminary digestion step.[21] Adjustment of the reaction conditions allows differentiation between organically and inorganically bound mercury. Magos[228] digested biological samples with acid cysteine. Subsequently, reduction with $SnCl_2$ released only inorganic mercury but reduction with alkaline $SnCl_2-CdCl_2$ released all mercury. Both procedures exploit the differences in rate of hydrolysis of mercury compounds. Baltisberger and Knudson used hydrogen peroxide to decompose organomercurials in a preliminary oxidation.[228a] A further differential reduction method has also been used to determine mercury.[209]

In the cold vapour procedure, excess of oxidant remaining after digestion is destroyed by addition of a reducing agent such as hydroxylammonium sulphate or ascorbic acid. The stannous sulphate or chloride which reduces the mercury to the metal is added immediately before the aeration. If the reducing agent is omitted, the response to mercury is linear but somewhat lower. A number of techniques and modifications have been described which reduce interference and increase sensitivity. A common interference is water vapour, which is carried into the spectrophotometric cell from the reduction vessel and tends to condense on the cell walls. Water has been removed by passing the gas stream through a drying tube,[5,193,231-233,329] usually containing magnesium perchlorate. However, the use of such a drying tube has been reported to lead to broadening of the absorption peaks as well as the introduction of memory effects.[234] Additionally, there is a danger that mercury may be lost by adsorption. It has been claimed that no interference from water is encountered if the spectrophotometric cell is kept at 16° – 21°.[210] Lindstedt and Skare[235] warmed the gas stream to 200° before it entered the spectrophotometric cell – this also reduced the possibility of deposition of mercury on the walls of the apparatus. Drying agents were not required when the cell was heated to 200°.[236] Vapour from the reduction vessel has been diluted with air to prevent condensation of water in the spectrophotometric cell.[234] A similar approach described by Thorpe[14] involves the transfer by syringe of headspace vapour from the reaction mixture to the spectrophotometric cell. In contrast to the previous method, an equilibrium absorption reading may be taken although the flow-through method[234] is perhaps better suited to the analysis of large numbers of samples. Other procedures take no specific precautions against water vapour interference[237] or simply recommend a filter, *e.g.*, cotton wool and sintered glass.[238]

Sulphur-containing molecules and some cyclic organic compounds will interfere in the AAS measurement. Bubbling air through the sample under oxidizing conditions will remove some organic solvents before analysis.[5] Chau and Saitoh[15] extracted the mercury in lake waters with dithizone, which served both to concentrate mercury and reduce interferences, before proceeding with reduction and aeration of the sample. Dithizone extraction of the digested sample followed by thermal decomposition of the dithizonate and measurement of the absorption of the mercury vapour released, has been used to try to overcome interferences from other species absorbing at the reasonance wavelength of mercury.[91,239,240] Similarly, mercury has been precipitated from the digested sample as sulphide, which is collected and vaporized into a spectrophotometric cell.[25-27] A concentration step in which mercury from the original sea-water sample is reduced and carried by an air-stream into a smaller volume of permanganate before determination of mercury is described.[291] Since mercury readily amalgamates with noble metals, formation of an amalgam may be used to separate mercury from possible interfering species in the sample. The mercury may be trapped on gold, silver or copper after combustion of the sample or may be deposited from a solution after digestion. These methods will be discussed under the next section, on flameless techniques.

It is important for the attainment of maximum sensitivity that the volumes of the reduction cell and the spectrophotometric cell are in optimum ratio and that the dead volume in the system is at a minimum. This permits the highest concentration of mercury in the spectrophotometric cell. Although the "open" system, which records the maximum absorbance as the mercury is flushed through the cell, may give a higher instantaneous reading than is obtained for a closed circulating system, correction for non-atomic absorption by a continuum source[242] must usually be done on a second "run" of the sample. The circulating system permits such a correction to be made on the vapour measured by means of the mercury resonance lamp. In addition, the open system requires that a recorder be used to register the signal, which may be affected by gas flow-rate through the reduction cell. The closed system is independent of this, but the need to provide a pump complicates the apparatus and may increase mercury losses by adsorption. Larger volumes of sample may be used in the closed system without affecting sensitivity, making it suitable where wet-ashing procedures are required.

The cold vapour procedure has been automated. The samples may be digested separately before sampling by the automatic analyser.[212,218,225-227,235,243-245] Depending on the sample type, only a mild digestion may be required and this could be carried out by the automatic analyser.

The method has been standardized for determination of inorganic mercury in inorganic samples.[245a]

Flameless techniques. Flameless atomic absorption covers procedures where the mercury is released as elemental vapour either by combustion or thermal decomposition of the sample. The atomic absorption is commonly measured away from the decomposition point. Where the combustion procedure is followed, the gaseous combustion products often include interfering molecules for which a correction must be made. Both chemical and physical techniques have been used in efforts to solve this problem.

For air samples, the air has been passed directly into a cell for spectrophotometric measurement, interferences being negligible.[246] To reduce mercury compounds in air to the atomic state, samples were passed through a carbon column at 1350° before entering a silica tube for measurement of mercury, with the 184·9-nm resonance line.[247] Mercury in air has been adsorbed on iodine-impregnated charcoal before being released by heating.[224] This serves both to concentrate the mercury and to isolate it from possible interferences. Active charcoal alone has been used.[247a]

For direct combustion of rock and mineral samples a glass-wool filter between sample-decomposition chamber and spectrophotometric cell was satisfactory.[248] Direct absorbance measurement has also been made after direct heating of rocks.[249,250] Little interference (except perhaps from sulphurous minerals) would be expected from such samples. A stream of nitrogen, air or oxygen passing over the sample aids combustion and carries the released mercury into the spectrophotometric cell. Passing the combustion products over heated copper oxide, and mixing copper oxide plus silver vanadate[252] or sodium nitrate[253] with the sample has been used to aid the combustion. A mixture of silver and manganese oxides at 620° has been used for oxidation of gaseous organic products.[254]

Halides and sulphur compounds in the gas-stream may be removed by passage over heated silver.[251,253] Use of hot silver coils or heating with Na_2SO_3 and passing the vapours through a silica-gel trap[255] (at 400°) also aids in oxidation of vapours.[118] A magnesium perchlorate drying tube has been used to remove water.[248] Lindstrom[205] and Lidums[254] have used chemical absorption systems for the removal of interferences.

Sodium carbonate reduces tar formation from the thermal decomposition of samples such as coal, sugar and cellulose materials.[256] The alternative to removal of interferences from the mercury-carrying gas-stream is to remove the mercury from the sample itself, collecting it in a form in which it may readily be volatilized into the spectrophotometric cell. Although mercury has been collected as the dithizonate[91,239,240,257] and as the sulphide[25-27,54,258] a simpler method is probably amalgamation on gold, silver, or copper, or adsorption on a cool mixture of cobalt and manganese oxides.[254] Mercury is released for ultraviolet measurement by heating. One of the procedures with dithizone[257] amalgamates mercury, released by thermal decomposition of the complex, on gold foil before its release for photometry.

Although mercury absorbance has been measured in the vapour resulting from combustion after possible removal of some interferences[205,251,259,260] the majority of applications would require the further separation of mercury from other constituents in the vapour by amalgamation. Gold[118,253,261-263] is generally used in the form of powder or wire, but a fritted glass disc coated with gold, through which the combustion gases are drawn, has been described.[256] Several amalgamations and desorptions are common in the separation of mercury from organics and water vapour.[118] The methods depend on the gold remaining cool enough to be amalgamated by the mercury and there being a sufficiently clean surface for this. Though silver[262] has been investigated as an absorber for mercury,[264] gold has been used for amalgamation of mercury in analysis of stack gases from smelters[265] while platinum foil has been used for retention of mercury after combustion of blood and urine samples.[252]

Copper[263] has been used for amalgamation of mercury vapour released from rock samples. Copper may be less satisfactory for amalgamation if reactive compounds are present in the combustion vapour. The amalgamation procedures where mercury is subsequently released into the spectrophotometric cell have the advantage that all the mercury can be released into the cell at one time. Studies of the release of mercury from samples by combustion[259,260,266] and from amalgam by heating[264] show that gas flow and sample type will affect the rate of release and thus the absorbance reading in an "open" system.

Amalgamation of mercury produced either electrolytically or spontaneously from a solution of the sample, also isolates and concentrates the mercury. Silver wire has been used for spontaneous deposition[268] of mercury from sediment samples[267] as well as foods, minerals and environmental material, and mercury was released by heating the wire. Gold foil retained mercury from digested rock samples.[269]

Brandenberger and Bader[270] deposited mercury onto a copper wire from solution. Mercury was released into the evacuated spectrophotometric cell when the wire was heated by passage of a current.[270,272] Deposition on copper wire has also been used for the analysis of water samples[273] and radioactive samples,[274] and the Hg was also released, by resistance heating, into a spectrophotometric cell. Electrolytic deposition on other electrodes has been described.[275-276]

A combination of the reduction–aeration method and the amalgamation procedure, in which mercury released after reduction of the digested geological sample with stannous chloride is collected on gold wire clippings which are heated in a furnace to release mercury, has been described,[277] as has the similar use of silver foil.[278]

Correction for background absorption. In addition to the chemical and mechanical methods for separation of mercury from interferences in the absorption measurement in both flameless and cold vapour techniques, several instrumental techniques have been developed, testifying to the difficulty of obtaining adequate isolation.

One of the earliest attempts[27] measured the absorption of the vapour in two units, the first using the mercury line at 253·7 nm while the second had a wide spectral bandpass and continuum source. The contribution of atomic absorption to the measurement in the latter unit is very small and it thus gives a measure of any non-atomic absorption. This is somewhat cumbersome and the principle has been adapted for a single instrument with the two measurements being made simultaneously.[279,280]

Another technique uses pressure broadening of the 253·7-nm mercury emission line to determine the effect of other absorbers.[248,281,282] The central portion of the pressure-broadened line is absent because the light is passed through an absorption cell saturated with mercury vapour; thus mercury will not absorb when this beam passes through the cell, but broad-band absorbers will. This absorption is compared with that obtained for the usual mercury emission which is affected by both atomic and non-atomic broad-band absorption. Ling's instrument[281,282] corrects for this before the final absorption is read.

Removal of mercury by adsorption on palladium-impregnated glass wool allows measurement of residual absorption. This principle has been utilized[283] in a double-beam instrument where the gas-stream is split, one half travelling directly to an absorption cell while the other passes over the palladium chloride filter before entering the second absorption cell. The difference in signal is due to absorption by mercury.

In comparison with neutron activation, which has similar detection limits (1–10 ng),

non-flame atomic-absorption techniques are generally much less time-consuming and require relatively simple apparatus. They are being increasingly used.

Catalytic procedures

Catalysis by Hg^{2+}. Mercury in the Hg^{2+} form will catalyse the reaction between ferrocyanide, water and nitrosobenzene. Hadjiioannou[284] utilized this property in a method for the detection of mercury down to 0·1 ppm. The rate of formation of the reaction product is dependent on the amount of mercury present. The same reaction, which produces a violet compound, was followed on samples of soils and rocks where concentrations down to 30 ppM in a 1-g sample could be detected.[285] In these methods, the catalytic effect is dependent on the concentration of Hg^{2+} present. This requires that all mercury present must be brought into this form. For biological samples this is probably best accomplished by oxidative digestion.

Mercury(II) will also catalyse the reaction between ferrocyanide and 1,10-phenanthroline to yield ferroin and cyanide. The cyanide can be titrated coulometrically with iodine. The method determines down to 10 ppM of mercury.[285a]

Inhibition by Hg^{2+}. The inhibition of an enzyme reaction by mercury allows determination of the mercury in the range 0·004–0·02 ppm.[286] The system under observation was that of the inhibition of invertase (β-fructofuranosidase) in its hydrolysis of sucrose. Toren and Burger,[287] using the glucose–glucose oxidase reaction, were not able to reach such sensitivity by their procedure (0·1–0·4 ppm Hg^{2+}). They made use of the further rapid reaction of one of the reaction products (H_2O_2) with *o*-dianisidine, the reaction being followed spectrophotometrically. Because the system involves a coupled reaction, it may be expected to incur greater errors.

In the case of inhibition of biological reactions, many metals will have effects similar or opposite to that of mercury and a large number of interferences are possible. The methods thus have limited application.

Iodide catalyses the reaction between Ce(IV) and As(III) or Sb(III). Mercuric ion inhibits the catalytic effect of iodide to an extent depending on the amount of mercury present. The reactions are suitable for automation, and the automated procedures, eliminating operator variables, give the best results. A flow-through cell,[288] in which the progress of the reaction between As(III) and Ce(IV) in the presence of iodide and the mercury-containing sample could be followed, has been used to determine down to 0·2 ppm of mercury. The dynamic system reaches a steady-state concentration of Ce(IV), which is dependent on the concentration of mercury in the sample added. Bognár and Sárosi used the iodide-catalysed Ce(IV)–As(III), Ce(IV)–Sb(III) and the iodate–arsenite[289] reactions. The level of mercury in the sample determined the time required to achieve the steady-state condition (Landolt effect). For the Ce(IV)–As(III) and the Ce(IV)–Sb(III) systems, ferroin was present to enable this point to be observed. The sensitivity of this procedure is poorer, the working range being 1–10 ppm, but the iodate–arsenite system is useful for 0·2–2 ppm. The reaction between Ce(IV) and Sb(III) in the presence of ferroin has also been used by Mottola.[290] The Ce(IV)–As(III) reaction has also been followed photometrically.[291]

Elements which affect the rate of reaction between Ce(IV) and As(III) and Sb(III) must be absent. Additionally, the sample should be free from iodide or ions which react with iodide. A number of reactions for the determination of mercury, based on catalytic and inhibition effects, are discussed by Beck and Gaizer.[292]

X-Ray methods

X-Ray detection methods generally require a concentration step since the sensitivity is inadequate for many present requirements. Leroux *et al.*[293] determined mercury in solution by X-ray absorption but the method is incapable of measuring mercury at levels below 0·1%, making it unsuitable for many environmental mercury analyses.

To overcome this lack of sensitivity, mercury from the sample has been collected on ion-exchange paper. Mercury, present on the paper in microgram quantities, has then been determined by an X-ray emission procedure.[294] Another but less sensitive method has been described by Starchik *et al.*[295] (threshold sensitivity 1·9 mg).

The accuracy of X-ray procedures can be affected by matrix effects such as absorption by

other species present in the sample, enhancement and particle-size effects. Optimum excitation and detection energies must be chosen to minimize these effects.[296]

A recently described procedure has a greatly increased sensitivity.[297] Mercury vapour from the sample is mixed with an argon–nitrogen mixture, which intensifies emission at 253·7 nm when the vapour is subjected to X-ray irradiation. The limit of detection is below 1 ppM. The disadvantage of the method lies in the requirement that all mercury from the sample must be brought into the vapour phase.

The X-ray fluorescence determination of trace elements suffers from the disadvantages that the sensitivity (considerably lower than that of neutron-activation analysis or AAS) is affected by a large number of factors and any corrections for interference require involved calculations. In addition, fewer laboratories are equipped for this type of analysis than for atomic absorption.

Spectrographic emission methods

A number of attempts have been made to improve the sample preparation technique and thereby increase sensitivity. A spectrographic procedure for the determination of the mercury in wet digested biological samples involves collecting mercury as an amalgam when the digest is passed through a column of copper dust and, after drying with acetone, transfer of the copper dust to the cavity of a carbon electrode. This is then excited in a d.c. arc. Less than 10 μg of mercury in a sample may be recovered by this method.[298] A similar procedure also involves the collection of mercury on copper dust.[299]

A polystyrene-coated cavity in a carbon electrode has been used to hold dissolved sample[300] for spectrographic analysis. Mercury in sulphuric and acetic acids has been determined by evaporation with carbon powder and subsequent excitation of this carbon powder in a d.c. arc.[301] Although a sensitivity of 0.01 ppm is reported for sulphuric acid, a flameless atomic-absorption measurement on the carbon deposit allows the same sensitivity to be attained, while in the case of acetic acid, a sensitivity of 0·005 ppm is possible, compared with the 0·02 ppm by the spectrographic method. An increased sensitivity enabling detection of mercury down to 1 ppM, has been obtained for effluent samples by extracting with dithizone in carbon tetrachloride before absorption of the extract on carbon powder.[302] The carbon powder is then placed in a special electrode for spectrographic analysis.

To increase the sensitivity of the spectrographic determination of mercury, elements of lower ionization potential may be removed by controlled distillation. Separate evaporation is achieved by the use of specially designed electrodes and arcing conditions[303] which also produce more intense spectra. A low intensity a.c. arc and two electrodes, each carrying sample, have been used in the determination of 3×10^{-4}% mercury in minerals.[304]

An inductively-coupled high-frequency plasma source has been applied to the determination of mercury by atomic emission spectrometry at wavelengths below 200 nm.[305] One of the most significant developments in emission analysis has been the introduction of the helium plasma discharge. By this means 0·1 ppM of mercury[306] may be detected. The mercury from the sample must be introduced into the discharge region as elemental mercury in a stream of He carrier gas. The elemental mercury may be released either by direct combustion or by the reduction of mercury in solution and purging with carrier gas.

A method using a radiofrequency plasma into which elementary mercury from a solution of the sample is carried by a stream of helium, and measurement of the rise in emission intensity, has also been described.[307] The detection limit is given as 2 ng, noble metals and chloride ion being the strongest interferences.

Titration procedures

Indicator methods. The most common type of titration, where the end-point is detected by some type of visual indicator reaction, is not widely used for microtitrations. The end-point is more often detected by physical methods. Further, the very low concentrations of interest mean that mercury cannot usually be determined by direct titration. Usually, some kind of indirect procedure, back-titration or determination of a species the concentration of which is dependent on that of the mercury present, is used.

Thiosulphate was used as titrant for determination of down to 60 μg of mercury by the

Schulek cyanogen bromide procedure.[309] Two methods based on reduction of Hg^{2+} have been published. One, having a working range of 50–100 mg of Hg in the sample used,[310] is not sufficiently sensitive for many applications. The mercury is reduced to the metal by reaction with alkaline glucose. The metallic mercury reduces Fe(III) to Fe(II) and the Fe(II) formed is determined by titration with acidified ceric sulphate, *N*-phenylanthranilic acid being used as indicator. A large number of metal ions can interfere in the reaction and the mercury must be in the inorganic form. The second[311] is based on the reduction of Hg^{2+} to Hg_2^{2+} by ascorbic acid and titration of the unconsumed ascorbic acid with bromosuccinimide, with Methyl Red as indicator; 100 μg of mercury were determined but only in urine and food samples where mercury was added as $HgCl_2$. The method was not tested on organomercury compounds.

N-Carboxyalkyl derivatives of aminonaphthalenesulphonic acids can act as metallofluorescent indicators for titration of mercury with EDTA. However, these will probably not be useful for concentrations below 1 ppm.[312]

Thermometric titration. Thermometric titration with periodate[313] has been used to determine 1 mg/ml Hg. A much more sensitive procedure[314] developed by Burton and Irving used potassium iodide as titrant. The end-point was detected by the catalysis, by excess of iodide, of the oxidation of As(III) with Ce(IV); 0·1 ppm of mercury can be detected by this method but the system is subject to interference from species which will affect the reaction rate.

High-frequency titration. High-frequency titration in non-aqueous media has been used for the complexometric determination of mercury above 5 ppm with EDTA.[315]

Amperometric titrations. These methods are generally able to determine lower concentrations of mercury than thermometric or volumetric procedures can. However, even here, the lower limit of the working range is much higher than can be obtained with atomic absorption or neutron activation analysis.

Lotareva[316] titrated Hg^{2+} with sodium diethyldithiocarbamate solution and was able to determine 10–100 μg of mercury in a 15-ml sample. A more sensitive method involves the formation of the imidazolidine-20-thione complex. This enables 0·4–100 ppm of mercury to be determined.[317] 5-Bromo-8-mercaptoquinoline has also found use in amperometric titration, allowing mercury down to 0·18 ppm to be measured.[318] It is doubtful whether the amperometric titration of mercury with sulphide (used for analysing mercury–antimony sulphide ores) can be adapted to very low concentrations.[319]

Potentiometric titration. The iodide ion-selective electrode has been used as the end-point detector for potentiometric titration of mercury.[272,320] This procedure would also be expected to be less sensitive since the iodide electrode would show some instability at low iodide levelsand could be affected by other ions in solution.

Generally, the titrimetric procedures lack the sensitivity of other methods. The absence of the many interfering species which could react with the complexing or precipitating titrants must be ensured.

Polarographic techniques

The anodic stripping technique using a carbon electrode permits direct determination of mercury. The wax-coated graphite electrode originally used[321,322] has given way to the glassy carbon electrode, which increases the sensitivity. From 0·1 ppm down to 5 ppM of mercury can be determined by the procedure of Miwa *et al.*[323] Other approaches have involved extraction before the polarographic determination.[323,325] An extremely sensitive procedure which uses solvent extraction to isolate the mercury, followed by anodic stripping polarography, is described for the determination of mercury in high-purity lead.[324] The method will be limited to samples where similar interferences are encountered.

Some indirect polarographic procedures have been described.[325-327] Mercury can be determined from its effect on the height of a standard sulphide peak when sample is added.[326] Noble metals would interfere in the analysis. A modification of this procedure uses organosulphur compounds such as thiourea, thionalide, 2-mercaptobenzothiazole or dithio-oxamide instead of sulphide.[327]

Mercury is measured indirectly by a.c. polarography of dithizone solution, where the change in dithizone concentration after extraction of the mercury dithizone complex is related to the

amount of mercury in the sample.[325] Steps may be taken to minimize interferences from cations which form extractable complexes with dithizone. The use of a.c. polarography allows more accurate determination at low concentrations, although the anodic stripping procedure has greater sensitivity.

Although the polarographic procedure can achieve sensitivities down to the order of ppM, this is only possible where interferences can be eliminated. The sample must be brought into the correct form for analysis.

Coulometric production of iodide for use in titrations of mercury has been used for determination of microequivalent amounts of mercury in a sample.[328] Anodic stripping chronopotentiometry has allowed determination of 0·1–100 ppm of Hg.[329]

Miscellaneous techniques

Developed for the determination of mercury in air, a diffusion-chamber apparatus, capable of measuring down to 10^{-15} mole/cm^3 (approximately 0·05 ppm) is used to observe the formation of condensation nuclei under the influence of 253·7-nm radiation.[330] This procedure would require that the mercury be present in the atomic vapour form. Another apparatus[331] for determination of mercury in the elemental or reducible forms collects mercury on a gold or silver surface as amalgam. This is then heated to vaporize the mercury, which in the presence of air and ultraviolet radiation, forms HgO condensation nuclei which are counted. This procedure is applicable to liquid or solid samples from which mercury can be collected as an amalgam, either directly from solution or after reduction and aeration of the (dissolved) sample to convert mercury into the elemental form.

Adsorption of elemental mercury vapour on a thin gold film leads to resistance changes in the film. A portable instrument, capable of measuring 0·05 ng of mercury by using this phenomemon, has been constructed.[332] If mercury in the sample can be brought into the elemental vapour form, this method can be used. However, as in the combustion–amalgamation–atomic-absorption procedures, it is important that impurities present in the mercury vapour stream are not deposited on the surface of the gold film, thereby reducing its adsorption efficiency. In this procedure the vapour is scrubbed to eliminate interfering species (*e.g.*, H_2S) before reaching the gold film.

Spark-source mass-spectrometry has been used in conjunction with isotope dilution to measure traces of mercury in orchard leaves. The samples were wet-ashed and mercury electro-plated onto gold wire cathodes.[332a]

SUMMARY

Since analysis for trace amounts of mercury is most often carried out on environmental samples (tissue, water, air) most methods of analysis will encounter at least some interferences as well as being dependent on a preliminary digestion to bring mercury into solution in the desired form.

Because of their comparatively low sensitivity, X-ray fluorescence and spectrographic emission methods usually require a concentration step. In the case of the former the equipment is not found in many analytical laboratories. The volumetric and thermometric titration procedures lack the sensitivity of atomic absorption or neutron activation while methods based on catalysis or inhibition by Hg^{2+} are too susceptible to interferences to be generally recommended. Of the electrochemical techniques, polarography is probably the most sensitive but this will depend on the complexity of the sample to be analysed.

The susceptibility to interference from other constituents in the sample makes the colorimetric procedures less attractive, though in ideal conditions they could detect 0·05 ppm. Minimizing the interferences may make the procedure quite tedious. In addition, one of the most commonly used and sensitive reagents (dithizone) forms a complex which is very sensitive to light and temperature. All procedures in which reagents are added to remove interferences or to concentrate the mercury run the risk of introducing mercury as an impurity in the reagents. High blank values reduce the sensitivity of analysis.

Atomic fluorescence, having the advantages of not requiring a closed cell and thereby eliminating fogging of windows as well as being virtually unaffected by broad-band absorption,

may become more attractive with the improvement in light-sources and the adoption of the cold vapour or flameless procedures, although a closed system with all mercury from the sample present may be more sensitive.

Radiochemical procedures require activation sources or a supply of tracer, the availability of which probably reduces the degree of their usage. The methods are, however, very sensitive and as well as having much lower levels of activation require generally less manipulation than neutron-activation procedures. Isotope dilution methods are readily automated.

Neutron activation, although applicable to samples where there is an extremely low mercury content, is not widely used because of the equipment and instrumentation required. Detection of mercury at the 0·1-ppM level is possible. Considerable manipulation of the sample may be required to reduce interference, however. Nevertheless, in cases where the amount of sample is limited, neutron activation provides the only suitable means of non-destructive analysis.

In addition to differentiating between organically and inorganically bound mercury, chromatography may allow identification of the organomercurials present, making it a technique particularly useful in environmental studies.

Conventional atomic absorption has a poor sensitivity compared with that of the flameless and cold vapour modifications, which approaches that of neutron-activation. Concentration procedures such as amalgamation have the advantage of removing a considerable amount of interference with little danger of contamination and the mercury can be easily driven off the amalgam for flameless atomic-absorption measurement. The techniques are generally fairly simple and, if required, corrections for non-atomic absorption can be readily made. The cold vapour system has the disadvantages that absorbers such as water vapour may be present and that not all the mercury is present in the absorption cell at the same time, but these can be minimized by careful design of the system. The sample-combustion procedure has the advantage that the mercury is released without long digestion being required but this is offset to some extent by limitation on the size of organic samples which can be burnt completely in the system. Again, with modification of the system (traps for interferences or amalgamation and release of mercury) most such drawbacks can be overcome. The relative simplicity of the system and its sensitivity make it attractive for routine use for a wide variety of samples, although it is more difficult to automate, a solid sample usually being analysed. Most automated methods still reply on a separate digestion to bring mercury into the Hg^{2+} form before its introduction into the analyser.

The wide use already being made of the atomic-absorption procedures is indicative of their suitability for routine determinations. Analysts are familiar with the principles involved and the equipment can be assembled relatively easily and inexpensively. Since the sensitivity attainable is comparable to that of the most sensitive procedures, there is likely to be increasing use of the method when values for mercury content are sought.

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APPENDIX

The following tables constitute a guide to the types of sample which have been analysed by some of the methods described in the text. In cases where sample type is not specified the method has been applied to solutions containing Hg^{2+}. The concentration limits quoted are the approximate lower limits to which the procedure is applicable. In the flameless atomic-absorption procedures the lower useful limit of the method is often better described by the amount of mercury measurable. However, to facilitate comparison with alternative procedures these limits are quoted as concentrations on the basis of a 1-g sample. Where a larger sample may be used the method becomes more sensitive. The quoted lower useful limit of the method is an approximation to the nearest order of magnitude.

Colorimetric methods

Reagent	Sample type	Lower useful limit	References
	water		337
	air	0.15 μg	36
	soil	0.1 ppm	62
		0.01 ppm	61
	coal	1 ppm	56
		0.1 ppm	42, 43
		1 ppM	41
	metals	0.1 ppm	338
	plant material	0.1 ppm	45, 46, 47
		0.01 ppm	61
	animal tissue	1 ppm	55
		0.1 ppm	44, 47, 48
		0.01 ppm	39, 57
	urine	0.1 ppm	37
		0.01 ppm	38
		1 ppM	336
	blood	0.1 ppm	44
	eggs	0.1 ppm	53
Dithizone	organic matter	0.1 ppm	28, 94
Di-(2-naphthyl) thiocarbazone	air		35
	selenium	0.01 ppm	67
Diphenylcarbazone	organomercury residues	1 ppm	66
1-(2-Pyridylazo)-2-naphthol		1 ppm	69
4-(2-Pyridylazo)-resorcinol		0.1 ppm	77
1,3-bis-(4-Nitrophenyl)-triazene		1 ppm	70
4,4-bis(Dimethylamino)diphenylamine (Bindschedler's Green)		0.1 ppm	76
Methyl Green(C.I. Basic Green 5)		0.1 ppm	335
Brilliant Green (C.I. Basic Green 1)		0.1 ppm	83
Crystal Violet (C.I. Basic Violet 3)		0.01 ppm	81
		0.1 ppm	334
Ruhemann's Purple		0.1 ppm	89
Methylene Blue		0.1 ppm	85, 333
Xylenol Orange		1 ppm	84
Rhodamine B		1 ppm	82
Antipyrine dyes		0.1 ppm	80
Pyrazolone dyes		0.1 ppm	88
5-Nitrofurfuralsemicarbazone		0.1 ppm	72, 73
Thiothenoyltrifluoroacetone	water	0.1 ppm	75
Oxamide bis(phenylhydrazone)		0.1 ppm	68
N-Phenylbenzohydroxamic acid		0.1 ppm	71
Sulpharsazen		0.1 ppm	74
Metalphthalein		0.1 ppm	78
2,2′-Bipyridyl–Fe(II)		0.1 ppm	86, 87
bis-Antipyrinyl-4-dithioformato-Ni(II)		0.1 ppm	90

Neutron activation methods

Sample type	Lower useful limit	References
water	1 ppM	129
	0.1 ppM	110
	0.01 ppM	99, 109, 111, 133
air particulates	1 in 10^{15}	105
rocks	1 ppm	123, 126, 132
	0.1 ppM	120, 134
soils and sediments	10 ppM	115, 138
coal	10 ppM	97, 98, 138
metals	1 ppM	107
plant materials (including grains)	1 ppm	126
	0.1 ppm	112, 122
	10 ppM	138
	1 ppM	99, 103, 104, 108, 113, 116
animal tissue	10 ppM	97, 121, 122, 125, 130, 138
	1 ppM	96, 102, 119, 121, 139, 140, 141
milk	0.1 ppm	122
blood	10 ppM	98, 136
	1 ppM	19, 117
eggs	10 ppM	122, 141
chemicals and laboratory materials	10 ppM	121
	0.01 ppM	111

Flameless atomic-absorption methods

Sample type	Lower useful limit	References
water	10 ppM	253
	1 ppM	205
soils and sediments	10 ppM	253
rocks	10 ppM	248, 253
	0.1 ppM	260
coal	10 ppM	253
animal tissue	10 ppM	253
	0.1 ppm	251
urine	1 ppM	205
organic matter	0.01 ppM	255

2. Preliminary deposition

Sample type	Lower useful limit	References
water and effluents	0.1 ppM	25, 27, 267, 270, 272, 273, 278
air	10 ppM	269
	0.001 ppM	252
soils and sediments	10 ppM	269, 275
	0.1 ppm	278
rocks	10 ppM	263, 269, 275
	1 ppM	262
	0.1 ppM	254, 277
coal	0.1 ppM	118
inorganic chemicals	1 ppM	252
animal tissue	10 ppM	54, 257, 258
	1 ppM	252, 254, 261
urine	1 ppM	276
eggs	10 ppM	54
organic matter	1 ppM	254

Cold vapour atomic-absorption methods

Sample type	Lower useful limit		References
water and effluents	10	ppM	213, 214, 224
	1	ppM	201, 208, 210, 211
	0.1	ppM	5, 209, 212
	0.01	ppM	11, 15
	0.001	ppM	241
air	1	ppM	210
	10	ppM	224
soil and sediments	10	ppM	229
	1	ppM	211, 222
rocks	10	ppM	221
	1	ppM	208
coal	1	ppM	236
metals and inorganic chemicals	0.1	ppm	201
	1	ppM	203, 208
plant materials (including grains)	0.1	ppm	14
	10	ppM	92, 218, 220, 223, 227
	1	ppM	236
animal tissue	0.1	ppm	14, 219, 226, 243
	10	ppM	92, 214, 218, 220, 225, 227, 228
	1	ppM	211, 236
urine	1	ppM	211, 216, 217, 224, 235
blood	10	ppM	92, 226
	1	ppM	210
eggs	10	ppM	54

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COULOMETRIC INVESTIGATION OF THE DRYING METHODS FOR THE STANDARD REFERENCE MATERIALS POTASSIUM DICHROMATE AND SODIUM CARBONATE

TAKAYOSHI YOSHIMORI and NORIYUKI SAKAGUCHI

Faculty of Engineering, Science University of Tokyo, Kagurazaka, Shinjuku-ku, Tokyo, Japan

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Summary—The water content of dried potassium dichromate and sodium carbonate, which had been heated at various temperatures and then cooled in a "desiccated" atmosphere of argon, was measured by a coulometric microdetermination method. The amounts of water in the dried standard reference materials depended mainly on the heating temperature and only a little on the desiccant used. The dichromate and carbonate contained less than 50 ppm of water when they were heated at temperatures higher than 200° and 250° respectively and then cooled in an atmosphere of argon desiccated with magnesium perchlorate. Sulphuric acid was not advisable as the desiccant for sodium carbonate.

There are many differences in the drying procedures for "Standard Reference Materials" (SRMs) for volumetric analysis. In particular the procedures for potassium dichromate and sodium carbonate differ appreciably in text-books and research investigations. For example, Marinenko and Taylor dried the dichromate by two methods; first, the pulverized reagent was heated at 110° for 24 hr and then cooled in a desiccator containing magnesium perchlorate,[1] secondly, the reagent was dried for 6 hr at 130° and cooled in a phosphorus pentoxide desiccator.[2] Although they obtained excellent results for the purity of the reagent, there was no evidence that the samples were completely dry. Some authors[3–5] have shown that the dichromate can be dried by melting. They warn, however, that decomposition of the reagent to green chromium(III) oxide was sometimes observed in the melt. Yoshimori *et al.* purified the reagent by the zone-melting method, and obtained very pure products.[6] This suggests that the reagent may be dried at higher temperature without decomposition. The water in the dichromate is present in cavities in the crystals, which explains the role of the pulverizing.[7]

On the other hand, sodium carbonate is recommended by IUPAC[8] and the Society for Analytical Chemistry as an SRM,[9] and has been used as such in Japan for about 40 yr. According to the procedure shown by IUPAC and SAC, the reagent should be dried at $270 \pm 10°$ to constant weight, and Japanese Industrial Standards recommend heating at higher temperature (500–650°) for 40–50 min in a platinum crucible. Various drying conditions for this reagent, given in the literature, have been summarized by Laitinen.[11]

Newkirk and Laware[12] pointed out that the thermogravimetric investigations on the drying procedures for SRMs, are of little value, and Laitinen[13] had some doubts on the sensitivity of the thermobalance.

As the next stage, the heated reagents must be cooled in a desiccator before weighing. The hygroscopicities of the reagents in this process decrease their purities. Kolthoff[14] warned that the dried carbonate takes up moisture during the opening and closing of a container. By using the desiccator shown by Peck,[15] we can largely eliminate this problem. However, the selection of the desiccant and the adsorption of water vapour on the container (weighing bottle) may be the next sources of trouble. The wide range of the relative efficiencies of desiccants has been shown by Kolthoff and Elving[16] and by Trusell and Diehl.[17] Booth and McIntyre also indicated that the air in a desiccator took 2 hr to reach equilibrium after the lid was closed.[18]

For these reasons, Madej and Rokosz[19] prepared single crystals of some reagents. Following up this idea, Yoshimori and Tanaka analysed single crystals of commercial sodium chloride[20] and of sulphamic acid prepared by themselves.[21] Although the crystals had excellent purity and adsorbed little water on their surfaces, the purity differed somewhat

from crystal to crystal. Therefore, the crystals analysed were not suitable as ultimate standards but only as secondary reference materials for analysis of ordinary or somewhat better accuracy. Thus powder-type SRMs are still necessary.

Since we cannot weigh completely dry SRMs very easily, it is convenient for us to know what amount of water is present in the SRMs under practical weighing conditions and also what procedure is preferable.

In this paper, we demonstrate the coulometric measurement of the water content of dried and cooled potassium dichromate and sodium carbonate. The method involves the conversion of the water into ammonia, in an argon carrier, with sodium amide, followed by the coulometric titration of the ammonia with electrogenerated hypobromite ion.[22, 23]

EXPERIMENTAL

Apparatus

The apparatus used in this investigation was fundamentally the same as that of previous reports,[23, 24] and is shown in Fig. 1. The U-tube, which had a by-pass circuit with a stop-cock (K), was inserted between the argon-purification train and the entrance to the sample heating tube. The titration cell and the apparatus for coulometric titration were also the same as in the previous reports.

Procedure

The pulverized sample (0·2–0·3 g) of potassium dichromate or sodium carbonate was weighed into a quartz or platinum boat respectively, and the boat put into the heating tube. The sample was then heated at a definite temperature for 3 hr for the dichromate or 1 hr for the carbonate, under dried argon which was by-passed through the stop-cock (not through the U-tube). Then the stop-cock was closed and the gas was allowed to flow through the desiccant in the U-tube. Therefore, the argon then contained some water vapour from the desiccant itself. The sample was taken out of the furnace and allowed to cool to room temperature for 1·5 hr under the same argon stream. During this cooling, the water vapour could be adsorbed by the dried sample.

The argon was then again made to by-pass the U-tube, by opening of the stop-cock. The sample was again introduced into the furnace and heated at higher temperature (400° for potassium dichromate and 600° for sodium carbonate). The water released from the sample by this heating was converted into ammonia with sodium amide and the ammonia was determined by coulometric titration. The technique has been described in detail elsewhere.[22–24]

The amounts of water determined here may be both the residual moisture in the sample and the water trapped by the sample during the cooling process. Because the sample cannot come into contact with atmospheric moisture and is heated in dry argon, this procedure is not exactly the same as the ordinary drying process for SRMs, but we considered that it was suitable for investigation of the best drying temperature for SRMs and selection of the desiccant for the cooling desiccator.

RESULTS AND DISCUSSION

Potassium dichromate

As a preliminary investigation, weighed portions of the reagents were heated at various temperatures and the amounts of water released from the samples at each temperature were determined coulometrically. The results obtained are shown in Fig. 2. The amounts of water released from a commercial reagent (analytical grade) was much larger than those from the National Bureau of Standards (NBS) and also increased at temperatures above the melting point. This is one piece of evidence for the presence of organic impurities in

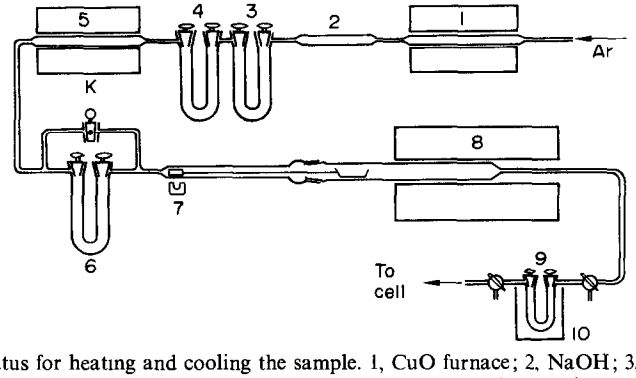

Fig. 1. Apparatus for heating and cooling the sample. 1, CuO furnace; 2, NaOH; 3, $Mg(ClO_4)_2$; 4, P_2O_5; 5, Ti furnace; 6, U-tube containing desiccant; 7, magnet; 8, heating furnace; 9. $NaNH_2$; 10, oil-bath.

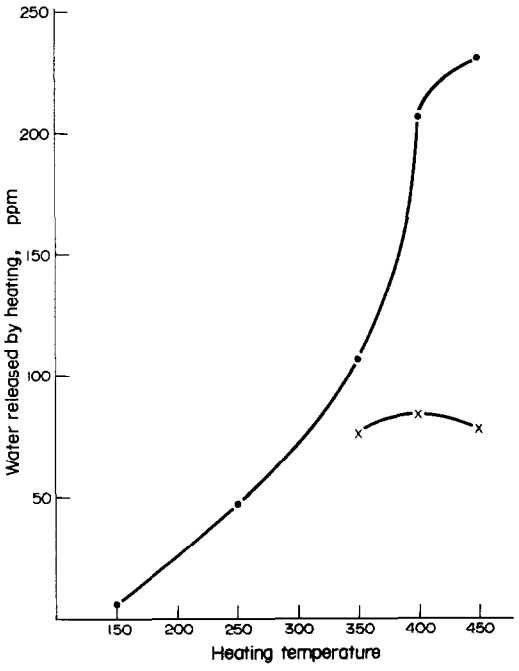

Fig. 2. The amounts of water released from potassium dichromates by heating at various temperatures. ●——● Commercial reagent (analytical grade). ×——× SRM 136c from NBS.

the commercial reagent. The results for the NBS material show that the dichromate released its water completely on heating at 400°.

The water contained in samples which were heated and cooled by the procedure described above was next determined, and the results are shown in Fig. 3. Much water was released from the commercial reagent and also extremely high results were sometimes obtained (not shown in the figure). In such cases a green compound [chromium(III) oxide] was found at the bottom of the melt after the determination. This is the other evidence

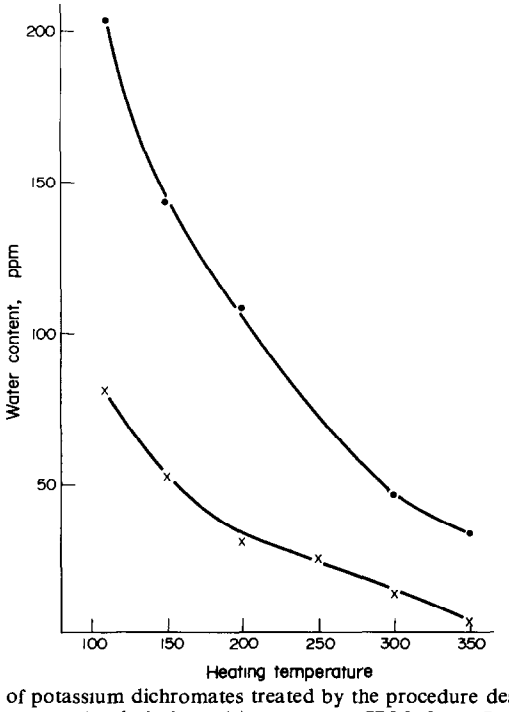

Fig. 3. Water contents of potassium dichromates treated by the procedure described in the text. ●——● Commercial reagent (analytical grade). ×——× SRM from Industrial Inspection Institute Japan (IIIJ). Desiccant H_2SO_4, heating time 3 hr.

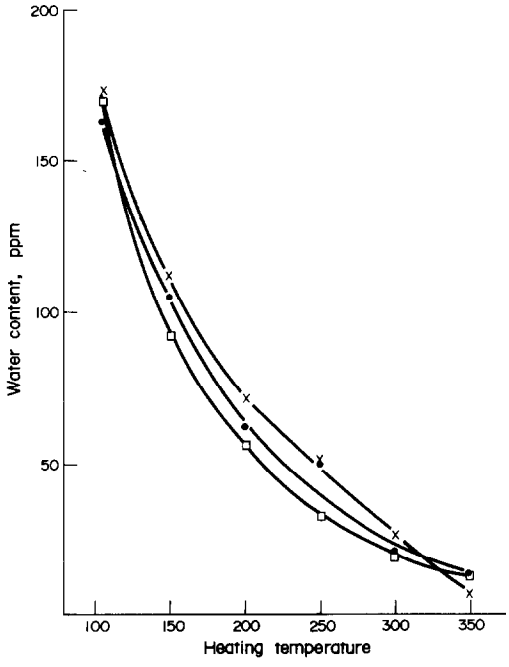

Fig. 4. Water contents of potassium dichromate SRMs treated by the procedure described in the text. □——□ SRM 136c (NBS), desiccant $Mg(ClO_4)_2$. ×——× SRM (IIIJ), desiccant $Mg(ClO_4)_2$. ●——● SRM (IIIJ), desiccant H_2SO_4. Heating time 3 hr.

for the presence of organic impurities in the reagent. In the examination of the SRM certified by the Industrial Inspection Institute (Japan), we could find no anomalous results and no green compound. Hence, if we wish to purify the reagent by recrystallization, we have to be extremely careful to avoid contamination by organic materials.

The Japanese and NBS (136c) samples were analysed by the given procedure in the investigation of the selection of desiccants, and the results are shown in Fig. 4. From these results, it is clear that the reagent must be dried at a temperature higher than 350°, if extremely dry reagent is needed. In the ordinary case, however, the pulverized dichromate may be dried at a temperature higher than 200°, if the accuracy of the following analysis allows 0·005% of moisture in the reagent. The efficiency of the drying agent in the desiccator is not so important if the heated sample is not stored for a long time. Magnesium perchlorate will keep the sample dry, though in blank experiments it released somewhat more water into the argon than sulphuric acid did. (This result is not proof that the acid is a better desiccant, since both the equilibrium water vapour pressure and the rate at which equilibrium is reached both have to be taken into account). We consider that adsorption of water by the glass container for the reagent,[23] and the moisture in the air which enters the desiccator on opening the lid,[18] cause more trouble than water vapour from the desiccant.

Sodium carbonate

The SRM certified by the Industrial Inspection Institute (Japan) was used in this investigation, and the results are shown in Fig. 5. Generally, the reagent contained more water than that in potassium dichromate. The carbonate, however, released water appreciably at 200°, and the procedure for heating the reagent at 270° which is recommended by IUPAC *etc.* is reasonable when the reagent is to be used as an SRM with ordinary accuracy. The completely dehydrated reagent may be obtainable by heating the carbonate at just above its melting point, in an atmosphere of carbon dioxide.[25] The experimental conditions adopted here seem not to warrant final heating at 600°, to obtain complete dehydration, but the observations of Newkirk and Aliferis[25] may support the use of this temperature.

The results in Fig. 5 also indicate that the heated carbonate should be cooled in a desiccator containing magnesium perchlorate. Although the sulphuric acid used in this investi-

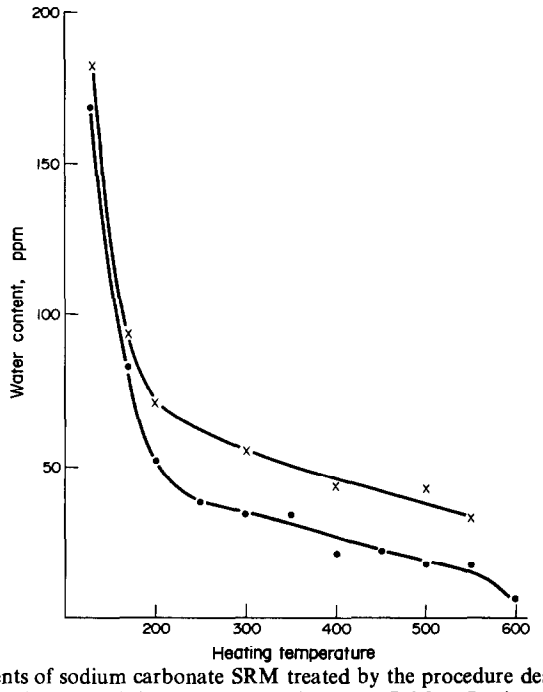

Fig. 5. Water contents of sodium carbonate SRM treated by the procedure described in the text. ●——● Desiccant $Mg(ClO_4)_2$; ×——× desiccant H_2SO_4. Heating time 1 hr.

gation was somewhat more effective than magnesium perchlorate, the water contained in the cooled carbonate when the acid was used as the desiccant always exceeded that when magnesium perchlorate was used. This phenomenon indicates that a trace of the acid was vaporized into the argon stream and reacted with the carbonate. The observations of Gore,[26] for reduced pressure conditions, also support the results in this figure. The carbonate, dried at 600° and cooled in argon passed through magnesium perchlorate, released 5·7 ppm of water on heating at 600°. This indicates the limit of the power of the desiccant and the hygroscopicity of the carbonate. Phosphorus pentoxide was not investigated here because it sometimes contains the trioxide.[27]

CONCLUSION

Potassium dichromate and sodium carbonate should be dried at temperatures higher than 200° and 250° respectively for 3 hr, and be allowed to cool in a desiccator containing magnesium perchlorate. By this procedure the water in the reagents is decreased to less than 50 ppm (0·005%). Melting procedures for these reagents are also advisable, when the investigator needs the completely dried reagents. Great care must be exercised to avoid errors arising from atmospheric moisture and water adsorbed on the container used for the reagents.

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SELECTIVE SEPARATION OF CHROMIUM FROM OTHER ELEMENTS BY ION-EXCHANGE—II*

ANION- AND CATION-EXCHANGE IN OXALIC ACID SOLUTIONS

ADOLF M. MULOKOZI and DONNATI M. S. MOSHA

Laboratory of Inorganic and General Analytical Chemistry, Chemistry Department, University of Dar es Salaam, P.O. Box 35061, Dar es Salaam, Tanzania.

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Summary—The kinetic inertness of the chromium(III) aquo-ion towards substitution reactions with oxalate has been exploited for selective separation of chromium from other elements. Most transition elements, with the notable exception of chromium, react rapidly with oxalate, and may be sorbed on a strongly basic anion-exchange resin as anionic oxalato complexes. On the other hand chromium sorbed on a cation-exchange resin is not eluted with oxalic acid solutions. This permits separation of chromium from elements which react rapidly with oxalate.

The separation of chromium, present at various levels of concentration in minerals, technical products and biological materials, is of general interest to analytical and clinical chemists. The element plays an important role in industry, and recently it has been associated with carcinogenic hazards.[1, 2] Consequently a number of elaborate procedures for separation and determination of the element in biological samples such as plasma, urine and faeces[3–6] have appeared in the literature. In this laboratory we have given priority to the determination of the element in mineral samples under an existing wide programme for study and evaluation of the local mineral potential. The element commonly found in association with chromium in minerals, industrial products and biological samples is iron, or to a less extent aluminium. We have therefore paid attention to the separation of chromium in systems containing iron and aluminium.[7]

Some of the successful methods for selective separation of chromium by ion-exchange involve anion- or cation-exchange of chromium(VI).[7–10] Procedures for ion-exchange separation of chromium(III) are rare, mainly because the element in this state shows a similar distribution coefficient to those of its accompanying elements, iron and aluminium.

The ion-exchange behaviour of chromium(III) is characterized by the tendency of the element to be held tenaciously on cation-exchange resins so that it is not easily desorbed. This is a consequence of the kinetic inertness of chromium(III).[11]

The kinetic inertness of chromium and a few other transition elements offers good prospects for general application in analytical chemistry. In a recent thorough treatment, Alimarin[12] demonstrated the immense possibilities for application of the kinetics of complex formation in analytical chemistry. In ion-exchange the kinetic inertness of chromium has found application in cation-exchange separation of the element from others in solutions containing citrate.[13] Similarly the separation of chromium with a chelating resin has been reported.[14]

Ligand-substitution reactions involving chromium have been widely investigated. In a thorough study of the literature, we discovered the kinetics of the reaction between the chromium(III) aquo-ion and oxalic acid[15–18] to be particularly favourable for our present investigation. Most transition elements react quickly with oxalic acid to form stable anionic complexes which exhibit large distribution coefficients[19] with strongly basic anion-exchange resins. On the other hand chromium(III) reacts extremely slowly in the

* Part I: *Analyst*, 1972, **97**, 820

cold to form sorbable oxalate complexes. Thus chromium(III) is not desorbed in appreciable amounts from a cation-exchange resin by cold oxalic acid solution, whereas the elution of other elements such as iron and aluminium takes place rapidly. When cold solutions of oxalic acid and chromium(III) are passed rapidly through an anion-exchange resin immediately after mixing, almost all the chromium (*ca.* 99%) is recovered in the effluent solution. Iron and aluminium are retained under those conditions.

EXPERIMENTAL

Reagents

Analytical-grade Amberlite IRA 400 and 401 resins supplied in the chloride form by Rohm and Haas were converted into the oxalate form. The resin in the chloride form was stirred for 24 hr in 1*M* sodium hydroxide. The resin, after filtering and washing with distilled water, was stirred for another 24 hr in a mixture that was 0·5*M* in oxalic acid and 0·5*M* in sodium oxalate. The resin was filtered off and washed with distilled water and with acetone. After air-drying the resin was placed in a vacuum oven at 45° for 12 hr. The dry resin obtained (Amberlite IRA 401) had a capacity of 4·4 meq/g based on oxalate content. This compares well with the value 4·3 quoted by the manufacturer.[20]

The Dowex 50 × 8 (14–52 BSS, hydrogen form) (Dow Chemical Co.) was purified by washing with hydrochloric acid followed by distilled water. After filtering, the resin was air-dried, and kept in a vacuum oven at 40° for 12 hr. The dry resin had a capacity of 4·5 meq/g based on titration of the acid liberated when a 1*N* solution of barium chloride was passed through a column packed with the resin. The manufacturer quotes the value 4·8 meq/g.[20]

Solutions containing 5 mg of chromium, aluminium or iron per ml were prepared from analytical-reagent grade potassium chromic sulphate, potassium aluminium sulphate and ferric chloride. The chromium solution was standardized according to a procedure previously described,[8] and the aluminium and iron solutions by EDTA titration with Xylenol Orange as indicator.[21]

All other reagents were of analytical-grade quality, and were used without further purification. The term "oxalic acid" refers to the dihydrate throughout.

Procedure

Kinetics of chromium sorption by Amberlite IRA 400. To a round-bottomed flask of 100 ml capacity were added 2 g of the dry resin in the oxalate form, 12·5 ml of 0·25*N* oxalic acid and 30·24 ml of distilled water. After a short period of shaking, 7·26 ml of chromium solution (36·30 mg Cr) were added, then the flask was immediately tightly stoppered and connected to a shaking device. After 1 hr of shaking, the resin was filtered off, and residual chromium in an aliquot of the filtrate was determined as chromate after destruction of oxalate with perchloric acid and oxidation of chromium with alkaline peroxide. The amount of chromium sorbed was obtained by difference. The same procedure was used to determine chromium sorbed during longer periods of shaking. In each experiment the total solution volume was 50 ml. In a separate series of experiments the effect of increasing oxalic acid concentration and addition of hydrochloric acid was investigated.

Elution characteristics of Cr, Al and Fe. A column of dimensions 3 cm^2 × 18 cm was packed with 35 ml of the wet resin Amberlite IRA 401 in the oxalate form (previously immersed in water for 24 hr). Then 20 ml of a solution containing 8 mg of Cr, 7·86 mg of Al, 26·3 mg of Fe were mixed with 15 ml of 0·15*M* oxalic acid and added. The solution was allowed to descend at the rate of 40 ml/min. Before the solution sank below the resin surface, the original container of chromium solution was washed with 20 ml of 2% oxalic acid solution and the washings passed through the column. Then 500 ml of 2% oxalic acid solution were passed through the column at the rate of 40 ml/min. The flow-rate was kept constant in the manner described elsewhere.[22] Fractions (25-ml) of the effluent solution were collected by means of an automatic fraction collector. When 500 ml of solution had been collected, the effluent solution contained nearly all the chromium (recovery 99%). Aluminium and iron still on the resin were eluted with 0·19*M* oxalic acid–0·3*M* hydrochloric acid, at a flow-rate of 5 ml/min.

Distribution coefficients for aluminium and iron. The distribution coefficients of aluminium and iron in mixtures of hydrochloric acid and oxalic acid were determined for Amberlite IRA 401 by the usual batch equilibration method.[23, 24] The maximum (theoretical) loading of the resin was not allowed to exceed 12%.

Separation with Dowex 50 × 8. The resin Dowex 50 × 8 (hydrogen form) was made ready for use by keeping it under distilled water for 12 hr. Then 35 ml of the wet resin were packed in a constant flow-rate ion-exchange column[22] of dimensions 3 cm^2 × 18 cm The resin in the column was loaded in separate experiments with varying amounts of chromium and aluminium In another series of experiments the column was loaded with chromium and iron. The solution containing a synthetic mixture of the elements in desirable weight ratios was passed through the column, followed by washing with distilled water in order to free the resin bed from the liberated acid.

Iron and aluminium were desorbed with 500 ml of 2% oxalic acid solution at a flow-rate of 40 ml/min. The desorption of chromium(III) from a cation-exchange resin is always difficult. Therefore chromium(III) was desorbed by oxidation to chromium(VI) with alkaline sodium peroxide solution according to a procedure described by Freeman.[4]

RESULTS AND DISCUSSION

Aluminium(III) and iron(III) are typical kinetically labile tervalent metal ions.[25] This explains why these ions are rapidly desorbed from a cation-exchange resin with oxalic acid solutions. The availability of oxalate and bioxalate ions in solution is an important factor in the formation of metal oxalate complexes which are absorbed on anion-exchange resins,

Table 1. Results of ion-exchange separation of binary mixtures of Cr–Al and Cr–Fe, using an anion-exchange column packed with Amberlite IRA 401

Chromium, *mg*		Aluminium, *mg*		Chromium, *mg*		Iron, *mg*	
Added	Found	Added	Found	Added	Found	Added	Found
30	29·5	10·0	10·0	20·0	19·6	20·1	20·0
25	24·7	13·0	12·9	25·0	24·7	23·5	23·5
40	39·4	16·0	15·7	26·5	26·2	25·6	25·3
15	14·8	18·0	18·0	27·4	27·1	15·0	14·7
20	19·6	20·5	20·3	28·4	28·0	25·9	25·6
16	15·6	25·6	25·2	30·0	29·5	26·1	26·0
12	11·5	30·1	29·6	35·5	35·1	30·0	29·2

and desorbed from cation-exchangers. Thus the suppression of dissociation of oxalic acid by addition of mineral acids or acetone, reduces the sorption of the metal on the anion-exchangers, and the desorption from cation-exchangers. Although iron and aluminium exhibit nearly similar distribution coefficients for cation-exchange resins in solutions of dilute hydrochloric acid, their separation factor S_{Fe}^{Al} may be improved considerably by a careful choice of oxalic acid–hydrochloric acid ratios. Thus selective desorption of those elements from cation-exchange resins is possible. In presence of chromium(III), selective desorption of iron and aluminium increases the time needed for the necessary column operation, so that some loss of chromium occurs. Table 1 shows typical results of separation of binary mixtures of Cr–Al and Cr–Fe. The analyses of the fractions show satisfactory recovery of all the elements. The recovery of chromium is, in this case, better than that obtained with an anion-exchange resin. This is because the reaction time for chromium(III) and oxalic acid is shortened, since the formation of chromium oxalate complexes is restricted within the column.

For our study of the kinetics of chromium sorption we used a resin of increased cross-linking (Amberlite IRA 400). It is to be expected, however, that the Amberlite IRA 401 we used for study of the elution characteristics of chromium, aluminium and iron, would show more favourable sorption kinetics and permit the higher flow-rates necessary for optimum recovery of chromium. Figure 1 shows the kinetics of chromium sorption by Amberlite IRA 400. A comparison of curves *a* and *b* shows clearly that higher concentrations of oxalic acid enhance chromium sorption. Addition of a small amount of hydrochloric acid (curve *c*) has a marked depressant effect on chromium sorption. In spite of use of an increased oxalic acid concentration the absorption of chromium is visibly suppressed in 0·04*M* hydrochloric acid. This effect is explained in terms of acid hydrolysis of the sorbable species, $Cr(C_2O_4)_3^{3-}$ and $Cr(H_2O)_2(C_2O_4)_2^-$, according to:

$$Cr(C_2O_4)_3^{3-} + 2H_3O^+ \rightleftharpoons Cr(H_2O)_2(C_2O_4)^- + H_2C_2O_4$$

$$Cr(H_2O)_2(C_2O_4)_2^- + 2H_3O^+ \rightleftharpoons Cr(H_2O)_4C_2O_4^+ + H_2C_2O_4$$

$$Cr(H_2O)_4C_2O_4^+ + 2H_3O^+ \rightleftharpoons Cr(H_2O)_6^{3+} + H_2C_2O_4$$

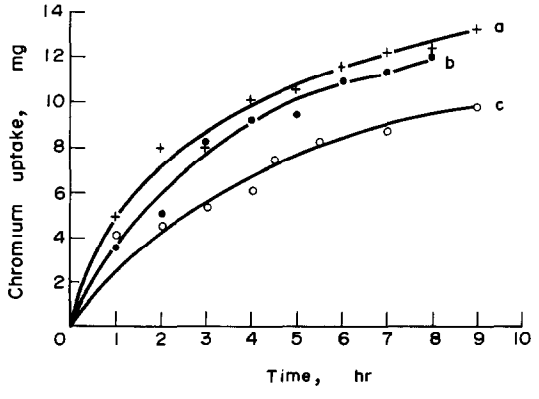

Fig. 1. Rate of uptake of chromium at 26°C by Amberlite IRA 400 (oxalate form) from oxalic acid media. [oxalic acid]: (*a*) 0·025*M*; (*b*) 0·031*M*; (*c*) 0·031*M* in 0·04*M* HCl.

Table 2. Cation-exchange separation of binary mixtures of Cr–Al and Cr–Fe

Chromium, *mg*		Aluminium, *mg*		Chromium, *mg*		Iron, *mg*	
Added	Found	Added	Found	Added	Found	Added	Found
10·2	10·1	30·5	30·4	12·0	11·9	30·0	30·0
12·5	12·4	26·0	26·0	12·5	12·4	26·5	26·4
15·0	14·8	25·5	26·6	15·1	15·0	25·0	25·1
16·5	16·4	21·7	21·7	17·5	17·3	24·5	24·2
18·0	17·8	20·0	20·0	18·0	15·0	23·1	23·1
19·5	19·4	21·0	20·9	20·1	20·0	20·5	20·4
20·0	19·8	17·5	17·6	22·5	22·4	20·0	20·1
21·5	21·4	18·6	18·5	25·4	25·2	19·5	19·4
22·0	21·9	16·0	16·1	26·2	26·1	18·1	18·1
25·0	24·8	10·0	10·0	26·5	26·4	16·5	16·4

Among the important factors which favour high recovery of chromium are acidity, low temperature, moderate concentration of oxalic acid, and short residence time of the solution in the resin bed. Since the formation of sorbable anionic chromium complexes starts immediately upon mixing of the chromium solution with oxalic acid, it is necessary to pass the resulting solution through the resin in the column without delay. Because of slight formation of sorbable oxalate complexes during the time of mixing of the solution and the passage of the resulting solution through the column, higher recovery than 99% for chromium is rare (Table 1).

Optimum conditions for separation of aluminium and iron

Babko and co-workers have determined the stability constants of various oxalate complexes of aluminium[26] and iron.[27] The stability of these complexes is sensitively influenced by the proton concentration. The separation of those elements is therefore facilitated by selective formation (or dissociation) of their complexes in oxalic acid–hydrochloric acid mixtures. In order to find the optimum conditions for separation of aluminium and iron, we have made a thorough study of the distribution coefficients of these elements for Amberlite IRA 401 in oxalic and hydrochloric acid mixtures. A comprehensive report of this study will appear in a subsequent communication. Relevant to our present study is the discovery that the maximum separation factor $S_{Fe}^{Al} = 3{\cdot}4$ is obtained with a 0·3*M* hydrochloric acid–0·018*M* oxalic acid mixture. Under these conditions the distribution coefficients are $D_{Fe} = 140$ and $D_{Al} = 36{\cdot}9$.

Elution characteristics of Cr, Al and Fe from Amberlite IRA 401

In 0–0·05*M* oxalic acid the distribution coefficients of iron and aluminium are nearly the same (~ 10^4). The distribution coefficient of aluminium falls more sharply with increasing proton concentration, an indication of increasing instability of aluminium complexes with acidity. This is why the separation of aluminium from iron is best carried out in oxalic acid solutions that are 0·3*M* with respect to hydrochloric acid. However, the presence of chromium in the same solution does not permit use of 0·3*M* hydrochloric acid, as both aluminium and chromium are then obtained in the same fraction. Although the presence of hydrochloric acid would suppress the sorption, it has been necessary to use oxalic acid free from hydrochloric acid for elution of chromium. Since large volumes of solution require longer duration to run through the column, it was necessary to limit the volume of sample solution to 35 ml in order to minimize the sorption of chromium. Figure 2 shows the elution curves of Cr, Al and Fe. A trailing effect is observed for chromium. This probably arises from formation of small amounts of chromium species which are sorbed tenaciously. To minimize this effect, the elution of residual chromium with 0·05*M* oxalic acid was carried out at high flow-rates (40 ml/min). Under these conditions 90% of the added chromium is found in the 160 ml collected in 4 min and 99% in 500 ml of eluate. Elution with 0·05*M* oxalic acid–0·3*M* hydrochloric acid produces a pure fraction of aluminium, followed by iron, which is desorbed rather slowly. Iron may be rapidly desorbed from the resin by elution with hydrochloric acid only.

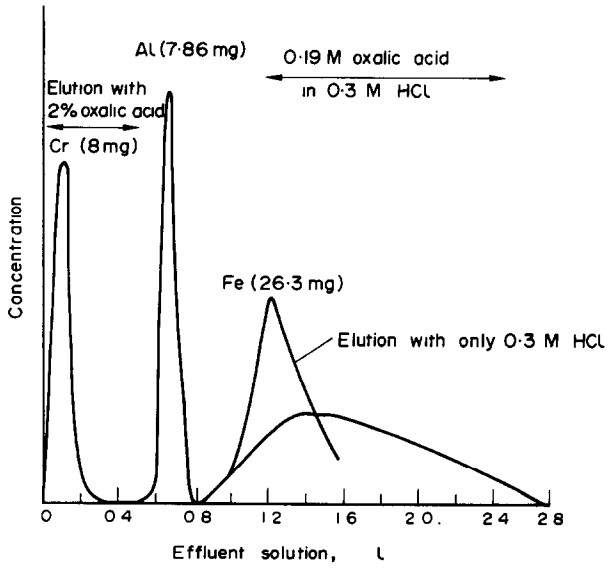

Fig. 2. Elution characteristics of chromium, aluminium and iron.

Recommended procedure for anion-exchange separation of binary mixtures Cr–Al and Cr–Fe

A solution containing not more than 50 mg of Cr and 30 mg of Al is first concentrated to approximately 10 ml by evaporation. The solution is then cooled in an ice-bath and 20 ml of cold 2% oxalic acid solution are added quickly. The mixture is shaken for 30 sec and passed without delay through a column (3 cm^2 × 18 cm) packed with 30 ml of 14–52 BSS Amberlite IRA 401 (oxalate form). A flow-rate of 40 ml/min is employed. The container is washed with 20 ml of 0·05*M* oxalic acid and before the solution level in the column has sunk below the surface of the resin, the washings are added. Residual chromium is removed from the column with 400 ml of 0·05*M* oxalic acid. The flow-rate of the effluent solution is maintained at 40 ml/min throughout. With practice, it is possible to complete the entire process within 12 min. Aluminium is then desorbed with 500 ml of 0·3*M* hydrochloric acid.

The separation of iron from chromium is carried out in the same way. Here the removal of residual chromium from the column is best carried out with 0·05*M* oxalic acid–0·2*M* hydrochloric acid. Iron is eluted with 0·3*M* hydrochloric acid. Typical results are shown in Table 1.

The desorption of Cr, Al and Fe from a cation-exchange resin is governed by the equilibria

$$(R^-)_3M(H_2O)_6^{3+} + H_2C_2O_4 \rightleftharpoons (R^-)M(H_2O)_4C_2O_4^+ + 2RH + 2H_2O$$

$$(R^-)M(H_2O)_4C_2O_4^+ + H_2C_2O_4 \rightleftharpoons M(H_2O)_2(C_2O_4)_2^- + H^+ + RH + 2H_2O$$

$$M(H_2O)_2(C_2O_4)_2^- + H_2C_2O_4 \rightleftharpoons M(C_2O_4)_3^{3-} + 3H^+ + 2H_2O$$

where RH is the resin in the hydrogen form and M is chromium, aluminium or iron. These reactions proceed rapidly for M = Al or Fe and extremely slowly with chromium. Thus aluminium and iron may be rapidly desorbed with cold solutions of oxalic acid, whereas chromium is retained on the resin. When cold oxalic acid solution is passed through the ion-exchange resin at high flow-rate (30–40 ml/min), both iron and aluminium are desorbed completely with 500 ml of the solution and 99·5% of the chromium is retained on the resin.

Recommended procedure for cation-exchange separation of chromium from either aluminium or iron

A solution containing chromium and with an acidity not exceeding 0·1*M* with respect to hydrochloric or sulphuric acid is passed through a column of dimensions 3 cm^2 × 18 cm containing 30 ml of Dowex 50 × 8 in the hydrogen form. The resin is washed with distilled water to remove any free acid liberated in the resin bed.

With 500-ml of an ice-cold 2% solution of oxalic acid, the column is freed from sorbed iron or aluminium at a flow-rate of 40 ml/min. Removal of iron or aluminium is complete when the thiocyanate and alizarin tests no longer show the presence of those ions in the effluent.[28] For desorption of chromium from the resin, warm alkaline hydrogen peroxide solution is used. Since the decomposing peroxide would generate bubbles in the resin, thereby restricting smooth flow of the solution, the peroxide treatment is best carried out outside the column. For this purpose, the resin is transferred to a beaker to which 20 ml of 10% sodium hydroxide solution are added. Distilled water (30 ml) is added, and the mixture is warmed to about 90°.

Hydrogen peroxide (4 ml) is added drop by drop from a dropping pipette, while the mixture in the beaker is stirred. When the reaction is complete, the resin is filtered off and washed with distilled water until the washings are no longer yellow. Starch indicator paper may be used to ascertain the absence of both chromate and peroxide in the resin.

The filtrate and washings are combined and then boiled for 30 min to destroy peroxide. Chromium may then be determined by titration with ammonium ferrous sulphate or sodium thiosulphate solution.[29]

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ULTRAVIOLET SPECTRA OF METAL IONS IN 6*M* HYDROCHLORIC ACID

LOUISE GOODKIN, MARK D. SEYMOUR* and JAMES S. FRITZ

Ames Laboratory, USAEC and Department of Chemistry Iowa State University, Ames, Iowa 50010, U.S.A.

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Summary—Ultraviolet absorption spectra of 66 metal ions in aqueous 6*M* hydrochloric acid were recorded and the spectra of 36 metal ions that absorb appreciably are reported. The absorption of these metal ions is sufficient to permit their detection in liquid chromatography.

Although ultraviolet spectrophotometry has found wide application for detection of organic compounds in liquid chromatography,[1] it has been largely overlooked for continuous monitoring of metal ions in column effluents. In a few instances, however, the absorbance of metal chloride complexes in the ultraviolet spectral region has been used successfully as the basis for automatic detection of metal ions in liquid chromatography.[2–4] This has been accomplished in two ways. If the eluent contains chloride, the ultraviolet absorption of the eluted complex will be sufficient for detection.[2,3] If no chloride or insufficient chloride is used in the separating medium, chloride ions (usually as concentrated hydrochloric acid) can be mixed with the column effluent before the spectrophotometric monitoring.[4] Quantitation is contingent upon chromatographic resolution from interfering ions and rapid formation of the absorbing species when a mixing device is used.

Rogers *et al.* have demonstrated the utility of hydrochloric acid as a reagent for the spectrophotometric determination of metals, but no complete spectral study has been published.[5–7]

To explore the scope of ultraviolet spectrophotometry for detection of metal ions in liquid chromatography, the spectra of 66 metal ions in 6*M* hydrochloric acid medium were obtained. The results of this study are the subject of this communication.

EXPERIMENTAL

Apparatus

A Cary Model 14, Serial 19, recording spectrophotometer with 1·00-cm cells was used to obtain the spectra.

Procedure

The selection of 6*M* hydrochloric acid medium was somewhat arbitrary. It is the centre of the hydrochloric acid range used for metal separations by anion-exchange; most metal ions that form chloride complexes will do so in 6*M* hydrochloric acid.

For most metal ions, spectra were recorded at two different concentrations of the ion. One concentration was chosen so that the absorbance at the wavelength of maximum absorption fell in the range 0·200–0·800. The second concentration was 10 times the first, thus allowing more accurate determination of molar absorptivities at wavelengths away from the maximum.

Reagents

With a few exceptions, solutions of metal ions were prepared from reagent grade oxides, chlorides or high purity metals by dissolving them in 6*M* or 12*M* hydrochloric acid and adjusting the concentration of acid to 6*M* if necessary. High purity lanthanide oxides were obtained from the Ames Laboratory.

Except for gold chloride, palladium chloride, rhodium chloride and chloroplatinic acid, weighings based on formula weights were taken as correct; no independent standardizations were undertaken. For gold chloride and chloroplatinic acid the assays provided by the Baker Chemical Company were used. Rhodium chloride obtained from Sargent–Welch was assayed by the method of Syrokomskii and Proshenkova,[8] and palladium chloride obtained from Engelhard was titrated with EDTA.[9]

A solution of arsenic(III) was prepared by dissolving As_2O_3 in aqueous sodium hydroxide and diluting with hydrochloric acid and water so that the solution was 6*M* in hydrochloric acid.

* Present address: The Procter and Gamble Company, Miami Valley Laboratories, Box 39175, Cincinnati, Ohio 45239, U.S.A.

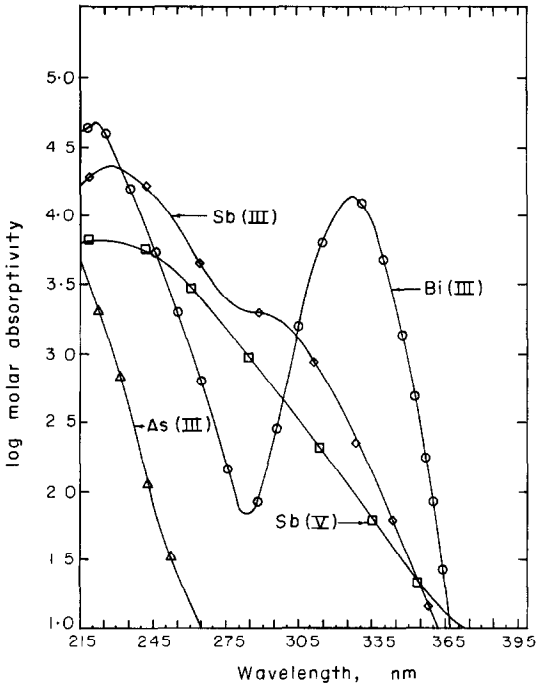

Fig. 1. Absorption spectra in aqueous 6*M* hydrochloric acid.

Solutions of cerium(III) and silver(I) were prepared by evaporating to dryness solutions of the nitrates and redissolving the residues in 6*M* hydrochloric acid. Two evaporations were carried out for each metal. A similar procedure was used for uranium(VI), but that solution was prepared from the acetate.

An aqueous solution of chromium(VI) was prepared from potassium dichromate. An aliquot of the solution was diluted with concentrated hydrochloric acid and water so that the final concentration of hydrochloric acid was 6*M*. The spectrum was run immediately because chromium(VI) is unstable in 6*M* hydrochloric acid. The spectrum agrees with that reported by Haight, Richardson and Coburn.[10]

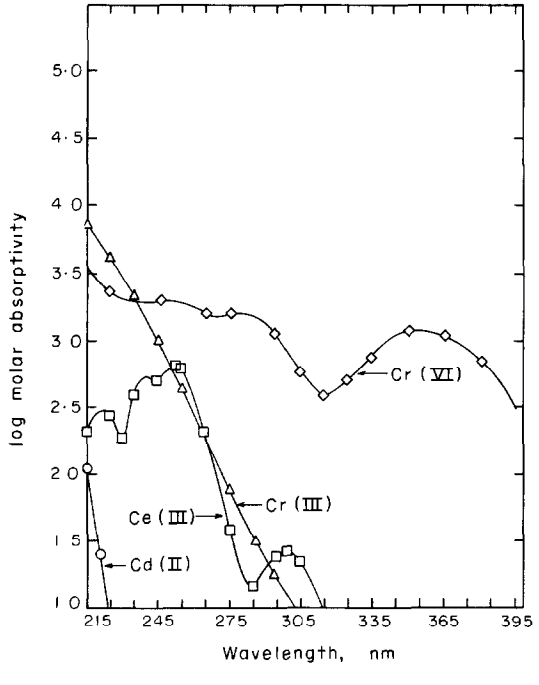

Fig. 2. Absorption spectra in aqueous 6*M* hydrochloric acid.

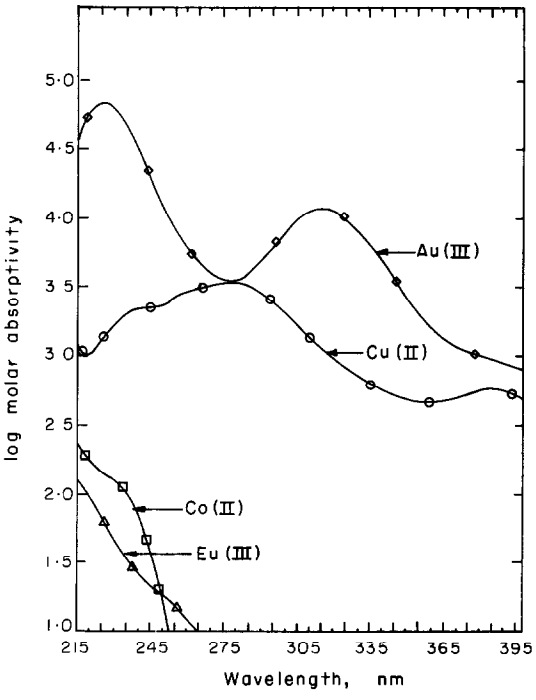

Fig. 3. Absorption spectra in aqueous 6*M* hydrochloric acid.

Because tin(II) and titanium(III) are oxidized in air, aluminium metal was added to the solutions of these ions, and the solutions were then boiled and subsequently cooled under an atmosphere of carbon dioxide.

Vanadium(V) is unstable in 6*M* hydrochloric acid, so hydrogen peroxide was added to the solution to convert all of the vanadium into vanadium(V). The solution was then boiled to effect destruction of the peroxo complex and the spectrum was recorded immediately. A solution of vanadium(IV) was prepared by boiling a solution of vanadium(V) with ethanolic hydrochloric acid.

A solution of ruthenium(IV) was prepared from ruthenium trichloride. Conversion of ruthenium(III) into ruthenium(IV) was accomplished by allowing the solution to stand for 4 days. The spectrum of ruthenium(IV) agrees with that reported by Wehner and Hindman.[11]

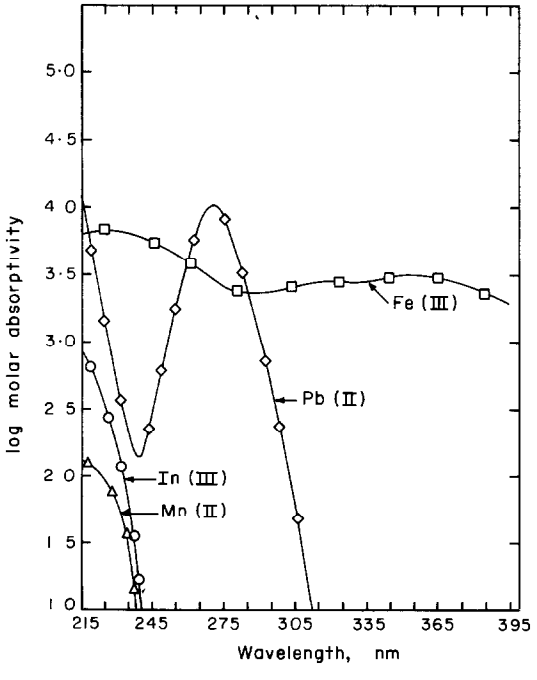

Fig. 4. Absorption spectra in aqueous 6*M* hydrochloric acid.

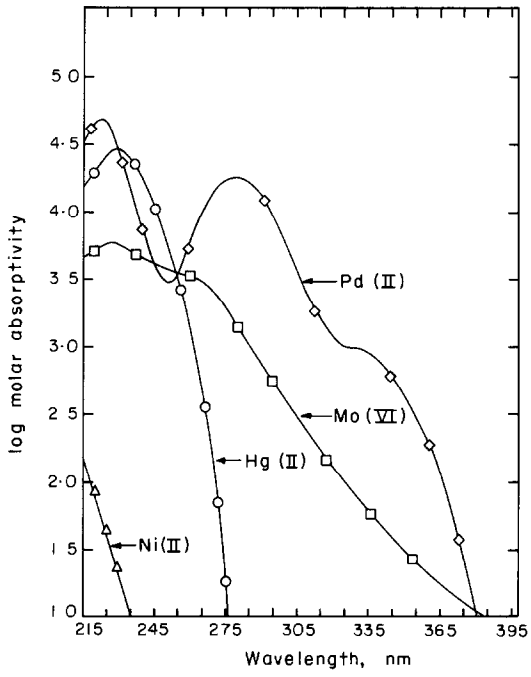

Fig. 5. Absorption spectra in aqueous 6*M* hydrochloric acid.

RESULTS AND DISCUSSION

The spectra of 36 metal ions are shown in Figs. 1–9. Table 1 gives a summary of the ions examined, their wavelengths of maximum absorption, and the molar absorptivities at those wavelengths. Examination of these data shows that over the 215–400 nm spectral range used, over half (35) of the metal ions tested have molar absorptivities greater than 100 l. mole^{-1}.cm^{-1}. Thirteen of the metal ions tested have molar absorptivities greater than $1{\cdot}0 \times 10^4$ l. mole^{-1}.cm^{-1}.

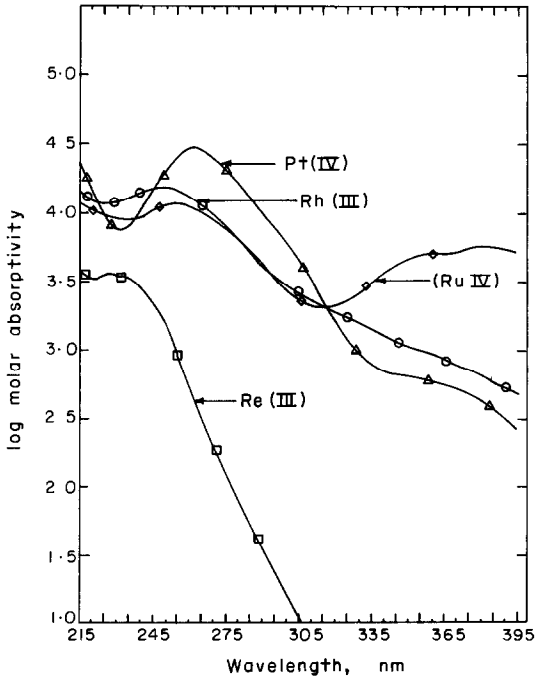

Fig. 6. Absorption spectra in aqueous 6*M* hydrochloric acid.

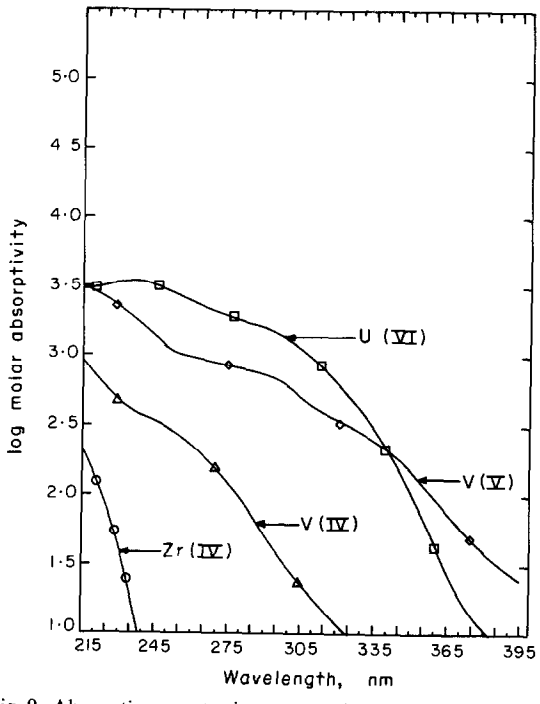

Fig. 9. Absorption spectra in aqueous 6*M* hydrochloric acid.

Table 1. Absorption maxima and ϵ_{max} for metal ions in 6*M* hydrochloric acid

Metal ion	λ_{max}, *nm*	ϵ_{max}, *l. mole*$^{-1}$.*cm*$^{-1}$
Aluminium(III)	N*	
Antimony(III)	229	$2{\cdot}2 \times 10^4$
Antimony(V)	225	$6{\cdot}6 \times 10^3$
Arsenic(III)	215†	$4{\cdot}5 \times 10^3$
Arsenic(V)	N	
Barium(II)	N	
Beryllium(II)	N	
Bismuth(III)	222	$4{\cdot}6 \times 10^4$
	327	$1{\cdot}4 \times 10^4$
Cadmium(II)	215†	$1{\cdot}1 \times 10^2$
Calcium(II)	N	
Cerium(III)	222	$3{\cdot}3 \times 10^2$
	240	$5{\cdot}6 \times 10^2$
	253	$6{\cdot}8 \times 10^2$
	300	$2{\cdot}7 \times 10^2$
Caesium(I)	N	
Chromium(III)	215†	$7{\cdot}1 \times 10^3$
Chromium(VI)	248	$2{\cdot}1 \times 10^3$
	280	$1{\cdot}6 \times 10^3$
	355	$1{\cdot}2 \times 10^3$
Cobalt(II)	215†	$2{\cdot}2 \times 10^2$
Copper(II)	275	$3{\cdot}4 \times 10^3$
	385	$5{\cdot}7 \times 10^2$
Dysprosium(III)	N	
Erbium(III)	N	
Europium(III)	215†	$1{\cdot}2 \times 10^2$
Gadolinium(III)	N	
Germanium	N	
Gold(III)	225	$6{\cdot}8 \times 10^4$
	313	$1{\cdot}1 \times 10^4$
Hafnium(IV)	N	
Holmium(III)	N	
Indium(III)	215†	$8{\cdot}5 \times 10^2$
Iridium(IV)	215†	$1{\cdot}8 \times 10^3$
Iron(III)	225	$7{\cdot}0 \times 10^3$
	320	$2{\cdot}9 \times 10^3$
	360	$3{\cdot}1 \times 10^3$

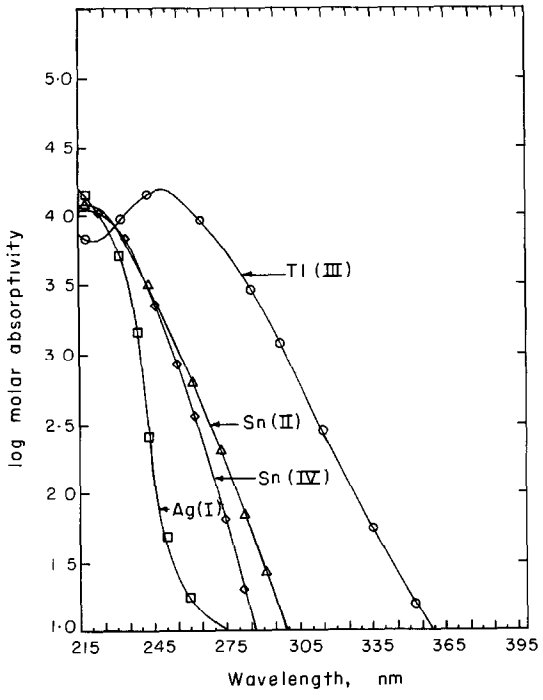

Fig. 7. Absorption spectra in aqueous 6*M* hydrochloric acid.

Most of the metals that absorb can be detected at 225 nm, but several can be detected quite selectively at other wavelengths. Bismuth(III), chromium(VI), copper(II), gold(III), iron(III), molybdenum(VI), palladium(II), platinum(IV), rhodium(III), ruthenium(IV), uranium(VI) and vanadium(V) absorb throughout the spectral region from 215 to 400 nm. These metal ions would interfere in the detection of other metal ions by ultraviolet spectrophotometry in 6*M* hydrochloric acid if no separation were made.

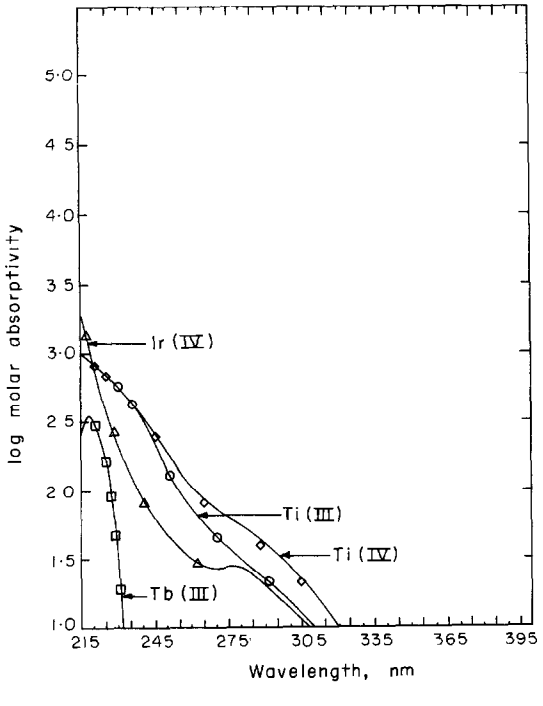

Fig. 8. Absorption spectra in aqueous 6*M* hydrochloric acid.

Table 1. (*Continued*

Metal ion	λ_{max}, *nm*	ϵ_{max}, *l. mole*$^{-1}$*.cm*$^{-1}$
Lanthanum(III)	N	
Lead(II)	271	$1{\cdot}1 \times 10^4$
Lithium(I)	N	
Lutetium(III)	N	
Magnesium(II)	N	
Manganese(II)	215†	$1{\cdot}4 \times 10^2$
Mercury(II)	229	$2{\cdot}7 \times 10^4$
Molybdenum(VI)	227	$5{\cdot}7 \times 10^3$
Neodymium(III)	N	
Nickel(II)	215†	$1{\cdot}5 \times 10^2$
Niobium(V)	I§	
Palladium(II)	222	$4{\cdot}8 \times 10^4$
	280	$1{\cdot}8 \times 10^4$
Platinum(IV)	262	$2{\cdot}7 \times 10^4$
Potassium(I)	N	
Praseodymium(III)	N	
Rhenium(VII)	227	$3{\cdot}5 \times 10^3$
Rhodium(III)	250	$1{\cdot}5 \times 10^4$
Ruthenium(IV)	255	$1{\cdot}1 \times 10^4$
	380	$5{\cdot}3 \times 10^3$
Samarium(III)	N	
Scandium(III)	N	
Silver(I)	215	$1{\cdot}5 \times 10^4$
Sodium(I)	N	
Strontium(II)	N	
Tantalum(V)	I	
Terbium(III)	219	$3{\cdot}3 \times 10^2$
Thallium(III)	248	$1{\cdot}5 \times 10^4$
Thorium(IV)	N	
Thulium(III)	N	
Tin(II)	216	$1{\cdot}2 \times 10^4$
Tin(IV)	218	$1{\cdot}1 \times 10^4$
Titanium(III)	215†	$9{\cdot}7 \times 10^2$
Titanium(IV)	215†	$9{\cdot}6 \times 10^2$
Tungsten(VI)	I	
Uranium(VI)	236	$3{\cdot}4 \times 10^3$
Vanadium(IV)	215†	$9{\cdot}0 \times 10^2$
Vanadium(V)	215†	$3{\cdot}1 \times 10^3$
Ytterbium(III)	N	
Zinc(II)	N	
Zirconium(IV)	N	

* N, $\epsilon < 100$.
† No maximum from 215 to 395 nm, ϵ at 215 nm.
§ I, insoluble in 6*M* HCl.

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A STUDY OF SOME PYRIDYLAZO DYESTUFFS AS CHROMOGENIC REAGENTS AND THE ELUCIDATION OF THE NATURE OF THEIR METAL COMPLEX SPECTRA

D. A. JOHNSON and T. M. FLORENCE

Australian Atomic Energy Commission, Research Establishment, Lucas Heights, NSW, Australia 2232

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Summary—A series of dyestuffs having the same basic structure as 2-(2-pyridylazo)-5-diethylaminophenol (PADAP) but varying in their substituents on the 5-positions of both rings has been prepared. Dissociation constants for three such dialkylaminophenol derivatives have been determined, the pK_{OH} values being of the same order as that reported for 4-(2-pyridylazo)resorcinol (PAR), while the pK_{NH} values are lower. Two different 5-bromo-PADAP complexes are formed with the uranyl ion, one between pH 2 and 5 which is a neutral complex and probably a dimer, and the other an unstable neutral complex which forms between pH 5·5 and 8 and is a 1:1:1 ternary hydroxo-complex. A stable 1:1:1 ternary fluoro-complex is also formed between pH and 6 and 8. Double maxima occur in the spectra of all the metal complexes of these dyes. Evidence given shows the double peaks to originate from the one moiety and to be directly related to the presence of a substituent on the benzene ring *para* to the azo linkage. A tautomeric equilibrium with two imine tautomers in addition to the azo form of the complex is postulated and it is suggested that they correspond to the three composite bands given by computer analysis of the spectrum.

2-(2-Pyridylazo)-5-diethylaminophenol (PADAP) and its derivatives are a relatively new class of spectrophotometric reagent. They have the same chelating system as 4-(2-pyridylazo)resorcinol (PAR) but are twice as sensitive as PAR for the determination of most metals, having molar absorptivities in the region of 1×10^5 l. mole^{-1}. cm^{-1} for the transition metal complexes.[1–6] 2-(5-Bromo-2-pyridylazo)-5-diethylaminophenol (Br-PADAP) has been shown to be a very sensitive reagent for the determination of uranium(VI) and is used as the basis of a specific method for the determination of uranium in ores.[6] The real nature of the complex formation between uranium(VI) and Br-PADAP has not yet been determined, and its elucidation is the object of this paper. Attention was also given to investigating the origin of the double maxima observed in the metal complex spectra, and to obtaining some qualitative information on a range of metal–Br-PADAP complexes.

EXPERIMENTAL

Reagents

The reagents were prepared by coupling the appropriate aminophenols with the substituted 2-pyridyldiazoate and then recrystallizing from ethanolic solution.

The preparation of 2-(5-bromo-2-pyridylazo)-5-diethylaminophenol (Br-PADAP) has been described elsewhere.[1,6]

Analysis* Calc., C 51·58%, H 4·91%, N 16·04%, O 4·58%, Br 22·9%
Found, C 51·6%, H 4·9%, N 16·2%, O 4·9%, Br 22·4%.

2-(5-Chloro-2-pyridylazo)-5-dimethylaminophenol (Cl-PADAP) was prepared by coupling 3-dimethylaminophenol with 5-chloro-2-pyridyldiazoate.

Analysis Calc., C 59·11%, H 5·62%, N 18·38%, O 5·25%, Cl 11·3%
Found, C 58·2%, H 5·7%, N 18·4%, O 5·7%, Cl 11·6%.

2-(5-Bromo-2-pyridylazo)-5-dimethylaminophenol (Br-(diMe)'-PADAP) was prepared by coupling 3-dimethylaminophenol with 5-bromo-2-pyridyldiazoate.

Analysis Calc., C 48·61%, H 4·08%, N 17·45%, Br 24·9%
Found, C 48·1%, H 4·0%, N 16·6%, Br 24·2%.

A further test of purity of these compounds was made by coulometric titration of the reducible azo-nitrogen. After degassing and prereduction at −0·09 V *vs.* SCE, the buffered (pH 4) ethanolic dye solutions were reduced at −0·6 V *vs.* SCE. If four-electron reductions are assumed in each case, purities of 100% were indicated for Br-PADAP and Cl-PADAP and 98% for Br-(diMe)'-PADAP.

The following compounds were prepared solely for comparative spectra of the metal complexes; 2-(5-methyl-2-pyridylazo)-5-diethylaminophenol (5-Me-PADAP), 2-(5-iodo-2-pyridylazo)-5-diethylaminophenol (5-I-PADAP),

* Microanalyses carried out at CSIRO Microanalytical Laboratories, Melbourne.

2-(2-pyridylazo)-5-diethylaminophenol (PADAP), 2-(2-quinolylazo)-5-diethylaminophenol (QUA-DAP), 2-(2-pyridylazo)-5-aminophenol (PAAP); all had a purity in excess of 90% according to the coulometric titrations.

Attempts to prepare 5-nitro-PADAP and the pyrimidylazo analogue of PADAP were unsuccessful because the appropriate diazoates could not be made. Nickless[7] also found that 2-pyrimidyldiazoate could not be prepared by the Tschitschibabin[8] method. It appears that a strongly electron-withdrawing group such as a 5- or 3-nitro or another ring nitrogen atom eliminates a 2-amino group by forming the imine tautomer,[9] thus preventing salt formation at the 2-position when the amine reacts with sodium amide. A sample of 2-(2-pyridylazo)-phenol (*o*-PAP) was kindly provided by Dr. D. Betteridge of University College, Swansea, UK.

Apparatus

Spectrophotometers. Visible spectra were determined with a Hitachi EPS 3T Recording Spectrophotometer using 1-cm cells, while accurate absorbance measurements were made on a Cary 16 Manual Spectrophotometer using matched 1-cm cells. All measurements were made at 25 ± 1° unless otherwise stated.

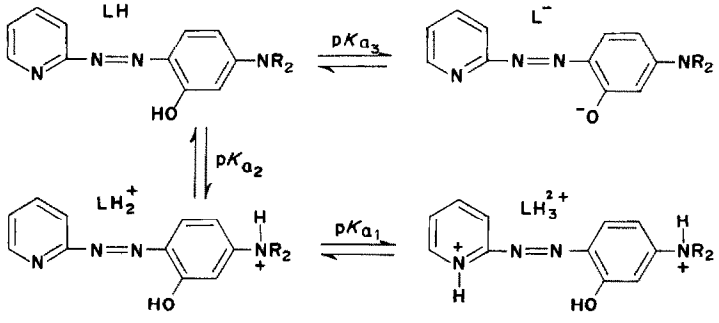
Preparation of solutions. The ionic strength of solutions was usually $\mu = 0{\cdot}1$ and was obtained by adjustment with Merck GR sodium perchlorate. All solutions were in 50% v/v ethanol (Merck GR ethanol). Doubly distilled demineralized water was used throughout, and for pK_{OH} determinations was boiled to remove CO_2. The buffer used at pH 4·1 was pyridine/perchloric acid, and at pH 7·3 triethanolamine/perchloric acid.

RESULTS AND DISCUSSION

Acid–base equilibria

The acid dissociation constants of the three analysed dyes, Br-PADAP, Cl-PADAP and Br-(diMe)' -PADAP were determined by spectrophotometric techniques.[10,11]

The 3-alkylaminophenol derivatives of 2-pyridylazo compounds exhibit three dissociation steps as shown in the following scheme.



The pK_{a_3} values (pK_{OH}) were determined by a graphical method,[10] using nine different sodium hydroxide concentrations and absorbances measured at four wavelengths.

An attempt to determine pK_{a1} and pK_{a2} by potentiometric titration was unsuccessful because the solubility of the dyes in 50% ethanol was not sufficient to make a $10^{-2}M$ solution. Likewise, the acetone/water, dioxan/water and dimethylformamide/water systems were inadequate. The spectrophotometric technique of Kok-Peng Ang[11] for the determination of overlapping dissociation constants was employed. This was used in conjunction with the computer program devised by Heys[12] specifically for treatment of such data. A comparison of results obtained by Kok-Peng Ang's time-consuming calculation with those obtained by the matrix technique of Heys shows the results to be identical within experimental error, *e.g.*, Cl-PADAP $pK_{a1} = 0{\cdot}05$, $pK_{a2} = 2{\cdot}19$ (Kok-Peng Ang) and $pK_{a1} = 0{\cdot}03$, $pK_{a2} = 2{\cdot}14$ (Heys). The ionic strength for these determinations was 1·0. The pK_a values were calculated by using the Heys program on an IBM360 computer and are summarized in Table 1.

The pK_{OH} values observed were of the order expected from values reported in the literature[13,14] for related PAR derivatives. Strictly speaking, one cannot assign pK_{a1} and pK_{a2}. The pK_a value reported[15] for the $N(CH_3)_2$ group in pyridine-2-azo-dimethylaniline is 4·5

Table 1. Acid dissociation constants

Dye	pK_{a1}	pK_{a2}	pK_{a3}
Br-PADAP	0·1 ± 0·1	2·02 ± 0·05	11·30 ± 0·04
Cl-PADAP	0·0 ± 0·1	2·14 ± 0·05	11·39 ± 0·05
Br-(diMe)' -PADAP	0·1 ± 0·1	2·21 ± 0·05	11·15 ± 0·04

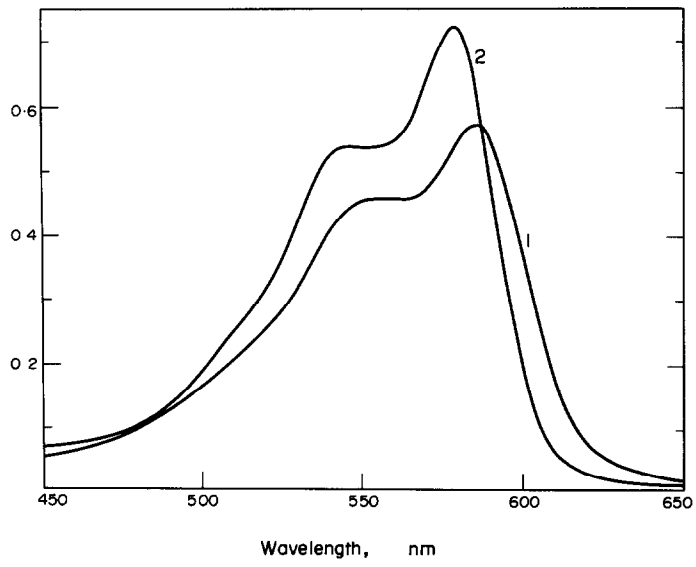


Fig. 1. Spectra of uranium(VI) Br-PADAP complexes. $C_R = 1{\cdot}00 \times 10^{-5}M$, $C_M = 1{\cdot}00 \times 10^{-3}M$. 1—pH 4·1, 2—pH 7·3 in presence of excess of NaF.

while pK_a values for pyridyl nitrogen atoms in related azo dyes generally lie between 3 and 1·0. One might therefore speculate that the lowest pK_a value relates to the pyridyl nitrogen atom while the second relates to the diethylamino group. Nevertheless, both values are considerably lower than the expected values.

Bromo-PADAP complexes of uranium (VI)

As Br-PADAP has recently found wide use as a very sensitive reagent for the spectrophotometric determination of uranium,[6] it was appropriate that this system be the subject of an intensive study, rather than uranyl complex formation by one of the other dyes prepared.

Dependence of complex formation on pH. Complex formation was studied in the pH range 3–8 with both dye and uranyl ion concentrations of $1{\cdot}00 \times 10^{-5}M$. Spectra (Fig. 1) measured after 2 hr indicated the formation of a single complex having double maxima at 554 and 586 nm with only one isosbestic point between unreacted dye and complex, at 400 nm. Absorbances measured after 2 hr and again after three days were the same. Plots of pH *vs.* absorbance (Fig. 2) at 554 and 586 nm show a marked pH-dependence with maximum complex formation at pH 4·1. Both curves have the same shape, indicating that probably only one complex is present.

The composition of the complex at pH 4·1 was determined by Job's method of continuous variation and the mole-ratio method. A pyridine/perchloric acid buffer was used rather than an acetate system because the latter forms an interfering uranyl complex. A metal to ligand ratio of 1:1 was indicated by both methods. The true molar absorptivity of the complex was found, by using a 100-fold excess of uranyl ion, to be $4{\cdot}65 \times 10^4$ l. mole^{-1}. cm^{-1} at 554 nm and $5{\cdot}63 \times 10^4$ at 586 nm. All the polar and many of the less-polar solvents tested extracted this complex.

It should be noted that at pH 7·6 an unstable complex with maxima at 546 and 580 nm forms initially but rapidly decomposes. A series of solutions at this pH measured quickly after first standing for 30 min, indicated a metal to ligand ratio of 1:1. After a further 30 min standing the complex had almost completely decomposed. The molar absorbance of this complex determined in the presence of a 100-fold excess of uranium and measured after 20 min was $6{\cdot}4 \times 10^4$ l. mole^{-1}. cm^{-1} at 580 nm. This complex is also extractable.

Complex formation in the presence of fluoride. It was observed that if sodium fluoride is added to a solution of Br-PADAP and uranyl ion buffered to pH 7·6, a very slow increase in pink colour occurs. This new complex is pink in the presence of excess of dye,

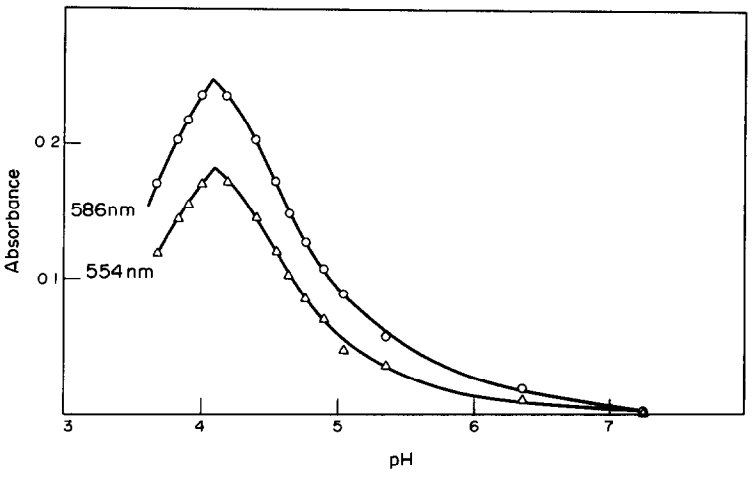


Fig. 2. pH–absorbance plots measured at 554 and 586 nm. $C_R = C_M = 1{\cdot}00 \times 10^{-5}M$.

whereas a mauve complex is formed under similar conditions at pH 4·1. The order of addition of reagents was found to be unimportant when equilibrium was established. A quantitative study of the effect of fluoride ion concentration varying from 1 to 3000 molar ratio to uranium was made. Figure 3 indicates that above a molar ratio of 2000 (F:U), the complex formation becomes independent of fluoride concentration. The spectrum of the complex (curve 2 in Fig. 1) shows double maxima at 542 and 578 nm, $\epsilon_{542} = 5{\cdot}51 \times 10^4, \epsilon_{578} = 7{\cdot}32 \times 10^4$ l. mole^{-1}. cm^{-1}.

Dependence of complex formation on pH, in the presence of fluoride. Complex formation in the range pH 4–8·4 with equimolar uranyl ion and Br-PADAP concentrations ($1{\cdot}00 \times 10^{-5}M$) and a fluoride concentration of $2 \times 10^{-2}M$ was investigated. Maximum complex formation occurs at pH 7·3 (Fig. 4) while at pH 5 and pH 8 it is negligible. The composition of the complex as determined by Job's method and the mole-ratio method is 1:1. This complex is also extractable into many organic solvents.

Nature of the Br-PADAP uranium complexes. Three different uranyl complexes have been shown to occur, the spectrum of each having double maxima and each being extractable into a wide range of organic solvents. They remained extractable in the presence of

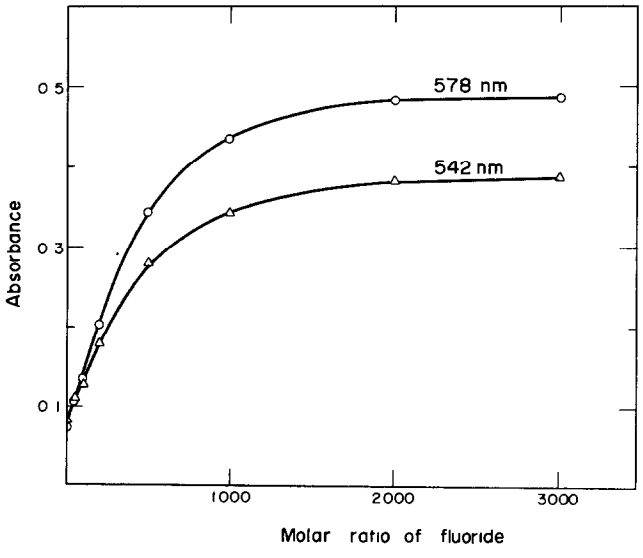


Fig. 3. Fluoride dependence of complex formation at pH 7·6, measured at 542 and 578 nm. $C_R = C_M = 1{\cdot}00 \times 10^{-5}M$.

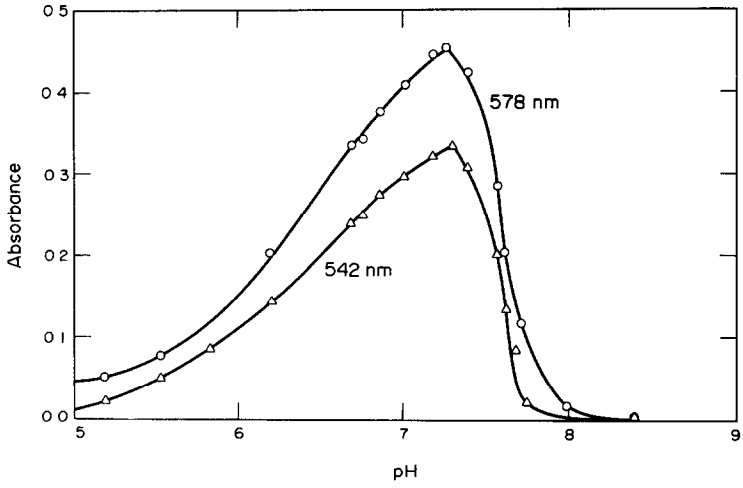
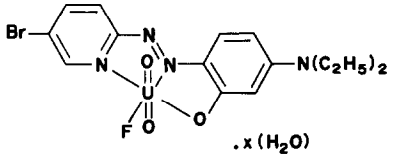


Fig. 4. pH–absorbance plots in the presence of fluoride, measured at 542 and 578 nm. $C_R = C_M = 1{\cdot}00 \times 10^{-5}M$, NaF = $2{\cdot}0 \times 10^{-2}M$.

a gross excess of the anions NO_3^-, Cl^-, ClO_4^-, SO_3^{2-}, $Cr_2O_7^{2-}$, thus eliminating the possibility of their being ion-association complexes. Examination of the Br-PADAP molecule shows that the dye when complexed exhibits a single negative charge by loss of the hydroxyl proton, while the uranyl ion has two positive charges. Charge neutrality of the 1:1 complex requires that an additional singly negatively charged ligand be involved in the complex formation. In light of the evidence that fluoride ion added to a solution at pH 7·3 in which the complex has decayed causes a different stable complex to form and that to obtain charge neutrality a single negative charge is required, it was suspected that fluoride ion might enter the complex as an auxiliary ligand.

In order to investigate this possibility the complex was analysed for fluoride. An aliquot of a chloroform extract of the complex was equilibrated with distilled water by shaking for 24 hr. The complex decomposed, leaving the free dye in the chloroform phase and produced in the aqueous phase exactly equimolar concentrations of uranyl ion and fluoride ion. A more rapid method of decomposing the complex by shaking with a pH-4 acetate buffer also gave a fluoride analysis corresponding to a formula UO_2(Br-PADAP$^-$)F. Thus it can be concluded that the complex formed at pH 7·3 in the presence of excess of fluoride has this composition. There are probably two water molecules also associated with it since these would then satisfy the usual co-ordination number of six for the complex of uranyl ion. One can therefore draw a tentative structure assuming that Br-PADAP co-ordinates through the same atoms as does PAR.



Confirmation that fluoride enters the complex at pH 7·3 leads to the obvious conclusion that in the absence of fluoride the 1:1 complex which first forms, only to decompose rapidly, is in fact the hydroxo-analogue of the fluoro-complex, UO_2(Br-PADAP$^-$)OH. Its absorption spectrum is almost identical to that of the fluoro-complex but with its double maxima displaced by bathochromic shifts of 4 and 2 nm. It appears that when uranium(VI) reacts with the dye at pH 7·3, the rate of reaction of the dye with the small proportion of UO_2OH^+ present is more rapid than the polymerization of UO_2OH^+. Formation of the more stable hydroxo-uranyl polymer eventually eliminates UO_2OH^+ from the complex.

The ability of other anionic ligands (*e.g.*, Ce^-, Br^-, CN^-, SCN^-) to enter into complex formation in the manner of fluoride was tested, but in each instance the spectrum was identical to that of the postulated UO_2(Br-PADAP$^-$)OH complex and the complex decomposed as does UO_2(Br-PADAP$^-$)OH. Also, tests of extracts for the presence of these ions, by the same technique as used to prove the presence of fluoride ion, proved negative. This indicates that the complex formed in each case was the hydroxo-complex and that these anions do not act as ligands in this system. Thus a dual role for fluoride ion is signified; it is an auxiliary ligand in the complex and a complexing agent which inhibits the polymerization of hydrolysed uranyl ion.

The spectrum of the complex formed at pH 4·1 is clearly different from that of the hydroxo-complex formed at pH 7·3. Peaks occur at 546 and 580 nm ($\epsilon = 6{\cdot}40 \times 10^4$) for the hydroxo-complex, while the species at pH 4·1 has maxima at longer wavelengths of 552 and 586 nm ($\epsilon = 5{\cdot}63 \times 10^4$). This complex, like that formed at pH 7·3, is neutral, requiring a minimum of 20% ethanol to keep it in solution. As ion-association has been ruled out for this system, then the only other possibility for a 1:1 neutral complex to exist is as a hydroxo-bridged complex $ML(OH)_2ML$. The dimerization *via* hydroxo-bridges satisfies charge requirements and would be consistent with the observation of a bathochromic shift by virtue of the interaction of the two chromophoric systems.[16] Polymerization is also indicated by the curved nature of the mole-ratio plot, but this alone is not sufficient proof. The 1:1 complex formed in aqueous media at pH 4·1 was found to be extracted into chloroform as a 1:2 complex, indicating that in aqueous medium there must be a very small amount of 1:2 complex in equilibrium with the 1:1 dimer. The real nature of the complex at pH 4·1 remains a matter of speculation.

Stability constants. Conditional stability constants for the two stable complexes in 50% ethanol were determined.[17] For the hydroxo-bridged species at pH 4·1 with both uranyl ion and Br-PADAP concentrations of $1{\cdot}00 \times 10^{-5}M$ and an ionic strength of 0·1, $\beta' = 1{\cdot}32 \times 10^5$ measured at 554 nm, and $1{\cdot}30 \times 10^5$ measured at 586 nm. The fluoro-complex at pH 7·27 with dye and uranium concentrations $1{\cdot}00 \times 10^{-5}M$ and $\mu = 0{\cdot}1$ has a conditional stability constant of $\beta' = 4{\cdot}51 \times 10^5$ measured at 542 nm, and $4{\cdot}42 \times 10^5$ measured at 578 nm. The ratios of the heights of the two peaks for the complex, when corrected for

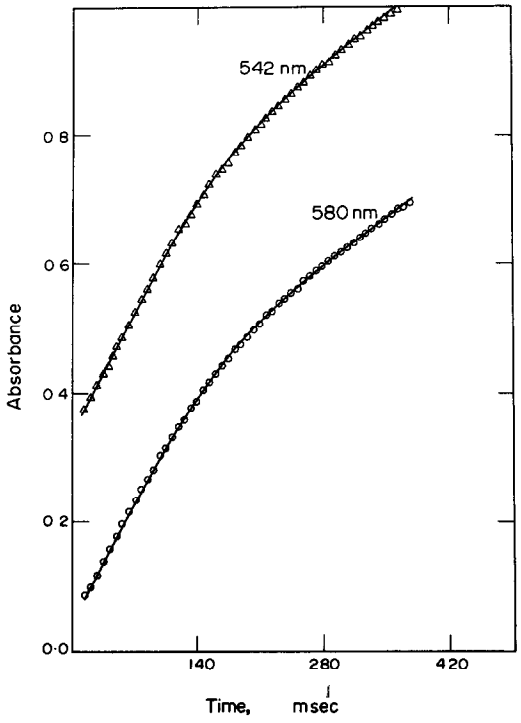


Fig. 5. Absorbance–time plots for complex formation in the presence of fluoride at pH 7·3, measured at 542 and 580 nm. $C_R = C_M = 1{\cdot}0 \times 10^{-4}M$, NaF = $2{\cdot}0 \times 10^{-1}M$.

Table 2. Spectral data of metal–Br-PADAP complexes

Metal ion	pH*	Absorption max, *nm* A	B	Bathochromic shifts, *nm* A	B	Splitting, *nm*	Molar absorptivity, 10^4 *l.mole*$^{-1}$.*cm*$^{-1}$ A	B	Absorbance ratio A/B	Mole ratio M:L
Mn(II)	10	525	560	80	115	35	8·8	8·8	1·00	1:2
Fe(II)	8	523	557	78	112	34	6·6	8·2	0·81	1:2
Co(II)	8	554	588	111	145	34	8·7	9·3	0·97	1:2
Ni(II)	8	526	559	81	114	33	9·8	11·7	0·88	1:2
Zn(II)	8	522	553	77	108	31	11·6	13·3	0·87	1:2
Cu(II)	8	NR†	560	—	115	NR†	—	11·6	—	1:2
Fe(III)	8	542	594	97	149	46	7·2	8·2	0·88	—
Eu(III)	8	536	568	91	123	32	5·3	5·5	0·96	—
Zr(IV)	4·8	544	580	99	135	36	2·4	3·1	0·79	—
V(V)	8	NR†	600	—	155	—	—	6·0	—	—
U(VI).F	8	546	578·5	101	134	33	5·5	7·3	0·76	1:1
U(VI).OH	8	547	580	102	135	33	4·9	6·4	0·77	1:1
U(VI)	4	552	586	107	141	34	4·5	5·6	0·79	1:1

* pH for maximum absorbance.

† NR—not resolved.

Note. Justification for visually estimating peaks is demonstrated by a computer analysis of a spectrum by using a curve-resolution program. There is no difference between the visually estimated peak separation and the computed value.

dye absorbance, are the same at all pH values. The β' values for each complex determined at the two wavelengths of the double peaks are identical within experimental error, confirming that the two peaks originate from a single complex.

Rate of complex formation. The rate of formation of the fluoro-complex at pH 7·3 in 50% ethanol was monitored at the wavelengths of both maxima, with an Aminco Stopped Flow Spectrophotometer. Equimolar solutions of Br-PADAP and uranyl ion were prepared, the pH of each being such that when the acidic uranium solution was mixed in equal proportion with the alkaline dye solution, the resultant solution was at pH 7·3. The $1{\cdot}00 \times 10^{-4} M$ solutions were mixed in the instrument cell by a pneumatic syringe system. After 4 msec mixing time the transmission was measured at 7-msec intervals up to 385 msec.

The absorbance–time curves shown in Fig. 5 adequately demonstrate that the rate of reaction indicated by the slopes at any given time is the same at both wavelengths. A rate constant could not be calculated, owing to the lack of information in the literature on the equilibrium constants for the hydrolysis of uranyl ion in ethanolic media. However, there is sufficient evidence to confirm that the double maxima observed in the spectra of both complexes have their origin in the splitting of energy levels of the chromophore in a single molecular species.

The analytical potential of Br-PADAP

The reactions of Br-PADAP with a number of metal ions were screened in order to determine possible applications of the dye to spectrophotometric analysis. Table 2 lists the spectral data for these complexes, determined at the optimum pH. The spectra of all these complexes of Br-PADAP exhibit the same double peak character observed for the uranyl complexes. While the peak separation for the copper(II) complex is not as well resolved as in the other spectra shown in Fig. 6, the double peak character is easily recognizable.

The reagent Br-PADAP should be compared with PAR, which has the same basic chelate structure and is widely used as a spectrophotometric reagent. Analyses using PAR require measurement of absorbances at wavelengths between 494 and 550 nm, which makes simultaneous determinations impossible. With Br-PADAP complexes the maxima occur over a wider range of wavelengths, 522–600 nm. Cobalt(II) and zinc for example, may be determined simultaneously at pH 2·8 by measuring at 590 and 520 nm respectively. Cobalt can be determined in the presence of at least a fifty-fold excess of zinc, the Beer's law plot being linear to at least this level.

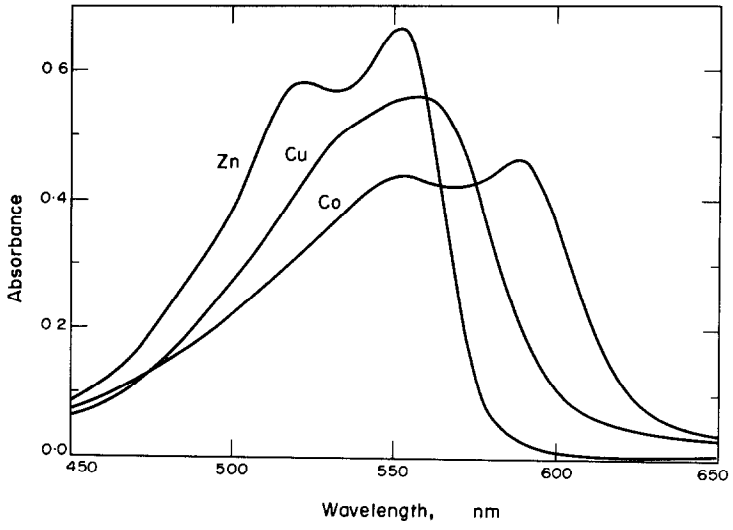


Fig. 6. Spectra of the Br-PADAP complexes of zinc, copper and cobalt at pH 8. $C_R = 1{\cdot}00 \times 10^{-5} M$, $C_M = 2{\cdot}0 \times 10^{-4} M$.

The principal advantage of Br-PADAP over PAR is its considerably improved sensitivity. In most cases it is increased by a factor of 2 and, in the case of bismuth,[1] it is increased by a factor of 5. This reagent must rank among the most sensitive known, having molar absorptivities of the order of 10^5 for its transition metal complexes. Another advantage is the extractability of many of the Br-PADAP complexes, enabling far greater selectivity to be obtained than with PAR, the complexes of which are generally charged and non-extractable. A practical example of these advantages of Br-PADAP over PAR is for the spectrophotometric determination of uranium(VI) in ores. The molar absorptivity of the uranium(VI) Br-PADAP fluoro-complex is twice that of the uranium(VI) PAR complex and in the presence of a mixed complexing solution[18] is even more selective than PAR. A preliminary extraction into TOPO, followed by direct colour development in the organic phase with Br-PADAP provides a specific method of uranium determination suitable when gross amounts of interfering ions are present. The uranium(VI) PAR complex is not extracted by organic solvents.

The influence of substituents on the spectra of the metal–dye complexes

A comparison of the spectral data of *o*-PAP and PAR with those of Br-PADAP is given in Table 3. One general observation can be made for pyridylazo dyestuffs possessing an *ortho* hydroxy group. That is, the more electronegative the substituent in the *para* position on the benzene ring, the higher the molar absorptivity of the metal complex. Hammett

Table 3. Comparative spectral data for complexes of Br-PADAP, PAR and *o*-PAP.

	Br-PADAP		PAR[19]		*o*-PAP[19]	
Metal	ϵ, 10^4 *l. mole*$^{-1}$.*cm*$^{-1}$	λ_{max}, *nm*	ϵ, 10^4 *l. mole*$^{-1}$.*cm*$^{-1}$	λ_{max}, *nm*	ϵ, 10^4 *l. mole*$^{-1}$.*cm*$^{-1}$	λ_{max}, *nm*
Cu(II)	11·6	560	5·89	510	1·98	547
Ni(II)	11·7	559	7·3	494	2·26	543
Co(II)	9·3	558	5·6	510	1·28	533
Zn(II)	13·3	553	6·34	495	2·30	520
Mn(II)	8·80	560	—	—	—	—
U(VI)	7·3	578	3·85	530	—	—
Bi(III)	5·8*	590	1·07	515	—	—
V(V)	6·0	600	3·6	550	—	—

* Reference 1.

Table 4. Spectral data for uranyl complexes of PADAP derivatives

	I-PADAP	Br-PADAP	Cl-PADAP	PADAP	Me-PADAP	Br-(diMe)$^{1-}$ PADAP	QUADAP
λ_{max}, *nm*	583 550	579 546	576 544	564 532	568 536	576 543	564 532
ϵ, 10^3 *l. mole*$^{-1}$*.cm*$^{-1}$	71·2 58·0	73·2 55·7	71·0 53·1	76·0 59·6	72·0 59·0	62·0 47·5	76·0 59·6

substituent constants for the diethylamino and hydroxy groups in *para* positions are $\sigma = -0{\cdot}70$ and $-0{\cdot}37$ respectively and that for the O^- group is $\sigma = -0{\cdot}52$.

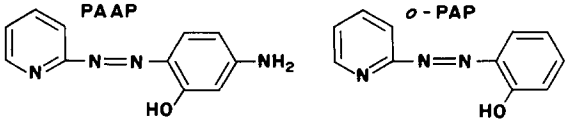
The influence of the substituent in the 5-position of the pyridine ring is relatively minor compared to that of the benzene ring substituent when considering molar absorptivities of the complexes. This is seen when comparing the uranyl complexes of the various diethylaminophenol derivatives with differing groups in the 5-position of the pyridyl ring.

Table 4 shows that, with the exception of Br-(di-Me)^1-PADAP, the molar absorptivities are all $(7{\cdot}3 \pm 0{\cdot}3) \times 10^4$ l. mole^{-1}. cm^{-1}, regardless of whether the substituent is electron-withdrawing or electron-repelling. The substituent has a more marked effect on the wavelength of the absorption maxima, with halogen substituents causing much larger bathochromic shifts than the other substituents. Compared to PADAP, the halogen derivatives have complexes which absorb at longer wavelengths in the order of Cl-PADAP < Br-PADAP < I-PADAP, an order consistent with the decreasing electronegativity. The dyes Br-(di-Me)^1-PADAP and QUADRAP were included in this Table for convenience. Comparison of PADAP and QUADAP indicates that the 2-pyridine and 2-quinoline groups are equivalent in this chromophoric system by virtue of having the same λ_{max} and molar absorptivities.

The influence of substituents on the occurrence of double maxima in the spectra of the dyes and metal–dye complexes

A recent study in these laboratories[20] has provided convincing evidence that both the protonated and molecular forms of PAR do exist as azo and quinhydrazone tautomers in aqueous solution. The existence of these tautomers had been suggested by Savvin[21] on the basis of simple Hückel MO theory, but no experimental proof had been reported in support of this conclusion. In the study referred to, spectra of the protonated forms of PAR, 3-PAR, 4-PAR and *o*-PAP showed clear evidence of having composite absorption bands which exhibit isosbestic points in various ethanol/water mixtures. These protonated compounds also exhibited fluorescence due to the presence of quinhydrazone forms in equilibrium with the azo forms. All the compounds possess a hydroxy group *ortho* to the azo linkage. On the other hand the phenol derivatives with a *para* hydroxy group, *i.e.*, *p*-PAP, 3-(*p*-PAP) and 4-(*p*-PAP), show in their protonated forms only single symmetrical absorption bands with no evidence of isosbestic points, and they do not fluoresce. This demonstrates that only the derivatives with an *ortho* hydroxy substituent exhibit tautomerism. The monoprotonated form of Br-PADAP exhibits overlapping peak characteristics, having a shoulder at 60 nm longer wavelength than the maximum, but this aspect could not be investigated owing to complications from the overlap of pK_a values.

Spectra of some metal complexes of PAR, *o*-PAP and PAAP were examined to determine whether the double-peak character is present. The uranium-complex spectra are shown in Fig. 7. Uranium and all other metal complexes of *o*-PAP display only single symmetrical bands in the spectra while PAR complexes show definite evidence of overlapping peaks.



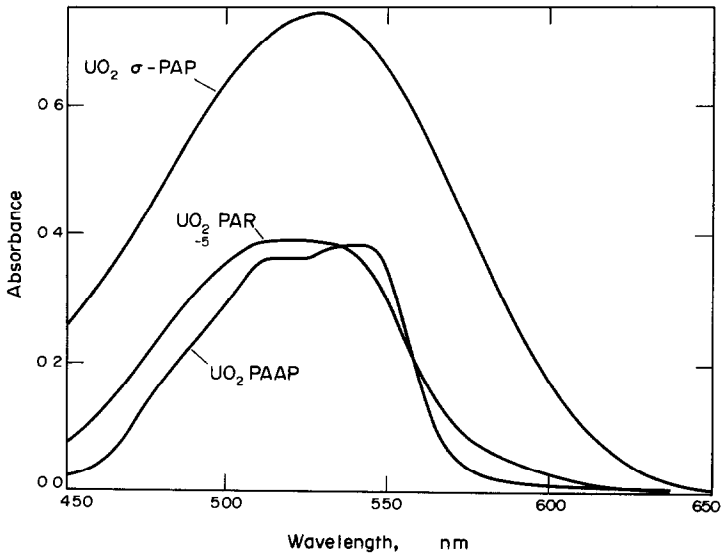
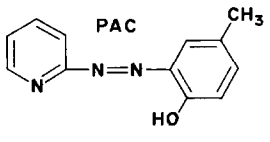


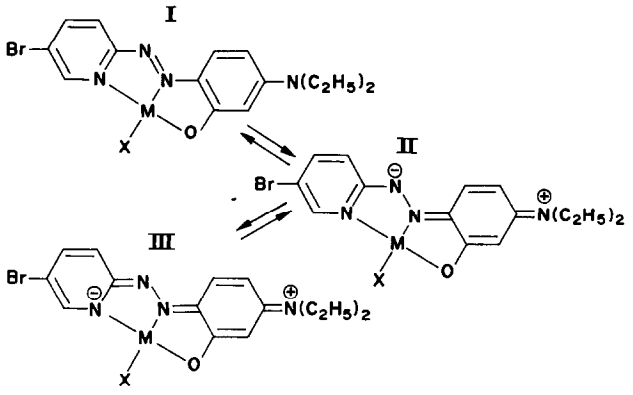
Fig. 7. Spectra of the uranyl complexes of *o*-PAP, PAR and PAAP. $C_M = 1.0 \times 10^{-3}M$, *o*-PAP = $4.0 \times 10^{-5}M$, PAR = $1.0 \times 10^{-5}M$, PAAP = $1.0 \times 10^{-5}M$.

The spectrum of the uranium–PAAP complex at pH 8 is strikingly similar to that of the uranium–PAR complex. Its λ_{max} is within a few nm of that of the PAR complex and the molar absorptivity is the same. The overlap of peaks is more accentuated than for uranium–PAR. It is revealing to compare the influence of this highly electronegative $-NH_2$ group (Hammett substituent constant $\sigma_{para} = -0.66$) with the $-N(C_2H_5)_2$ group ($\sigma_{para} = -0.70$) which would seem to have an almost equal inductive effect. The $-N(C_2H_5)_2$ group is bulky and as shown by molecular models protrudes out of the plane of the planar metal–dye complex, whereas the $-NH_2$ group in PAAP lies within the plane. Although the *para* diethylamino group is not unique in giving overlapping bands in the complex spectra it has significantly greater effect than the amino group on the absorption of light by the chromophoric system. The vast differences in intensities and λ_{max} between the spectra of PAAP and PADAP complexes may be related to the ability of the diethylamino group to carry the π-electron system out of the plane of the chromophore. Savvin[22] attributes the double maxima in the spectrum of monoprotonated Arsenazo III to the interaction of π-electrons from two chromophores in the one molecule lying in different planes; however, in the system under consideration neither the amino nor the diethylamino group alone is a chromophore, they are merely auxochromes.

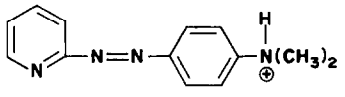
In addition to the *o*-PAP complexes giving only single absorption bands, the related dye 2-(2-pyridylazo)-4-methylphenol (PAC) also shows single symmetrical bands in its metal-complex spectra.[13] Thus the evidence indicates that the occurrence of multiple peaks in the spectra of metal–dye complexes of this type is dependent on the presence of a substituent *para* to the azo group on the benzene ring.



A substituent capable of mesomerism may permit a tautomeric equilibrium to exist in the complex. One can draw two possible mesomeric structures **II** and **III** in addition to **I**, the azo form of UO_2(Br-PADAP$^-$)F. Chelation leads to the transfer of a strongly electropositive charge to the chromophoric system so that in the extreme mesomeric structures **II** and **III**, an effect approaching protonation of the diethylamino nitrogen atom is observed.

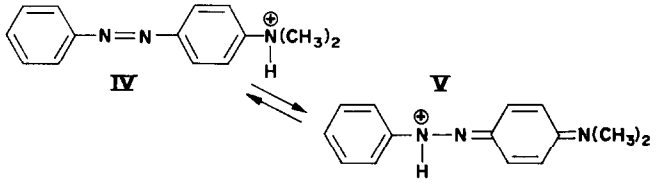


In this respect the spectrum of the protonated form of 2-(pyridyl)-4-*N*,*N*-diethylaniline, PADA,[15] is informative. It shows a maximum at 560 nm with a molar absorptivity of $3{\cdot}90 \times 10^4$ l. mole^{-1}. cm^{-1}. This wavelength is remarkably close to the wavelength of the B peak in the complexes of PADAP (Table 4). Cilento *et al.*[23] have sought to explain the absorption spectrum of H^+PADA in terms of resonance structures which would involve an imine structure similar to that shown in **II** above.



PADA

Similarly, Hanztsch *et al.*[24,25] have pointed out that the spectrum of protonated *N*,*N*,*N*-trimethyl-*p*-phenylazoaniline is similar to that of azobenzene while that of the conjugate acid of *N*,*N*-dimethyl-*p*-phenylazoaniline is quite different with bands at 350 and 520 nm. They assign these bands to a tautomeric equilibrium between the azoanilinium form **IV** at 350 nm and the azoammonium form **V** at 520 nm.



Comparison of metal complex formation with protonation is not an uncommon approach to the interpretation of spectra. Savvin[22] has pointed out the similarity of the spectra of monoprotonated Arsenazo III and its metal complexes. Evidence for tautomeric equilibria in the UO_2(Br-PADAP$^-$)F complex is indicated by its spectral behaviour at different temperatures. At 0° the ratio of peak heights A/B is 0·73 while at 50° the ratio is 0·77, indicating a shift in the tautomeric equilibrium.

In contrast to the protonated form of *o*-PAP which exhibits tautomerism, the metal complexes of *o*-PAP, as stated previously, show only single absorption bands. This may now be explained by the fact that while tautomeric structures can be drawn for H^+*o*-PAP the same cannot be done for its metal complexes because of the absence of any *para* substituent capable of mesomerism.

The UO_2(Br-PADAP$^-$)F spectrum was resolved by using the computer program of Biggers and Bell.[27] Initially, resolution into two bands was attempted by varying the parameters λ_{max}, absorbance, bandwidth and Gaussian fraction. Invariably a poor fit on the short wavelength side of the spectrum was obtained. Close examination of the spectrum shows a small hump on that part of the curve, so a third band was used in the curve synthesis. Manipulation of the aforementioned variables produced a composite curve of good fit to the experimental data (Fig. 8). Asterisks denote experimental points and superimposed closely over these points is the resultant synthetic curve from the three component curves below. Computed parameters for the component curves are shown in Table 5.

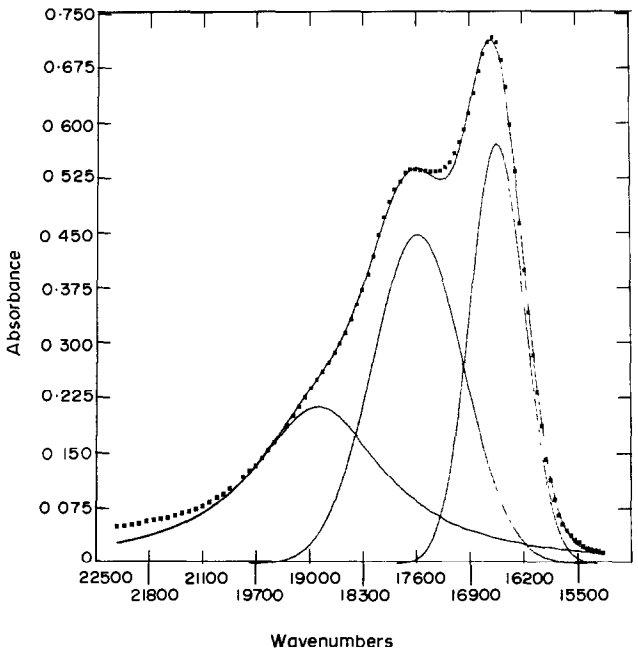


Fig. 8. Computer plot of resolved spectrum of UO_2(Br-PADAP$^-$)F. Asterisks denote experimentally observed points Full line through them is resultant synthetic curve produced by the component curves below.

Table 5. Parameters for component curves used in synthesis of UO_2(Br-PADAP$^-$)F spectrum

Parameter	Band 1	Band 2	Band 3
Wavelength, *nm*	510·5	547·0	580·0
Absorbance	0·212	0·450	0·570
Half-bandwidth, *nm*	54·7	42·0	28·09
Gauss fraction	0·0	1·0	1·00
Lorentz fraction	1·0	0·0	0·00

The two longer-wavelength component peaks at 547 and 580 nm are very close to those estimated visually as being at 546 and 578·5 nm and used in the tables. The real peak height ratio (major peaks) of 0·79 obtained from this analysis is also very close to the estimated observed value. Visual examination of all the metal complexes of Br-PADAP and the complexes of related dialkylaminophenol derivatives reveals that a third band is evident in all the spectra and is always manifested by a small hump on the short-wavelength side of the spectrum.

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SPEKTROCHEMISCHE BESTIMMUNG VON SULFAT BZW. CHLORID MIT ROENTGENFLUORESZENZ NACH ANREICHERUNG DURCH MITFÄLLUNG AN $BaCrO_4$ BZW. AgSCN AUS VERDÜNNTEN LÖSUNGEN

B. MAGYAR und G. KAUFMANN

Laboratorium für Anorganische Chemie, Eidg. Techn. Hochschule, Zürich, Schweiz

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Zusammenfassung—Sulfat und Chlorid wurden aus verdünnten Lösungen (10^{-5}–$10^{-4}M$) an $BaCrO_4$ bzw. AgSCN als Träger quantitativ mitgefällt. Beide Ionen wurden im Niederschlag mit Hilfe der Röntgenfluoreszenz-Spektrometrie (RFS) bestimmt wobei das Intensitätsverhältnis I_S/I_{Cr} bzw. I_{Cl}/I_S der K_α-Linien als Maß für die mitgefällte SO_4^{2-} bzw. Cl^--Menge diente. Diese Kombination der Mitfällung als Anreicherungsmethode und der RFS als Meßmethode ermöglichte die Bestimmung beider Ionen in 50–100 ml Leitungswasser mit einer Reproduzierbarkeit von *ca.* 3 Prozent relativem Fehler.

Die molare Fluoreszenzintensität von Lösungen verschiedener Elemente, d.h. die Proportionalitätskontante K_A zwischen Nettointensität N_A und Molarität [A], zeigt eine starke Abhängigkeit von der Ordnungszahl Z des Elementes A.[1]

Leichte Elemente, wie z.B. Schwefel und Chlor haben kleine K_A-Werte und können in Lösung mit der Röntgenfluoreszenz-Spektrometrie (RFS) nur in großer Konzentration ([A] > 0,01M) gut bestimmt werden. Aus verdünnteren Lösungen müssen diese Elemente angereichert werden. Die Mitfällung der Ionen dieser Elemente an geeigneten Trägern ist die einfachste und schnellste Anreicherungsmethode, welche sich mit der RFS sehr gut kombinieren läßt. Der Niederschlag wird dabei an einem Membranfilter gesammelt, welcher im Spektrometer direkt bestrahlt werden kann. Stork und Jung[2] verwendeten Silberbromid bzw. -jodid als Träger bei der Mitfällung von Chlorid. Luke[3] benutzte Selenat, um Sulfat mit einer an Bariumsulfat gesättigten Lösung von Barium(II) in 50%-igem Alkohol mitzufällen. Ob diese Träger auch als Spurenfänger wirken, wurde nicht untersucht. Als Spurenfänger sollen hier solche Hauptkomponenten von Mischfällungen bezeichnet werden, welche bei ihrer gleichzeitigen Fällung aus verdünnter Lösung das mitzufällende Ion auch dann mitreißen, wenn das Löslichkeitsprodukt der Spurenkomponente nicht überschritten wird.

Bei der Suche nach weiteren geeigneten Trägern für Sulfat bzw. Chlorid fanden wir, daß sich Bariumchromat bzw. AgSCN ebenfalls gut eignen. Die Anwendbarkeit und Wirkungsweise dieser Träger bei der Anreicherung von Sulfat bzw. Chlorid aus stark verdünnten Lösungen wird in dieser Arbeit diskutiert.

MESSTECHNIK UND FÄLLUNGSBEDINGUNGEN

Die Fluoreszenzintensitäten wurden unter standardisierten Meßbedingungen[1] mit einem Vakuumspektrometer (Philips PW 1540) ermittelt. Die Fällungen wurden an Sartorius-Membranfiltern (0,45 μm Porengrösse, 47 mm Durchmesser) filtriert und über konzentrierter Phosphorsäure im Vakuumexsikkator bei *ca.* 15 Torr 20 Minuten getrocknet. Die Membranfilter wurden jedoch vor dem Trocknen über einen Ring gespannt, wobei die Seite mit dem Niederschlag noch mit einer 6 μm dicken Mylarfolie zugedeckt wurde. Derart eingespannte Filterscheiben wurden im Probenhalter des Spektrometers eingesetzt und während der Bestrahlung gedreht.

Die Fällungen wurden im allgemeinen durch Zugießen einer Lösung von Barium (II) bzw. Silber (I) zu den Lösungen von Sulfat bzw. Chlorid, welche zuerst mit Kaliumchromat bzw. mit Ammoniumthiocyanat sowie mit allen übrigen Zusätzen versetzt wurden, hergestellt. Die übrigen Fällungsbedingungen sind an den betreffenden Stellen angegeben, wobei Q die Menge des betreffenden Stoffes oder Ions, V das Totalvolumen aller Zusätze, P den zugesetzten Puffer, T_F die Temperatur bei der Fällung, T_A die Temperatur beim Altern des Niederschlages und t_W die Wartezeit zwischen Fällen und Filtrieren bedeuten.

RESULTATE UND DISKUSSION

Auswertung

Trägt man die Peakintensität I_A des zu bestimmenden Elementes A gegen die gefällte Menge Q_A auf, erhält man ohne bzw. mit kleinen, konstanten Mengen des Trägerions B Geraden.[3] Die Linearität zwischen I_A und der zur Fällung vorgelegten Menge wird aber nur erhalten, wenn A quantitativ ausfällt, der Niederschlag vollständig auf das Filter transferiert und homogen verteilt wird. Ebenfalls darf die Schichtdicke nur Bruchteile der Austrittstiefe für die Fluoreszenzstrahlung betragen, da sonst die Fluoreszenz tief liegender Schichten durch Absorption verloren geht. Das Intensitätsverhältnis I_{Ag}/I_{B_r} diente als Maß für die mitgefällte Chloridmenge bei einer indirekten Chloridbestimmung.[2] Dieses Verhältnis hängt einerseits von der Chloridmenge linear ab und anderseits ist es von der Menge und der Verteilung des Niederschlages auf dem Filterpapier weitgehend unabhängig. Daher ist die quantitative Überführung des Niederschlages auf das Filter nicht nötig, was einen großen praktischen Vorteil bedeutet. Beide Auswertungsmethoden geben aber fehlerhafte Resultate, wenn außer dem zu bestimmenden Ion A und dem Bezugsion B störende Ionen anwesend sind, welche mit dem Fällungsmittel ebenfalls ausgefällt werden.

Wir benützen daher das Verhältnis der Peakintensitäten I_A/I_B für das Mengenverhältnis Q_A/Q_B beider Ionen A und B. I_A/I_B ist ebenfalls weitgehend unabhängig von der Menge und der Verteilung des Niederschlages auf dem Filter. Zudem ist der Einfluß von eventuell mitgefällten Ionen auf dieses Verhältnis viel kleiner als auf I_A bzw. I_C/I_B, wobei C das Kation des Fällungsmittels bedeutet. I_A/I_B wird nämlich nur indirekt, über Veränderung des Massenabsorptionskoeffizienten μ des Niederschlages beeinflußt.

Eigentlich sollte das Verhältnis der Nettointensitäten N_A/N_B benützt werden. Die Streustrahlung ist aber bei der Bestrahlung von Fällungen an dünnen Membranfiltern gewöhnlich klein, so daß in Abwesenheit von Interelementeffekten die folgende Proportionalität gelten sollte:

$$k.(Q_A/Q_B) = N_A/N_B \simeq I_A/I_B \tag{1}$$

Experimentell findet man die Bestätigung dieser linearen Beziehung nur in einem engen Meßbereich. Dagegen erhält man immer Geraden, wenn man log (I_B/I_A) gegen log (Q_B/Q_A) aufträgt. Die Beziehung

$$\log (I_B/I_A) = q + p.\log (Q_B/Q_A) \tag{2}$$

wurde durch Ermittlung von I_B/I_A für Fällungen mit bekannten Mengen der Ionen B und A geprüft und bestätigt (s. Abb. 1). Die verschiedenen Mengenverhältnisse wurden durch Variation von Q_A (Geraden a, c, e) beim Konstanthalten von Q_B bzw. durch Zugabe verschiedener Mengen des Bezugsions B zu der gleichen Menge des zu bestimmenden Ions A (Serie b und d) eingestellt.

Die Zahlen in Abb. 1 bedeuten berechnete Schichtdicken. Die Dicke x' der am Filterpapier verteilten Fällungen kann nämlich nicht gemessen werden. Zudem ist für die Absorption der Primär- und der Fluoreszenzstrahlung die Flächenbelegung $x'.d'$ maßgebend, wobei d' das spezifische Füllgewicht bedeutet. Diese Rechengröße kann man sich schlecht vorstellen und soll hier durch eine berechnete Probendicke x ersetzt werden. Um x zu berechnen, denkt man sich den feinkristallinen Niederschlag als einen scheibenförmigen Einkristall mit der Basisfläche von der effektiven Filteroberfläche $F(=9{,}6\ \text{cm}^2)$ und nimmt die Höhe des fiktiven Einkristalls als Probendicke x:

$$x = (Q_A.M_{r,CA}/d_{CA} + Q_B.M_{r,CB}/d_{CB})/F \tag{3}$$

Hierbei bedeutet Q die Menge, M_r die relative Molmasse und d die Dichte der entsprechenden Komponente (Q = Mole, x = cm). Bei vergleichbarer Absorption beider Fluoreszenzstrahlungen und in Abwesenheit von Korngrößen-Effekten sollte man unabhängig von den Fällungsbedingungen und von der Probendicke die gleiche Gerade erhalten. Diesem Idealfall kommt das System Ag(SCN, Cl) ziemlich nahe.

Eine Möglichkeit, um die gegenseitige Beeinflussung der Strahlungen verschiedener Elemente durch Absorption und Interelementenanregung zu verhindern, besteht in der

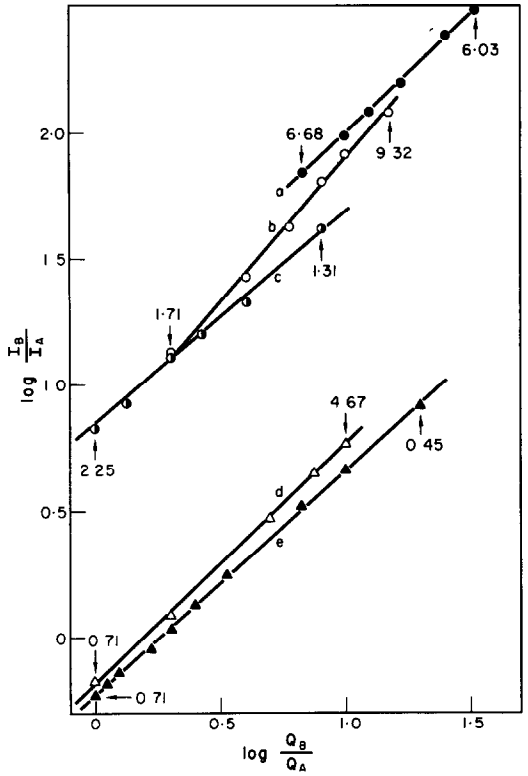

Abb. 1. Abhängigkeit des Verhältnisses der Peakintensitäten vom Molverhältnis, Fällungsbedingungen (Q = μMole, V = ml, t_W = Minuten) $T_F \sim T_A \sim 25°C$

Serie	A (Q_A)	B (Q_B)	C (Q_C)	Puffer*	V	t_W
a	SO_4^{2-} (3–15)	CrO_4^{2-} (100)	Ba^{2+} (2.Q_B)	0,1*M* TEA-P	50	5
b	SO_4^{2-} (10)	CrO_4^{2-} (20–150)	Ba^{2+} (Q_B + 20)	0,04*M* TEA-P	25	20
c	SO_4^{2-} (2,5–20)	CrO_4^{2-} (20)	Ba^{2+} (2.Q_B)	0,04*M* TEA-P	25	15
d	Cl^- (10)	SCN^- (10–100)	Ag^+ (Q_B + 20)	0,5*M* HAc	var†	20
e	Cl^- (0·5–10)	SCN^- (10)	Ag^+ (2.Q_B)	0,5*M* HAc·	25	15

* TEA-P = Äquimolare Mischung von Triäthanolamin (TEA) und TEA·H^+ HAc = Essigsäure
† var = Das Volumen wurde in Abhängigkeit der Chloridmenge so variiert, daß [Cl] vor der Fällung $2.10^{-4}M$ betrug.

Verwendung von Proben, deren Dicke x viel kleiner als die Austrittstiefe x_a für die betreffende Strahlung ist. Die Eindringtiefe x_e für die Primärstrahlung und auch x_a wurden für die vier Komponenten der beiden Mischfällungen berechnet und in der Tabelle 1 zusammengestellt.

Die Dicke der Mischfällungen von Ag(SCN,Cl) variiert zwischen 0,45 und 4,67 μm. Die berechnete Schichtdicke der dünnsten Probe entspricht *ca.* 4 bzw. 6% der Austrittstiefe der

Tabelle 1. Berechnete Eindringtiefe x_e [= $(2{,}303/\mu_p.d)(\log I°_P/I_p).\sin\alpha$] der Primärstrahlung P und Austrittstiefe x_a [= $(2{,}303/\mu_F.d)(\log I_F/I°_F).\sin\beta$] der Fluoreszenzstrahlung F für 100-fache Abschwächung ($I°_P/I_P = I_F/I°_F = 100$) und für einen Winkel α von 45° zwischen dem Lot des primären Strahlenkegels und der Probenoberfläche bzw. für einen Winkel β von 45° zwischen der Kollimatorachse und der Probenoberfläche (d = Dichte, μ = Massenabsorptionskoeffizient). Die Werte gelten für Einkristalle und dicht gepreßte Pillen.

Matrix	d,g/cm³	x_e,* cm 0,559 Å	0,7 Å	Cr, K_z	x_a, cm Cl, K_z	S, K_z
AgSCN	3,92	—	$4{,}92.10^{-2}$	—	$7{,}10.10^{-4}$	$1{,}15.10^{-3}$
AgCl	5,56	—	$2{,}75.10^{-2}$	—	$1{,}05.10^{-3}$	$7{,}22.10^{-4}$
$BaCrO_4$	4,50	$4{,}76.10^{-2}$	$2{,}56.10^{-2}$	$2{,}94.10^{-3}$	—	$7{,}09.10^{-4}$
$BaSO_4$	4,50	$5{,}46.10^{-2}$	$2{,}94.10^{-2}$	$2{,}53.10^{-3}$	—	$6{,}47.10^{-4}$

* Als repräsentative Wellenlänge wurde λ (Ag, K_z) der verwendeten Silberröhre für die Anregung von Cr mit 50 kV bzw. die Wellenlänge bei der maximalen Intensität der Bremsstrahlung (0,7 Å) für die Anregung von Cl und S mit 24 kV angenommen.

S,K_z- bzw. Cl,K_z-Linie für AgSCN (Hauptkomponente). In dieser Probe werden beide Strahlungen nur unwesentlich absorbiert. Die Dicke der Proben nimmt innerhalb der Serie d sehr stark zu. Die Absorption der beiden Strahlungen ist aber ungefähr gleich stark (vergleichbare x_a-Werte), was die große Ähnlichkeit der q- und p-Werte dieser Geraden verständlich macht.

Die Eichgerade für die Bestimmung von Schwefel in der Mischfällung Ba(CrO_4, SO_4) wird durch die Menge des Bezugsions CrO_4^{2-} stark beeinflußt. In der Serie c beträgt die durchschnittliche Schichtdicke *ca.* 25 bzw. 6% der Austrittstiefe für die S,K_z- bzw. Cr, K_z-Linie aus $BaCrO_4$. Erhöht man die Chromatmenge auf 100 μMole (Serie a), so erreicht x beinahe x_a für die S,K_z-Linie. Diese Strahlung wird daher in der Probe sehr stark absorbiert. Die Probe bleibt dagegen für die viel härtere Cr,K_z-Strahlung und natürlich für die Primärstrahlung weitgehend durchlässig. Diese Verschiedenheit der Absorption der S,K_z- und Cr,K_z-Linien verursacht die Zunahme des q-Wertes von 0,831 auf 1,044 bei der Erhöhung der Trägermenge von 20 auf 100 μMole. In der Serie b variiert die Schichtdicke sehr stark. Die relative Absorption der Strahlungen beider Elemente Schwefel und Chrom ändert sich dementsprechend innerhalb der Serie ebenfalls beträchtlich. Die Beziehung (2) gilt trotzdem erstaunlich gut.

In einem engen Meßbereich besteht auch die Proportionalität (1). Allerdings muß bei kleinen Konzentrationen von A in der Mischfällung eine Untergrundkorrektion an I_A vorgenommen werden. Wird allen Eichfällungen und allen zu analysierenden Proben die gleiche Menge des Bezugsions zugesetzt, so erhält man Q_A aus der folgenden Beziehung:

$$Q_A = r + s.(I_A/I_B) \tag{4}$$

Der Ordinatenabschnitt r sollte mit $-s.I_A^\circ/I_B$ übereinstimmen, wobei I_A°/I_B an einer A-freien Probe (Blindprobe, Index o) direkt ermittelt werden kann. Als Beispiel sollen die Meßresultate für Eichfällungen mit 100 μMole CrO_4^{2-} und mit 1 bis 10 μMole SO_4^{2-} sowie für die Eichfällung mit 10 μMole SCN^- und 0,5 bis 6 μMole Cl^- in Form der Beziehung (4) angegeben werden (Q = μMole):

$$Q(SO_4^{2-}) = (-0{,}229 \pm 0{,}080) + (993 \pm 13).(I_S/I_{Cr})$$
$$Q(Cl^-) = (-0{,}243 \pm 0{,}026) + (5{,}75 \pm 0{,}04).(I_{Cl}/I_S)$$

Wirkungsweise des Trägers

Um die Rolle von AgSCN bzw. $BaCrO_4$ bei der Mitfällung von Chlorid bzw. Sulfat zu klären, wurde der Einfluß der Verdünnung auf das Intensitätsverhältnis I_A/I_B untersucht. Die Ba(CrO_4,SO_4)-Mischfällung neigt stark zur Bildung von übersättigten Lösungen und konnte aus stark verdünnten Lösungen nicht ausgefällt werden. In Abb. 2 geben die Pfeile die Anfangskonzentration $[A]_a$ an, dessen Produkt mit der überschüssigen Konzentration des Fällungskations C (Ba^{2+} bzw. Ag^+) gleich dem Löslichkeitsprodukt von CA ist. Letzteres wurde zu $[CA]^2_{ges}$ angenommen, wobei [CA] die molare Löslichkeit in reinem Wasser bedeutet. AgSCN scheint nach der anfangs gegebenen Definition kein echter Spurenfänger zu sein, da das Löslichkeitsprodukt von AgCl überschritten werden muß, damit Chlorid durch Ag^+ ausgefällt wird. Die Rolle von AgSCN ist also auf Trägerfunktion und auf die Lieferung des Bezugselementes beschränkt. Ohne den Träger CB würde aber CA bei hoher Verdünnung nicht ausfallen, da es im allgemeinen übersättigte Lösungen bildet (besonders ausgeprägt bei $BaSO_4$, s. Zitat [5]).

Störung durch Fremdionen

Die S,K_z- und die Ba,L_z-Linien haben eine kleinere Wellenlängendifferenz und werden daher von der Matrix und von Materialien im Strahlengang ungefähr gleich stark absorbiert. Aus diesem Grunde wäre Barium ein besseres Bezugselement als Chrom. Barium eignet sich jedoch wegen seiner unkontrollierten Mitfällung in Anwesenheit von gewissen Begleitionen wie HCO_3^-, HPO_4^{2-}, $C_2O_4^{2-}$, SeO_4^{2-} usw. als Bezugselement weniger gut.

Um den Einfluß solcher Störionen zu untersuchen, wurden Fällungen mit konstanter Menge von SO_4^{2-} und CrO_4^{2-} gemacht, wobei jeweils ein Störion D in verschiedenen Molverhältnissen Q_D/Q_S zugesetzt wurde. Wie die Abb. 3 zeigt, wird das Verhältnis I_S/I_{Cr}

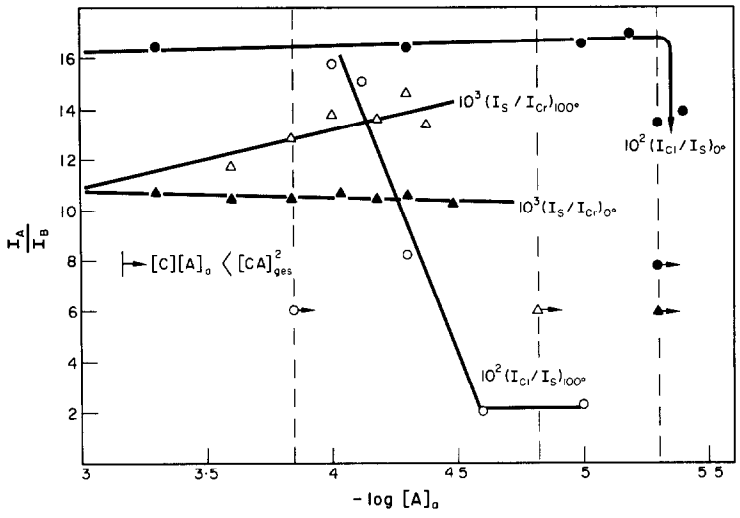

Abb. 2. Einfluß der Verdünnung auf I_A/I_B. Fällungsbedingungen: V entsprechend der vorgewählten Anfangskonzentration $[A]_a$ variiert. ▲ $Q(SO_4^{2-}) = 10$ μMole, $Q(CrO_4^{2-}) = 100$ μMole, P: je 5 mMole TEA und TEA. HCl, $T_F = T_A \sim 0°C$, $t_W = 60$ Min. △ wie ▲ jedoch $T_F \sim 100°C$, sofort filtriert bei 90–100°C. ● $Q(Cl^-) = 10$ μMole, $Q(SCN^-) = 100$ μMole, P: 0,5M HAc, $T_F \sim 100°C$, $T_A \sim 0°C$, $t_W = 60$ Min. ⊙ wie ●, jedoch sofort filtriert bei 90–100°C.

nur wenig durch Phosphat bzw. Oxalat beeinflußt. Das Verhältnis $I(S,K_z)/I(Ba,L_z)$ verkleinert sich dagegen sehr stark, da die Menge des Bezugsions Ba^{2+} zunimmt. Eine möglichst störungsfreie Analysenmethode muß daher auf dem Intensitätsverhältnis I_S/I_{Cr} basieren.

ANWENDUNG ZUR ANALYSE VON LEITUNGSWASSER

Man verwendete Zürcher Leitungswasser, welches zuerst durch ein Membranfilter mit 0,2 μm Porengröße filtriert wurde.

Bestimmung von Sulfat

Eine 50-ml Leitungswasser-Probe und 5 bzw. 10 ml 10^{-3} M Schwefelsäure wurden mit deionisiertem Wasser zu *ca.* 100 ml ergänzt, mit 5 ml Triäthanolamin-Puffer (je 0,2M an TEA und TEA.HCl) und 10 ml $10^{-2}M$ Kaliumchromat versetzt. Man goß 20 ml $10^{-2}M$ Bariumchloridlösung zu und ließ die Suspensionen 20 Minuten stehen. Gleichzeitig wurden noch Fällungen mit 100 ml deionisiertem Wasser (Blindprobe) bzw. mit 100 ml Leitungswasser hergestellt. Man bereitete die Proben zur Meßung, wie früher beschrieben wurde, vor. Die Intensität der S,K_z-bzw. Cr,K_z-Linie wurde nach der Impulsvorwahl-Meßtechnik ermittelt, wobei für I_S 2-mal je 2.10^4 und für I_{Cr} 2-mal je 2.10^5 Impulse akkumuliert wurden. In der Tabelle 2 ist das Resultat von vier Wiederholungen, welche in Abständen von einigen Tagen an der gleichen Wasserprobe gemacht wurden, angegeben.

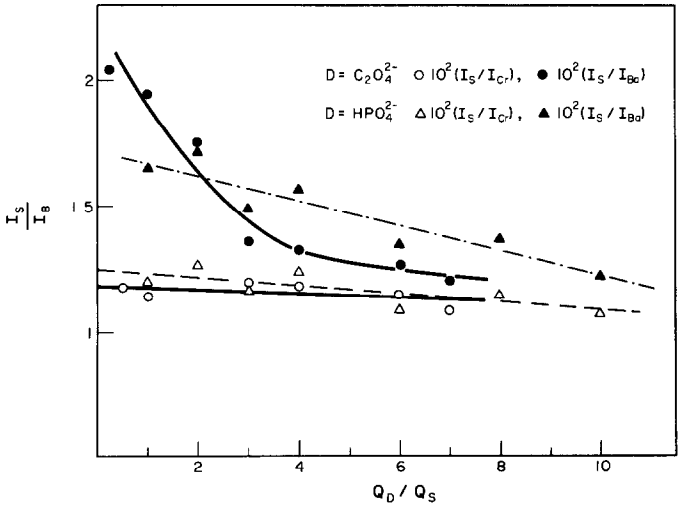

Abb. 3. Störung durch Mitfällung von Oxalat und Phosphat. Fällungsbedingungen: $V = 100$ ml, $Q(SO_4^{2-}) = 10$ μMole, $Q(CrO_4^{2-}) = 100$ μMole, P: je 5 mMole TEA und TEA.HCl, $T_F = T_A \simeq 25°C$, $t_W = 10$ Min.

Dabei wurde die Blindprobe [$Q(SO_4^{2-}) = 0$], die Eichproben mit 5 bzw. 10 μMole SO_4^{2-} sowie die Fällungen mit 50 bzw. 100 ml Leitungswasser, welche die gesuchten Sulfatmengen von x_{50} bzw. x_{100} enthielten, gleichzeitig präpariert und ausgemessen. Der angegebene Fehler für das betreffende Intensitätsverhältnis bedeutet die einfache Standardabweichung aus je vier wiederholten Fällungen. Die Sulfatkonzentration wurde für jede Wiederholung mit der gleichzeitig bestimmten Eichkonstante ermittelt, wobei zur Berechnung der Sulfatmenge Beziehung (4) benutzt wurde. Die angegebene, einfache Standardabweichung für die Sulfatkonzentration basiert daher auf 8 Fällungen.

Tabelle 2. Reproduzierbarkeit (Standardabweichung σ) der Sulfatbestimmung in Leitungswasser

$Q(SO_4^{2-})$, μMole:	0	5	10	x_{50}	x_{100}
$10^5.(I_S/I_{Cl})$:	195	789	1359	1149	2064
$10^5.\sigma$:	58	34	67	41	90

Resultat: $Q(SO_4^{2-})$ nach Gleichung (4), $[SO_4^{2-}] = (1{,}619 \pm 0{,}061).10^{-4}M$.

Um möglichst ähnliche Beschaffenheit der Fällungen zu gewährleisten und damit den Präparationsfehler möglichst klein zu halten, sowie um den Meßfehler zu reduzieren, welcher von der langzeitigen Instabilität des Spektrometers herrührt, sollten die Fällungen und die Eichfällungen gleichzeitig präpariert und gemessen werden. Da diese Regel bei der Sulfatbestimmung befolgt wurde, ist das Resultat mit einem kleineren Fehler als die einzelnen zu verschiedener Zeit bestimmten (I_S/I_{Cl})-Werte behaftet.

Bestimmung von Chlorid

Chlorid konnte in ähnlicher Weise wie das SO_4^{2-} bestimmt werden [Empfohlene Fällungsbedingungen: $Q(NH_4SCN) = 100$ μMole, $Q(AgNO_3) = 200$ μMole, P: 0,5M Essigsäure, $T_F = T_A \sim 25°$, $t_W \simeq 10$ Min.].

Man erhielt $1{,}13.10^{-4}M$ für $[Cl^-]$, wobei jedoch keine Untersuchung über die Reproduzierbarkeit durchgeführt wurde. Die Standardabweichung der [Cl]-Bestimmung dürfte jedoch kaum schlechter als diejenige der $[SO_4^{2-}]$-Bestimmung sein, da die Eichkonstanten, d.h. die Regressionskoeffizienten r und s der Gleichung (4) für das System Ag(SCN,Cl) sehr kleine Standardabweichung aufweisen (s. oben).

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Summary—Sulphate and chloride are quantitatively co-precipitated from dilute solutions (10^{-5}–$10^{-4}M$) with $BaCrO_4$ and AgSCN respectively, and determined in the precipitate by X-ray fluorescence spectroscopy. Ratios of count-rates I_S/I_{Cl} and I_{Cl}/I_S for the appropriate K_γ-lines are used for quantitative evaluation by comparison with reference standards prepared the same way. The method enables both sulphate and chloride to be determined in 50–100 ml of tap-water with a reproducibility of about 3%.

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ANWENDUNG VON IONENAUSTAUSCHVERFAHREN ZUR BESTIMMUNG VON SPURENELEMENTEN IN NATÜRLICHEN WÄSSERN—V

BLEI

J. KORKISCH und A. SORIO

Analytisches Institut der Universität, Abteilung: Rohmaterialanalyse nuklearer Brennstoffe, Währingerstraße 38, A-1090 Wien, Österreich

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Zusammenfassung—Eine Methode wird beschrieben, die es ermöglicht ppM-Mengen Blei aus natürlichen Wässern zu isolieren und der Endbestimmung mittels Spektrophotometrie oder Atomabsorption zugänglich zu machen. Die Wasserprobe wird durch Zugabe von konzentrierter Bromwasserstoffsäure 0,15*M* an dieser Säure gemacht, filtriert und anschließend durch eine Säule des stark basischen Anionenaustauscherharzes Dowex 1, X8 (Bromidform) fließen gelassen. Dabei wird das Blei nicht nur am Ionenaustauscher quantitative adsorbiert, sondern auch gleichzeitig von den meisten anderen, in der Wasserprobe anwesenden Begleitelementen getrennt. Das Blei wird mit 6*M* Salzsäure eluiert und im Eluat, unter Anwendung der Dithizonmethode spektrophotometrisch oder mittels Atomabsorptionsspektrophotometrie bestimmt. Die Methode wurde zur Bestimmung des Bleis in Trinkwasser- und Donauwasserproben herangezogen, wobei Bleigehalte im Konzentrationsbereich von 2 bis 14 ppM gefunden wurden.

Zur Lösung von Umweltschutzproblemen im Zusammenhang mit der Toxizität des Bleis werden analytische Methoden benötigt, die eine serienmäßige Bestimmung des Bleis in natürlichen Wässern gestatten. Die dabei normalerweise zu bestimmenden Bleikonzentrationen sind sehr gering (im ppM-Bereich) so daß zur Bleibestimmung nur Verfahren herangezogen werden können deren Empfindlichkeit entsprechend hoch ist bzw. es sind solche Methoden zu verwenden, die eine der Bestimmung vorangehende, einfache Anreicherung des Bleis aus Proben natürlicher Wässer ermöglichen.

Auf Grund von Literaturangaben[1–13] ist ersichtlich, daß nur relativ wenige Methoden beschrieben wurden, die es gestatten das Blei ohne vorangehende Anreicherung und gleichzeitiger Abtrennung von den Begleitelementen mittels Verfahren beruhend auf Voltammetrie,[1,2] Polarographie,[3–7] Atomabsorption,[8,9] Spektrophotometrie,[10,11] Emissionsspektrographie[12] und Massenspektroskopie[13] zu bestimmen. Bei vielen dieser Verfahren ist es erforderlich die zu analysierende Wasserprobe einzudampfen, um die Empfindlichkeit und Genauigkeit der Bleibestimmungen zu erhöhen.

Die Mehrzahl der im Zusammenhang mit der Bleibestimmung in natürlichen Wässern benützten Methoden beruhen jedoch auf Abtrennverfahren die in Kombination mit geeigneten Bestimmungsmethoden für Blei angewendet werden. Die am häufigsten benützten Abtrennmethoden beruhen auf Extraktionen von Chelaten des Bleis mit Dithizon,[14–23] Ammoniumpyrrolidin-1-carbodithioat,[8,24] Ammoniumtetramethylendithiocarbamat,[25] Hexahydroazepin-1-carbodithioat[26] und Arsazen.[27] Durch die Extraktion dieser Chelate mittels geeigneter organischer Lösungsmittel wie Chloroform,[15–21,23] Tetrachlorkohlenstoff,[22] Methylisobutylketon,[8,25] Heptan-2-on,[24] Butylacetat[26] und Butanol[27] wird nicht

nur eine Trennung des Bleis von störenden Begleitelementen bewirkt, sondern meistens auch die direkte Bleibestimmung in den organischen Extrakten mittels Spektrophotometrie[18–21,23] oder Atomabsorption[8,24–26] ermöglicht.

Andere Verfahren die zur Bleiabtrennung aus natürlichen Wässern herangezogen wurden beruhen auf der Adsorption des Bleis auf Kationenaustauscherharzen,[28 31] Dünnschichtchromatographie[14] und auf der Kopräzipitation des Bleis mit Kalciumcarbonat[32–34] oder Zinkphosphat.[35]

Obwohl zur Trennung des Bleis von vielen Begleitelementen sehr oft stark basische Anionenaustauscherharze verwendet werden[36,37] hat dieses Trennungsprinzip zur Bleianalyse von natürlichen Wässern bis jetzt keine Anwendung gefunden. Wie jedoch in der vorliegenden Arbeit gezeigt wird, ist das beschriebene Anionenaustauschverfahren sehr gut geeignet, um Blei aus Wässern zu isolieren, wonach dieses Element spektrophotometrisch oder mittels Atomabsorption störungsfrei bestimmt werden kann.

EXPERIMENTELLER TEIL

Losungen und Reagenzien

Ionenaustauscher. Es wurde der stark basische Anionenaustauscher Dowex 1, X8 (100–200 mesh; Chloridform) verwendet. Vor dem Einfüllen in die Ionenaustauschersäule werden 4 g des Austauscherharzes mit einigen Millilitern 6*M* Salzsäure aufgeschlämmt und das Harz so vollständig als möglich in die mit der gleichen Säure gefüllte Ionenaustauschersäule gebracht. Danach wird mit 50 ml 6*M* Salzsäure gefolgt von einem gleichen Volumen an Wasser nachgewaschen. Hierauf wird mit 50 ml 1.5*M* Bromwasserstoffsäure und anschließend mit 50 ml 0.15*M* Bromwasserstoffsäure gewaschen um den Ionenaustauscher in die Bromidform überzuführen.

Blei-Standardlösungen. Ausgehend von einer mittels ÄDTA-Titrationen eingestellten Bleinitratstammlösung, die 20 mg Blei/ml 0,5 vol.%iger Salpetersäure enthielt, wurden 0.15*M* bromwasserstoffsaure und 6*M* chlorwasserstoffsaure Standardlösungen mit Bleigehalten im Konzentrationsbereich von 0,2 bis 200 ppm hergestellt.

Wäßrige Dithizonlösung. Dithizonstandardlösung (6 ml; 1 g Dithizon pro Liter Chloroform; diese Lösung ist kühl zu lagern) wurde in einem Schütteltrichter genau 2 Minuten lang mit 10 ml 0,5*M* Ammoniaklösung geschüttelt und der Chloroformextrakt verworfen Die wäßrige Phase wird durch ein angefeuchtetes Filter filtriert und das Filtrat (die wäßrige Dithizonlösung) zur spektrophotometrischen Bleibestimmung verwendet.

Ammoniakalische Komplexierungslösung. Natriumsulfit (3 g; $Na_2SO_3.7H_2O$) wurde in 340 ml konzentrierter Ammoniaklösung und 680 ml Wasser gelöst und mit 30 ml einer Kaliumcyanidlösung (10 g/Liter) vermischt.

Andere Reagenzien. Ferner wurden verwendet: Chloroform, Kaliumbromid, 6*M* Salzsäure, 0.15*M*, 1.5*M* und konzentrierte Bromwasserstoffsäure, 0,5 vol.%ige Salpetersäure und konzentrierte Perchlorsäure.

Apparaturen

Für die Bestimmung des Bleis mittels Atomabsorption wurde ein Perkin–Elmer 303 Atomabsorptionsspektrophotometer in Verbindung mit einem Hitachi–Perkin–Elmer Recorder 56 verwendet. Die Messungen wurden mittels einer Bleihohlkathodenlampe bei 283,3 nm unter Anwendung der folgenden instrumentellen Einstellungen ausgeführt: Gitter—ultraviolett; Skalendehnung—bis auf das 30 Fache; Spalt—4 (1 mm; 0,7 nm spektrale Spaltbreite); Lampenstrom—8 mA; Brenner—Dreischlitzbrennerkopf; Acetylendruck—8 psig (Einstellung 9,0 auf dem Rotameter); Luftdruck—30 psig (Einstellung 9,0 auf dem Rotameter); Dämpfung—bis zu 5. Unter diesen Bedingungen und bei Durchführung der Messungen in 0,5 vol.% Salpetersäure wird eine Empfindlichkeit von 0,6 ppm Blei für 1% Absorption erzielt.

Für die photometrischen Bestimmungen des Bleis wurde ein Beckman Spektralphotometer, Modell DB-GT und 1-cm Küvetten verwendet.

Die Ionenaustauschtrennungen wurden in Austauschersäulen eines früher[38] angegebenen Typs ausgeführt.

Vorbereitung der Wasserprobe

Ein Liter der Wasserprobe wird sofort nach der Probenahme mit 18,5 ml konzentrierter Bromwasserstoffsäure angesäuert und dann im Laboratorium durch ein dichtes Filter filtriert. Danach wird das Filtrat einige Stunden (vorzugsweise über Nacht) stehengelassen wodurch Kohlendioxyd und andere Gase, die durch Gasblasenbildung das Austauschverfahren stören würden, entfernt werden. Für die unten beschriebene Ionenaustauschtrennung werden 200 ml des Filtrats (die Sorptionslösung) benützt.

Für Untersuchungen hinsichtlich des Einflußes von in Wasserproben anwesenden organischen Bestandteilen auf die Bleiabtrennung (siehe Resultate und Diskussion) werden 200 ml des Filtrats auf dem Sandbad (einer Heiz-

platte oder unter einer Infrarotlampe) zur Trockne eingedampft. Der Rückstand wird mit 5 ml konzentrierter Perchlorsäure aufgenommen und die Lösung, zwecks Zerstörung organischer Substanzen, auf dem Sandbad zur Trockne gebracht. Anschließend werden 5 ml konzentrierte Bromwasserstoffsäure zugegeben, die Lösung auf dem Wasserbad zur Trockne eingedampft und der Eindampfrückstand in 50 ml 0,15*M* Bromwasserstoffsaure aufgenommen. Dieser Lösung wird 1 g Kaliumbromid zugesetzt und nach längerem Stehenlassen (vorzugsweise über Nacht) wird das ausgefällte Kaliumperchlorat abfiltriert. Nach dem Waschen des Niederschlags mit 0,15*M* Bromwasserstoffsäure wird das Filtrat mit derselben Säure auf 200 ml verdünnt (die Sorptionslösung).

Ionenaustauschtrennung

Die, wie oben angegeben, hergestellten 200 ml Sorptionslösung werden durch eine mit 4 g des Anionenaustauschers beschickte Säule (vorbehandelt mit je 50 ml 1,5*M* und 0,15*M* Bromwasserstoffsäure), mit einer dem Gegendruck des Harzbettes entsprechenden Geschwindigkeit (etwa 1,5 ml/Minute) fließen gelassen. Anschließend wird mit 50 ml 0,15*M* Bromwasserstoffsäure nachgewaschen und das Blei mit 50 ml 6*M* Salzsäure eluiert (Bleieluat).

Quantitative Bestimmung des Bleis

Spektrophotometrische Methode.[21] Das Bleieluat wird auf dem Wasserbad zur Trockne eingedampft, der Eindampfruckstand in 1 ml 6*M* Salzsäure aufgenommen und die Lösung unter Nachwaschen mit insgesamt 50 ml Wasser in einen Scheidetrichter gebracht. Danach werden 30 ml der ammoniakalischen Komplexierungslösung zugesetzt, kurz durchgeschüttelt und nach Zugabe von 0,5 ml wäßriger Dithizonlösung erneut kurze Zeit geschüttelt. Anschließend werden 10 ml Chloroform zugegeben und das Bleidithizonat durch genau 1 Minute langes Schütteln extrahiert. Nach der Phasentrennung wird der Chloroformextrakt durch ein trockenes Filter filtriert und seine Extinktion bei 510 nm gegenüber einer analog hergestellten Reagensleerlösung (ein Dithizon–Chloroformextrakt der in Abwesenheit von Blei aber unter genauester Einhaltung der obigen Arbeitsvorschrift erhalten wurde) gemessen. Aus der gemessenen Extinktion des Extrakts wird dann mit Hilfe einer analog aufgestellten Eichkurve im Konzentrationsbereich von 0 bis 20 μg Blei/10 ml Chloroformextrakt der Bleigehalt der Probelösung ermittelt; 10 μg Blei entsprechen einer Extinktion von 0,381.

Zwecks direkter Bestimmung des Bleis in Wasserproben werden 200 ml der mit Bromwasserstoffsäure angesäuerten Probe (siehe oben) auf dem Wasserbad zur Trockne eingedampft und der Rückstand genauso wie der Eindampfrückstand des Bleieluats (siehe oben) weiterbehandelt.

Da die untersuchten Wasserproben nur ppM-Mengen an Blei enthielten, war es immer nötig den Bleigehalt aller verwendeten Reagenzien (vom Ansäuern der Wasserprobe bis zur Bleibestimmung) zu ermitteln und diesen dann bei der Auswertung der Analysenergebnisse in Rechnung zu stellen. Dies war natürlich auch bei Anwendung der unten beschriebenen atomabsorptionsspektrophotometrischen Methode erforderlich.

Atomabsorptionsmethode. Das Bleieluat wird auf dem Wasserbad zur Trockne eingedampft, der Eindampfrückstand in 5 ml 0,5 vol.%iger Salpetersäure aufgenommen und nach 30 Minuten wird die Lösung in einen 10-ml-Meßkolben gebracht wobei mit derselben Säure nachgewaschen und zur Marke aufgefüllt wird. Unlösliche Anteile, welche die zum Ansaugen der Lösung in die Luft-Acetylenflamme benützte Kapillare verstopfen könnten, müssen vor Bestimmung des Bleis durch Filtration (trockenes Filter) abgetrennt werden. Die Eichkurve wird durch Ansaugen von geeigneten, analog hergestellten Bleistandardlösungen aufgestellt.

RESULTATE UND DISKUSSION

Stark basische Anionenaustauscher weisen gegenüber Blei eine relativ hohe Selektivität auf vorausgesetzt, daß dieses Element als anionischer Bromidkomplex vorliegt.[36,39] Aus Messungen der Gleichgewichtsverteilungskoeffizienten des Bleis an Dowex 1, X8 unter Anwendung der in dieser Arbeit verwendeten bromwasserstoffsauren Lösungen geht hervor, daß dieser Koeffizient in 0,15*M* Bromwasserstoffsäure einen Wert von $3{,}40 \cdot 10^3$ (bei Beladung des Harzes mit 1 mg Pb) aufweist. In Gegenwart von 5 oder 10 mg Kaliumbromid/ml 0,15*M* Bromwasserstoffsäure wurde bei derselben Beladung ein wesentlich niedrigerer Verteilungskoeffizient von 950 ermittelt woraus folgt, daß die Bleiadsorption in Gegenwart von Salzen erwartungsgemäß[36] erniedrigt wird. Besonders deutlich wird dieser Salzeffekt durch die in Tabelle 1 gezeigten Resultate von Bleibestimmungen im Wiener Trinkwasser veranschaulicht. Aus diesen geht hervor, daß der in den Wasserproben ermittelte Bleigehalt, abgesehen von geringen Schwankungen, unabhängig vom Volumen der Wasserprobe ist, vorausgesetzt wenn dieses ein Liter nicht überschreitet. Wird mehr als

Tabelle 1. Resultate von spektrophotometrischen Bleibestimmungen in Wiener Trinkwasser

Volumen der zur Analyse verwendeten Wasserprobe, *l*.*	Bleigehalt, *μg/l*.
0,1	14,0
0,1	14,0
0,2	14,1
0,2	13,7
0,5	14,1
0,5	13,9
1,0	14,0
1,0	13,8
2,0	12,6
3,0	6,0
5,0	1,5

* Die Probenahme erfolgte im April 1974 im Analytischen Institut der Universität Wien.

Tabelle 2. Einfluß von Fremdionen auf die Abtrennung und spektrophotometrische Bestimmung des Bleis

Der Wasserprobe* zugesetztes Fremdion (1 mg)	Bleigehalt, *μg/l*.
Zn(II)	13,7
Cd(II)	13,7
Hg(II)	13,5
Bi(III)	13,2
Sn(II)	13,0
Tl(I)	13,7
Mo(VI)	13,5
Ag(I)	12,6
Cu(II)	13,2
Ohne Zusatz	13,2

* Als Wasserprobe wurden jeweils 200 ml Wiener Trinkwasser verwendet und unter Anwendung der Arbeitsvorschrift analysiert.

Tabelle 3. Einfluß der Bleikonzentration auf die Bleiausbeute

Der Wasserprobe* zugesetzte Bleimenge, *μg*	Im 6*M* HCl-Eluat wiedergefundene Bleimenge†, μg
10	10,1
20	17,9
100	117
1000	1083

* Als Wasserprobe wurden jeweils 1000 ml Wiener Trinkwasser verwendet und unter Anwendung der im experimentellen Teil beschriebenen Arbeitsvorschrift analysiert.

† Abzüglich der in der Wasserprobe und in den Reagenzien enthaltenen Bleikonzentrationen.

ein Liter Wasserprobe der in der Arbeitsvorschrift beschriebenen Anionenaustauschoperation unterworfen, so wird das Blei in zunehmenden Ausmaß durch die in der Probe anwesenden Anionen der Erdalkalimentalle (Bromide und Sulfate) vom Harz verdrängt wodurch beträchtliche Bleiverluste eintreten. So wurde z.B. bei Anwendung einer 5 Liter Wasserprobe ein um etwa eine Zehnerpotenz niedrigerer Bleigehalt gefunden (siehe Tabelle 1). Auf Grund dieser Tatsache werden bei der Ionenaustauschtrennung nur 200 ml der Sorptionslösung verwendet obwohl auch eine quantitative Anreicherung des Bleis, entsprechend den in Tabelle 1 gezeigten Resultaten, aus 1000-ml Proben möglich ist. Dieses kleinere Probevolumen von 200 ml wird jedoch deshalb empfohlen damit das Blei auch aus Wasserproben, die einen höheren Salzgeholt als Wiener Trinkwasser aufweisen, quantitativ abgetrennt werden kann.

Kein Einfluß auf die Adsorption des Bleis am Anionenaustauscher wird dagegen in Anwesenheit von Schwermetallionen hervorgerufen, selbst wenn diese analog zum Blei als anionische Bromidkomplexe vom Harz adsorbiert werden wie z.B. Cadmium[40] und Wismut. Die Ergebnisse diesbezüglicher Untersuchungen werden in Tabelle 2 gezeigt in der auch Metallionen angeführt sind, die wie Zink und Kupfer aus 0,15 *M* Bromwasserstoffsäure nicht vom Austauscher adsorbiert und damit schon während der Sorption quantitativ vom Blei getrennt werden. Da bei der Elution des Bleis mit 6*M* Salzsäure (siehe Arbeitsvorschrift) die als anionische Bromidkomplexe adsorbierten Fremdionen wie z.B. Cadmium und Wismut nicht eluierbar sind, wird eine Eluat erhalten in dem das Blei störungsfrei bestimmt werden kann.

Untersuchungen hinsichtlich des Einflußes der Bleikonzentration auf die Bleiausbeute ergaben die in Tabelle 3 gezeigten Resultate aus denen hervorgeht, daß selbst eine Bleimenge von 1 mg/Liter vollständig vom Austauscher adsorbiert und quantitativ im Eluat wiedergefunden wurde. Dadurch wird der Anwendungsbereich der Methode wesentlich erweitert, eine Tatsache die von Bedeutung ist wenn die Methode zur Analyse von relativ bleireichen Gewässern (z.B. Abwässer) angewendet werden soll.

In Tabelle 4 werden die Resultate von Bleibestimmungen in Donauwasserproben gezeigt. Wie ein Vergleich der in Kolonne A II angeführten Bleigehalte mit den entsprechenden Werten der Kolonnen A I und B I und II zeigt, ist eine der Ionenaustauschtrennung vorangehende Zerstörung organischer Substanzen nicht erforderlich. Diese ist nicht nur zeitraubend, sondern es werden auch durch die zur Naßveraschung benötigten Reagenzien Bleimengen eingeschleppt die größenordnungsmäßig den Bleigehalten der Donauwasserproben entsprechen.

Wie ferner aus Tabelle 4 ersichtlich ist, weisen jene Analysen die in Gegenwart und in Abwesenheit von als Spike zugesetzten Bleistandardmengen durchgeführt wurden in vielen Fällen eine relativ gute Übereinstimmung auf, woraus geschlossen werden kann, daß die Bleiabtrennung quantitativ erfolgte und auch nicht von den im Donauwasser anwesenden organischen Substanzen ($\equiv$0,5–1,0 ml 0,1*M* Kaliumpermanganat pro Liter) gestört wird (die in den Kolonnen B I und II angeführten Resultate wurden ohne vorangehende Zerstörung organischer Substanzen ermittelt). Demgegenüber wurden bei der direkten Anwendung der spektrophotometrischen Methode Bleigehalte gefunden, die wesentlich höher sind als die nach vorangehenden Ionenaustausch erhaltenen. Die Ursache dafür ist auf die Anwesenheit von Schwermetallionen (z.B. Zink) zurückzuführen, die analog zum Blei mit Dithizon–Chloroform extrahierbar sind und dann bei der spektrophotometrischen Bleibestimmung einen beträchtlichen positiven Fehler hervorrufen.

Nicht meßbar waren die Bleigehalte der Donauwasserproben bei direkter Anwendung

Tabelle 4. Resultate von Bleibestimmungen in Donauwasserproben

Probenbezeichnung*	Bleigehalt, μg/l. Bleibestimmung nach vorangehendem Ionenaustausch				Direkte spektrophotometrisch Bleibestimmung†
	A		B		
	I	II	I	II	
1. Donau bei Linz-Magreiten (R)	5,5	5,5	3,0	7,0 (20)	11,5
2. Donau bei Linz-Steyregg (L)	9,0	11,0	7,1	8,5 (20)	15,0
3. Donau bei Langenstein (L)	5,5	5,0	7,3	5,5 (20)	20,0
4. Donau bei Mauthausen-Ost (L)	9,0	10,0	10,9	8,2 (20)	21,5
5. Donau bei Ysperdorf (L)	3,7	7,5	10,3	5,5 (20)	25,0
6. Donau bei Persenbeug (L)	2,0	2,8	6,2	2,5 (20)	18,0
7. Donau bei Dürnstein (L)	3,7	6,0	7,0	4,5 (20)	25,0
8. Donau bei Traismauer-Ost (R)	3,7	4,0	6,6	6,0 (20)	26,0
9. Donau bei Klosterneuburg (Fähre) (R)	4,3	7,0	5,8	5,5 (20)	26,0
10. Donau bei Wien-Lobau (Ölhafen) (L)	9,0	9,5	7,3	10,0 (20)	37,0

A I = Spektrophotometrisch bestimmter Bleigehalt ohne vorangehende Zerstörung organischer Substanzen.
A II = Spektrophotometrisch bestimmter Bleigehalt nach Zerstörung organischer Substanzen.
B I = Atomabsorptionsspektrophotometrisch bestimmter Bleigehalt.
B II = Atomabsorptionsspektrophotometrisch bestimmter Bleigehalt nach Abzug der vor der Anionenaustauschtrennung als Spike zugesetzten Bleimenge (die eingeklammerten Zahlen geben an, wieviel μg-Blei-Spike verwendet wurde).

* Die Probenahme erfolgte am 20 April 1974; (R) = rechtes Donauufer; (L) = linkes Donauufer

† Da die in dieser Kolonne gezeigten Resultate nur in Gegenwart von Cyanid als Maskierungsmittel ermittelt wurden is es verstandlich, daß diese Bleigehalte wesentlich höher sind (hervorgerufen durch Koextraktion von Dithizonaten anderer in den Wässern vorhandener Metallspüren) als die in Kolonnen A und B angeführten.

der Atomabsorptionsmethode (Empfindlichkeit nur 100 ppM) woraus folgt, daß angenähert verläßliche Bleibestimmungen mittels Atomabsorptionsspektrophotometrie erst nach Abtrennung des Bleis aus den Wasserproben möglich sind.

Die beschriebene Methode wurde auch zur Bestimmung des Bleis in der Fresh Water Sample W-3 (International Atomic Energy Agency, Intercomparison Run June–December 1973) herangezogen und ein Bleigehalt von 295 ppM ermittelt. Der theoretische Bleigehalt dieser Probe wird mit 305 ppM angegeben.

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Summary—A method is described which makes possible the separation of lead from natural waters at the ppM level, and its final determination by spectrophotometry or atomic absorption. The sample is made 0·15*M* in hydrobromic acid, filtered, and passed through Dowex 1 X8 (bromide form). The lead is sorbed on the resin and most of the other elements present are separated from it. The lead is eluted with 6*M* hydrochloric acid and determined by the dithizone method or by atomic-absorption. The method was used to determine lead in drinking water and water from the Danube, lead concentrations in the range 2–14 ppM being found.

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ANWENDUNG VON IONENAUSTAUSCHVERFAHREN ZUR BESTIMMUNG VON SPURENELEMENTEN IN NATÜRLICHEN WÄSSERN—VI

ZINK

J. KORKISCH, L. GÖDL und H. GROSS

Analytisches Institut der Universität, Abteilung: Rohmaterialanalyse nuklearer Brennstoffe, Währingerstraße 38, A-1090 Wien, Österreich

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Zusammenfassung—Eine Methode wird beschrieben, die es gestattet ppM-Mengen Zink aus natürlichen Wässern zu isolieren und der Endbestimmung mittels Atomabsorptionspektrophotometrie zugänglich zu machen. Die Wasserprobe wird mit Salzsäure angesäuert, filtriert und nach Zugabe von Kaliumthiocyanat durch eine Säule des stark basischen Anionenaustauschers Dowex 1, X8 (Thiocyanatform) fließen gelassen. Dabei wird das Zink als anionischer Thiocyanatkomplex quantitativ adsorbiert und gleichzeitig von den meisten in der Wasserprobe anwesenden Begleitelementen getrennt. Nach dem Nachwaschen mit einem salzsauren, gemischt wäßrig-organischen Lösungsmittelsystem und 1*M* Salzsäure wird das Zink mit 0,15*M* Bromwasserstoffsäure eluiert und direkt im Eluat mittels Atomabsorption bestimmt. Die Methode wurde zur Bestimmung des Zinks in österreichischen Gewässern herangezogen wobei Gehalte im Konzentrationsbereich von 18 bis 685 ppM Zink gefunden wurden.

Zinkbestimmungen in natürlichen Wässern liefern wertvolle Daten nicht nur im Zusammenhang mit Problemen des Umweltschutzes, sondern auch in Hinblick auf die Geochemie dieses Elementes und der hydrogeochemischen Prospektion auf Zink. In der Literatur werden daher eine große Anzahl von Methoden zur Zinkbestimmung in Süß- und Meerwasserproben sowie Abwässern beschrieben die auf Spektrophotometrie,[1–12] Polarographie,[13–15] Voltammetrie,[16–18] Atomabsorptionsspektrophotometrie,[19,20] Atomfluoreszenzspektroskopie,[21] Röntgenstrahlenfluoreszenz,[22] Emissionsspektroskopie,[23] ÄDTA-Titration[24–27] und radiochemischen Methoden[28–31] beruhen.

Obwohl es mit vielen der angeführten Verfahren möglich ist das Zink direkt in den Wasserproben zu bestimmen[5–7,14,17–21,25–27] ist es häufig erforderlich, vor allem in Anwesenheit sehr geringer Zinkmengen, die Analysenprobe einzudampfen[13,15,23] oder das Zink mittels geeigneter Abtrennungsmethoden zu isolieren wozu am häufigsten die Flüssig–Flüssig Extraktion von Komplexen des Zinks mit organischen Reagenzien herangezogen wird. Die dazu verwendeten Extraktionssysteme sind: Dithizon–Chloroform (oder Tetrachlorkohlenstoff),[2,4,8–10,28] Diäthyldithiocarbamat–Äthylacetat[24] (oder Toluol und Isoamylalkohol[3] bzw. Chloroform[11]), Di-2-naphthylthiocarbazon–Chloroform,[1] 6-Methoxy-3-methyl-2-[4-(*N*-methylanilino)phenylazo] benzothiazoliumchlorid–Thiocyanat–Benzol–TBP[12] und Aliquat-336–Xylol.[31] Einige dieser Reagenzien wie z.B. Dithizon sind gleichzeitig auch empfindliche Farbreagenzien, so daß das Zink nach Extraktion in die organische Phase direkt in dieser spektrophotometrisch bestimmt werden kann.[1,2,4,8–10,12,28] Andere zur Abtrennung des Zinks aus Wässern benützte Verfahren sind: Chromatographie auf einer mit Dithizon impregnierten Zelluloseacetatsäule,[30] Adsorption des Zinks auf Chitosan,[16] dem stark sauren Kationenaustauscher Amberlite

IR-120[22] oder auf einem stark basischen Anionenaustauscher aus etwa 2*M* salzsaurer Lösung nach vorangehender Abtrennung des Zinks durch Kopräzipitation mit Eisenhydroxyd.[29] Auch ein Adsorptionsverfahren beruhend auf Kolloidflotation mit Dodecylamin als Surfaktant kann zur Isolierung des Zinks herangezogen werden.[32]

In früheren Arbeiten dieser Reihe werden Methoden beschrieben, die es ermöglichen die in natürlichen Wässern vorhandenen Spurenelemente Kobalt,[33,34] Cadmium[34] und Uran[34] ohne vorangehendes Eindampfen der Analysenproben durch Anwendung von Anionenaustausch in Thiocyanatsystemen abzutrennen und der spektrophotometrischen Endbestimmung zugänglich zu machen. Da auch Zink analog zu den obengenannten Elementen einen anionischen Thiocyanatkomplex bildet, kann dieses Element, wie in der vorliegenden Arbeit beschrieben wird, direkt aus der Wasserprobe auf dem stark basischen Anionenaustauscher Dowex 1 quantitativ adsorbiert und nach der Elution atomabsorptionsspektrophotometrisch bestimmt werden.

EXPERIMENTELLER TEIL

Lösungen und Reagenzien

Ionenaustauscher. Es wurde der stark basische Anionenaustauscher Dowex 1, X8 (100–200 mesh; Chloridform) verwendet. Vor dem Einfüllen in die Ionenaustauschersäule werden 4 g des Anionenaustauscherharzes in wenigen ml der Vorbehandlungslösung (siehe unten) aufgeschlämmt und nach Ablauf von etwa 15 Minuten wird der Austauscher so vollständig als möglich in die mit derselben Lösung gefüllte Ionenaustauschersäule gebracht. Danach wird mit 50 ml der Vorbehandlungslösung nachgewaschen, um den Austauscher weitestgehend in die Thiocyanatform überzuführen.

Zink-Standardlösungen. Ausgehend von einer Stammlösung die 1,0 mg Zn (als Zinkchlorid) pro ml 6*M* Salzsäure enthielt (der Zinkgehalt dieser Lösung wurde durch ÄDTA-Titrationen ermittelt), wurden durch Verdünnen mit 6*M* Salzsäure oder 0,15*M* Bromwasserstoffsäure, Lösungen mit Zinkgehalten im Konzentrationsbereich von 0,1 bis 10 ppm hergestellt.

Vorbehandlungslösung. Salzsäure, 0,1*M*, die pro 100 ml Lösung 1 g Kaliumthiocyanat enthält.

THF–MG–HCl-Mischung. Mischung bestehend aus 50 vol.% Tetrahydrofuran, 40 vol.% Methylglykol und 10 vol.% 6*M* Salzsäure; siehe Beiträge I und IV dieser Reihe.[33,34]

Andere Reagenzien. Ferner wurden verwendet: Kaliumthiocyanat (*p.a.*), 1*M* und konzentrierte Salzsäure sowie 0,15*M* Bromwasserstoffsäure.

Apparaturen

Zur Bestimmung des Zinks mittels Atomabsorption wurde ein Perkin-Elmer 303 Atomabsorptionsspektrophotometer in Verbindung mit einen Hitachi-Perkin-Elmer Recorder 56 verwendet. Die Messungen wurden mittels einer Zinkhohlkathodenlampe bei 213,8 nm unter Anwendung der folgenden instrumentellen Einstellungen ausgeführt: Gitter–ultraviolett; Skalendehnung–bis auf das 10Fache; Spalt—5 (3 mm; 2 nm spektrale Spaltbreite); Lampenstrom—15 mA; Brenner—Dreischlitzbrennerkopf; Acetylendruck—8 psig (Einstellung 10 auf dem Rotameter); Luftdruck—30 psig (Einstellung 10,5 auf dem Rotameter); Dämpfung—bis auf 4. Unter diesen Bedingungen weist die Empfindlichkeit der Zinkbestimmung für 1% Absorption Werte von 0,019 bzw. 0,017 ppm auf wenn die Messungen in 0,15*M* Bromwasserstoffsäure bzw. 0,1*M* Chlorwasserstoffsäure (direkte Bestimmung des Zinks in den Wasserproben) ausgeführt werden.

Die Ionenaustauschtrennungen wurden in Austauschersäulen eines in einer früheren Arbeit[35] angegebenen Typs ausgeführt.

Bestimmung der Verteilungskoeffizienten

Die Gleichgewichtsverteilungskoeffizienten (K_d-Werte) des Zinks wurden unter Anwendung der Batch-Methode bestimmt.[36]

Vorbereitung der Wasserprobe

Ein Liter der Wasserprobe wird so bald als möglich nach der Probenahme mit 10 ml konzentrierter Salzsäure angesäuert und durch ein dichtes Filter filtriert. Dem Filtrat werden 10 g Kaliumthiocyanat zugesetzt, gut durchgemischt bis sich das Reagens aufgelöst hat und danach wird die Mischung (die Sorptionslösung) etwa eine Stunde stehengelassen. Wird für die Analyse ein kleineres oder größeres Volumen als 1 Liter benötigt, so ist es natürlich erforderlich die der Wasserprobe zuzugebenden Mengen an Salzsäure und Kaliumthiocyanat entsprechend zu variieren.

Ionenaustauschtrennung

Die Sorptionslösung (siehe oben) wird durch eine mit 4 g des Ionenaustauscherharzes beschickte Säule (die vorher mit 50 ml der Vorbehandlungslösung gewaschen wurde), mit einer dem Gegendruck des Harzbettes entsprechenden Geschwindigkeit (etwa 140 ml/Stunde) fließen gelassen. Anschließend wird zuerst mit 50 ml der THF–MG–HCl-Mischung (wobei die, durch den am Harz adsorbierten Thiocyanatkomplex des Eisens während der Sorption gebildete, rote Adsorptionszone vollständig verschwindet) und dann mit 20 ml 1*M* Salzsäure nachgewaschen, um koadsorbierte Fremdionen wie Eisen, Uran und Kobalt weitestgehend zu entfernen. Hierauf wird das Zink mit 100 ml 0,15*M* Bromwasserstoffsäure eluiert (Zinkeluat).

Quantitative Bestimmung des Zinks

Das Zinkeluat wird mittels einer Kapillare in die Luft–Acetylenflamme gesaugt und die Absorption bei 213,8 nm gemessen. Die Eichkurve wird durch Ansaugen von geeigneten, analog hergestellten Zinkstandardlösungen aufgestellt.

Die direkte Zinkbestimmung in den untersuchten Wässern erfolgte analog durch Ansaugen der filtrierten 0,1*M* salzsauren Proben.

Obwohl die zur Abtrennung und Bestimmung des Zinks benützten Reagenzien nur verschwindend geringe Mengen dieses Elementes enthielten, ist es immer ratsam ihre Zinkkonzentrationen unter Anwendung des oben beschriebenen Verfahrens zu ermitteln wobei 1 Liter destilliertes Wasser als Wasserprobe eingesetzt wird.

RESULTATE UND DISKUSSION

Das Prinzip der beschriebenen Methode zur Abtrennung des Zinks aus natürlichen Wässern beruht darauf, daß das Zink mit Thiocyanationen einen sehr stabilen anionischen Komplex bildet, der aus verdünnt salzsaurer Lösung sehr stark auf dem stark basischen Anionenaustauscher Dowex 1 adsorbiert wird. Unter den angegebenen Bedingungen, d.h. in Gegenwart von 10 ml konzentrierter Salzsäure und 10 g Kaliumthiocyanat pro Liter Wasserprobe, wurde für Zink ein Verteilungskoeffizient von 28×10^3 ermittelt. Wie aus Tabelle 1 ersichtlich, ist dieser Koeffizient sowohl von der Salzsäuremolarität als auch von der Thiocyanatkonzentration abhängig. Die Ursache dafür, der der Verteilungskoeffizient mit ansteigender Thiocyanatkonzentration zunimmt ist auf zunehmende Komplexbildung des Zinks mit Thiocyanation zurückzuführen; andererseits weist der Anstieg des Koeffizienten mit zunehmender Salzsäuremolarität (vor allem im Bereich niedriger Thiocyanatkonzentrationen) darauf hin, daß das Zink in zunehmenden Ausmaß auch als anionischer Chloridkomplex adsorbiert wird.

Auf Grund dieses sehr hohen Verteilungskoeffizienten kann das Zink auch aus einem sehr großen Volumen der Wasserprobe quantitativ abgetrennt werden. Diesbezügliche Versuche ergaben die in Tabelle 2 gezeigten Ergebnisse aus denen hervorgeht, daß bei Anwendung der im experimentellen Teil beschriebenen Arbeitsmethode durchwegs übereinstimmende Resultate erzielt werden, und zwar unabhängig davon ob das Zink aus 0,5 oder 5 Liter der Wasserprobe abgetrennt wird.

Wie aus Tabelle 3 ersichtlich ist, ermöglicht es der hohe Verteilungskoeffizient des Zinks auch relativ große Zinkmengen am Austauscher zu adsorbieren wodurch der Anwendungsbereich der Methode wesentlich erweitert wird d.h. es können mit ihr nicht nur μg-

Tabelle 1. Verteilungskoeffizienten des Zinks in Abhängigkeit von der Salzsäure- und Thiocyanatkonzentration (1 g Dowex 1; 1 mg Zn in 20 ml Lösung)

[HCl], *M*	[KSCN], *g/l.* 1	5	10	20
0,0	230	380	$25{,}0 \times 10^3$	$25{,}0 \times 10^3$
0,1	448	$2{,}60 \times 10^3$	$28{,}0 \times 10^3$	$28{,}0 \times 10^3$
0,5	456	$10{,}0 \times 10^3$	$31{,}0 \times 10^3$	$28{,}0 \times 10^3$
1,0	$1{,}40 \times 10^3$	$14{,}0 \times 10^3$	$31{,}0 \times 10^3$	$50{,}0 \times 10^3$

Tabelle 2. Resultate von Zinkbestimmungen im Wiener Trinkwasser

Volumen der zur Analyse verwendeten Wasserprobe*, *l.*	Zinkgehalt, *μg/l.*
0,5	47,6
1,0	47,0
2,0	47,5
3,0	46,0
5,0	48,2

* Die Probenahme erfolgte im April 1974 im Analytischen Institut der Universität Wien.

Tabelle 3. Einfluß der Zinkkonzentration auf die Zinkausbeute

Der Wasserprobe* zugesetzte Zinkmenge, *μg*	Im 0,15*M* HBr-Eluat wiedergefundene Zinkmenge, *μg*
0	47
100	144
500	535
1000	1060
2000	1980
5000	4900

* Als Wasserprobe wurde jeweils 1 Liter Wiener Trinkwasser verwendet und unter Anwendung der Arbeitsvorschrift analysiert.

sondern auch mg-Mengen an Zink quantitativ abgetrennt werden. Dies ist von Bedeutung wenn die Methode zur Analyse von Abwässern aus Industrie und Gewerbe angewendet werden soll.

Eine weitere Folgeerscheinung, die sich aus der sehr starken Adsorption des Zinks ergibt ist, daß die Zinkabtrennung durch Metallionen, die als anionische Thiocyanatkomplexe am Harz adsorbierbar sind,[33,34] nicht gestört wird. Wie aus Tabelle 4 ersichtlich, ist selbst in Gegenwart von 50 mg Eisen keine Verdrängung des Zinks zu beobachten. Von den in

Tabelle 4. Einfluß von koadsorbierten Fremdionen auf die Abtrennung des Zinks

Der Wasserprobe* zugesetztes Fremdion	Zinkgehalt, *μg/l.*
Fe(III) (50 μg)	48,0
Fe(III) (500 μg)	47,0
Fe(III) (5000 μg)	47,0
Fe(III) (50000 μg)	48,0
Hg(II) (5000 μg)	47,0
Ag(I) (500 μg)	45,5
Mo(VI) (5000 μg)	46,5
Co(II) (5000 μg)	46,5
Cu(II) (5000 μg)	46,5
V(V) (5000 μg)	46,5
Cd(II) (5000 μg)	46,5
UO_2(II) (5000 μg)	48,0
Ohne Zusatz	47,5

* Als Wasserprobe wurde jeweils 1 Liter Wiener Trinkwasser verwendet und unter Anwendung der Arbeitsvorschrift analysiert.

Tabelle 5. Elutionsverhalten des als Thiocyanatkomplex auf Dowex 1 (4 g Säule) adsorbierten Zinks*

Elutionsmittel	Zinkgehalt des Eluats, μg
1. 50 ml THF–MG–HCl-Mischung + 20 ml 1*M* HCl + 100 ml 0,15*M* HBr	47,5
2. 20 ml 1*M* HCl + 100 ml 1*M* HNO_3	47,0
3. 20 ml 1*M* HCl + 100 ml 1*M* $HClO_4$	45,0
4. 100 ml H_2O	14,0
5. 20 ml 1*M* HCl + 100 ml 1*M* H_2SO_4	11,0
6. 20 ml 1*M* HCl + 100 ml 0,15*M* HBr	<2
7. 20 ml H_2O + 100 ml 0,15*M* HBr	<1

* Zur Analyse gelangte jeweils 1 Liter mit 10 ml konzentrierter Salzsäure angesäuertes Wiener Trinkwasser das 10 g Kaliumthiocyanat enthielt.

dieser Tabelle angeführten, koadsorbierten Elementen werden Eisen und Molybdän bei dem der Sorption des Zinks nachfolgenden Waschen des Anionenaustauschers mit THF–MG–HCl-Mischung (siehe Arbeitsvorschrift) teilweise entfernt. Die Restmengen dieser Elemente sowie auch Kupfer, Kobalt, Vanadin und Uran werden dann beim Nachwaschen mit 1*M* Salzsäure eluiert (siehe Arbeitsvorschrift). Da auch bei der Elution des Zinks mit 0,15*M* Bromwasserstoffsäure das Cadmium nicht miteluierbar ist,[34] wird bei Anwendung der Anionenaustauschtrennung ein Eluat erhalten welches nur Zink enthält, so daß dieses störungsfrei bestimmt werden kann.

Tabelle 6. Resultate von atomabsorptionsspektrophotometrisch bestimmten Zinkgehalten in österreichischen Wasserproben

Probenbezeichnung und Datum der Probenahme	Zinkgehalt, $\mu g/l$. A	B	C
198/5 Wiesergraben, 1 km oberhalb Grafendorf, Oberes Gailtal, Südkärnten; 10.8.1973	18	22 (50)	20
198/6 Reißkofelbach, oberhalb Reißkofelbad, bei Grafendorf, Oberes Gailtal, Südkärnten; 10.8.1973	430	400 (500)	33,8
DR 2 Gnoppnitzbach, 10 km oberhalb Greifenburg, Drautal, Kärnten; 11.8.1973	78	78 (50)	23
Sb.2 Imlaubach oberhalb Imlau, an der B159 Werfen-Bischofschofen, Salzburg; 12.8.1973	36	38 (50)	35,6
Fieberbrunn, Tirol; 25.8.1973	685	670 (500)	34,5
200/1 Nötschgraben oberhalb Förk bei Nötsch, Gailtal, Kärnten; 6.8.1973	50	50 (50)	48,5
S15 Salzach unterhalb Bruck an der Glocknerstraße, Salzburg; 16.6.1973	32	34 (50)	27,7
196/4 Aus dem Tuffbad 1420 m, Tirol; 26.8.1973	86	80 (50)	30
197/6 Sittmooserbach, bei Sittmoos (Bachbrücke), Lesachtal, Südkärnten; 7.8.1973	525	490 (500)	23,0
197/8 Dellacherbach, 1 km oberhalb Dellach, Oberes Gailtal, Südkärnten; 7.8.1973	94	87 (50)	34,3

A = Zinkgehalt ermittelt nach Abtrennung des Zinks mittels Anionenaustausches (diese Methode).

B = Zinkgehalt ermittelt nach Abtrennung des Zinks mittels Anionenaustausches (diese Methode) und nach Abzug einer als Spike vor der Ionenaustauschtrennung zugesetzten Zinkmenge (die Zahl in der Klammer gibt die μg-Menge des als Spike zugesetzten Zinks an).

C = Zinkgehalt ermittelt durch direkte atomabsorptionsspektrophotometrische Bestimmung des Zinks in der Wasserprobe.

Untersuchungen hinsichtlich des Elutionsverhaltens des als Thiocyanatkomplex adsorbierten Zinks ergaben die in Tabelle 5 gezeigten Resultate. Aus diesen ist ersichtlich, daß nur mittels der Elutionsmittel 1 und 2 eine quantitative Elution des Zinks erzielt werden kann. Mit Ausnahme von Elutionssystem 1 bei dem das Zink der Arbeitsvorschrift entsprechend nur im 0,15*M* bromwasserstoffsauren Eluat bestimmt wurde, erfolgte die Zinkbestimmung bei Anwendung der Systeme 2 bis 7 in den vereinigten Eluaten dieser Elutionsmittel.

In der Tabelle 6 werden die Ergebnisse von Zinkbestimmungen in Wasserproben aus einigen österreichischen Gewässern gezeigt. Diese Analysen wurden unter Anwendung der beschriebenen Methode in Gegenwart und in Abwesenheit von als Spike zugesetzten Zinkstandardmengen durchgeführt. Wie ein Vergleich der in Kolonnen A und B angeführten Zinkgehalte zeigt, besteht in fast allen Fällen eine relativ gute Übereinstimmung der Werte woraus folgt, daß mittels der verwendeten Methode eine quantitative Abtrennung des Zinks ermöglicht wird. Demgegenüber weichen die durch direkte atomabsorptionsspektrophotometrische Messungen ermittelten Zinkgehalte (siehe Kolonne C der Tabelle 6) sehr häufig von den nach Ionenaustausch des Zinks ermittelten Resultaten ab und ergeben, besonders bei hohem Zinkgehalt der Wasserproben, oft um etwa eine Zehnerpotenz geringere Werte. Diese Wasserproben, die geringere Werte lieferten, enthalten auch ppm-Mengen an Phosphat welches vielleicht die direkte atomabsorptionsspektrophotometrische Messung stören könnte.

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Summary—A method is described for the separation of ppM levels of zinc in natural waters and final determination by atomic absorption. The sample is acidified, filtered, treated with potassium thiocyanate, and passed through Dowex 1 × 8 (thiocyanate form). The anionic zinc thiocyanate complex is sorbed and separated from most of the accompanying elements. The column is washed with an aqueous-organic hydrochloric acid solution and with 1*M* hydrochloric acid, and the zinc is then eluted with 0·15*M* hydrobromic acid and determined directly in the eluate by atomic-absorption. The method was used for determining zinc in some Austrian waters, zinc contents in the range 18–685 ppM being found.

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ANWENDUNG VON IONENAUSTAUSCHVERFAHREN ZUR BESTIMMUNG VON SPURENELEMENTEN IN NATÜRLICHEN WÄSSERN—VII

KUPFER

J. KORKISCH, L. GÖDL und H. GROSS

Analytisches Institut der Universität, Abteilung: Rohmaterialanalyse nuklearer Brennstoffe, Währingerstraße 38. A-1090 Wien, Österreich

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Zusammenfassung—Eine Methode wird beschrieben, die es ermöglicht ppM-Mengen Kupfer aus natürlichen Wässern zu isolieren und der Endbestimmung mittels Atomabsorptionsspektrophotometrie zugänglich zu machen. Die Wasserprobe wird mit konzentrierter Salzsäure angesäuert, filtriert und nach Zugabe von Ascorbinsäure wird die 0,1*M* salzsaure Lösung durch eine Säule des Anionenaustauscherharzes Dowex 1, X8 (Chloridform) fließen gelassen. Das als anionischer Cu(I)-Chlorokomplex adsorbierte Kupfer wird dabei von den meisten in der Wasserprobe anwesenden Begleitelementen getrennt. Nach Elution mit 1*M* Salpetersäure wird das Kupfer mittels Atomabsorptionsspektrophotometrie bestimmt. Die Methode wurde zur Bestimmung des Kupfers in österreichischen Gewässern herangezogen wobei Gehalte im Konzentrationsbereich von 10 bis 39 ppM Kupfer gefunden wurden.

Da die Ermittlung des Kupfergehaltes natürlicher Wässer sowohl im Rahmen des Umweltschutzes als auch für die hydrogeochemische Prospektion auf Kupfer von großer Bedeutung ist, werden in der Literatur eine große Anzahl von Methoden zur Kupferbestimmung beschrieben die auf Spektrophotometrie,[1–43] Polarographie,[44–54] Atomabsorptionsspektrophotometrie,[55–62] Titration[63–65] und radiochemischen Methoden[66,67] beruhen. Obwohl es eine große Anzahl dieser Verfahren ermöglicht das Kupfer ohne vorangehende Anreicherung und Abtrennung von den Begleitelementen zu bestimmen, beruhen viele Methoden zur Kupferbestimmung in Wässern auf Abtrennverfahren die in Kombination mit geeigneten Bestimmungsmethoden angewendet werden. Die am häufigsten benützten Abtrennmethoden beruhen auf Extraktionen von Chelaten des Kupfers wozu folgende Extraktionssysteme zur Anwendung gelangen: Diäthyldithiocarbamat–Chloroform[5,12,14,24,36] (oder Xylol[1]), Dibenzyldithiocarbamat–Tetrachlorkohlenstoff,[27,29,31] Tetramethylendithiocarbamat–Äthylacetat[57] (oder Methylisobutylketon[60]), Ammoniumpyrrolidin-1-carbodithioat–Methylisobutylketon[55] und Dithizon–Chloroform[2] (oder Tetrachlorkohlenstoff[34]). Durch die Extraktion dieser Chelate wird nicht nur eine Trennung des Kupfers von störenden Begleitelementen bewirkt, sondern meistens auch die direkte Kupferbestimmung in den organischen Extrakten mittels Atomabsorption[55,57,60] oder Spektrophotometrie[5,12,14,24,27,29,31,34,36] ermöglicht.

Zur Kupferabtrennung wurden auch organische Hochpolymere herangezogen die es ermöglichen das Kupfer entweder durch Kationenaustausch oder Chelatbildung aus den natürlichen Wässern zu isolieren. Zur Anwendung gelangten Dowex 50,[5,62] Amberlite IR-120,[4] Dowex A-1[61] und Poly(triaminophenolglyoxal) auf Chromosorb W.[55] Andere Verfahren zur Kupferabtrennung beruhen auf Papierchromatographie,[2,3] Kopräzipitation

mit Kalciumcarbonat[51] und Kocristallisation mit 5,7-Dibrom-8-hydroxychinolin und darauffolgender Anionenaustauschtrennung.[56]

Obwohl zur Trennung des Kupfers von Begleitelementen öfters stark basische Anionenaustauscherharze verwendet werden[68] ist bis jetzt kein mit der in der vorliegenden Arbeit beschriebenen Methode identisches Verfahren entwickelt worden. Dieses ist zur direkten Abtrennung des Kupfers aus Wässern geeignet, und zwar ohne vorangehendes Eindampfen der Probe oder Vorkonzentration des Kupfers durch z.B. Kocristallisation.

EXPERIMENTELLER TEIL

Lösungen und Reagenzien

Ionenaustauscher. Es wurde der stark basische Anionenaustauscher Dowex 1, X8 (100–200 mesh; Chloridform) verwendet. Vor dem Einfüllen in die Ionenaustauschersäule werden 4 g des Harzes in wenigen ml 3*M* Salzsäure aufgeschlämmt und nach Ablauf von etwa 15 Minuten wird der Austauscher so vollständig als möglich in die mit derselben Säure gefüllte Ionenaustauschersäule gebracht. Danach wird mit 100 ml 3*M* Salzsäure, 50 ml destillierten Wasser und 50 ml Vorbehandlungslösung (siehe unten) in dieser Reihenfolge nachgewaschen.

Kupfer-Standardlösungen. Ausgehend von einer Stammlösung die 1,00 mg Cu(II) (als Chlorid) pro ml 6*M* Salzsäure enthielt wurden durch Verdünnen mit 6*M* Salzsäure Lösungen mit Kupfergehalten im Konzentrationsbereich von 0,2 bis 20 ppm hergestellt. Für die atomabsorptionsspektrophotometrischen Messungen wurden Standardlösungen des Kupfers in 1*M* Salpetersäure bereitet die Kupfergehalte im Konzentrationsbereich von 0,2 bis 10 ppm enthielten.

Vorbehandlungslösung. Ascorbinsäure (0,5 g) gelöst in 100 ml 0,1*M* Salzsäure (frisch bereitet bis höchstens einen Tag alt).

Andere Reagenzien. Ferner wurden verwendet: Ascorbinsäure, 1*M* Salpetersäure, 0,1*M*, 3*M* und konzentrierte Salzsäure.

Apparaturen

Zur Bestimmung des Kupfers mittels Atomabsorption wurde ein Perkin–Elmer 303 Atomabsorptionsspektrophotometer in Verbindung mit einen Hitachi-Perkin-Elmer Recorder 56 verwendet. Die Messungen wurden mittels einer Kupferhohlkathodenlampe bei 324,7 nm unter Anwendung der folgenden instrumentellen Einstellungen ausgeführt: Gitter—ultraviolett; Skalendehnung—bis auf das 10Fache; Spalt—4 (1 mm; 0,7 nm spektrale Spaltbreite); Lampenstrom—15 mA; Brenner—Standardbrennerkopf (flach); Acetylendruck—8 psig (Einstellung 9,0 auf dem Rotameter); Luftdruck—30 psig (Einstellung 9,0 auf dem Rotameter); Dämpfung—bis zu 4.

Unter diesen Bedingungen weist die Empfindlichkeit der Kupferbestimmung für 1% Absorption einen Wert von 0,096 ppm auf wenn die Messungen in 1*M* Salpetersäure ausgeführt werden.

Die Ionenaustauschtrennungen wurden in Austauschersäulen eines in einer früheren Arbeit[69] angegebenen Typs ausgeführt.

Bestimmung der Verteilungskoeffizienten

Die Gleichgewichtsverteilungskoeffizienten (K_d-Werte) des Kupfers wurden unter Anwendung der Batch-Methode bestimmt.[70]

Vorbereitung der Wasserprobe

Die Wasserprobe (200 ml) wird so bald als möglich nach der Probenahme mit 2 ml konzentrierter Salzsäure angesäuert und durch ein dichtes Filter filtriert. Dem Filtrat wird 1 g Ascorbinsäure zugesetzt, gut durchgemischt bis sich das Reduktionsmittel aufgelöst hat und danach wird die Mischung (die Sorptionslösung) etwa 1 Stunde lang stehengelassen. Ist für die Analyse ein kleineres Volumen als 200 ml ausreichend, so ist es natürlich erforderlich die der Wasserprobe zuzugebenden Mengen an Salzsäure und Ascorbinsäure entsprechend zu variieren.

Ionenaustauschtrennung

Die Sorptionslösung (siehe oben) wird durch eine mit 4 g des Ionenaustauscherharzes beschickte Säule (die vorher mit 50 ml der Vorbehandlungslösung gewaschen wurde), mit einer dem Gegendruck des Harzbettes entsprechenden Geschwindigkeit (etwa 70 ml/Stunde) fließen gelassen. Anschließend wird mit 10 ml der Vorbehandlungslösung nachgewaschen und das Kupfer mit 100 ml 1*M* Salpetersäure eluiert (Kupfereluat).

Quantitative Bestimmung des Kupfers

Das Kupfereluat (siehe oben) wird auf dem Wasserbad zur Trockne eingedampft, der Eindampfrückstand in 10 ml 1*M* Salpetersäure aufgenommen und die Lösung mittels einer Kapillare in die Luft-Acetylenflamme

gesaugt und die Absorption bei 324,7 nm gemessen. Die Eichkurve wird durch Ansaugen von geeigneten, analog hergestellten Kupferstandardlösungen aufgestellt. Beim Eindampfen des Kupfereluats muß natürlich sehr darauf geachtet werden, daß dieses nicht mit Kupfer verunreinigt wird wie z.B. bei Verwendung eines kupfernen Wasserbades. Enthält der Eindampfrückstand des Kupfereluats eine größere Menge in 1*M* Salpetersäure unlöslicher, organischer Substanzen, so müssen diese durch Naßveraschung mit konzentrierter Perchlorsäure entfernt werden. Zu diesen Zweck wird der Rückstand mit 10 ml Perchlorsäure versetzt und unter einer Infrarotlampe zur Trockne eingedampft. Danach wird der Eindampfrückstand in 5 ml 6*M* Salzsäure aufgenommen, die Lösung auf dem Wasserbad zur Trockne gebracht und wie oben beschrieben weiter verfahren.

Die direkte Kupferbestimmung in den untersuchten Wässern erfolgte durch Ansaugen der 0,1*M* salzsauren Proben (in Abwesenheit von Ascorbinsäure). Unter diesen Bedingungen weist die Empfindlichkeit der Kupferbestimmung für 1% Absorption einen Wert von 0,093 ppm auf.

Zur direkten spektrophotometrischen Bestimmung des Kupfers in Wasserproben wurde die von Kovařik und Vinš[14] beschriebene Methode verwendet. Dieses Verfahren beruht auf Chloroformextraktion des Kupferdiäthyldithiocarbamatkomplexes und Messung der Extinktion bei 500 nm.

Kupferbestimmungen im Kupfereluat können auch spektrophotometrisch nach Zerstörung organischer Substanzen (siehe oben) ausgeführt werden.[68]

Obwohl die zur Abtrennung und Bestimmung des Kupfers benützten Reagenzien nur verschwindend geringe Mengen dieses Elementes enthalten, ist es immer ratsam ihre Kupferkonzentrationen unter Anwendung der oben beschriebenen Arbeitsvorschrift zu ermitteln wobei 200 ml destilliertes Wasser als Wasserprobe eingesetzt wird.

RESULTATE UND DISKUSSION

Stark basische Anionenaustauscher weisen gegenüber Kupfer(II)-ionen eine relativ geringe Selektivität auf, so daß die Adsorption dieses Elementes nur aus Wasserproben erfolgen kann die vorher eingedampft wurden. In diesem Fall ist es möglich das Kupfer, nach Aufnahme des Eindampfrückstandes in einer Methanol–HBr–Mischung, von praktisch allen Begleitelementen auf einer Säule des Harzes Dowex 1, X8 zu trennen und der störungsfreien Bestimmung mittels Atomabsorptionsspektrophotometrie zuzuführen. Dieses Verfahren wurde zur Kupferbestimmung in geologischen Materialien herangezogen,[68] ist aber naturgemäß ohne vorangehendes Eindampfen der Probe nicht zur Kupferanalyse von Wässern geeignet. Ebenso unbrauchbar für diesen Zweck sind Methoden die auf der Adsorption des anionischen Kupfer(II)-chlorokomplexes beruhen, da dieser nur aus 6–10*M* salzsauren Lösungen eine nennenswerte Adsorption auf stark basischen Anionenaustauschern aufweist. Ganz andere Adsorptionsverhältnisse werden jedoch beobachtet, wenn das Kupfer in der einwertigen Form vorliegt; unter diesen Umständen ist es möglich dieses Element aus schwach salzsaurer Lösung als anionischen Kupfer(I)-chlorokomplex an Dowex 1 relativ stark zu adsorbieren.[71] Diese Tatsache wurde zur Isolierung des Kupfers aus *o*-Diphenoloxydase[72] herangezogen und stellt auch das Prinzip der in der vorliegenden Arbeit beschriebenen Abtrennmethode dar.

Durch Messungen der Gleichgewichtsverteilungskoeffizienten des Kupfers an Dowex 1, X8 in verdünnt salzsauren Lösungen, die 5 g Ascorbinsäure pro Liter enthielten, wurden die in Tabelle 1 gezeigten Resultate erhalten aus denen hervorgeht, daß das Kupfer am

Tabelle 1. Verteilungskoeffizienten des Kupfer(I) in Abhängigkeit von der Salzsäurekonzentration (1 g Dowex 1; 1 mg Kupfer gelöst in 20 ml Salzsäure + 100 mg Ascorbinsäure)

Salzsäuremolarität	Verteilungskoeffizient
0,1	480
0,5	397
1,0	274
2,0	202
4,0	72
6,0	32

Tabelle 2. Resultate von Kupferbestimmungen im Wiener Trinkwasser

Volumen der zur Analyse verwendeten Wasserprobe,* *l.*	Kupfergehalt, *µg/l.*	Volumen der zur Analyse verwendeten Wasserprobe,* *l.*	Kupfergehalt, *µg/l.*
0,1	9,8	0,8	9,1
0,2	11,2	0,9	9,0
0,3	10,5	1,0	7,7
0,4	11,8	2,0	5,5
0,5	10,6	3,0	3,7
0,6	10,1	5,0	2,1
0,7	10,0		

* Die Probenahme erfolgte im Mai 1974 im Analytischen Institut der Universität Wien.

Tabelle 3. Einfluß der Kupferkonzentration auf die Kupferausbeute

Der Wasserprobe* zugesetzte Kupfermenge, *µg*	Im 1*M* HNO_3-Eluat wiedergefundene Kupfermenge, *µg*	
	A	B
0	12	2,5
50	38	52
100	80	100
500	280	500
1000	480	970
5000	2300	4600

* Als Wasserprobe wurde Wiener Trinkwasser verwendet.

A = Kupfergehalt des Eluats nach Abtrennung des Kupfers aus einer 1000 ml Wasserprobe.

B = Kupfergehalt des Eluats nach Abtrennung des Kupfers aus einer 200 ml Wasserprobe (siehe Vorbereitung der Wasserprobe).

Tabelle 4. Einfluß von Fremdionen auf die Abtrennung des Kupfers

Der Wasserprobe* zugesetzte Ionen	Kupfergehalt des Eluats, *µg*
20 *µg* Cu + kein Zusatz	19,8
20 *µg* Cu + 1 mg Zn(II) (als Chlorid)	20,4
20 *µg* Cu + 1 mg Cd(II) (als Chlorid)	19,6
20 *µg* Cu + 1 mg Hg(II) (als Chlorid)	19,6
20 *µg* Cu + 1 mg Bi(III) (als Chlorid)	20,2
20 *µg* Cu + 1 mg Sn(II) (als Chlorid)	19,6
20 *µg* Cu + 1 mg Pb(II) (als Nitrat)	19,6
20 *µg* Cu + 1 mg Ag(I) (als Nitrat)	20,4
20 *µg* Cu + 1 mg Au(III) (als Chlorid)	20,0
20 *µg* Cu + 10 mg Cl^- (als NaCl)	19,8
20 *µg* Cu + 100 mg Cl^- (als NaCl)	19,6
20 *µg* Cu + 1000 mg Cl^- (als NaCl)	20,8
20 *µg* Cu + 10 mg SO_4^{2-} (als Na_2SO_4)	19,8
20 *µg* Cu + 100 mg SO_4^{2-} (als Na_2SO_4)	20,0
20 *µg* Cu + 1000 mg SO_4^{2-} (als Na_2SO_4)	19,1
20 *µg* Cu + 100 mg NO_3^- (als $NaNO_3$)	19,6
20 *µg* Cu + 100 mg PO_4^{3-} (als Na_2HPO_4)	19,8
20 *µg* Cu + 100 mg ClO_4^- (als $NaClO_4$)	18,4

* Als Wasserprobe wurden jeweils 200 ml destilliertes Wasser verwendet und unter Anwendung der Arbeitsvorschrift analysiert.

besten aus ascorbinsäurehaltiger 0,1*M* Salzsäure adsorbiert wird, da in dieser der Verteilungskoeffizient den höchsten Wert aufweist. Wie am Beispiel der Bleiadsorption aus 0,15*M* Bromwasserstoffsäure gezeigt wurde[73] (siehe Beitrag V dieser Reihe) ist jedoch auch bei der Kupferadsorption aus 0,1*M* Salzsäure damit zu rechnen, daß diese in Gegenwart von Salzen erniedrigt wird. Besonders deutlich wird dieser Salzeffekt durch die in den Tabellen 2 und 3 gezeigten Ergebnissen von Kupferbestimmungen im Wiener Trinkwasser veranschaulicht. Aus diesen Resultaten geht hervor, daß der in den Wasserproben ermittelte Kupfergehalt sehr stark vom Volumen der Wasserprobe abhängig ist und daß konstante Kupferwerte erst dann erhalten werden wenn das Volumen 700 ml unterschreitet. Werden größere Volumina als diese 700 ml der beschriebenen Anionenaustauschoperation unterworfen, so wird der Kupfer(I)-chlorokomplex in zunehmenden Ausmaß durch die in der Wasserprobe anwesenden Anionen der Erdalkalimetalle (Chloride und Sulfate) vom Harz verdrängt wodurch beträchtliche Kupferverluste eintreten. Auf Grund dieser Tatsache werden bei der Ionenaustauschtrennung nur 200 ml der Wasserprobe verwendet aus der selbst größer Kupfermengen quantitativ am Harz adsorbierbar sind. Diese Tatsache geht aus den in Tabelle 3 gezeigten Versuchsergebnissen hervor und schafft die Möglichkeit diese Methode auch zur Analyse von relativ kupferreichen Wasserproben (z.B. Abwässer aus Industrie und Gewerbe) heranzuziehen.

Bei Anwendung von 200 ml Wasserprobe wird die Adsorption des Kupfers am Anionenaustauscher weder durch die Anwesenheit von als Chlorokomplexen adsorbierbaren Metallionen noch durch hohe Konzentrationen an Anionen (mit Ausnahme von Perchlorat) gestört. Die Ergebnisse diesbezüglicher Untersuchungen werden in Tabelle 4 gezeigt. Bei der Elution des Kupfers mit 1*M* Salpetersäure (siehe Arbeitsvorschrift) werden mit Ausnahme von Gold alle koadsorbierten Ionen zusammen mit dem Kupfer eluiert, rufen aber keinerlei Störungen bei den atomabsorptionsspektrophotometrischen Messungen hervor.

Tabelle 5. Einfluß der Ascorbinsäurekonzentration und Reduktionsdauer auf die Kupferausbeute*

Reduktionsdauer	Ascorbinsäure *g*/200 *ml*	Wiedergefundene Kupfermenge, *µg*					
		0,0	0,1	0,5	1,0	2,0	5,0
15 Minuten		0,0	64	82	102	100	102
30 Minuten		0,0	64	82	100	102	100
1 Stunde		0,0	64	83	100	102	98
2 Stunden		0,0	66	83	98	102	98
5 Stunden		0,0	68	96	100	102	100

* Jeweils 200 ml Wiener Trinkwasser wurden mit 2 ml konzentrierter Salzsäure, 100 µg Kupfer und einer bestimmten Ascorbinsäuremenge versetzt und nach Ablauf der angegebenen Reduktionsdauer durch die Ionenaustauschersäule fließen gelassen.

Untersuchungen hinsichtlich des Einflußes der Ascorbinsäurekonzentration und der Reduktionsdauer auf die Kupferausbeute ergaben die in Tabelle 5 gezeigten Resultate. Aus diesen geht hervor, daß das Kupfer in Gegenwart von 1 bis 5 g Ascorbinsäure/200 ml Wasserprobe und einer Reduktionsdauer von 15 Minuten bis 5 Stunden (Reduktionsdauer = Zeitintervall ab Zusatz der Ascorbinsäure bis zum Beginn der Sorption) quantitativ im Eluat wiedergefunden wurde. In Abwesenheit von Ascorbinsäure wird dagegen überhaupt kein Kupfer vom Anionenaustauscher festgehalten und demzufolge beträgt die im Eluat

wiedergefundene Kupfermenge 0,0 μg (siehe Tabelle 5). Diese Tatsache liefert den eindeutigen Beweis dafür, daß das Kupfer nur als anionischer Kupfer(I)-chlorokomplex adsorbierbar ist*, während Kupfer(II)-ion aus 0,1*M* Salzsäure nicht vom Austauscher festgehalten wird.

Tabelle 6. Elutionsverhalten des auf Dowex 1 (4 g Säule) adsorbierten Kupfer(I)-chlorokomplexes*

Elutionsmittel	Kupfergehalt des Eluats, μg
1. 100 ml 1,5*M* Bromwasserstoffsäure	250
2. 100 ml 3*M* Bromwasserstoffsäure	275
3. 100 ml 6*M* Bromwasserstoffsäure	665
4. 100 ml 9*M* Bromwasserstoffsäure	1050
5. 100 ml 1·5*M* Chlorwasserstoffsäure	215
6. 100 ml 3*M* Chlorwasserstoffsäure	220
7. 100 ml 6*M* Chlorwasserstoffsäure	580
8. 100 ml 9*M* Chlorwasserstoffsäure	845
9. 100 ml 1*M* Salpetersäure	995
10. 100 ml 1*M* Perchlorsäure	985
11. 100 ml 1*M* Schwefelsäure	950

* Jeweils 1000 μg Kupfer wurden aus 200 ml 0,1*M* Salzsäure die 1g Ascorbinsäure enthielt am Ionenaustauscher adsorbiert.

Aus Tabelle 6 ist ersichtlich, daß mittels 1*M* Salpetersäure eine quantitative Elution des Kupfers ermöglicht wird, dagegen aber nicht bei Anwendung von salzsauren bzw. verdünnt bromwasserstoffsauren Lösungen. Ebenso geeignet wie Salpetersäure sind auch perchlor- und schwefelsaure Elutionsmittel (siehe Elutionsmittel 10 und 11 in Tabelle 6).

In Tabelle 7 werden die Resultate von Kupferbestimmungen in 10 aus österreichischen Gewässern stammenden Wasserproben gezeigt. Wie ein Vergleich der in Kolonne A angeführten Kupfergehalte mit den entsprechenden, eingeklammerten Werten derselben Kolonne zeigt, ist eine der Ionenaustauschtrennung vorangehende Zerstörung organischer Substanzen nicht erforderlich. Zu diesen Zweck wurde der angesäuerten Wasserprobe soviel 0,1*M* Kaliumpermanganatlösung zugesetzt bis die Probe eindeutig violett gefärbt war. Nach Ablauf einer Stunde wurden 2 g Ascorbinsäure zugegeben und die Ionenaustauschtrennung wie in der Arbeitsvorschrift angegeben durchgeführt.

Wie ferner aus Tabelle 7 ersichtlich ist, weichen die durch direkte atomabsorptionsspektrophotometrische Messungen ermittelten Kupfergehalte (siehe Kolonne B) sehr häufig von den nach Ionenaustausch des Kupfers gefundenen Resultaten ab. Die Ursache dafür beruht darauf, daß nach Durchführung der Anionenaustauschtrennung (Kolonne A) eine Meßlösung von 10 ml erhalten wird (siehe Arbeitsvorschrift) die eine um einen Faktor 20 höhere Kupferkonzentration aufweist wodurch naturgemäß wesentlich genauere Kupferbestimmungen möglich sind als bei Anwendung der direkten Methode (Kolonne B).

Die durch direkte Spektrophotometrie[14] ermittelten Kupfergehalte (siehe Kolonne C der Tabelle 7) stimmen oft nicht mit den Resultaten der Kolonnen A und B überein woraus geschlossen werden kann, daß in den Wasserproben anwesende Schwermetallionen oder auch andere Bestandteile die spektrophotometrische Kupferbestimmung stören.

* Ein ähnliches Adsorptionsverhalten zeigt auch der Kupfer(I)-bromokomplex welcher bei der Reduktion mittels Ascorbinsäure in 0,15*M* Bromwasserstoffsäure gebildet wird.

Tabelle 7. Resultate von Kupferbestimmungen in österreichischen Wasserproben

Probenbezeichnung und Datum der Probenahme	Kupfergehalt, μg/l. A	B	C
203/1 Diexerbach nördl. von Obertrixen bei Straßenbrücke oberhalb Mühle, Kärnten; 16.7.1973	38,5 (39,5)	37,4	32,0
186/1 Feistritzbach, an der Straße nach Hochfeistritz hinter 4. Straßenbrücke von der Hauptstraße bei Mühle, Kärnten; 16.7.1973	13,0 (13,0)	15,0	20,0
186/2 Tisäckerbach, westl. Eberstein an der Straße nach Kulm bei der 1. Brücke, Kärnten; 16.7.1973	32,5 (32,5)	31,8	32,8
186/3 Schreckenbach östl unter St. Paul, Kärnten; 16.7.1973	33,5 (33,5)	35,5	34,8
187/1 Löllingbach, östl. Lölling, südl. Stöckl, Kärnten; 16.7.1973	28,7 (29,5)	31,8	32,0
116/1 Silzerbach, unterhalb Wasserfall, Tirol; 26 8.1973	29,7 (30,5)	30,0	27,6
145/1 Leonhardsbach, Oberangern, Tirol; 26.8.1973	23,0 (23,0)	22,4	20,0
S 11 Stuhlfeldnerbach oberhalb Stuhlfelden, Pinzgau, Salzburg; 16.6.1973	15,3 (15,3)	15,0	20,0
117/3 Reitherbach, Tirol; 26.8.1973	32,5 (32,5)	35,5	26,4
117/4 Zirlerbach, Tirol; 26.8.1973	33,5 (34,5)	37,4	25,0

A = Atomabsorptionsspektrophotometrisch bestimmter Kupfergehalt nach vorangehender Ionenaustauschtrennung. Die eingeklammerten Zahlen geben den Kupfergehalt an der nach Zerstörung der in der Wasserprobe anwesenden organischen Substanzen ermittelt wurde.

B = Kupfergehalt bestimmt durch direkte Atomabsorptionsspektrophotometrie (ohne vorangehende Ionenaustauschtrennung).

C = Kupfergehalt bestimmt durch direkte Spektrophotometrie[14] (ohne vorangehende Ionenaustauschtrennung).

Die beschriebene Methode wurde auch zur Bestimmung des Kupfers in der Fresh Water Sample W-3 (International Atomic Energy Agency, Intercomparison Run, June–December 1973) herangezogen und ein Kupfergehalt von 16,0 ppM ermittelt. Der theoretische Kupfergehalt dieser Probe wird mit 14,6 ppM angegeben.

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Summary—A method is described which makes it possible to separate ppM levels of copper from natural waters and complete the determination by atomic-absorption. The sample is made 0·1*M* in hydrochloric acid, filtered, treated with ascorbic acid and passed through Dowex 1 X8 (chloride form). The anionic copper(I) chloro-complex is sorbed and the copper separated from most other elements present. After elution with 1*M* nitric acid, the copper is determined by atomic absorption. The method has been used to determine copper concentrations in the range 10–39 ppM, in some Austrian waters.

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BESTIMMUNG VON ZINK IN SALZSÄURE, GALLIUMARSENID UND GALLIUMALUMINIUMARSENID DURCH FLAMMENLOSE ATOMABSORPTION

K. DITTRICH und W. ZEPPAN

Sektion Chemie der Karl-Marx-Universität, Leipzig-701, Liebigstraße 18, DDR

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Zusammenfassung—Ein Eigenbau-AAS-Gerät und Kohlenstabatomisator wurden verwendet und hier beschrieben. Die apparativen Parameter wurden optimiert. Der Einfluß der Matrix auf die Empfindlichkeit der Bestimmung sowie die Ursachen der unspezifischen Absorption werden diskutiert. Die Nachweisgrenze der Methode liegt je nach Bedingungen bei 2–25 × 10^{-11}g bzw. 3–20 ppM bezogen auf 1 ml 1*M* Salzsäure oder 2,5–30 ppm bezogen auf 0,1–1 mg Galliumarsenid.

Über die Bestimmung von Zinkspuren mittels flammenloser Atomabsorption vor allem in organischen Materialien und verdünnten Lösungen wurden bereits einige Methoden veröffentlicht.[1–5]

Die hohe Empfindlichkeit, die guten Nachweisgrenzen und die gute Reproduzierbarkeit der flammenlosen Atomabsorption lassen diese Methode für die Bestimmung von Zinkspuren in Mikroausgangsmengen als geeignet erscheinen.

Unsere Aufgabe war es, Zinkspuren in Salzsäure, Galliumarsenid-und Galliumaluminiumarsenid-Materialien zu bestimmen. Das Zink wird als Dotierungselement in $A_{III}B_V$-Halbleiter eingebaut, ist aber auch oft als Verunreinigung in diesen enthalten. Sowohl für die Kontrolle des Herstellungsprozesses als auch für die Bestimmung der Eigenschaften des Halbleitermaterials ist die Ermittlung der Dotierungskonzentration von großer Bedeutung. Die Methode sollte anwendbar sein für Ausgangsmengen von 0,1 bis 10 mg Halbleitermaterial und zur Zeitersparnis und Verminderung der Verunreinigungsgefahr ohne Abtrennung der Matrix erfolgen. Wir wendeten einen von uns entwickelten elektrothermischen Atomisator, der dem Konzept von Belyaev[6] entsprach, für die Bestimmung an und untersuchten die Matrixeffekte über das Verdampfungsverhalten der Substanz.

EXPERIMENTELLER TEIL

Apparatur

Für alle Untersuchungen benutzten wir ein Eigenbau-Atomabsorptionsspektralphotometer entsprechend unserer früheren Mitteilung,[7] in dem die Zerstäuber–Brenner-Kombination durch einen elektrothermischen Atomisator ersetzt wurde.

Die Abbildung 1 zeigt die Auf- und Seitenansicht des Atomisators. Der Atomisator ist in der Höhe, in der Richtung zur optischen Achse und im rechten Winkel zu dieser bewegbar (Justierschrauben F). Zwischen die Kontaktflächen (K) der beiden Graphitbacken (C) werden kurze, runde Graphit- oder Kohlestäbe geklemmt, auf die die Analysenlösungen mittels einer Mikrolitерspritze bzw.-pipette aufgegeben werden können. Die Graphitbacken haben eine Stärke von 5 mm. Die Probeträger (siehe Abb. 2) wurden aus Spektralkohlen der Qualität T O (VEB EKL Berlin, DDR) hergestellt. Die Probeträger wurden durch Wechselstrom, der über die Kontakte (A—Abb. 1) zu den Graphitbacken geleitet wird, aufgeheizt. Zwei Niederspannungstransformatoren gestatten es, Ströme bis zu 800 A bei maximal 10 V (Parallelschaltung) bzw. 400 A bei maximal 20 V (Reihenschaltung) an die Kontakte zu legen. Zur Erreichung der gewünschten Probeträgertemperatur erfolgte die Einstellung der Stromparameter auf der Primärseite über einen Regeltransformator vom Typ SST 250/20, der an einen automatischen Spannungskonstanthalter vom Typ NR 220/20 angeschlossen war.

Die Kontrolle von Spannung und Stromstärke erfolgte auf der Primär- und Sekundärseite durch entsprechende Meßinstrumente. Die Registrierung der Absorptionssignale erfolgte mittels eines Kompensationsbandschreibers vom Typ G_1B_1 (VEB C. Zeiss, Jena), der eine Einstellzeit für den Vollausschlag von 1 Sekunde besitzt. Als Meßgröße verwendeten wir die Peakhöhe des Absorptionssignals.Folgende apparative Parameter wurden eingestellt: Lampenstrom 6 mA, Spaltbreite 100 μm, Zinklinie 213,9 nm.

Reagenzien

Zinkchlorid-Lösung, hergestellt aus $ZnSO_4 . 7H_2O$ und 1*M* HCl

Galliumchlorid-Lösung, hergestellt aus 99,9999%igem Gallium und HCl suprapur.

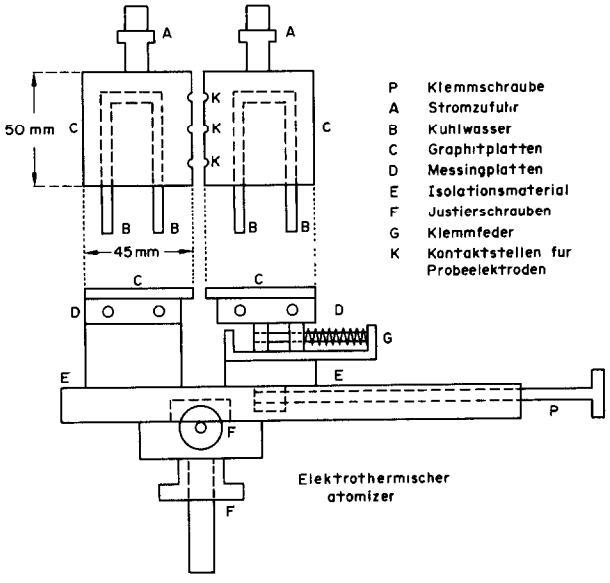

Abb.1. Schema des elektrothermischen Atomisators.

Arsensäure-Lösung, hergestellt aus As_2O_3 *p.a.*
Aluminiumchlorid-Lösung, hergestellt aus 99,999%igem Aluminium und HCl Suprapur.
Salzsäure. Suprapur konzentrierte und 1*M*.
Salpetersäure. Suprapur, konzentrierte.
Galliumarsenid und *Galliumaluminiumarsenid* mit und ohne Zinkdotierung.

Allgemeine Arbeitsvorschrift

Die Herstellung der zu analysierenden Lösungen des GaAs, $Ga_{0,9}Al_{0,1}As$ und der einzelnen Komponenten erfolgte durch Auflösen der Substanzen in einem 1:1 Gemisch suprapurer konzentrierter Salz- und Salpetersäure in staubarmer Atmosphäre. Diese Lösungen wurden eingedampft und in 1*M* Salzsäure aufgenommen. Von diese Lösungen wurden 1–50 µl auf den Probeträger des Atomisators gegeben. Es wird in Abhängigkeit vom Lösungsvolumen 10–15 Sekunden bei 90° (1,1 V) und 5–7 Sekunden bei 140° (1,3 V) getrocknet und anschließend durch elektrische Erwärmung bei Atomisatorspannungen zwischen 3 und 5 V (s.u.) verdampft.

RESULTATE UND DISKUSSION

Zinkbestimmung in Salzsäure

Optimierung der apparativen Parameter

Zur Erreichung reproduzierbarer, vom Aufzeichnungssystem unabhängiger Signale ist es erforderlich, die Signaldauer größer als die Einstellzeit des Aufzeichnungssystems zu gestalten,[8] da sonst das Signal vom Aufzeichnungssystem beeinflußt wird. Die Steuerung der Signaldauer ist über folgende Parameter möglich: (*a*) die Form und die Dimension des zu erhitzenden Probeträgers; (*b*) die Größe der Atomisatorspannung und die Geschwindigkeit, mit der die Atomisatorspannung an den Atomisator angelegt wird; (*c*) die durch den Atomisator strömende Gasmenge.

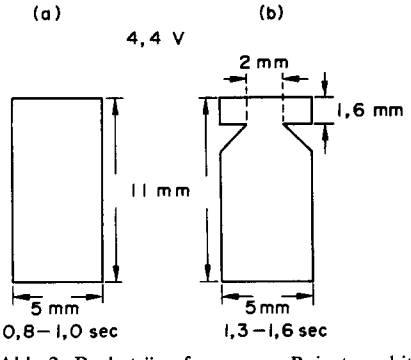

Abb. 2. Probeträgerformen aus Reinstgraphit.

Wir testeten den Einfluß der Probeträgerform und den der Größe der Atomisatorspannung auf die Signaldauer. Die benötigte Spannung wurde reproduzierbar mit der gleichen Geschwindigkeit an den Atomisator angelegt. Die Optimierung erfolgte für Zinksalze.

Es kamen zwei Probeträger zum Einsatz (siehe Abb. 2). Die Absorptionssignale wurden mit einem Impulsoszillographen registriert. Die Zeit, gemessen vom Beginn des Zinkabsorptionssignals bis zu dessen Maximum, vergrößert sich für die Form *b* gegenüber der Form *a* von 1,0 auf 1,5 Sekunden. Die Ursache hierfür ist der an der Verjüngung des Probeträgers der Form *b* entstehende Wärmestau. Hieraus resultiert eine langsamere Erwärmung des oberen Teiles des Probeträgers, eine langsamere Verdampfung der Zinkteilchen und damit ein länger dauerndes Signal. Wir wählten aus den genannten Gründen die Probeträgerform *b* für alle weiteren Messungen aus. Der Einfluß der Atomisatorspannung auf die Höhe und Form des Absorptionssignales konnte bei der Probeträgerform *b* bereits mit dem Schreiber ermittelt werden.

Einfluß der Atomisatorspannung

Auf der Abbildung 3 wird für drei Atomisatorspannungen die Abhängigkeit der Absorption von der Zeit dargestellt. Die Signale wurden mit einer Schreibergeschwindigkeit von 10 mm/sec aufgezeichnet. Es ist zu sehen, daß sich die Signaldauer mit zunehmender Spannung verkürzt. Bei den Spannungen 4,4 V und 5 V wird außerdem ein Schreiberausschlag über die 0%-Absorptionslinie sichtbar. Dieser Ausschlag entspricht einer Emission, die durch die Strahlung des glühenden Probeträgers verursacht wird. Damit ergeben sich zwei Ursachen für die Abnahme der Signalhöhe oberhalb der Atomisatorspannung von 4,4 V: die Kontinuumstrahlung des glühenden Probeträgers und die Trägheit des Aufzeichnungssystems bezogen auf die Verdampfungsgeschwindigkeit.

Um die störende Strahlung des Probeträgers ohne Modulation des Lichtes der Hohlkathodenlampe auszuschalten, setzten wir vor den Monochromatorspalt eine Blende, die das gesamte Abbild des Probeträgers ausblendete. Bei der Atomisatorspannung von 4,4 V erreichten wir dadurch eine etwas vergrößerte Empfindlichkeit. Für noch höhere Atomisatorspannungen resultiert keine zusätzliche Empfindlichkeitssteigerung. Die mit steigender Spannung zunehmende Schnelligkeit der Zinkverdampfung beeinflußt demnach die Signalhöhe stärker. Der Schreiber kann den schnellen Signaländerungen nicht mehr befriedigend folgen.

Eine Untersuchung der Kühl- und Transportwirkung des den Atomisator umgebenden Gases erfolgte nicht, da dieser Effekt in unserem Fall nur durch Konvektion bestimmt wurde.

Stellung des Probeträgers zum Strahlengang der HKL

Bekanntlich ist die Lebensdauer der für die atomare Absorption verantwortlichen freien Atome bei der gewählten Atomisierungsart begrenzt. Ihre größte Konzentration wird jeweils nur in einem sehr begrenzten Volumen oberhalb des Atomisators gefunden.[9–10] Die Anzahl der freien Atome verkleinert sich mit zunehmender Entfernung

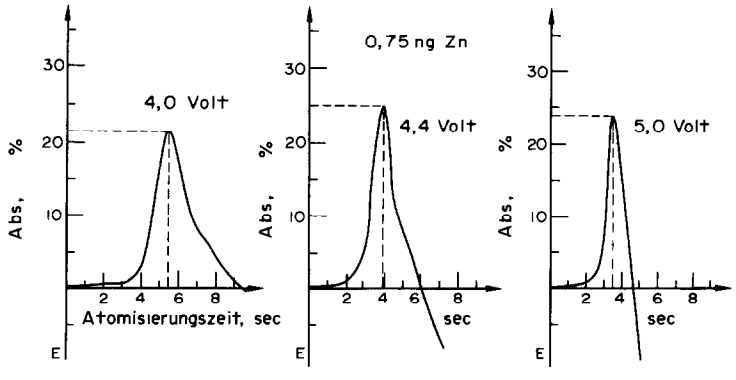

Abb. 3. Abhängigkeit der Absorption von der Zeit bei verschiedenen Atomisatorspannungen.

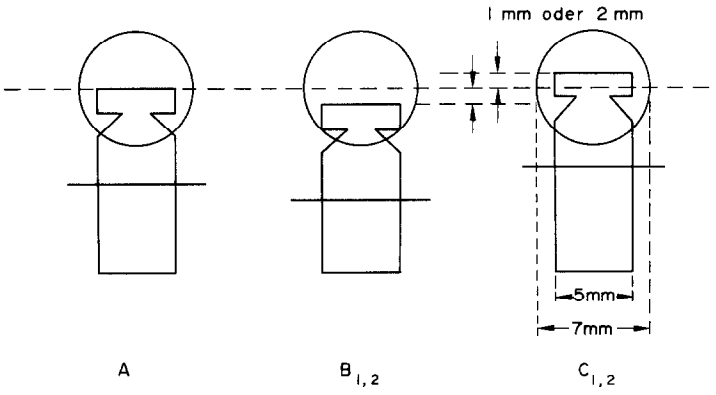

Abb. 4. Untersuchte Stellungen des Probeträgers relativ zum Abbild der Hohlkathodenlampe.

vom Probeträger durch Kondensation der Atome in der kalten Atmosphäre und durch chemische Reaktionen mit den Gasteilchen der Luft. Wir untersuchten die in Abb. 4 gezeigten Stellungen des Probeträgers zum Lichtfleck der Hohlkathodenlampe. Die Positionen A und C_1 ergeben die größten Absorptionssignale. Aus diesem Grunde wurde der Probeträger stets so einjustiert, daß sein oberes Ende im Lichtfleckzentrum der Hohlkathodenlampe stand.

Untersuchungen zur Reproduzierbarkeit

Infolge des Arbeitens ohne Schutzgasatmosphäre treten durch Verbrennen des Kohlenstoffs des Probeträgers und an den Kontaktstellen der Graphitbacken des Atomisators Veränderungen auf. Durch diesen Abbrand verkleinern sich die Probeträger, die Dimensionen der Kontaktflächen und damit die elektrische Leitfähigkeit. Diese Veränderungen können Anlaß für unterschiedliche Absorptionssignale für ein und dieselbe Zinkkonzentration sein. Außerdem beobachteten wir eine zunehmende Porösität des Probeträgers.

Zur Klärung des Einflusses dieser Abbrandeffekte auf die Reproduzierbarkeit der Zinkabsorptionssignale wurden für eine Zinkkonzentration auf drei Probeträgern je 10 Absorptionssignale aufgenommen (siehe Tabelle 1). Vergleicht man die Werte der Spalte 4 untereinander, so ist keine auf einem systematischen Fehler beruhende Abweichung festzustellen.

Diese Untersuchungen wurden in gleicher Weise für 5 verschiedene Zinkmengen durchgeführt und ergaben entsprechende Ergebnisse. Wir können demnach feststellen, daß die oben aufgeführten Abbrandeffekte an den Probeträgern und den Graphitbacken die Reproduzierbarkeit der Zinkabsorptionssignale innerhalb von 10 Messungen nicht verschlechtern. Damit wurde nachgewiesen, daß die Verwendung einer Inertgasatmosphäre bei den verhältnismäßig niedrigen Temperaturen der Zinkbestimmung nicht notwendig ist.

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Der Probeträger wird so zwischen die Graphitbacken des Atomisators eingespannt, daß sein unteres Ende mit den unteren Enden der Graphitbacken eine Fläche bildet und sein oberes Ende im Lichtfleckzentrum der Hohlkathodenlampe steht. Vor der ersten Messung wird jeder Probeträger gereinigt, indem 10 Sekunden eine Spannung von 5 V angelegt wird.

Die Lösungen werden mit einer Mikroliterpipette auf den Probeträger gegeben. Danach wird in Abhängigkeit vom Lösungsvolumen (s.o.) getrocknet und bei 4,4 V atomisiert. Die Emission des glühenden Probeträgers wird

Tabelle 1. Überprüfung der Reproduzierbarkeit der Absorptionsmessungen

Probeträger	Zahl der Messungen	Mittelwert, % Absorption	Abweichung der Signale vom Mittelwert in Prozent (rel.)
1	10	37	4
2	10	37	1
3	10	34,5	7,5
1,2,3	30	36	5

Tabelle 2. Ergebnisse der atomabsorptionsspektralphotometrischen Zinkbestimmung

Lösungsvolumen, µl	Temperatur des Probeträgers, °C	Empfindlichkeit bez. auf 1% Abs., pg	Konzentrationsgebiet mit linearer Extinktionsfunktion, ng	Nachweisgrenze (2s-Krit.) abs., pg	Nachweisgrenze (2s-Krit.) rel., ppM*	Variationskoeffizient 0,5 ng Zn, %
1	20	21	0,07–1,0	20	20	18
10	20	31	0,2–3,0	150	15	15
10	90	26	0,2–2,0	120	12	16
50	90	29	0,2–3,0	150	3	14

* Parts per milliard.

durch eine Blende am Monochromatorspalt ausgeschaltet. Als Meßgröße wird die Peakhöhe des Zinkabsorptionssignales ausgewertet. Nach Umrechnung in Extinktionswerte erfolgt die Errechnung der Ausgleichsgeraden, der Standardabweichungen und der Variationskoeffizienten mit Hilfe eines Rechenprogrammes am Kleinrechner C 8205. Die Tabelle 2 gibt die von uns ermittelten Ergebnisse an.

Zinkbestimmung GaAs-haltiger Lösungen

Untersuchung des Absorptionssignals

Gegenüber einer reinen 1*M* salzsauren Zinklösung, die einen einzigen Absorptionspeak bei flammenloser Verdampfung ergibt, erhalten wir für 1*M* salzsaure Zinklösungen, in denen GaAs- und GaAlAs-Matrix aufgelöst war, bei einer Papiervorschubgeschwindigkeit des Schreibers von 30 mm/min ein deutliches Mehrpeaksignal (Abb. 5).

Der 2. Peak ist der spezifische Zinkpeak. Seine Höhe ist von der vorhandenen Zinkmenge abhängig. Die beiden anderen Peaks sind unspezifisch, ihre Höhe hängt von der im Probenvolumen anwesenden Menge der Matrix ab. Auch die Höhe des Zinkpeaks wird von der Menge der Matrix beeinflußt.

Durch Messungen mit der Zink-Hohlkathodenlampe und einer Deuteriumlampe wurde versucht, die verschiedenen Absorptionsanteile an der Stelle des Zinkpeaks (213,9 nm) aufzuklären (siehe Tabelle 3). Tabelle 3 zeigt, daß etwa 3% der Absorption durch die thermische Ausdehnung des Graphitprobeträgers entstehen. Der von der Matrixkonzentration abhängige, unspezifische Signalanteil entsteht vorwiegend durch Lichtstreuung schnell kondensierter Matrixspezies. Der spezifische Signalanteil wird durch Zinkblindgehalte der Matrix und der Reagenzien hervorgerufen. Wie aus der Tabelle 3 zu entnehmen ist, waren die Blindgehalte relativ konstant. Aus weiteren Untersuchungen ging hervor, daß sie sich bezogen auf ein Probevolumen von 10 µl für eine GaAs-Matrixkonzentration von 1 mg/ml zwischen 300 und 600 pg Zink und für eine GaAs-Matrixkonzentration von 10 mg/ml zwischen 600 und 800 pg Zink bewegten. Daraus ist zu entnehmen, daß nicht so sehr das zu untersuchende Material als vielmehr das Lösungsmittel und der Lösungsprozeß für die Verunreinigung verantwortlich sind.

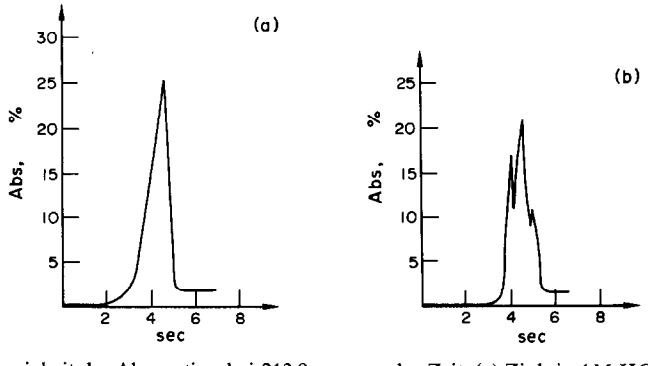

Abb. 5. Abhängigkeit der Absorption bei 213,9 nm von der Zeit. (*a*) Zink in 1*M* HCl, (*b*) Zink in 1*M* HCl in Gegenwart von GaAs-Spezies.

Tabelle 3. Die Abhängigkeit der Absorption bei 213,9 nm (Zn) von der Konzentration an GaAs. (Probevolumen: 10 µl; Atomisatorspannung: 4,4 V)

GaAs bzw. $Ga_{0,9}Al_{0,1}As$, *mg/ml*	Extinktion gemessen mit der Deuteriumlampe bei 213,9 *nm*	Extinktion gemessen mit der Zink-Hohlkathodenlampe bei 213,9 *nm*	spezifische Extinktion
1	0,018*	0,071	0,053
5	0,022*	0,075	0,053
10	0,029*	0,092	0,063
25	0,043*	0,102	0,059

* 0,013 Extinktionseinheiten sind auf die thermische Ausdehnung des Probeträgers zurückzuführen.

Einfluß der Atomisatorspannung auf die spezifische Absorption

Es wurde der Einfluß der Atomisatorspannung zwischen 4,0 und 5,0 V in Gegenwart verschiedener Matrixmengen auf die Signalhöhe des Zinkpeaks untersucht: 4,4 V ergab sich als optimale Atomisatorspannung. Sowohl bei höheren als auch bein niedrigeren Atomisatorspannungen ergaben sich verminderte Empfindlichkeiten. Die Abnahme der Empfindlichkeit bei niedrigeren Spannungen wird verursacht durch die Verminderung der Verdampfungsgeschwindigkeit des Zinks infolge der Matrix. Das relativ langsame Aufzeichnungssystem und Matrixeffekte im Plasma sind die Ursache für die Abnahme der Empfindlichkeit bei höheren Spannungen.

Einfluß der Lösungsmenge auf die spezifische Absorption

Es wurden Lösungsvolumina zwischen 1 und 10 µl untersucht. Die Empfindlichkeit ist bei kleinen Probevolumina größer. Eine lineare Abhängigkeit der Extinktion findet man für 1 µl bis zu 1 ng Zink und für 10 µl bis zu 3 ng Zink. Wird die matrixhaltige Probelösung auf einen auf 90° erwärmten Probeträger gegeben, so ergibt sich bei einem Probevolumen von 10 µl eine geringfügige Empfindlichkeitssteigerung.

Untersuchung der Matrixeffekte

Als Matrixeffekte bezeichnen wir Wechselwirkungen zwischen den Spezies des zu bestimmenden Elementes und Spezies der Probe, der Umgebungsatmosphäre und des Probeträgers. Diese Wechselwirkungen können sich auf die Richtigkeit, Genauigkeit und Empfindlichkeit der Bestimmung auswirken, sie können in der Gasphase und in der kondensierten Phase erfolgen, und sie können chemischer und physikalischer Natur sein.

Wir stellten fest, daß die GaAs- und die GaAlAs-Matrix einen Depressionseffekt auf die Absorption freier Zinkatome ausübt. Die Steigungen der Eichgeraden der Zinkbestimmung nehmen mit steigendem Matrixgehalt im Probevolumen ab (s. Abb. 6). Die Ursachen dieses Depressionseffektes sind folgende: Die Zinkatome verdampfen in die relativ kalte Atmosphäre über dem Proberträger. Dort bilden sie durch Oxydation und Kondensation größere Teilchen, die für die spezifische Absorption nicht zur Verfügung stehen. Diese Kondensation erfolgt wesentlich stärker in Gegenwart eines Überschusses anderer Spezies, vor allem, wenn diese einen sehr hohen Siedepunkt besitzen (z.B. Ga, Al und deren Oxide). Diese Spezies können als Kondensationskeime wirken, die die Zinkatome einschließen. Sie können dabei Mischkristalle und auch Verbindungen bilden. Alle diese Effekte führen zur Verminderung der Zahl der freien, zur Absorption fähigen Zinkatome im Plasma. Die Verwendung eine Argonatmosphäre bringt in dieser Hinsicht ebenfalls keine Vorteile, da auch die nichtoxydierten Teilchen infolge des hohen Siedepunktes und der verhältnismäßig niedrigen Temperaturen schnell kondensieren. Auch Festkörperreaktionen im Probeträger sind zu berücksichtigen. Entsteht z.B. während des Trocknungs-und Verdampfungsprozesses ein zinkhaltiges, schwerflüchtiges Ga_2O_3-Teilchen, so ist die Verdampfung des Zinks gegenüber der Verdampfung aus einem Rückstand, der aus einer salzsauren Zinklösung verbleibt, auf jeden Fall verzögert. Dies führt ebenfalls zu einer Redu-

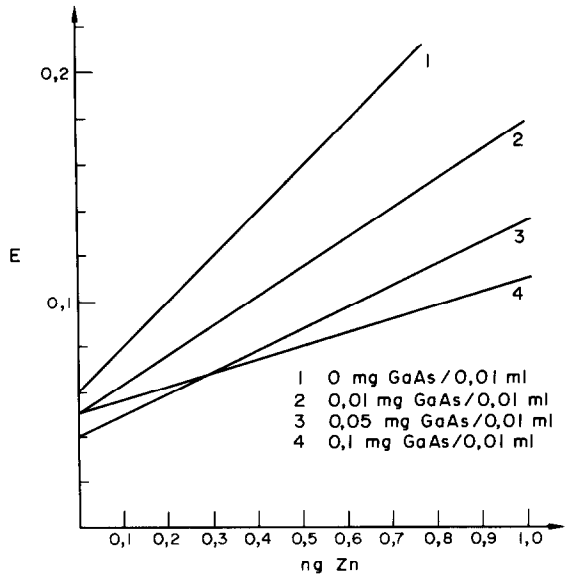

Abb. 6. Abhängigkeit der Empfindlichkeit der Zinkbestimmung von der Matrixkonzentration.

zierung der maximalen Konzentration der freien Zinkatome im Plasma. Zur eingehenden Untersuchung der unspezifischen Matrixeffekte wurden die Absorptionssignale bei 213,9 nm in 1*M* salzsaurem Medium in Anwesenheit der GaAs oder GaAlAs-Matrix bei einer Papiervorschubgeschwindigkeit des Schreibers von 10 mm/sec aufgezeichnet. Es ergaben sich die in Abb. 7 gezeigten Signale. In der Abb. 7 sind fünf Peaks zu sehen, die in einem Zeitraum zwischen 1,5 und 6,5 sec nach Zuschalten der Atomisatorspannung erscheinen.

Für eine Zuordnung der aufgezeichneten unspezifischen Peaks zu bestimmten Spezies ist eine Temperaturbestimmung und eine Elementbestimmung erforderlich. Da die Temperaturmessung dieses Plasmas sehr schwierig ist, wurde die Temperatur des Probeträgerkopfes mit einem Pt–Pt/Rh-Thermoelement bestimmt. Das Thermoelement, das an der Verbindungsstelle zu einer Kugel zusammengeschmolzen wurde, wurde in eine kleine Bohrung auf der Oberfläche des Probeträgers gebracht. Zur besseren Kontaktnahme zwischen Thermoelement und Probeträger wurde in die Bohrung Kohlepulver gestopft und das Thermoelement mit PVC-Leim befestigt. Der Fehler der Temperaturmessung liegt bei etwa $\pm$ 30°. Das Ergebnis der Temperaturmessung ist Abb. 8 zu entnehmen. Ein Vergleich der Abbildungen 7 und 8 ermöglicht es, den 5 Peaks folgende Temperaturen zuzuordnen.

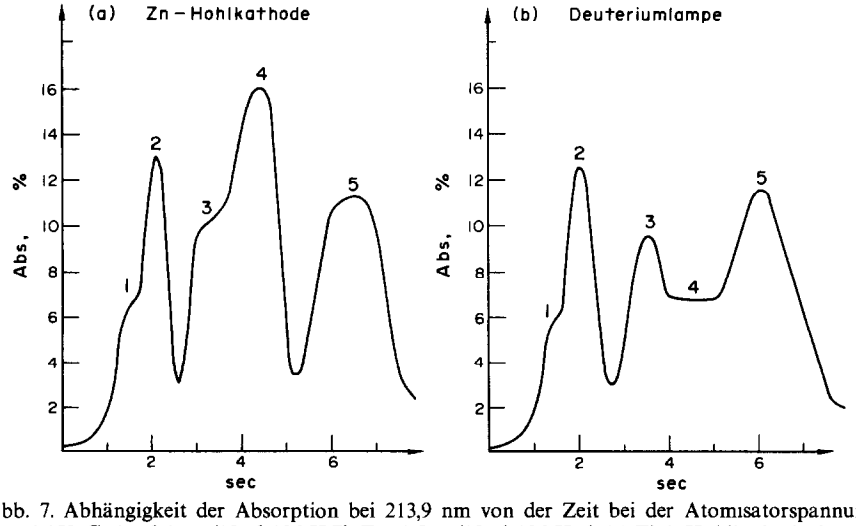

Abb. 7. Abhängigkeit der Absorption bei 213,9 nm von der Zeit bei der Atomisatorspannung von 4,4 V. GaAs: 0,1 mg/10 µl 1*M* HCl, Zn: 0,5 ng/10 µl 1*M* HCl. (*a*) Zink-Hohlkathodenlampe, (*b*) Deuteriumlampe.

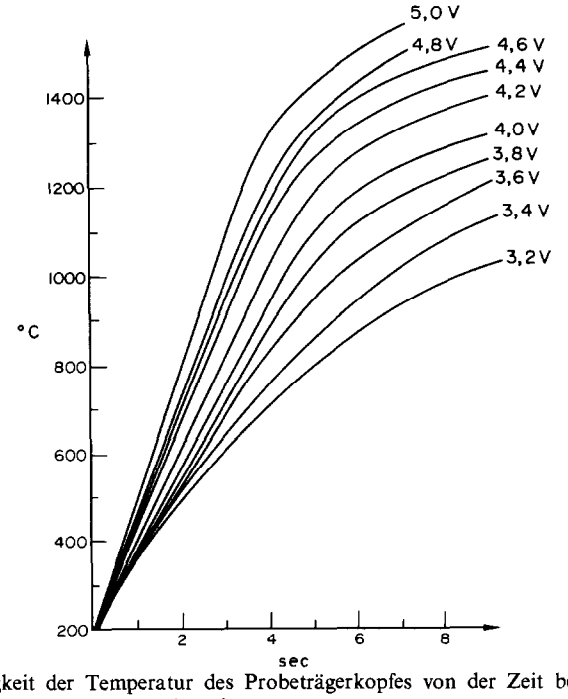

Abb. 8. Abhängigkeit der Temperatur des Probeträgerkopfes von der Zeit bei verschiedenen Atomisatorspannungen.

1. Peak 360–540°
2. Peak 550–750°
3. Peak 900–1100°
4. Peak 1100–1160°
5. Peak 1360–1410°

Zur Bestimmung der Elemente, die für die unspezifischen Peaks verantwortlich sind, wurden 1*M* salzsaure Lösungen mit einem Gehalt von GaAs 10 mg/ml bzw. Ga 5 mg/ml bzw. As 5 mg/ml untersucht. Es wurde die Absorption zinkhaltiger und zinkfreier Lösungen vermessen. Das eingesetzte Probevolumen war 10 μl, die Atomisatorspannung 4,4 V und die Papiervorschubgeschwindigkeit des Schreibers 10 mm/sec.

Abbildung 9 stellt die Ergebnisse dar. Es ist zu erkennen, daß Peak 1 und 2 dem Arsen, Peak 3 und 5 dem Gallium und Peak 4 dem Zink zuzuordnen sind. Es ist möglich, durch programmierte Temperatur das Arsen aus dem Probeträger zu entfernen. Dies bringt jedoch in analytischer Hinsicht keinen positiven Effekt, so daß auf dieser Basis keine Bestimmungsmethode ausgearbeitet wurde.

Berücksichtigt man, daß die 1*M* salzsauren Lösungen folgende Ionen enthalten: Ga^{3+}, AsO_4^{3-}, Al^{3+}, Zn^{2+} und Cl^-, so befinden sich nach dem Trocknungsprozeß im Probeträger folgende Verbindungen: As_2O_5, $GaCl_3$, $ZnCl_2$, ZnO, GaOCl, $GaAsO_4$, $Zn_3(AsO_4)_2$.

Diese Verbindungen können bei den festgestellten Peaktemperaturen hauptsächlich wie folgt reagieren.

1. $As_2O_5 \xrightarrow{315°} As_2O_3 + O_2$
2. $As_2O_3 + 3C \xrightarrow{400\text{–}500°} 2As + 3CO$
3. $GaCl_3, GaOCl, Ga(OH)_3 \xrightarrow{200\text{–}500°} Ga_2O_3$
4. $Ga_2O_3 + 3C \xrightarrow{600°} Ga_2O \xrightarrow{600°} 2Ga + 3CO$
5. $Ga_{feinverteilt} + 1/2N_2 \xrightarrow{1000°} GaN$
6. $2Ga + 2C \xrightarrow{1200°} Ga_2C_2$
7. $GaAsO_4 + 4C \xrightarrow{500\text{–}1000°} Ga + As + 4CO$

Die Reaktion 5 halten wir für möglich, da Gallium mit Ammoniak bei 1100° und pyrophores Gallium bereits bei 100° zu Galliumnitrid reagieren.[11] In unserem Fall liegt feinverteiltes Gallium vor: eine Reaktion mit Stickstoff bei 1000° ist also nicht auszuschließen. Das nach Reaktion 6 gebildete Galliumcarbid ist im Dampfzustand stabil im Gleichgewicht mit Galliumdampf und festem Kohlenstoff.[11]

Lösungen in denen 10% des Gallium durch Aluminium ersetzt waren, zeigten im Signalbild keinen Unterschied zu reinen Galliumlösungen gleicher Konzentration. Reine Aluminiumlösungen (Al bis zu 2,5 mg/ml) ergeben kein unspezifisches Absorptionssignal bei 213,9 nm. Das ist verständlich, wenn man berücksichtigt, daß das entstehende Aluminiumoxid (Fp 2050°) erst ab 1565° mit dem Kohlenstoff des Probeträgers zu verdampfbarem Aluminiumcarbid reagiert. Durch Kombination der Elementbestimmung und Temperaturmessung ergeben sich folgende Schlußfolgerungen für die Ursachen der unspezifischen Peaks.

1. Peak: Temperatur: 360–540°, Element: As. Es handelt sich um As_2O_3 (Kp 465°), welches in geringem Ausmaß parallel zur Reaktion 2 verdampft.

2. Peak: Temperatur: 450–750°, Element: As. Es handelt sich um sublimiertes, elementares Arsen oder dessen Folgeoxydationsprodukte.

3. Peak: Temperatur: 900–1100°, Element: Ga. Es handelt sich um sublimiertes Ga_2O (Sblp. 600°), welches als Zwischenprodukt nach Reaktion 4 entsteht. Evtl. kann auch GaN, das nach Reaktion 5 entstehen könnte, zur Absorption bzw. Streuung beitragen.

4. Peak: Temperatur: 1100–1160°, Element: Zn.

5. Peak: Temperatur: 1360–1410°, Element: Ga. Es handelt sich um Galliumcarbide, die nach Reaktion 6 entstehen.

Weiterhin ist aus der Abbildung 9 zu erkennen, daß die spezifische Absorption, die 1 ng Zink in 10 µl hervorruft, sehr von der Matrixart abhängt. Der höchste Wert wird für

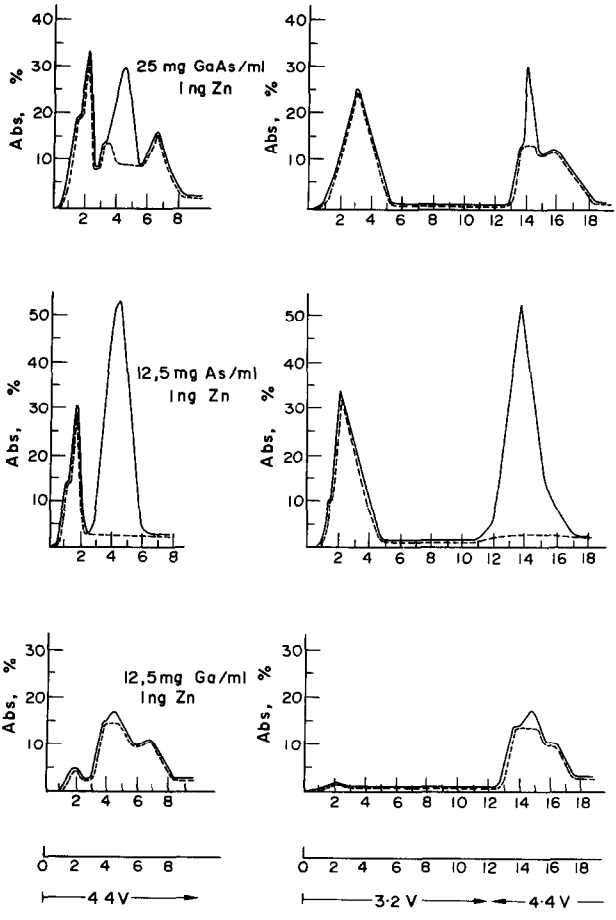

Abb. 9. Abhängigkeit der Absorption bei 213,9 nm von der Zeit für Zinkspuren in 1*M* HCl in Gegenwart verschiedener Matrices. —— Zink-Hohlkathodenlampe; ---- Deuteriumlampe.

arsenhaltige Lösungen, der kleinste für nur galliumhaltige Lösungen erhalten. Daraus ist zu schlußfolgern, daß in der Verdampfungsbeeinflussung des Zink die eigentliche Depressionsursache für die spezifische Absorption zu sehen ist und Matrixeffekte im Plasma nur eine geringe Rolle spielen.

Verwunderlich erscheinen zunächst die Werte für Lösungen, die nur Gallium bzw. Galliumarsenid-Spezies enthalten. Wahrscheinlich bildet sich im Probeträger beim Trocknungsprozeß in Gegenwart von Galliumarsenid-Spezies neben Galliumtrioxid eine größere Menge Galliumarsenat. In arsenfreien Lösungen entsteht beim Trocknungsprozeß fast nur Galliumtrioxid. Das Galliumtrioxid ist schwer flüchtig und hält das eingeschlossene Zink sehr stark fest, das Galliumarsenat dagegen zersetzt sich bei steigender Temperatur über Galliumarsenid zu Gallium und Arsen, welches sich verflüchtigt. Infolge dieser Zersetzung des Galliumarsenats wird das in diesen Partikeln enthaltene Zink freigesetzt und kann verdampfen.

Arbeitsvorschrift für die Bestimmung des Zink in GaAs und $Ga_{0,9}Al_{0,1}As$

Für die Bestimmung des Zinkgehaltes in GaAs und $Ga_{0.9}Al_{0.1}As$ werden Probemengen von 0,1 bis 10 mg in kleine Teflonbecher eingewogen. Die Substanzen werden mit 0,1 bis 1 ml eines Gemisches aus konzentrierter Salzsäure und konzentrierter Salpetersäure (1:1) gelöst. Nach Beendigung der spontan einsetzenden Reaktion wird die Säure vorsichtig abgedampft. Der Rückstand wird in 0,1 oder 1,0 ml 1*M* Salzsäure (je nach Einwaage) aufgenommen. Wegen der Verunreinigungsgefahr ist während der Probenvorbereitung möglichst unter völligem Staubausschluß zu arbeiten. Es ist aus dem gleichen Grund empfehlenswert, sofort nach der Probenvorbereitung die Bestimmungen durchzuführen. Ein 10-µl Teil der Probelösungen wird mit einer Mikrolitерspritze auf den Probeträger gegeben. Danach wird 15 sec bei 90° und 10 sec bei 140° getrocknet und anschließend bei 4,4 V atomisiert. Für eine Analysenprobe werden zur Verbesserung der Genauigkeit 5 Absorptionsmessungen durchgeführt. Als Meßwert wird die Höhe des Zinkpeaks ausgewertet. Bei der Auswertung ist die Matrixkonzentration zu berücksichtigen. Es ist erforderlich, die Eichkurven und die unspezifische Absorption an der Stelle des Zinkpeaks ständig durch Vermessen entsprechender Eichlösungen mit der Zink-Hohlkathodenlampe und der Deuteriumlampe zu überprüfen. Die Tabelle 4 gibt die von uns ermittelten Ergebnisse wieder.

Tabelle 4. Ergebnisse der Bestimmung von Zink in Galliumarsenid.

Einwaage GaAs, *mg*	Analysenvolumen, *µl*	Empfindlichkeit bezogen auf 1%A 0,0044 E, *ng*	Lineares analytisches Gebiet, *ng*	Nachweisgrenzen 3-*s*-Kriterium absolut, *pg*	relativ, *ppm* (GaAs)	Variationskoeffizient bei 0,5 ng Zn (P = 95%),%
0,1	1	0,035	0,1 –1	30	30	5
0,1	10	0,03	0,15–3	150	15	12
1,0	1	0,025	0,2 –1	120	12	10
1,0	10	0,1	0,25–3	250	2,5	15

Parameter—Zn-HKL—6 mA, 213,9 nm; Spalt—0,1 mm; Trocknen—15 sec 90°C; 10 sec 140°C; Atomisieren —3 sec 4,4 V; 280 A.
Probevolumen: 100 µl, Dreifachmessung.

Anwendung der Arbeitsvorschrift

Es wurde der Verunreinigungsgehalt an Zink von Chrom-, Selen-, Tellur- und Zinndotierten Galliumarsenid-Halbleitern bestimmt. Da sich der Gehalt nahe der Nachweisgrenze befand, wurden die Ergebnisse durch die Anwendung einer Zusatzmethode überprüft. Es ergab sich ein Verunreinigungsgehalt von 1,5 ppm Zink bezogen auf Galliumarsenid mit einem Variationskoeffizienten von 50%. Dieser Wert wurde durch Neutronenaktivierungsanalyse bestätigt.

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Summary—A home-made AAS-instrument and a home-made carbon-rod atomizer are described. The instrumental parameters were optimized. The influence of the matrix on the sensitivity, and the reasons for non-specific absorption are discussed. The detection limit of the method is 2–25 × 10^{-11}g or 3–20 ppM relative to 1 ml of 1*M* hydrochloric acid or 2·5–30 ppm relative to 0·1–1 mg of gallium arsenide.

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SHORT COMMUNICATIONS

TITRIMETRIC DETERMINATION OF MERCAPTANS WITH CHLORAMINE-T

(*Received* 4 *June* 1974. *Accepted* 27 *August* 1974)

Chloramine-T has been widely used as a titrimetric oxidant, replacing the more expensive iodine and the less stable hypochlorite.[1,2] In the present investigation, its use has been extended to the determination of various mercaptans.

EXPERIMENTAL

Reagents

Chloramine-T,[2] iodine cyanide,[3] thioglycollic acid and 2-mercaptopropionic acid[4] were purified according to the procedures reported in the literature cited. All the other chemicals used were of guaranteed purity.

The solutions of chloramine-T (0·05*M*) and iodine cyanide (0·04*M*) were prepared in doubly distilled water and 0·1*M* hydrochloric acid, respectively. Thio-*p*-cresol was dissolved in the minimum quantity of ethanol and then diluted with water to give a 0·025*M* solution. The solutions (0·025*M*) of 2-mercaptoethanol, thioglycollic acid, cysteamine hydrochloride, 2- and 3-mercaptopropionic acids and thiomalic acid were prepared in doubly distilled water and those of other mercaptans in glacial acetic acid. The solutions of various mercaptans and chloramine-T were standardized according to reported methods.[1,2]

Procedures

Direct titrations. An aliquot of the mercaptan solution (1–5 ml) was diluted with distilled water (20–30 ml). Potassium iodide (~0·5 g) was added and the solution titrated with standard chloramine-T solution, with starch (1 ml of 1% solution), carbon tetrachloride, chloroform, carbon disulphide and benzene (2 ml) as indicators. Enough concentrated hydrochloric acid was added to the 2-mercaptoethanol solution before the titration to make the acid concentration 0·55*M*.

Potentiometric titrations. A known volume of the mercaptan solution (2–10 ml) was taken in a 100-ml titration cell, diluted to about 50 ml with water, and then titrated as above, with the potentiometric titration outfit described earlier.[5]

Back-titrations. An aliquot of mercaptan solution (1–5 ml) was diluted with water (20–30 ml) and treated with excess of standard chloramine-T solution (5–20 ml); 2*M* hydrochloric acid (1–2 ml) was also added to the titrand in the titrations of cysteamine hydrochloride and 2-mercaptoethanol. The contents were allowed to stand, with occasional shaking, in a stoppered flask, for the time indicated in Table 1. The unconsumed chloramine-T was then titrated with standard thiosulphate solution.[2]

Iodine cyanide method. Iodine cyanide solution (1–3 ml) was added to an aliquot of mercaptan solution (1–5 ml) in a stoppered flask. The mixture was diluted to about 20 ml with 5*M* hydrochloric acid and/or water to adjust the acidity of the solution to the value given in Table 1, and then titrated with standard chloramine-T, chloroform or carbon tetrachloride (~5 ml) being used as indicator. The solution was shaken vigorously after each addition of titrant, until the colour abruptly changed from violet to colourless.

The titrations were repeated at least thrice at each concentration level. Some typical results are given in Table 1.

Table 1. Determination of various mercaptans with chloramine-T

	Visual determination			Potentiometric determination			Back-titration method			ICN method		
Mercaptan	Taken, *mg*	Found, *mg*	Mean relative deviation, %	Taken, *mg*	Found, *mg*	Mean relative deviation, %	Taken, *mg*	Found,† *mg*	Time, *hr*	Taken, *mg*	Found, *mg*	[HCl], *M*
Propyl mercaptan	7·44	7·45	0·14	12·13	12·11	0·09	7·44	7·43	1*	—	—	—
Allyl mercaptan	7·76	7·75	0·13	—	—	—	15·52	15·53	0·08	—	—	—
2-Mercaptoethanol	3·64	3·65	0·02	8·15	8·14	0·20	8·87	8·90	2·00	8·87	8·89	3
Cysteamine hydrochloride	5·68	5·67	0·12	12·11	12·09	0·09	5·68	5·67	1·5	5·68	5·66	0·6
2-Aminobenzene-thiol	5·80	5·81	0·22	7·62	7·60	0·17	—	—	—	—	—	—
Thio-*p*-cresol	10·50	10·52	0·05	18·12	18·14	0·07	10·15	10·20	0·5‡	—	—	—
Thioglycollic acid	5·13	5·12	0·19	12·63	12·61	0·09	5·13	5·12	3	21·24	21·26	1·8–2·1
2-Mercapto-propionic acid	4·12	4·11	0·06	12·60	12·58	0·08	4·12	4·13	2	4·12	4·11	1·5
2-Mercaptobenzoic acid	—	—	—	—	—	—	7·68	7·67	3	—	—	—
Thiomalic acid	—	—	—	—	—	—	5·60	5·59	0·5	5·60	5·61	0·9–1·5
3-Mercaptopro-pionic acid	—	—	—	—	—	—	7·20	7·19	2	6·80	6·79	2

* The contents were heated at 40–43°.

† These determinations correspond to a chloramine-T/mercaptan molar ratio of 3:1.

‡ This determination corresponds to a chloramine-T/mercaptan molar ratio of 2:1.

RESULTS AND DISCUSSION

Propyl mercaptan, allyl mercaptan, 2-mercaptoethanol, thio-*p*-cresol, 2-mercaptobenzenethiol, cysteamine hydrochloride, 2-mercaptopropionic acid and thioglycollic acid react in 2:1 molar ratio with chloramine-T in the presence of iodide, forming the corresponding disulphides. In the potentiometric titrations, there is no sudden jump in potential corresponding to a mercaptan/chloramine-T molar ratio of 2:1 in the absence of iodide, indicating that the addition of iodide is essential not only for detecting the end-point with indicators such as starch, but also because the oxidation to disulphide is essentially a reaction of iodine with the mercaptans:

$$CH_3C_6H_4SO_2NCl^- Na^+ + 2I^- + 2H^+ \rightarrow I_2 + CH_3C_6H_4SO_2NH_2 + Cl^- + Na^+$$

$$2RSH + I_2 \rightarrow RSSR + 2HI$$

Chloramine-T is known to oxidize certain polyhydroxy alcohols but it does not oxidize ethanol.[6] It is logical, therefore, that only the thiol group in 2-mercaptoethanol is oxidized. Thiomalic acid, 3-mercaptopropionic acid and 2-mercaptobenzoic acid do not react quantitatively in the 2:1 molar ratio, and the amount of chloramine-T consumed is somewhat greater than that expected theoretically. This is in keeping with the observation of Danehy and Oester[7] that mercaptans having a free β-carbonyl group are strongly inclined to further oxidation.

Benzene is far the best extraction indicator and the non-aqueous layer becomes light violet at the end-point. In all other cases, a drop of titrant in excess is required for a clearly detectable colour change. The colour disappears after 2–3 min in the titration of allyl mercaptan, probably because of addition of the iodine formed to the double bond in the allyl group. Potentiometric titration of this mercaptan is not possible.

The other potentiometric titrations are possible in the presence of iodide and the jump in the potential at the equivalence point is fairly large ($\sim$75 mV/0·05 ml of the titrant) in every case.

The oxidation of the mercaptans with chloramine-T in the absence of iodide is a function of time. If the mercaptans are allowed to stand with excess of chloramine-T for the times indicated in Table 1, they react in molar ratio 1:3, and the corresponding sulphonic acids are formed:

$$RSH + 3CH_3C_6H_4SO_2NCl^- Na^+ + 3H_2O \rightarrow RSO_3H + 3CH_3C_6H_4SO_2NH_2 + 3Na^+ + 3Cl^-$$

Excess of chloramine-T has already been reported to oxidize thioglycollic acid to the sulphonic acid.[7] Thio-*p*-cresol reacts with excess of chloramine-T in 1:2 molar ratio. It appears difficult to account for this stoichiometry.

Chloramine-T instantaneously reacts with 2-mercaptoethanol, cysteamine hydrochloride, 2-mercaptopropionic acid, 3-mercaptopropionic acid, thiomalic acid and thioglycollic acid in the molar ratio 3:1 in the presence of iodine cyanide. The end-point cannot be accurately detected in the titrations of 2-aminobenzenethiol, allyl mercaptan and thio-*p*-cresol, and 2-mercaptobenzoic acid and propyl mercaptan do not react quantitatively in the molar ratio 1:3 with chloramine-T in the presence of iodine cyanide. It may be mentioned that iodine cyanide[4] or chloramine-T, when present alone, will oxidize the mercaptans only to disulphide in a direct titration. In the present titrations, iodine cyanide acts as a catalyst and preoxidizer, and itself is reduced to iodine, which imparts a violet colour to the carbon tetrachloride layer. The iodide is completely oxidized back to I^+ by chloramine-T at the end-point. There is no mercaptan present to reduce it again and the solution becomes colourless owing to the formation of iodine cyanide.

In almost all the reported visual titrations of chloramine-T, iodide has been added to the titrand and it has, therefore, been concluded that the substance to be determined must be a stronger reducing agent than the iodide, otherwise iodine would separate on adding the titrant.[2] The iodine cyanide method is advantageous in the sense that iodide need not be added and even the reductants weaker than iodide can be determined.

The direct titrations of the mercaptans, with or without addition of iodine cyanide, are fast and quantitative. As little as 0·5 mg of the mercaptan can be determined in 50 ml of solution with $\pm$0·25% error. Acetate, chloride, bromide, iodide, urea, acetone and ethyl acetate do not interfere even when present in large excess. However, hydrazines, thiocyanate and thiocarbonyl compounds such as thiourea interfere in these titrations.

Department of Chemistry
Panjab University
Chandigarh, India

RAM CHAND PAUL
SATISH KUMAR SHARMA
NARESH KUMAR
RAM PARKASH

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Summary—Propyl mercaptan, allyl mercaptan, 2-mercaptoethanol, cysteamine hydrochloride, thio-*p*-cresol, 2-aminobenzenethiol, 2-mercaptopropionic acid and thioglycollic acid react with chloramine-T in 2:1 molar ratio in the presence of iodide, forming the corresponding disulphides. Mercaptans having a free β-carbonyl group do not react quantitatively. The oxidation of the mercaptans is a function of time, and the corresponding sulphonic acids are formed on allowing them to stand with excess of chloramine-T. The oxidation to sulphonic acid is, however, instantaneous in the presence of iodine cyanide which acts as a catalyst and preoxidizer. This method is simple, accurate and rapid, and as little as 0·5 mg of the mercaptan can be determined with $\pm$0·25% error.

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DIRECT PHOTOMETRIC TITRATION OF TELLURIUM

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Surprisingly few titrimetric methods are available for the determination of tellurium and most of these are indirect and laborious.[1–15] We have developed a direct photometric titration method for the determination of tellurium(IV) with dichromate, based on our observation that the reaction between tellurium(IV) and dichromate is fast in nitric or perchloric acid media. The initial oxidation state of the tellurium is not important. Tellurium(VI) can be quantitatively reduced to tellurium(IV) by heating with hydrochloric acid,[11] and elemental tellurium quantitatively oxidized to tellurium(IV) by dissolving it in 1:1 nitric acid;[6] tellurium(−II) can be converted into tellurium(IV) by treatment with nitric acid.[16]

EXPERIMENTAL

Apparatus

The photometric titrations were done with a Klett-Summerson photoelectric colorimeter with a No. 40 filter (bandpass 380–430 nm) and a rectangular 2 × 4 × 8 cm glass cell (2 cm path-length). Extraneous light was excluded by a cover having two holes—one for the burette tip, the other for an inlet tube for passage of carbon dioxide to stir the solution.

Reagents

Potassium dichromate, 0,1*N*.

Tellurium(IV) solution. An approximately 0·025*M* solution was prepared by dissolving sodium tellurite in water, and its strength determined.[11]

Tellurium(VI) solution. An approximately 0·025*M* solution in 0·5*M* hydrochloric acid was prepared from sodium tellurate, and its strength checked.[11]

Nitric acid free from nitrous oxide. Prepared by treating 75 ml of concentrated nitric acid with 25 ml of 4% aqueous urea solution, boiling for 2 min, and finally diluting with water to obtain approximately 8*M* nitric acid.

Procedure

To 1–10 ml of 0·025*M* tellurium(IV) (3–30 mg of tellurium) in the titration cell, add enough 8*M* nitric acid and water to give a total volume of 40 ml of 2–6*M* nitric acid. Adjust the absorbance to read zero (λ = 380–430 nm) and titrate with 0·1*N* potassium dichromate in the usual way, taking absorbance readings not less than 60 sec after the addition of titrant, and plot volume of dichromate *vs.* corrected absorbance. The intersection of the two straight lines gives the end-point. Instead of nitric acid, 1–4*M* percholoric acid can be used, or 1–3*M* sulphuric acid, but with the latter the readings must not be taken sooner than 120 sec after addition of reagent.

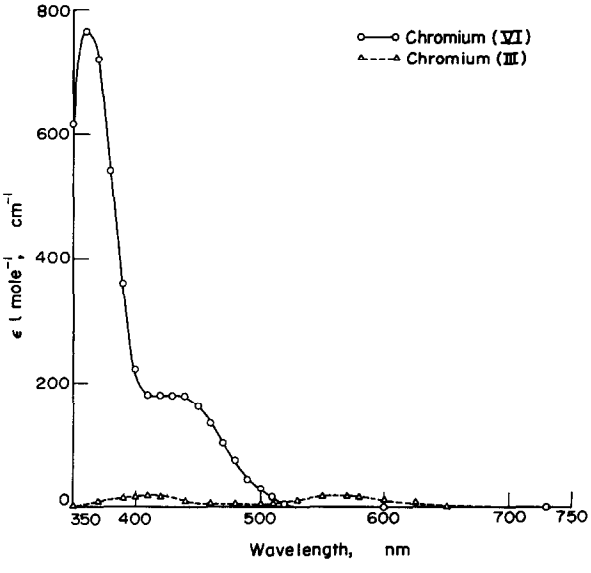

Fig. 1. Absorption spectra of Cr(VI) and Cr(III) in 2*M* nitric acid.

RESULTS AND DISCUSSION

Choice of conditions

Tellurium(VI) and (IV) do not absorb over the range 350–750 nm. Figure 1 shows that chromium(III) has no significant absorption peak in the same range, and the titration should obviously be monitored *via* the chromium(VI) absorption at 360–450 nm.

Interferences

Selenium(VI) and (IV) do not interfere, nor do chloride and phosphate in concentrations up to 0·05 and 0·2*M* respectively, but higher concentrations retard the reaction and the results become erratic. Any other species oxidizable by dichromate under the conditions used will interfere.

Attempts to develop a visual end-point or potentiometric method failed because indicators are irreversibly oxidized and stable potentials are not attained.

Precision and accuracy

Solutions containing known amounts of tellurium(IV) were analysed six times according to the recommended procedure. Averages and relative standard deviations (from the range) were; 25·58 mg, 0·6% (25·52 mg taken); 12·77 mg, 0·5% (12·76 mg taken); 6·39 mg, 0·4% (6·38 mg taken). Table 1 shows typical results for the range 5–60 mg of tellurium.

Table 1.

Amount of tellurium, *mg*	
Taken	Found
4·785	$4·7_9$
8·948	$8·9_3$
15·31	$15·3_7$
25·52	$25·4_1$
62·43*	$62·0_4$
49·95*	$49·8_3$
31·56†	$31·6_4$
19·0†	$18·8_7$

* Oxidation of metallic tellurium with nitric acid and estimation of Te(IV).

† Reduction of Te(VI) to Te(IV) and subsequent estimation.

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Department of Chemistry
Andhra University
Waltair, India

L. S. A. DIKSHITULU
DINDI SATYANARAYANA

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Summary—A direct photometric titration method has been developed for the determination of tellurium. Tellurium(IV) is titrated with potassium dichromate in 2–6*M* nitric acid (or 1–4*M* perchloric acid) at 380–430 nm (blue-violet filter). Selenium(IV) does not interfere.

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PRECIPITATION OF MOLYBDENUM(V) AS THE HYDROXIDE AND ITS SEPARATION FROM RHENIUM

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Existing precipitation methods for separation of rhenium from molybdenum are based on the precipitation of molybdenum(VI) as the salt of an organic base[1] or a heavy metal cation[2] or as an insoluble chelate with oxine[2] or α-benzoinoxime.[3] Traces of molybdenum are left behind in solution and have to be removed by other methods such as solvent extraction, before rhenium can be estimated by the often-used thiocyanate method.[4a] The bulkiness of the chelate limits application of the methods to a few milligrams of molybdenum to avoid loss of rhenium by adsorption. Precipitation of molybdate with collectors[5,6] has hitherto been used only for 10–20 μg of molybdenum per ml.

Mo(VI) and Re(VII) do not precipitate as hydroxides in slightly acid or alkaline media whereas Mo(V) does, although the exact conditions have not previously been established. As Mo(VI) can be reduced[7a] to Mo(V) without affecting Re(VII),[8] a possibility exists for separating the two elements simply by adjusting the pH. Accordingly, we present below a study of these two aspects.

EXPERIMENTAL

Reagents and solutions

Molybdenum solution. Sodium molybdate dihydrate was dissolved in water, and the solution standardized and diluted to give 500, 100 and 10 μg/ml concentrations.

Rhenium solution, 1 mg/ml. An appropriate weight of potassium perrhenate ("Spec. pure", Johnson–Matthey) was dissolved in water. Lower concentrations were obtained by suitable dilution.

Zirconium solution, 5 mg/ml. Zirconium oxychloride octahydrate was dissolved in 0·1*M* hydrochloric acid.

Solutions of other elements, 10 or 20 mg/ml. Prepared by dissolving suitable salts in water or dilute hydrochloric acid.

Samples. Synthetic samples were prepared by mixing solutions of the elements to give the composition shown in Table 1. Molybdenites (Mexico, 200 mg; Norway, 400 mg) were opened out with concentrated nitric acid.[4b] After destruction of the nitrate with hydrochloric acid, the solution was adjusted to pH 8–9 with sodium hydroxide. Any precipitate was filtered off and washed thrice with 5-ml portions of water. The filtrate and washings were boiled with hydrogen peroxide, the excess of which was then removed. The solution was then adjusted to a volume of 20 ml and 1·6*M* in hydrochloric acid and submitted to procedure (*iii*) below.

Separation procedures

(*i*) *Precipitation of 10–100 mg of molybdenum(V) as the hydroxide.* A solution containing 10–100 mg of molybdenum was adjusted to be 1·5–1·6*M* in hydrochloric acid and 20 ml in volume. It was boiled with 500 mg of hydrazine sulphate for 3–4 min in a covered beaker with occasional stirring. The solution was cooled to room temperature and the pH adjusted to 5·0–5·8 (pH-meter) with ammonia, the solution being cooled as the temperature rose. The solution was heated to 60–70°, a little filter paper pulp at pH 5·0–5·8 was added and the precipitate was filtered off an a Whatman No. 41 paper and washed thrice with 3–5-ml portions of water adjusted to pH 5·0–5·8. The filtrate and washings were made just alkaline with sodium hydroxide and boiled with a few drops of hydrogen peroxide, the excess of which was then removed. The solution was evaporated to about 30 ml and procedure (*ii*) applied. To minimize oxidation, the molybdenum(V) hydroxide was handled without delay.

(*ii*) *Precipitation of ≤ 10 mg of molybdenum(V) with zirconium as collector.* Procedure (*i*) was followed after addition of enough zirconium solution to give a Zr/Mo w/w ratio of at least 20.

(*iii*) *Separation of rhenium from molybdenum.* Solutions of rhenium and molybdenum were treated by procedures (*i*) and/or (*ii*) as appropriate to the amount of molybdenum present.

The filtrate and washings were evaporated to suitable volume, cooled to room temperature and taken for determination of rhenium.

Determination of the elements. Milligram amounts of molybdenum were determined by the cerimetric[7b] or oxinate[9] method, microgram amounts by the thiocyanate method.[4c] Rhenium was determined by the thiocyanate method[4a] and isoamyl alcohol extraction. Suitable conventional methods were used for estimation of other elements.

RESULTS AND DISCUSSION

Precipitation of mg/ml concentrations of molybdenum(V)

Molybdenum(VI) is quantitatively reduced to a brown molybdenum(V) species by hydrazine in 1–2*M* hydrochloric acid.[7a] From solutions containing 1 mg of molybdenum(V) per ml, precipitation starts at pH 2·4. It reaches a maximum of about 97·5% between pH 5·0 and 5·8 (Fig. 1, curve B) and varies only slightly with higher concentrations of molybdenum (Fig. 1, curve A). The brown precipitate quickly flocculates on heating to 60–70°. Stronger heating is avoided to minimize oxidation. Addition of filter paper pulp hastens filtration. Both the pulp and the wash-water should be adjusted to pH 5·0–5·8 to keep the solubility of the precipitate to the minimum. The precipitate should be kept covered throughout and filtration and washing of the precipitate completed as quickly as possible to minimize oxidation. If the pH is over-stepped and readjusted or filtration is delayed for 20 min, slightly lower results are obtained, probably owing to oxidation. After oxidation of molybdenum(V), the filtrate and washings are evaporated to 20–30 ml, before procedure (*ii*) is used to precipitate the residual molybdenum.

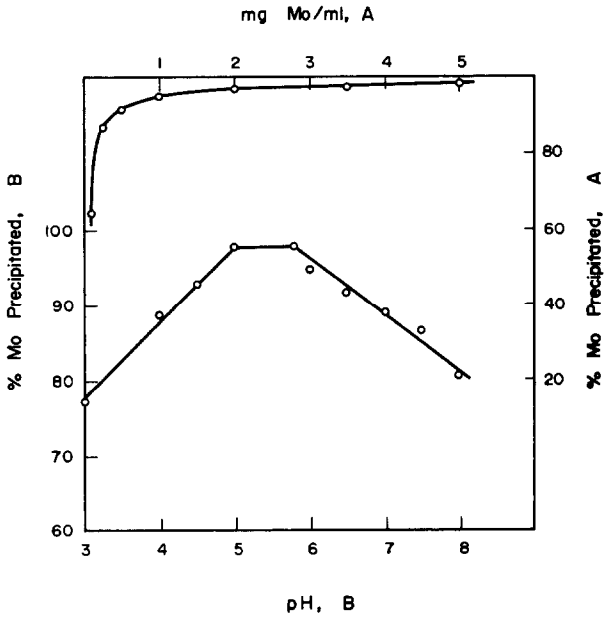

Fig. 1. Dependence of molybdenum precipitation on its concentration and pH (curves and corresponding scales on axes indicated by same letter). *A*—pH 5·8 and 20 min waiting before filtration, *B*—Mo 1 mg/ml and immediate filtration.

Tartrate, citrate, oxalate, EDTA, phosphate, and arsenate in sufficient amount, completely suppress the precipitation of molybdenum(V) as hydroxide.

Precipitation of molybdenum(V) in concentrations of < 1 mg/ml

The precipitation of molybdenum(V) hydroxide falls off rapidly at molybdenum concentrations < 1 mg/ml (Fig. 1, curve A), so it is not possible to recover the residual molybdenum in procedure (*i*) by its repetition. Precipitation with Be(II), Zn(II), Sn(II), Al(III), Th(IV), Zr(IV) as collectors at 1 mg/ml concentration was therefore investigated. Except with Zr(IV), the degree of precipitation increases with molybdenum concentration up to 0·25 mg/ml, above which it levels off (Fig. 2, curves *C-G*), some molybdenum always being left in solution. Zirconium(IV) gives complete precipitation at Zr/Mo w/w $\geqslant$ 10 (Fig. 2, curve *H*), independent of molybdenum concentration (up to 0·5 mg Mo/ml).

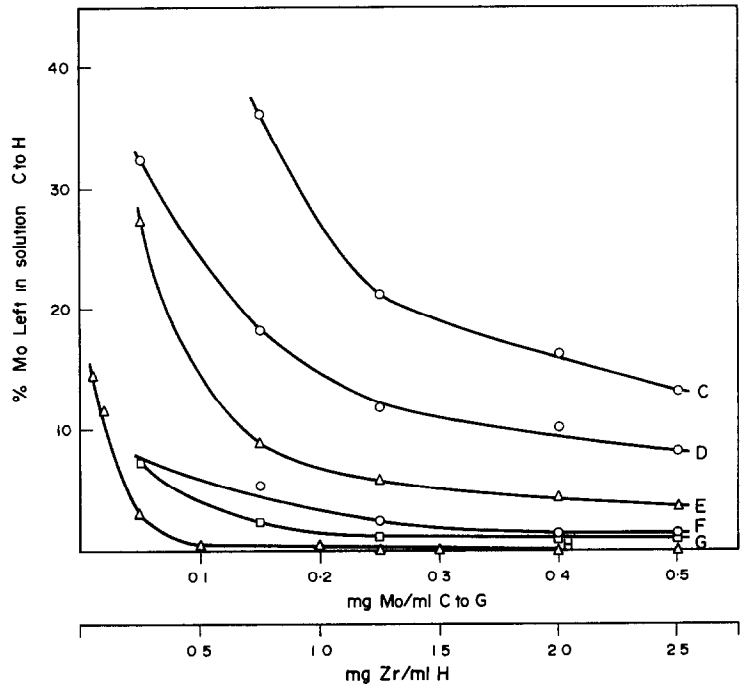

Fig. 2. Dependence of molybdenum precipitation on collector (curves and corresponding scales on axes indicated by same letter). pH 5·8 and 20 min waiting before filtration. *C*—Zn 1 mg/ml; *D*—Be 1 mg/ml; *E*—Al 1 mg/ml; *F*—Sn(II) 1 mg/ml; *G*—Th 1 mg/ml; *H*—Mo 0·25 mg/ml.

Thus if procedures (*i*) and (*ii*) are applied consecutively, large amounts of molybdenum can be quantitatively precipitated as molybdenum(V) hydroxide. The precipitation is not affected by sodium, ammonium, chloride, sulphate, silicate and acetate ions, even in very high concentrations.

Separation of rhenium(VII) from molybdenum(V)

Rhenium(VII) is not reduced by hydrazine in 1–2*M* hydrochloric acid,[8] and does not precipitate as hydroxide. Therefore, a separation from molybdenum is effected by applying procedure (*i*) followed by (*ii*). As molybdenum(VI) is also collected by Zr(IV) quantitatively,[6] the molybdenum in the filtrate need not be reduced in procedure (*ii*), thus saving time.

A single separation requires about 45 min. Rhenium is not adsorbed on the molybdenum(V) hydroxide. This was tested by the thiocyanate method[4] after separation of the molybdenum by the tribenzylamine[8] and thiocyanate[10] extractions.

When other elements are also to be separated as hydroxides,[2] the hydrazine sulphate concentration should not be more than 5 mg/ml in excess of that required for reduction, as it suppresses the precipitation of some of them.

Table 1. Analysis of samples by the proposed method

Sample composition Mo, *mg*	Re, *μg*	Re found, *μg*
5	40	39·5
10	30	30·0
15	20	19·5
20	10, 30, 50	10, 29·5, 50
30	10	10·0
50	10	10·0
100	20	19·5
Molybdenite (Mexico)	0·012%	0·011$_7$%
Molybdenite (Norway)	0·0036%	0·0037%

The results in Table 1 show that the method can be satisfactorily applied to the analysis of molybdenites and other molybdenum–rhenium samples and offers a simple solution to the problem of separation of rhenium from large amounts of its natural associate, molybdenum.

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Department of Chemistry
Kurukshetra University
Kurukshetra 132119, Haryana, India

V. YATIRAJAM
USHA AHUJA
L. R. KAKKAR

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Summary—A study of the conditions for precipitation of molybdenum(V) hydroxide shows that for Mo concentration ≥ 1 mg/ml about 97·5% of the Mo can be precipitated between pH 5 and 5·8. Lower concentrations of molybdenum(V) or molybdenum(VI) can be precipitated quantitatively by using 20 times the amount of zirconium as collector, at the same pH. On this basis, a simple method is given for quantitative separation of rhenium from large amounts of molybdenum and is attested by analysis of synthetic and molybdenite samples.

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QUANTITATIVE GOLDBESTIMMUNG IN FILMMATERIALIEN MITTELS FLAMMENLOSER ATOMABSORPTION

(*Eingegangen am* 9. *Juli* 1974. *Angenommen am* 17. *September* 1974)

Es wurde eine AAS Methode ausgearbeitet, die es ermöglicht, das den Filmmaterialien als Sensibilisator zugesetzte Gold quantitativ zu bestimmen. Da im allgemeinen das Gold nur in geringsten Mengen (10^{-7}–10^{-8} g/cm^2) zugesetzt wird, mußte eine sehr empfindliche Methode ausgewählt werden. Uns erschien das Verfahren der flammenlosen Atomisierung als besonders geeignet, da es gegenüber anderen Methoden einige entscheidende Vorteile besitzt, wie z.B. Verwendung äußerst geringer Probenvolumina, hohe Selektivität und eine sehr gute Nachweisgrenze. Die bisher veröffentlichten Ergebnisse der AAS Bestimmung von Gold mittels Flamme erwiesen sich für die Lösung des Problems als unzureichend.[1–4]

EXPERIMENTELLER TEIL

Geräte

Für alle Messungen wurde ein Eigenbau-Atomabsorptionsspektralphotometer[5] verwendet.

Alle Bestimmungen wurden mit den nachstehend aufgeführten Parametern, die sich im Verlauf der Versuche als optimal erwiesen hatten, vorgenommen: Analytische Wellenlänge 242,8 nm; Lampenstrom 20 mA; Spaltbreite 0,1 mm; Probeträgerform a (siehe Abb. 2); Probeträgerlänge 8 mm; Atomisatorspannung 4,5 V; Argonströmungsgeschwindigkeit 20 l. h.

Der von uns verwendete elektrothermische Atomisator (Abb. 1) ist eine Weiterentwicklung des bereits von uns beschriebenen Atomisators.[5] Zwischen die Graphitbacken G werden kleine Stifte aus Reinstgraphit als Probeträger geklemmt. Der Atomisator ist in Richtung der optischen Achse, senkrecht dazu und in der Höhe verstellbar.

Die Stromversorgung des Atomisators (maximal 800 A bei 10 V) erfolgt über zwei parallel geschaltete Niederspannungstransformatoren und einen 20 A Sparstelltransformator, an den 220 V angelegt werden. Der Atomisator wird mit Wasser gekühlt. Beim Anlegen von Spannungen zwischen 3,0 und 5,0 V fließen Ströme zwischen 50 und 250 A durch den Probeträger, der auf Grund seines Widerstandes so hoch aufgeheizt wird, daß die Probe verdampft und dissoziiert. Um den Abbrand des Probeträgers und der Graphitbacken auf ein Minimum zu reduzieren, ließen wir den Atomisierungsvorgang unter Argonatmosphäre ablaufen. Die von uns zu diesem Zweck verwendete Glasglocke kann mittels eines 60 mm Schliffes direkt auf den Atomisator aufgesetzt werden. Die Dosierung der Probelösung erfolgt mit einer Mikroliterspritze direkt auf den Probeträger.

Zur Unterscheidung zwischen spezifischer und unspezifischer Absorption wird eine Deuteriumlampe verwendet, die im rechten Winkel zur optischen Achse des Atomabsorptionsspektralphotometers angebracht wird. Mit Hilfe eines einklappbaren Spiegels ist es möglich, abwechselnd das Licht der Hohlkathodenlampe und der Deuteriumlampe durch die Absorptionszelle zu schicken, so daß eine Korrektur der nichtspezifischen Absorption nicht direkt, sondern nur mit zwei Messungen möglich ist.

Reagenzien

Gold(III)-Stammlösung. Gold (1 g) wurde in 25 ml Königswasser gelöst. Die Lösung wurde eingedampft und der Rückstand in 1 Liter 1*M* Salzsäure (stabilisiert durch 0,4 g Kaliumchlorat) aufgelöst.

Gold(III)-Analysenlösungen. Diese wurden erhalten durch Verdünnen der Stammlösung mit 1*M* Salzsäure (stabilisiert mit 1,6 g Kaliumchlorat/Liter).

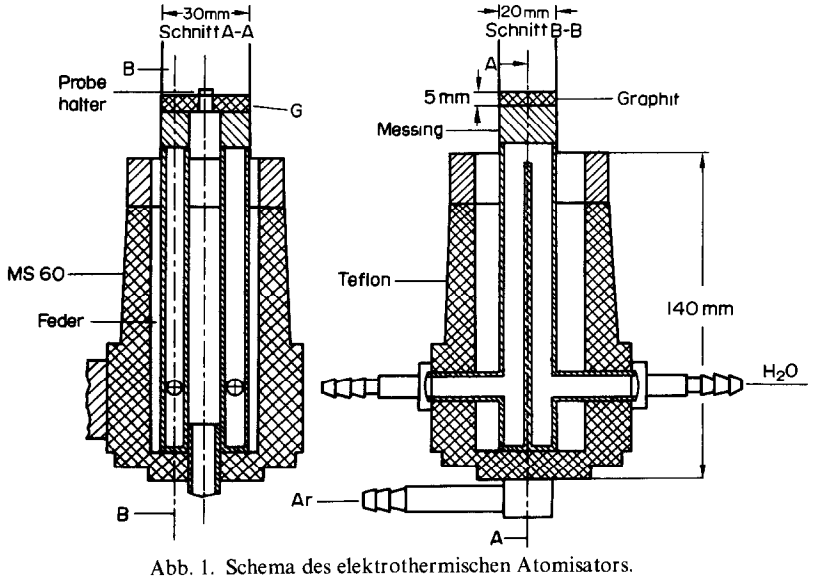

Abb. 1. Schema des elektrothermischen Atomisators.

Methylisobutylketon. Das MIBK wurde vor der Verwendung 3 Stunden unter Rückfluß über Kaliumpermanganat gekocht und anschließend über eine 1-m Vigreux-Kolonne destilliert. Verwendet wurde die Fraktion, die bei 114–117° überging. Das MIBK wurde mit Bromwasserstoffsäure (10%-ig) gesättigt.

Des weiteren kamen zum Einsatz: HBr (*p.a.*); HNO_3 (*p.a.*); H_2O_2 (*p.a.*); NaCN (*p.a.*); $Na_2S_2O_3$ (*p.a.*); KBr (*p.a.*).

Allgemeine Arbeitsvorschrift für die Goldbestimmung

Nach dem Reinigen des Probeträgers durch mehrmaliges Aufheizen bei 4,5 V gibt man mit einer 10-µl Pipette die wäßrige (bzw. organische) Goldlösung durch eine Öffnung der Glasglocke auf den auf 90° vorgeheizten Probeträger. Das Lösungsmittel (1*M* Salzsäure, 10%-ige Bromwasserstoffsäure, bzw. Methylisobutylketon) wird bei 0,6 V (MIBK bei 0,4 V) verdampft. Anschließend wird noch 10 Sekunden bei 1,0 V getrocknet. Dann wird sofort die Atomisatorspannung (s.u.) an den Probeträger angelegt, wodurch die Probe innerhalb von 2 Sekunden verdampft und atomisiert wird. Das Signal wird mit einem Kompensationsbandschreiber aufgezeichnet. Als Meßgröße wird die Peakhöhe des Absorptionssignales verwendet.

ERGEBNISSE UND DISKUSSION

Optimierung der Verdampfung und Atomisierung der Probe

Wie bereits früher berichtet wurde,[5] kann die Verdampfung und Atomisierung durch die Probeträgerform und die elektrischen Parameter beeinflußt werden. Im Zusammenhang mit unserem Aufzeichnungssytem kamen wir zu folgenden Ergebnissen.

Probeträgerform. Die von uns verwendete Probeträgerform ist in Abb. 2 zu sehen. Die Oberkante des Probeträgers befand sich stets im Lichtfleckzentrum der Hohlkathodenlampe.

Elektrische Parameter. (*a*) Bei Spannungen von 3,0 V und 120 A ist nur eine geringe Konzentrationsabhängigkeit festzustellen. (*b*) Von 3,0 bis 4,5 V nimmt die Höhe des Absorptionssignales zu. (*c*) Ab einer Spannung von 4,5 V verringert sich die Signalhöhe wieder, da der Atomisierungsvorgang für das Aufzeichnungssystem bereits zu schnell wird.

Wir konnten feststellen, daß das Gold in zwei Formen verdampft. Ein kleiner Teil des Goldes verdampft während des Aufheizens als $AuCl_3$ und dissoziiert in der Dampfphase. Der größere Teil wird im Probeträger zu elementarem Gold reduziert, welches direkt verdampft. Dieser Absorptionspeak wurde zur analytischen Bestimmung verwendet.

Ergebnisse der Goldbestimmung in wäßriger Phase

Eine Zusammenfassung der gefundenen Ergebnisse zeigt die Tabelle 1. Zur Bestimmung des in photographischen Materialien enthaltenen Goldes muß die Gelatine zerstört und der Rückstand in Lösung überführt werden. Wir wählten für die Zerstörung der Gelatine den enzymatischen Abbau mit Mezymfortelösung (0,1%-ig an Mezymforte/0,05 *M* an Ammoniumchlorid).[6] Durch mehrmaliges Abrauchen mit einem Gemisch aus gleichen Teilen Salpetersäure (conc.) und Wasserstoffperoxid (30%-ig) wurde der organische Rückstand zerstört und das Gold in die Gold(III)-form überführt. Nach dieser Operation bestand der Rückstand hauptsächlich aus Silberbromid, welches z.B. in folgenden Lösungen gelöst werden kann: 1. Bromwasserstoffsäure (48%-ig); 2. Natriumthiosulfatlösung (2*M*); 3. Natriumcyanidlösung (2*M*); 4. Kaliumbromid/Bromwasserstoffsäure-Lösungen; 5. Ammoniumbromid/Bromwasserstoffsäure-Lösungen verschiedener Konzentrationen.

Es zeigte sich jedoch, daß diese Lösungsmittel für die flammenlose Atomisierung bei Verwendung eines Gleichlichtgerätes nicht eingesetzt werden konnten, da verschiedene Matrixeffekte auftraten, die hauptsächlich den Verdampfungsprozess beeinflußten. Bei Verwendung von Bromwasserstoffsäure (48%-ig) erhielten wir zwar Goldsignale, diese zeigten jedoch keine Konzentrationsabhängigkeit. Bei den anderen verwendeten Lösungsmitteln erhielten wir an der Stelle des Goldpeaks eine sehr hohe unspezifische Absorption. Eine Trennung des spezifischen vom unspezifischen Signal gelang weder durch fraktionierte Verdampfung noch durch Erhöhung der Papiervorschubgeschwindigkeit am Schreiber.

Ergebnisse der Goldbestimmung in organischer Phase

Da die sofortige Bestimmung des Goldes nach Lösen des Rückstandes nicht möglich war, extrahierten wir das Gold. Als wäßrige Phase verwendeten wir das Lösungsmittel Kaliumbromid/Bromwasserstoffsäure (4 *M* an KBr/10%-ig an HBr) und als organische Phase HBr-gesättigtes Methylisobutylketon.

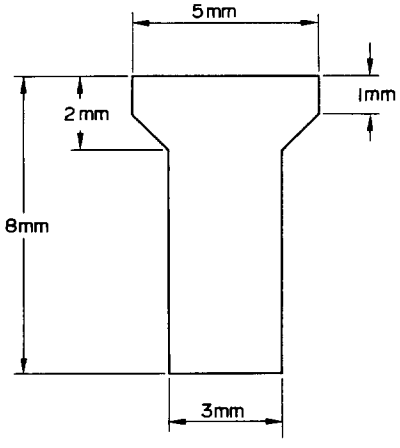

Abb. 2. Probeträgerform aus Reinstgraphit.

Tabelle 1. Ergebnisse der AAS-Bestimmung von Gold in wäßrigen Lösungen *[1]

Lösungsmittel	Lösungsvolumen, µl	Empfindlichkeit bez. auf 1% Abs., ng	Konzentrationsgebiet mit linearer Extinktionsfunktion, ng	Nachweisgrenze (3 s-Krit.) abs., ng	rel., ppm	Variationskoeffizient bei 1 ng Au, %
HCl (1*M*)	10	0,11	0,3–3,0	0,28	0,028	16,5
HBr (10%-ig)	10	0,08	0,3–3,0	0,30	0,030	23,0

* Die analytische Bestimmung des Goldes wurde in 1*M* HCl und in 10%-iger HBr vorgenommen. Es wurden jeweils 10 µl Lösungsvolumen eingesetzt. Zur Verbesserung des Vertrauensintervalls wurde eine Dreifachbestimmung durchgeführt; eine Korrektur über die Deuteriumlampe war nicht erforderlich.

Arbeitsvorschrift

Filmflächen (1–2 cm^2) werden aus dem Film herausgestanzt, in kleine Bechergläser (1,7 cm Durchmesser/1,5 cm Höhe) gegeben und mit 1 ml Mezymfortelösung (0,1%-ig an Mezymforte/0,05*M* an Ammoniumchlorid) bedeckt. Der Abbau der Gelatine erfolgte bei 38° innerhalb von 30 Minuten bis 2 Stunden. Nach Entfernen der Filmunterlage wird die trübe AgX-Sole mit einer IR-Lampe zur Trockne eingedampft. Der Rückstand wird mit einem Gemisch aus 8 Tropfen Wasserstoffperoxid (30%-ig) und 8 Tropfen Salpetersäure (conc.) aufgenommen.

Tabelle 2. Bestimmung von Gold (Au) in Filmmaterialien

Probe, cm^2	Empfindlichkeit bez. auf 1% Abs., ng	Konzentrationsgebiet mit linearer Extinktionsfunktion, ng	Nachweisgrenze (3 s-Krit.) abs., ng	rel., ng/cm^2 Film	Variationskoeffizient bei 5 ng Au, %
1	0,17	0,7–10	0,7	14	11,0
2	0,17	0,7–10	0,7	7	11,0

Hierbei werden die organischen Bestandteile oxydiert und das elementare Gold in die Gold(III)-form überführt. Nach Beendigung der Reaktion dampft man wieder zur Trockne ein und oxydiert nochmals mit 16 Tropfen Königswasser. Diese Lösung wird wieder eingedampft. Der Rückstand wird in 0,5 ml einer Lösung (4 *M* an KBr/10%-ig an HBr) aufgelöst und in ein Extraktionsröhrchen, in das bereits 200 µl MIBK (gesättigt an HBr) dosiert wurden, gegeben. Die Bechergläser werden mit 200 µl KBr/HBr-Lösung ausgespült und diese Menge zu den 0,5 ml hinzugefügt. Dann füllt man mit KBr/HBr-Lösung auf 1 ml auf, um die Volumenveränderung des MIBK konstant und reproduzierbar zu gestalten, und extrahiert 30 Sekunden. Jeweils 10 µl der MIBK-Lösung werden auf den Probeträger gebracht und atomisiert. Wir empfehlen, die extrahierten Lösungen sofort zu vermessen, da nach einiger Zeit Kaliumbromid auskristallisiert.

Die Parameter der Goldbestimmung im wäßrigen Medium werden übernommen, lediglich die Atomisatorspannung wurde auf 4,7 V verändert. Zur Erhöhung der Genauigkeit wurden Dreifachbestimmungen durchgeführt. Die von uns gefundeden Ergebnisse sind in der Tabelle 2 zu sehen.

Sektion Chemie der Karl-Marx-Universität
701 Leipzig, Liebigstraße 18, DDR

KLAUS DITTRICH®
WOLFGANG MOTHES

LITERATUR

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Summary—A graphite rod electrothermal atomizer has been used for the AAS determination of traces of gold in hydrochloric and in hydrobromic acid solutions, and also after extraction into HBr-saturated methyl isobutyl ketone. Photographic film samples were decomposed first by enzyme action then by nitric acid/peroxide oxidation, and the gold was extracted into MIBK. For 10-µl aliquots of solution the 3*s* limits of detection were 3×10^{-10} g for aqueous solutions, 7×10^{-10} g for MIBK, and 7×10^{-9} g/cm^2 for film.

Talanta, Vol. 22, pp 321–325 Pergamon Press, 1975 Printed in Great Britain

ANALYTICAL DATA

MASS SPECTRA OF METAL CHLORIDES

(*Received* 19 *June* 1974. *Accepted* 11 *September* 1974)

Activation analysis and spark-source mass spectrometry have been used to test the purity of standard metal samples and reagents. In previous papers,[1,2] we have reported the mass spectra of metal halides and the determination of mercury halides by use of a conventional electron-impact mass spectrometer. The method was found useful for testing the purity of metal samples (with the exception of alkali and alkaline earth metals). The impurities in the metals could be detected at the 100-ppM level. The mass spectra of ten chlorides are given.

EXPERIMENTAL

The mass spectrometer used was a JMS-01SG (JEOL Co.). The operating conditions were: accelerating voltage, 6 kV; ionization voltage, 75 V; ionization current, 200 μA; vacuum (in the ion source), 1×10^{-5} mmHg; sample temperature, 100–400°; main slit, 30 μm (the theoretical resolution was about 5000). A heated inlet system was used for liquid samples.

The standard metal sample was dissolved in nitric acid or *aqua regia* and the solution was evaporated to dryness, and a drop of hydrochloric acid added. Iron, tin and antimony were dissolved directly in hydrochloric acid. Titanium was dissolved in hydrofluoric acid and the solution was evaporated to dryness, and a drop of hydrochloric acid added. Germanium dioxide was dissolved in sodium hydroxide solution and the solution was acidified with hydrochloric acid. All metals and reagents were the super special grade from WAKO Pure Chemical Industries Ltd.

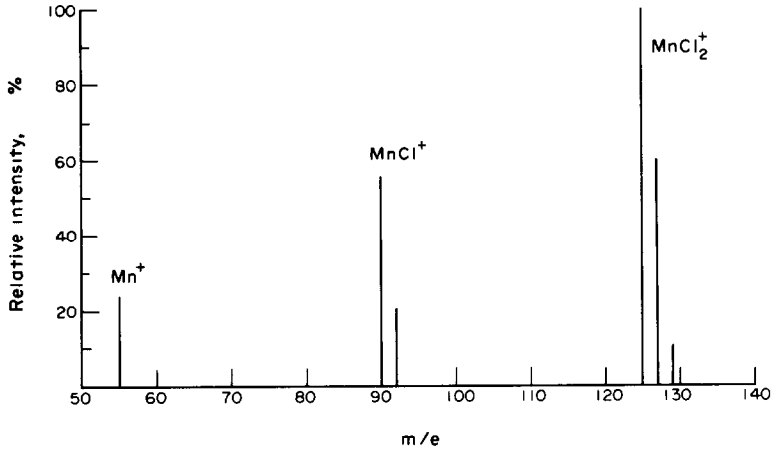


Fig. 1. Mass spectrum of manganese chloride. Sample temperature 380°.

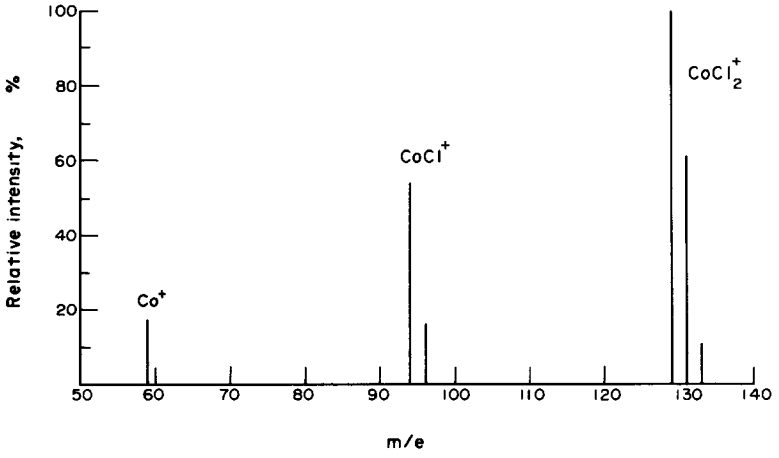


Fig. 2. Mass spectrum of cobalt chloride. Sample temperature 380°.

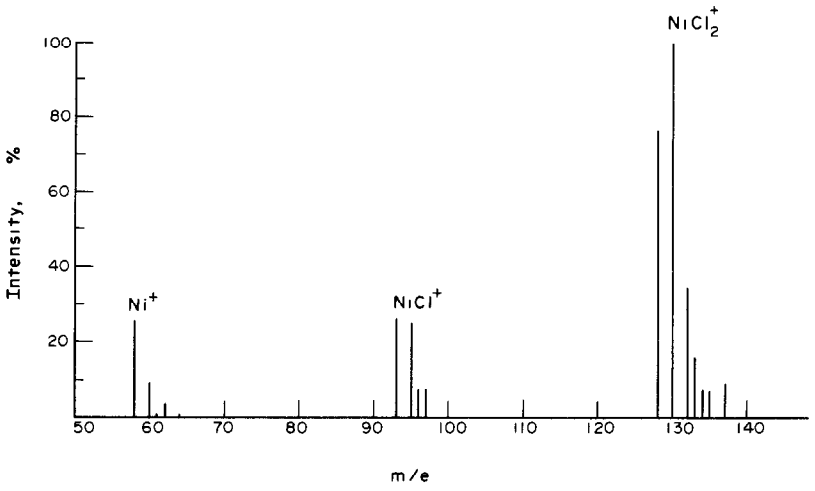


Fig. 3. Mass spectrum of nickel chloride. Sample temperature 400°.

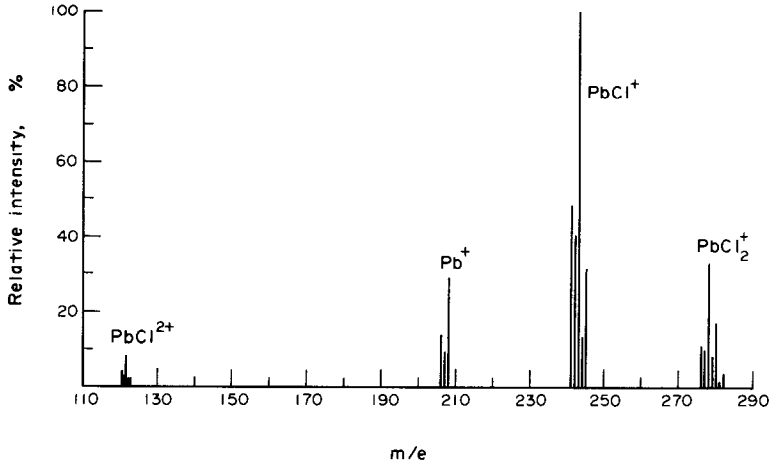


Fig. 4. Mass spectrum of lead chloride. Sample temperature 360°.

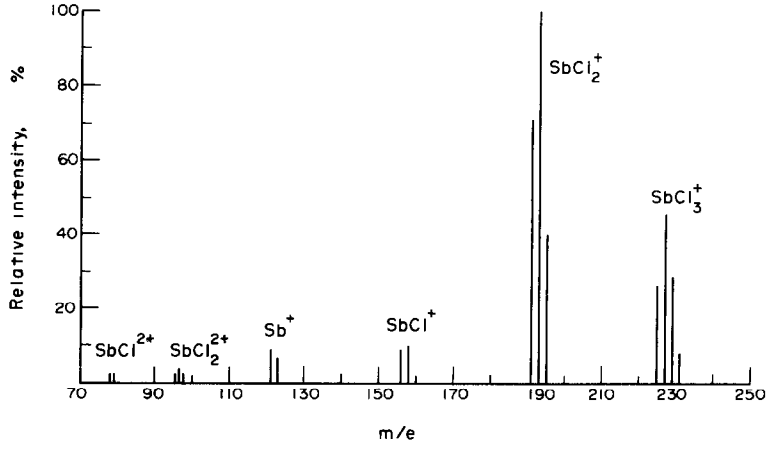


Fig. 5. Mass spectrum of antimony chloride. Sample temperature 120°.

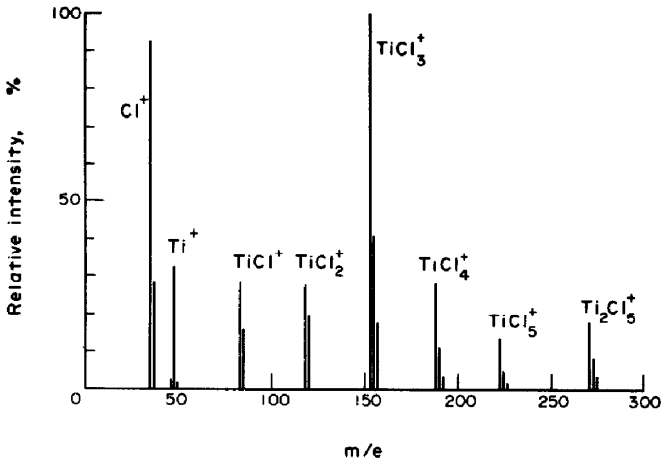
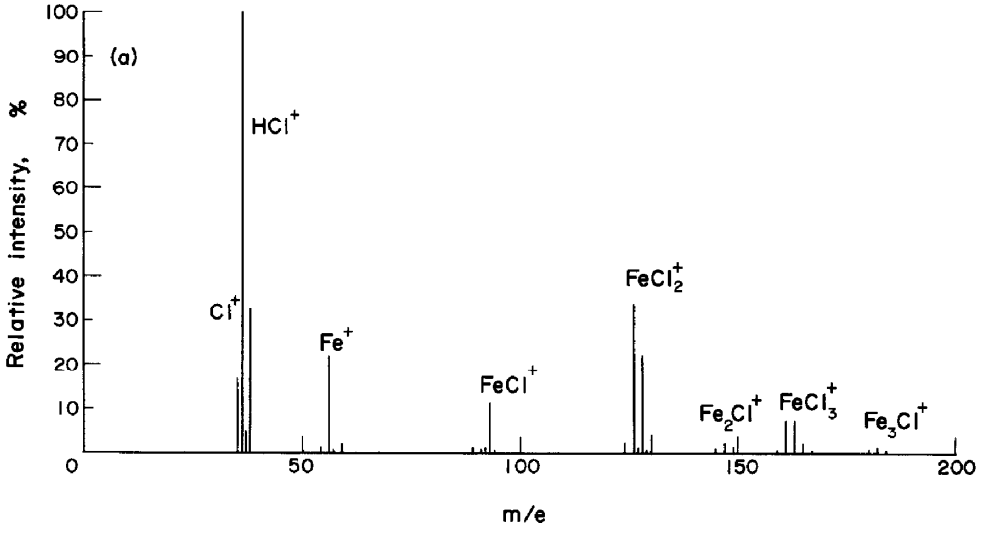


Fig. 6. Mass spectrum of titanium trichloride. Sample temperature 340°.



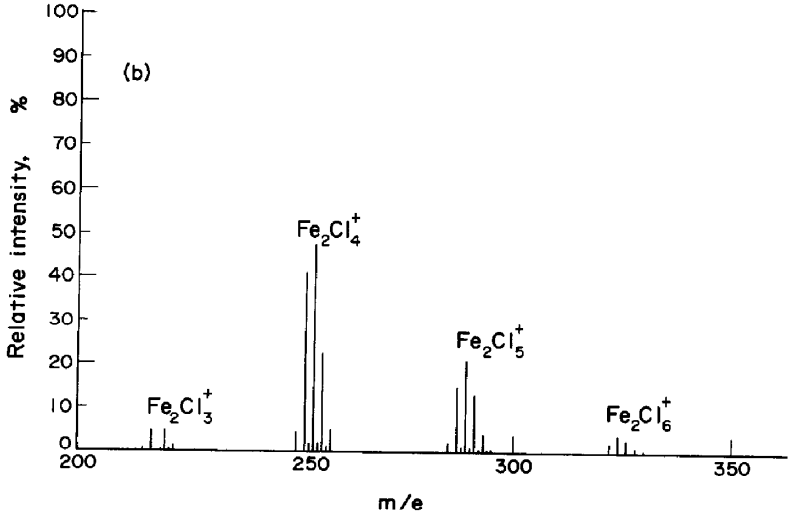


Fig. 7. Mass spectrum of ferric chloride. Sample temperature 200°.

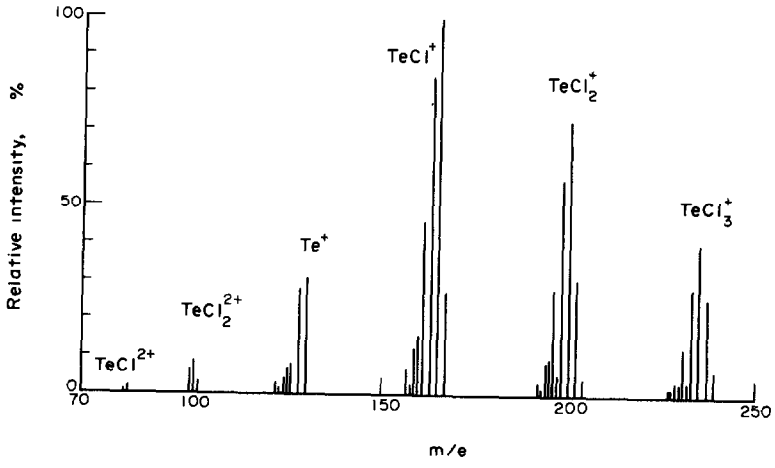


Fig. 8. Mass spectrum of tellurium tetrachloride. Sample temperature 130°.

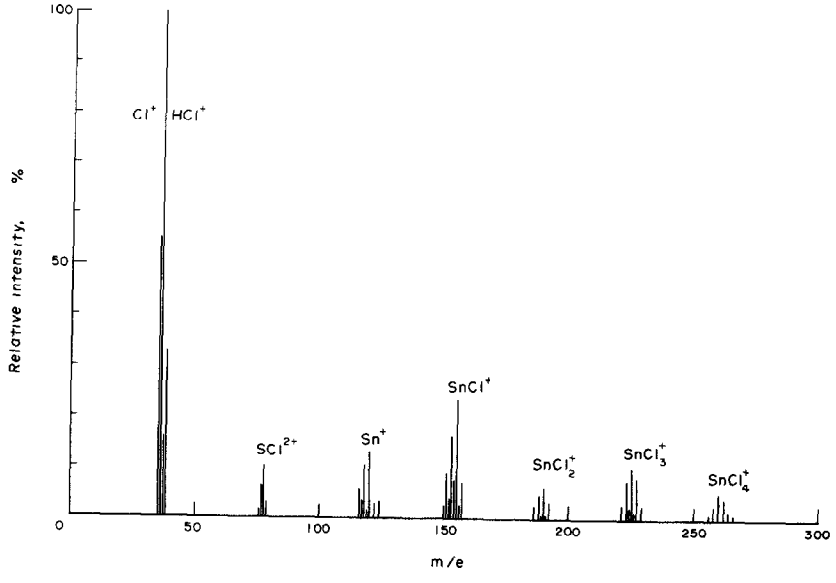


Fig. 9. Mass spectrum of stannic chloride. Sample temperature 100°.

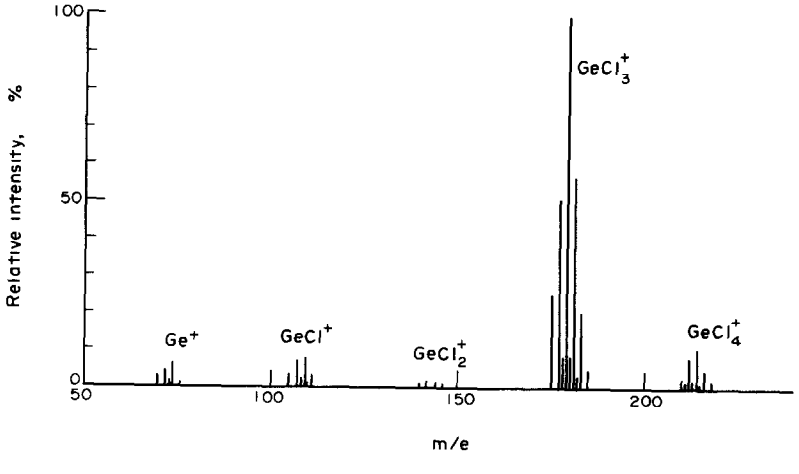


Fig. 10. Mass spectrum of germanium tetrachloride. Sample temperature 100°.

RESULTS

Simple mass spectra are obtained from chlorides of bivalent elements, such as $MnCl_2$, $CoCl_2$, and $NiCl_2$, but in the case of lead chloride, a doubly-charged ion, $PbCl_2^{2+}$, was observed and the spectrum is more complex.

The spectrum obtained from antimony trichloride was the simplest of those of the tervalent metal chlorides. The mass spectrum obtained from titanium trichloride was more complex, with peaks at *m/e* values higher than that of the molecule ion $TiCl_3^+$, corresponding to the ionic species $TiCl_4^+$, $TiCl_5^+$ and $Ti_2Cl_5^+$. The mass spectrum of ferric chloride is even more complex, having several peaks due to ions containing more than one iron atom, such as $Fe_2Cl_2^+$, $Fe_2Cl_3^+$, $Fe_2Cl_4^+$, $Fe_2Cl_5^+$, and $Fe_2Cl_6^+$. The mass spectrum of tellurium tetrachloride has doubly-charged ions, $TeCl^{2+}$ and $TeCl_2^{2+}$, but the spectrum is less complex than that of $TiCl_3$ or $FeCl_3$.

The mass spectra of the quadrivalent metal chlorides stannic tetrachloride and germanium tetrachloride are simpler than those of chlorides of tervalent elements. Diagramatic representations of the mass spectra are given in Figs. 1–10.

Department of Synthetic Chemistry
Faculty of Engineering
Nagoya University
Furo-cho, Chikusa-ku
Nagoya, 464 Japan

KOZO MATSUMOTO
NOBUTOSHI KIBA
TSUGIO TAKEUCHI

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Summary—The mass spectra of ten metal chlorides are given and may be used to test the purity of metals.

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ON THE ROLE OF ANALYTICAL CHEMISTRY IN SOLVENT EXTRACTION PROCESSING*

A. W. ASHBROOK

Extraction Metallurgy Division, Mines Branch, Department of Energy, Mines and Resources, Ottawa, Canada

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Summary—Analytical chemistry plays a vital role in both the development and operation of any chemical process, and the process of solvent extraction as applied in hydrometallurgical operations is no exception. Because of the increasing attention being given today to solvent extraction as a means of separating metals in solution, it seemed appropriate that the analytical chemistry associated with solvent extraction studies, process development, and operations be reviewed. In this review, consideration is given only to analysis of the aqueous and organic phases for the determination of solvent components, rather than to the determination of metals in these phases. Furthermore, the major emphasis is placed on analytical methods which are applicable to process studies and plant control, and which require a minimum of instrumentation and operator skill. The importance of sampling is discussed first, and problems encountered in obtaining representative samples from the solvent, aqueous, and slurry phases are considered in some detail. This is followed by a review of methods of analysis which are directly applicable, or are considered as having application, to the analysis of the organic and the aqueous phases of the solvent extraction process. Analytical methods for the determination of the various extractants, modifiers, and diluents presently being used, or considered for use, in commercial solvent extraction processes are surveyed. First, those methods which are applicable to the determination of reagents in the solvent phase are considered, followed by those which are available for analysis of the aqueous phase for the determination of soluble components of the solvent phase. In both cases extractants, modifiers, and diluents are considered separately. Finally, some of the more obvious analytical needs, and areas where research is required in order that a more complete understanding of the solvent extraction process can be obtained, are discussed.

Much interest has developed over the last few years in the application of solvent extraction to metallurgical processing, which is evident from the number of plants put into operation, and planned for the future.

On the other hand, there is apparently little interest being shown in the development or in the use of methods of analysis in this particular field. One might gather from the published data that the only analyses carried out in solvent extraction studies are those required to determine metal concentrations in aqueous (feed and raffinate) phases. Little concern is directed towards analysis of raffinates for solvent components, or extracts for metal and solvent components.

In more fundamental studies on the extraction of metals, particular attention is directed towards volume measurements, volume changes and metal ion concentrations in the aqueous phase where reactant concentrations are usually low. In process studies these quantities and concentrations are usually determined with much less accuracy and precision. In process studies it would seem that in order for the process to be optimized, it is important to determine metal concentrations in both phases, solvent losses in raffinates, and solvent composition and degradation over prolonged periods of time.

Little attention is being paid today to the loss of solvents other than to those effects such losses may have on the economics of a solvent extraction process. Thus, provided this loss, determined almost invariably by inventory, is not uneconomic for a given system, the actual determination is rarely of concern.

It is unlikely that this situation will obtain for long, because of public concern for damage to the environment which can result from the distribution of both organic and inorganic materials. We can foresee a need to determine the concentrations of solvent components which may occur in waste streams from solvent extraction processes. These will

have to be determined before the installation of a plant, necessitating their determination in bench or pilot plant studies.

The apparent lack of attention which has been paid to the analytical requirements associated with solvent extraction studies and processes is the reason for this dissertation, the main objective being to focus some attention on this most important, but often forgotten, area.

ANALYTICAL REQUIREMENTS

Methods

The analytical techniques and methods required in solvent extraction studies can be suitably divided into two classes: first, those required for fundamental and process studies, and second, those required for plant control purposes. This division is based essentially on the availability of skilled and qualified personnel, sophistication of equipment, and available time.

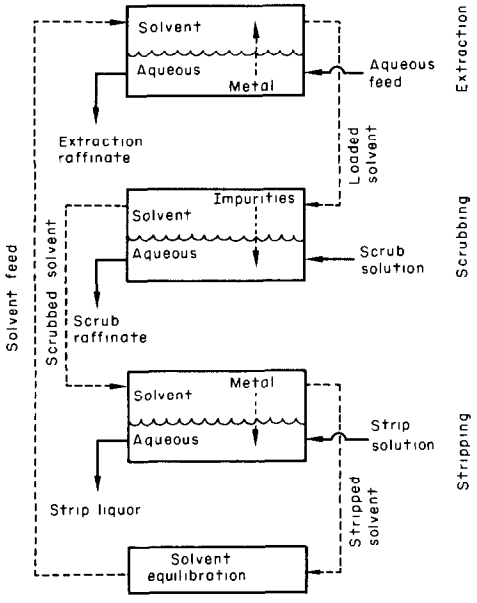


Fig. 1. The general process of solvent extraction as applied to metallurgical processing.

Research laboratories and universities are usually well endowed with skilled and learned analytical personnel, and with sophisticated equipment which can make analysis a much simpler operation than it is in plant operations, especially those in more remote areas. Furthermore, it is unlikely that methods of analysis used in the more fundamental solvent extraction studies are directly applicable to plant samples, for obvious reasons.

As a result, methods which may be considered simple in research laboratories cannot be used in operating plants because the cost of analysis would become prohibitive. There exists, therefore, a need for simple, accurate and precise procedures which can be carried out by relatively unskilled personnel with a minimum of equipment and reagents.

Samples

It is useful at this point to consider the type and nature of samples which require analysis if any process is to be optimized, and also those which may be required for control of materials detrimental to the environment.

Considering only the unit process of solvent extraction, there are essentially eight streams which require analysis of one or more components; aqueous feed, extraction raffinate, scrub solution, scrub raffinate, loaded solvent, strip solution, strip liquor and stripped solvent (Fig. 1).

Samples which may require analysis for environmental pollution purposes will be those which leave the plant either directly from the solvent extraction circuit, for example the extraction raffinate, or from a process or processes downstream from the solvent extraction circuit and dealing with its liquors. These will depend on the actual plant design, and therefore cannot be defined here. They could also include samples from settling ponds, *etc.*

It is apparent that the samples from a solvent extraction circuit will vary considerably; in two cases they are organic, and in the others aqueous in nature. It is also apparent that the methods of sampling will vary, and this subject will be discussed next.

Sampling

It is a self-evident truth that an analysis is only as good as the sample on which the analysis is performed. In far too many cases this axiom is either not recognized or is ignored, both in the plant and also in the laboratory. It cannot be stressed too strongly that usually a sample is only a representative of a whole or population, and is not in itself the population.

The degree to which a sample is representative of the population from which it is taken depends, in part, on its size and on the homogeneity of the population. Thus, sample size is a very important factor in any sampling scheme, and especially so when the homogeneity of the material being sampled is questionable.

Considerable thought must be given to sampling techniques if the analytical results are to be meaningful. The problem also involves the economics of both sampling and carrying out the analyses. The more samples which are taken and analysed the more certain will be the analytical result, but this must be weighed against the costs of sampling and analysis.

Sampling techniques for many types of materials have been described,[1,2] and the statistical approach has been well documented.[3] However, the sampling of streams in solvent extraction processes involves problems peculiar to such processes, and which do not appear to have been detailed in the literature. These are dealt with below in some detail.

The aqueous phase. Most extractants used in commercial solvent extraction processes are surface-active. Consequently they will be readily sorbed onto the surfaces of sample containers, and this fact must be taken into account in the sampling and analysis of solvent extraction streams.

The effect of surface adsorption will be greatest when only small amounts of solvent are present in the sample. As the solvent concentration decreases, the sample taken for analysis usually increases. This requires a larger sample container with a resultant increase in surface area available for adsorption. Problems also arise in the transfer of aliquots of the sample for analysis. For example, in the determination of low concentrations (ppm) of tertiary amine in aqueous solutions, it has been shown that adsorption of amine on the pipette can produce results that are up to 20% low.[4] This effect was overcome by rinsing the pipette at least five times with the sample solution before taking an aliquot for amine determination. Another example of amine adsorption onto surfaces has been given by Milun and Moyer,[5] who showed the loss of amine from an aqueous solution onto polyethylene, and onto "Desicote"-coated glass containers, to be a function of time. On glass containers coated with "Desicote", very little amine was adsorbed.

The problems of adsorption will occur when taking the sample in the plant, thus it is advisable to rinse the sample container several times with the solution being sampled before taking a sample for analysis. Specially prepared sample containers could also be used. It is also evident from Milun and Moyer's work[5] that samples should be analysed as soon as possible after they are taken.

To obtain consistent results on samples which contain, or are suspected to contain, entrained solvent it is preferable to remove this before analysis. In cases where inefficient plant operation results in visual amounts of solvent in the aqueous sample, analysis would not be too meaningful. If the dissolved portion of the solvent is to be determined, the entrained solvent must be removed.

The size of the sample originally taken from a process stream will be governed by several factors, such as the sensitivity of the methods of analysis, the amount of entrained solvent

expected, and the number of analyses to be carried out on the sample. One way of minimizing the effects of sorption of solvent on sample containers and pipettes is to make the sample size the same as that required for the analysis. In this way the whole sample is used, and the container can be washed with methanol or other reagent to remove sorbed solvent. A drawback to this method of sampling is that the sample taken may not be sufficiently large to be representative of the stream being sampled. It may, therefore, be necessary to make a compromise between sample size and the accuracy of the analysis.

The problem of entrained solvent in an aqueous sample is essentially one of non-homogeneity. For a meaningful analysis to be obtained, any sample must be homogeneous. Visual amounts of solvent in an aqueous sample, therefore, mean that any analyses carried out can provide only approximately true results, and this must be understood by both the analyst and engineer.

Slurries. The economic advantages to be gained by application of the so-called solvent-in-pulp process[6] to commercial operations are many. This process involves extraction of a metal from a leach slurry and obviates the need for filtration of the solid material. Several pilot plant studies have been made on this process, with particular successes.[7,8]

Sampling of slurry raffinates presents major problems. The rate at which solids in a slurry settle is dependent on solution viscosity, density and size of the solid particles, temperature, and so on. The greater the settling rate the less chance there is of obtaining a representative sample. In fact, it is doubtful if a truly representative sample from such a stream can be obtained.

The time between sampling and analysis may vary considerably. Ideally, the sample should be analysed immediately after sampling. This, unfortunately, is the exception rather than the rule.

There are essentially three points to consider in determining solvent losses in slurries. First, physical entrainment; this is more likely to occur in slurry than in liquid–liquid extraction because the solids can drag solvent into the raffinate sampling port of the contactor. Secondly, there is sorption of solvent onto the surfaces of the solid particles. This may be considered as a special type of entrainment, and in fact may give rise to entrainment if the sorption results in small globules of solvent adhering to the solids. Finally, there is the solubility of the solvent in the aqueous phase. Here again, it is expected that loss of the more polar constituents of the solvent will be greater than loss of the non-polar constituents.

It is probably impossible at present to determine quickly and accurately these three separate types of solvent loss. Entrainment losses, for example, are not readily obtained by volume measurement because the solids in the sample can trap droplets of solvent as they settle. From observations of slurry raffinate samples, it has been found that droplets of solvent are released from the settled solids over periods of hours and days, and these coalesce on the surface of the aqueous portion of the sample. The problem is not readily solved by agitation of the sample. For example, to agitate the solids so as to maintain them in a suspended state in order that the occluded solvent be freed requires sufficient agitation for the solvent released to be dispersed again in the suspension. As the solids settle after agitation, the solvent is again trapped.

Neglecting the problem described above, analysis of slurry samples can be accomplished in essentially two ways. The first approach is to use the whole sample for the determination, which would provide a total solvent loss. The other approach is to separate the solid and liquid phases and analyse each separately.

In the first method one major drawback is that in order for the sample to be in any way representative of the stream being sampled, it has to be larger than the aliquot taken for analysis. The problem then is how to take a representative aliquot from this large sample. In the second approach, the problems of entrapment of solvent, *etc.*, can be serious and vary from sample to sample. Further, analysis by the second method will take at least twice as long as by the first.

It is evident that the whole problem of sampling aqueous raffinates (liquid and slurry) is complex, and that many compromises may have to be made between the sampling and analytical procedures. Further, analysis of a single sample can provide quite erroneous and

misleading results; consequently solvent losses should only be viewed in the light of several analytical determinations.

The organic phase. Compared to sampling of aqueous raffinate streams, the sampling of organic phases is relatively free from problems. Here, the stream is much more homogeneous. The problems are then not so much in sampling the organic streams in the plant as in sampling in the laboratory.

Loaded solvents which may contain more than 20 kg of metal per m^3 are invariably viscous. This results not only from the metal concentration but also from the fact that relatively high concentrations of extractant are sometimes used to obtain high metal loadings to reduce the solvent throughput in the plant.

In transfer and measurement of such solutions by pipette, drainage of the pipette becomes a serious problem. The same situation obtains with aqueous solutions containing high concentrations of salts. One way of circumventing this problem is to use a wash-out pipette.

Aqueous or solid entrainment in organic samples can usually be removed quite readily by centrifuging, or, if the viscosity of the sample is not too high, by filtration through a phase-separating paper such as a Whatman 1PS.

ANALYTICAL METHODS

As was mentioned previously, methods of analysis for process control need to be simple, but with sensitivity and accuracy adequate for the purpose. For example, in the determination of extractant concentration in the solvent phase, a titrimetric procedure would offer the ease, accuracy and precision required, since the concentrations of extractants are usually greater than 5% v/v in the solvent. On the other hand, the determination of extractant loss in aqueous raffinates, probably of the order of a few ppm, would require much greater sensitivity, such as can be achieved by a colorimetric procedure.

In considering or reviewing available analytical methods it will be useful to separate them into those used for analysis of the organic phase, and those used for the aqueous phase. These two categories can then be suitably divided to deal with extractants, modifiers and diluents.

The organic phase

All extractants currently in use in commercial solvent extraction operations are liquids (Table 1), of viscosity such that they need to be diluted in order to improve dispersion in the organic phase, improve settling (coalescence) characteristics, and avoid emulsion formation. Diluents used, or those being studied for use,[9] range in nature from essentially pure aromatic to pure aliphatic, and are usually fractions from the distillation of petroleum products.

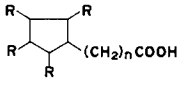
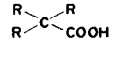
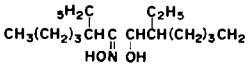
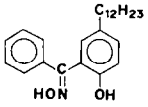
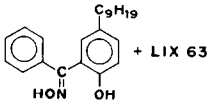
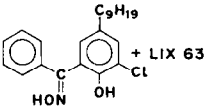
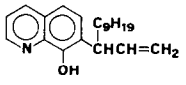
Concentrations of extractant in a diluent can range from 2 to 50% v/v. This solvent mixture may also contain a modifier to improve the solvent characteristics, but mainly to suppress the formation of a third phase. Modifiers are limited to aliphatic alcohols (such as 2-ethylhexanol and isodecanol), *p*-nonylphenol and tri-n-butyl phosphate (TBP).

Because of the generally active nature of the extractant, interference from the diluent and alcohol in the determination of the extractant does not usually occur, since both are relatively unreactive. The reactivity of the extractant towards other reagents depends on the active group, and it is convenient then to separate extractants in this way, since similar extractants can usually be determined by the same method. Extractants considered here will be divided into acidic, basic, neutral and chelating.

Acidic extractants. The one extractant in this class to have seen extensive use in commercial solvent extraction processes is di-(2-ethylhexyl)phosphoric acid (D2EHPA). Others which have been investigated are other alkyl phosphates, carboxylic acids (used in a Russian process for the separation of cobalt and nickel,[10] and the extraction of yttrium),[11] and sulphonic acids.

Titration in non-aqueous solution has been used extensively for the determination of these extractants in the organic phase. Basically the determination of these extractants presents no analytical problems by titrimetric methods, and general methods are available

Table 1. Some commercially available extractants

Extractant	Type	Structure	Supplier	Some refs to Uses	Some refs to Anal methods
Di(2-ethylhexyl)phosphoric acid	Acidic	$\left(CH_3(CH_2)_3CHCH_2O\right)_2POOH$ with CH_3CH_2	Union Carbide	127, 129–132	12, 69
Naphthenic acid			Shell Chemicals Exxon	133	12
Versatic acids			Shell Chemicals	133	12
LIX 63	Chelating		General Mills	134, 135	46, 98
LIX 64			General Mills	38	46, 98
LIX 64N		LIX 65N + LIX 63 (~1 vol %)	General Mills	38–43	46, 98
LIX 65N		 + LIX 63	General Mills		46, 98
LIX 70		 + LIX 63	General Mills	136	46, 98
LIX 71		LIX 70 + LIX 65N	General Mills	136	
LIX 73		LIX 70 + LIX 65N + LIX 63	General Mills		
Kelex 100			Ashland Chemicals	137–140	12, 99
Kelex 120		20 vol % Kelex 100 in p-nonylphenol	Ashland Chemicals		
Primary amines	Ion-association	$R{\cdot}NH_2$ ($R = C_{12}-C_{14}$)	Rohm & Haas	141 143	12, 97
Secondary amines		R_2NH ($R = C_{10}-C_{12}$)	Ashland Chemicals	144	
Tertiary amines		R_3N ($R = C_8-C_{10}$)	General Mills	145 150	
Quat ammonium halides		$(P_3N^+CH_3)Cl^-$ ($R = C_8-C_{10}$)		131, 151	
Tri-n-butyl phosphate	Solvating	$\left(CH_3(CH_2)_3O\right)_3P=O$	Ashland Chemicals	152–154	31, 82
Methyl isobutyl ketone		$(CH_3)_2CH_2CH_2\overset{O}{\overset{\|}{C}}CH$		155–157	

in any text on non-aqueous titrations. The use of both indicator and potentiometric methods for end-point determination is adequate. Indicators may be considered the more suitable because a pH meter is then not necessary.

A general method for the determination of an acidic extractant in a solvent would be by titration in chloroform solution with sodium methoxide solution.[12] Any of the normal indicators used in acid–base titrations may be used.

This general approach can only be used for solvents which contain no metals, acids, bases or other components which would interfere. For solvents which have been contacted with acidic or basic aqueous solutions containing metals, or have been equilibrated to form salts of the extractant (such as the sodium salt of D2EHPA) the sample must be treated before the determination of the extractant. Metals and salts can usually be stripped from the solvent with acids (20% v/v sulphuric acid), followed by water washing to remove entrained acid, and then titrated.

The concentration of sodium or ammonium salt of, say, D2EHPA in a solvent can be determined by titration with perchloric acid, again in chloroform solution, with Thymol Blue as the indicator.[12] The total D2EHPA can be determined as described above.

Thymol Blue is a versatile indicator since it has two pH ranges over which it can be used. With acid solution the colour change is from yellow to purple, and with base from

yellow to deep blue. These colour changes can be used to advantage in the determination of solvents which may contain mineral acids. Thus after stripping with acid, a solvent sample can be diluted with chloroform, and Thymol Blue added followed by base to a yellow → blue end-point. The mineral acid is converted into a salt (*e.g.*, sodium sulphate) and no longer interferes. Titration of the excess of base with perchloric acid to a blue → yellow end-point is followed by titration of the extractant to a yellow → purple end-point.[12]

Basic extractants. For all commercial operations, basic extractants are limited to primary, secondary and tertiary amines and quaternary ammonium halides. These are usually long chain fatty amines of fairly high molecular weight, and are used as metal extractants in acid or concentrated salt systems. Because the mechanism of metal extraction is one of anion-exchange (although this appears not to be absolutely necessary[13]) the amine-containing solvent requires equilibration with an acid to provide the exchangeable anion before it enters the metal extraction stage. Consequently this has to be taken into account in any method for the determination of amine concentration in the solvent phase.

Numerous volumetric methods employing titration in non-aqueous media have been proposed for the determination of both macro and micro amounts of amines. The non-aqueous media include acetic acid,[14] methyl ethyl ketone,[15] pyridine,[16] nitromethane,[17] "methyl Cellosolve",[18] dioxan,[19] benzene,[20] and some mixtures of these. The end-point is usually determined by indicator or potentiometrically. Non-aqueous titrations are also very useful for the determination of primary, secondary and tertiary amines in mixtures of these amines.

Amines generally used in solvent extraction processing are not particularly weak bases, thus they can be determined by titration in chloroform or similar media. Most methods appear to use acetic acid, in which the basicity of the amine is increased. Acetic acid has one advantage over hydrocarbons for total amine determinations, namely that any basicity differences between the amine components tend to cancel out in this medium.

For the titration of amines in non-aqueous media they must be present as "free amine", and since samples of amine-containing solvents from plant processes rarely contain the amine in this form, treatment before analysis is necessary. Any metals present in the solvent sample will also have to be removed.

Conversion of an amine salt into the free amine is readily accomplished by contacting it with a solution of sodium carbonate; metals can be removed by shaking with dilute sulphuric acid or sodium carbonate (for example, uranium). After stripping with acid the sample will have to be treated to remove the acid taken up by the amine.

In the case of amine-containing solvents used for the extraction of uranium, both uranium and sulphuric acid in the solvent sample can be removed by shaking with calcium hydroxide.[12]

Probably the best titrant for determination of amines is a solution of perchloric acid in dioxan; indicators include Thymol Blue, Gentian Violet and Crystal Violet. Potentiometric end-point determinations may also be used. Modifiers such as alcohols and TBP do not interfere.

Neutral extractants. In all commercial solvent extraction operations only one neutral extractant, TBP, is used in a diluted form. Methyl isobutyl ketone is used undiluted and thus does not require analysis in the solvent phase.

TBP has seen considerable use in the nuclear industry where it is used for the extraction and separation of radioactive species.[21] It has also been used successfully for the separation of zirconium and hafnium,[22] and for the separation of uranium from impurities before the production of high-grade UO_2 and UO_3.[23] TBP has also seen some use in the extraction of base metals.

Methods for the determination of TBP in kerosene-type diluents are of varied nature. Titrimetric,[24] colorimetric,[25] flame photometric,[26] gas chromatographic[27–29] and paper chromatographic[30] methods have been described.

One titrimetric method is based on the ability of TBP to form an adduct, $TBP.HNO_3$, under controlled conditions when contacted with nitric acid. The nitric acid thus extracted is titrated and the equivalent amount of TBP calculated.[31] An analogous method uses the

formation of a TBP–uranium complex, $UO_2(NO_3)_2 2TBP$, the uranium being determined by titration with EDTA, using Xylenol Orange as the indicator.[32] A similar method has been used for micro amounts of TBP, the uranium being determined colorimetrically with Arsenazo I.[32]

These methods are also suitable for the determination of butyl dibutylphosphonate, tributylphosphine oxide and trioctylphosphine oxide. Other colorimetric methods, again employing the extraction of uranium but measuring the colour of the yellow TBP–uranium complex, in both the visible and ultraviolet ranges, have been described.[33] Other reported methods involve turbidimetry,[34] dielectric properties,[35] specific gravity,[36] and decomposition followed by determination of phosphorus.[37]

In many of these procedures, metals must be removed from the sample before the determination of the extractant, which can usually be accomplished by stripping with acid or sodium carbonate solution.[12]

The most useful of the methods outlined above are the indirect titrimetric determination of TBP by contacting with nitric acid followed by titration with base, and the colorimetric approach using the colour of the extracted uranium complex as an indirect method for the determination of TBP.[12]

Chelating extractants. Commercially available chelating extractants are limited to the General Mills LIX reagents (substituted 2-hydroxybenzophenones) and the Ashland Chemicals Kelex 100 reagent (a substituted 8-hydroxyquinoline). While Kelex has not as yet seen use in commercial operations, LIX 64N has been used in several solvent extraction processes for the extraction of copper.[38–43]

Having a tertiary nitrogen atom, the Kelex extractant can be readily titrated in non-aqueous media as a tertiary amine.[12] However, this extractant contains some 8-hydroxyquinoline[44] which will also be titrated under these conditions, but for plant control processes this should not be a problem.

The LIX extractants are very weakly acidic in nature,[45] but can be readily titrated potentiometrically in non-aqueous media with strong base, provided the titration is done slowly.[46] This procedure does not distinguish between the isomers. Titration of these extractants with base gives rise to the formation of a yellow colour (anionic species) which may have possibilities for use as an internal indicator, but this approach has not been examined.

A procedure generally employed in plants using LIX extractants utilizes the loading capacity of the solvent for copper as a measure of the LIX concentration.[46] The copper loaded by the solvent may be determined colorimetrically (after dilution) or by stripping the copper and determining it in the strip liquor by a suitable method.

Modifiers. There appear to be no simple and accurate methods for the determination of modifiers (aliphatic alcohols, phenols and TBP) in the solvent phase. Most methods for the determination of alcohols, for example, are time-consuming and may require very close control.[47] One approach to the determination of alcohols in solvents is to use the red-brown complex formed between vanadium oxinate and an aliphatic alcohol.[48–52] A less sensitive approach is the use of acetylacetone in place of oxine,[51] which may be more suitable for alcohols in the 2–5% v/v range.

When used as a modifier, TBP may be determined as indicated previously, provided that the extractant does not extract acid or uranium.

The aqueous phase

The composition of raffinates from solvent extraction processes will vary within a process, and from process to process. In a single process the extraction and scrub raffinates may be expected to have fairly constant compositions, especially if the feed and scrub solution compositions are constant. Variations should then only occur as a result of upsets such as pump failure, solution surges, or during start-up after a shut-down period.

Raffinates from similar processes may vary significantly in composition as a result of different feed and scrub solutions. Because of such variations any given method of analysis may not be directly applicable to all raffinates from similar processes. For example, some processes used for preparation of a feed to a solvent extraction circuit, such as leaching,

filtration, thickening and precipitation, may use reagents which interfere with the determination of solvent extraction reagents in raffinate samples. It is advisable to determine beforehand whether such is the case. In fact, each method of analysis should be investigated thoroughly with regard to its applicability to the analysis of any sample. Attention must also be paid to sampling techniques in both the plant and in the laboratory. This point cannot be emphasized too strongly.

Few methods are available for the determination of solvent components in raffinates. Many methods have been reported for the determination of organic compounds such as acids, bases and alcohols, in water. In most cases these methods are not applicable to raffinate solutions, for obvious reasons. Further, raffinates will contain all the components of a solvent (extractant, diluent and modifier), which will not necessarily be in the ratio in which they are present in the solvent.

In reviewing methods for the analysis of solvent components in the aqueous phase it is again convenient to divide them into different categories as was done for the organic phase.

Acidic extractants. There are a number of methods reported in the literature for the determination of organic acids in aqueous solutions, many of which are not applicable to plant control. Thus carboxylic acids have been separated from the inorganic constituents of a solution by steam distillation. Shaova *et al.*[53] employed this approach, and determined monocarboxylic acids in the distillate by polarography. Gas chromatography has been used for the determination of carboxylic acids in aqueous solutions.[54,55] Low molecular-weight acids have been separated on ion-exchange resins and determined in the eluates by gas chromatography.[56] Others have used gas chromatography with varying degrees of success.[57–59] Baker[60] has reported the determination of volatile fatty acids in water at the 10-ppm level by gas chromatography. One problem with gas chromatography for the determination of total acids such as "Versatic" and naphthenic acids in aqueous solution is that these are not pure compounds, but mixtures of several similar acids. The concentration of the components also varies, to some degree, from batch to batch, or run to run. For example, Versatic 911, as received, contains at least five components, and these have been shown to vary significantly between two different samples.[4] Another point to remember is that the various components of the acid extractant may have different solubilities in the aqueous phase, which could present problems in interpreting the analyses in terms of extractant loss.

Colorimetric methods of analysis for acids include the use of Rhodamine and Butylrhodamine for aromatic carboxylic acids, in an extraction–photometric procedure.[61]

Methods which are probably the most appropriate for the determination of fatty acids in solvent extraction raffinates are those based on the formation of a metal–carboxylic acid complex. This approach is similar to that employed for the determination of D2EHPA, Kelex, and the LIX reagents. Such methods have been described,[62–68] and could almost certainly be modified to determine carboxylic acid extractants.

Except for one reported method,[69] there appear to be no methods in the literature for the quantitative determination of trace amounts of alkylphosphoric acids in solvent extraction raffinates. Alkylphosphates in aqueous solution have been determined indirectly by oxidation to phosphoric acid, followed by determination of the phosphorus by conventional methods. This approach assumes that all the phosphorus determined results from the organophosphate. The presence of TBP in the solvent, or phosphorus in the feed solution, nullifies this approach.

Phosphine oxides in aqueous solution have been determined by O'Laughlin, Sealock and Banks.[70] The method is based on the formation, in acid solution, of a yellow adduct between the phosphine oxide, titanium(IV) and thiocyanate, which is extracted into chloroform or carbon tetrachloride.

Basic extractants. The determination of micro and macro amounts of amines in aqueous solutions has been investigated quite thoroughly, and a number of methods have been reported in the literature. Most employ the formation of a coloured complex of the amine, and a photometric finish.

Critchfield and Johnson[71] determined primary amines in the presence of secondary and

tertiary amines by reacting the primary amine with an aqueous reagent containing cupric chloride, salicylaldehyde and triethanolamine. The complex formed was extracted into hexanol, and the copper in the hexanol determined photometrically with bis(2-hydroxyethyl)dithiocarbamic acid. The yellow-green colour formed between amines and alcoholic cupric chloride in aqueous solution, and extracted into chloroform, was used by Herschensen and Hume to determine total amine in aqueous solution.[72]

Silverstein[73] used Methyl Orange, at pH 3–4, to form an extractable coloured adduct for the determination of total amines. In the presence of salicylaldehyde, primary amines did not react. In the presence of acetic anhydride, only tertiary amines are determined. The procedure was modified by Larrick[74] for use in the field. Irving[75] employed Bromocresol Green for the determination of amines in $0–10^{-6}M$ solutions. The adduct was extracted into dichloroethane and determined colorimetrically. Trifluoroacetic anhydride was used by McCurdy and Reiser[76] to form trifluoracetyl derivatives of amines in aqueous solution, followed by extraction into n-hexane and determination by gas chromatography. Formation of *N*-substituted cinnamides of primary and secondary amines was the basis of a colorimetric method for the determination of these amines by Hong and Connors.[77]

The ability of small amounts of primary amines to reduce the absorption of a copper–EDTA solution at 720 nm was used by Citron and Mills[78] to determine primary amines. Succinaldehyde has also been used for the spectrophotometric determination of primary amines.[79,80]

Dyes have proved to be popular chromophoric reagents for amines. These include Bromocresol Purple,[81,82] Bromothymol Blue,[83] Bromocresol Green,[82] Phenol Red,[82] and Methyl Orange.[84] Other reagents include picric acid,[85] ninhydrin,[86] 3,5-dinitrobenzoyl chloride,[87] 3-chloro-3-(10,12-dioxodi-indeno-[1,2-*b*; 2′,1′-*e*]-phthalide,[88] aconitic anhydride,[89] and chloranil.[89]

The formation of an extractable complex in aqueous solution between amines and cobalt thiocyanate has been used for the determination of symmetrical fatty amines in raffinates from uranium solvent extraction plants.[90] This method has been modified to determine non-symmetrical amines.[91] Further modifications involve the use of ferric thiocyanate in place of the cobalt thiocyanate,[92] and the extraction of amine into carbon tetrachloride before the formation of the amine–cobalt thiocyanate complex.[93] Small amounts of long-chain amines in aqueous solutions have also been determined by using Erdmann's salt.[94]

Titrimetric methods for the determination of amines in aqueous solutions have included the use of eosin[5] and sodium lauryl sulphate.[95] Amine salts in aqueous solution have been converted into free amines in a "fore column" packed with an acid-coated support in a gas chromatograph. The amines were then determined by gas chromatography on an analytical column attached to the end of the "fore column".[96]

Of all these procedures, one using Bromophenol Blue as the chromophoric reagent,[97] and extraction of the amine–dye complex into chloroform, is probably the easiest to carry out, with adequate accuracy and precision at the ppm level in aqueous raffinates. All of the common amines (primary, secondary, tertiary and quaternary) can be determined by this method.

Neutral extractants. O'Laughlin *et al.*[70] have reported a spectrophotometric procedure for the determination of phosphine oxides in aqueous solutions, based on the formation of an extractable adduct formed between the oxide, titanium(IV) and thiocyanate. Cationic interference was not investigated. A similar approach in which a metal complex formed in the aqueous phase is extracted into an inert hydrocarbon, has been investigated for the determination of TBP.[4] Ferric thiocyanate, for example, can be used, but the method is not very sensitive. Further, in the presence of D2EHPA or similar extractants, this approach is not suitable because the D2EHPA forms an extractable species and interferes.

Perhaps the most promising approach to the determination of TBP in aqueous raffinates is by forming an extractable complex with a metal ion, and determining the metal in the extracted phase. For example, in a modification of the method of Nikolaev,[32] the uranyl nitrate–TBP complex $(UO_2)(NO_3)_2 . TBP$ is formed in aqueous solution, extracted into a suitable organic solution, and the uranium determined colorimetrically by a reagent

such as Arsenazo or bromopyridylazodiethylaminophenol. Alternatively, the TBP extracted into the organic phase (as a metal–TBP complex) may be determined by gas chromatography.

Chelating extractants. Methods for the determination of LIX extractants in the ppm range in aqueous raffinates have recently been reported,[98] as has a procedure for Kelex 100.[99] These methods make use of the fact that extractants present in the aqueous phase will complex with a metal ion, and under optimum experimental conditions can be extracted into an organic phase and be determined spectrophotometrically. The methods are simple and do not require elaborate apparatus.

Modifiers. Reagents of concern here are aliphatic alcohols, especially isodecanol and 2-ethylhexanol, nonylphenol and TBP. These reagents are used as modifiers in solvent systems which require modifiers.

Many methods have been reported for the determination of monoaliphatic alcohols in aqueous solution. Thus, Chalov and Volskaya[100] converted ethanol into ethyl nitrate by reaction with nitrous acid, formed an azo dye and determined this colorimetrically. Parker[101] used a similar method, which was later modified by Wellington[102] for microdetermination of monohydric aliphatic alcohols.

Oxidation of alcohols with various oxidants, and subsequent determination by spectrophotometry, have been reported. Ginther and Finch[103] oxidized isopropyl alcohol to acetone with potassium persulphate, followed by reaction of the acetone with alkaline salicylaldehyde to form the orange-red dihydroxybenzal acetone. Other oxidizing agents such as dichromate have been used, but the colour produced by this reagent has necessitated distillation of the acetone before its determination.[104–106] Critchfield and Hutchinson[107] used dichromate oxidation for the indirect determination of secondary alcohols, the ketone produced being determined colorimetrically as the 2,4-dinitrophenylhydrazone derivative. Excess of dichromate was reduced with hypophosphite.

Spectrophotometric determination of aliphatic alcohols with ceric ammonium sulphate as reagent have been reported.[108,109] These are not applicable to the microgram range. Other colorimetric methods involve reactions of alcohols with vanillin or *p*-dimethylaminobenzaldehyde,[110,111] chromotropic acid after oxidation,[112] and phenylhydrazine.[113]

Acetylation of primary and secondary alcohols, followed by hydroxamation, was used by Gutnikov and Schenk.[114] Titrimetric methods for the determination of alcohols in aqueous solution have been reported, based on the back-titration of excess of oxidant (permanganate, xenon trioxide, ceric sulphate) after oxidation of the alcohol.[115,116] Konishi *et al.*[117] have reported a procedure based on the oxidation of alcohols with excess of bromine chloride, the excess being titrated iodometrically. Gas chromatography has also been used to determine alcohols in aqueous solutions.[118]

Probably the procedure most studied for the determination of aliphatic alcohols in aqueous solution is that involving the formation of a red extractable vanadium(V) oxinate–alcohol complex.[48,52] Other vanadium complexes also give rise to red colours in the presence of alcohols, and have been suggested for the determination of alcohols.[52] But while these methods are sensitive and accurate for the determination of alcohols in water, they are not directly applicable to the determination of alcohols in solvent extraction raffinates. The reason for this is that raffinates contain trace or major amounts of metals which also form extractable coloured complexes with oxine, and consequently interfere. Separation of the alcohol is thus required before its determination. This same problem of interferences is common to all the methods, except perhaps gas chromatography.

There does not appear to be any satisfactory method available for the determination of monohydric aliphatic alcohols, in the ppm range, in raffinates from solvent extraction processes.

The same situation obtains in the case of TBP, when it is used as a modifier in the D2EHPA solvent system. The method of forming an extractable metal–TBP species is inapplicable since D2EHPA would (almost certainly) form a similar metal species and extract with the TBP–metal species. If the TBP could be extracted from the aqueous phase into an organic solvent, it could probably be determined by gas chromatography. In this case, any D2EHPA co-extracted would not interfere.

Diluents. The determination of kerosene-type diluents in aqueous solution presents many problems to the analyst. These materials are fractions of crude oil, and can contain many different types of hydrocarbons, ranging from aliphatic to aromatic. Further, variations in composition of the diluent, even though small, could affect both the analysis and the extraction of metals.

Determination of kerosenes, or similar materials, in aqueous solutions in the ppm range has been investigated by several workers.[119–124] The method described by Lee and Walden[125] is satisfactory for the determination of kerosene (Shell 140 Flash Naphtha) in aqueous solution provided no other organic compounds are present. Almost all organic materials give a turbidity under the conditions of the method. Thus the method is not suitable for the determination of kerosene in raffinates from solvent extraction processes.

Slurry raffinates

Methods used for the determination of amines, LIX and Kelex extractants have also been applied to the determination of these reagents in slurry raffinates.[12] The general technique is to extract the reagent from the slurry with methanol. In this way the water-soluble reagent and the adsorbed or entrained reagent can be determined separately if required. Problems associated with sampling of slurries were discussed earlier in this paper.

DISCUSSION

It is evident that there are many methods of analysis available for compounds similar in nature to those used in solvent extraction processes. It is also evident that the majority of these methods are not directly applicable to the determination of solvent extraction reagents, especially in raffinates. The number which may be applicable is further reduced if limited to the simpler methods suitable for plant control purposes. Thus there is a pressing need for analytical methods which are simple, rapid, accurate, precise, and of low cost.

Generally the determination of extractants in solvents poses few problems, mainly because the concentrations are sufficiently high for titrimetric methods to be applicable, and also because generally the other components of the solvent (diluent and modifier) are sufficiently inert for them not to interfere or interact during the determination. The use of mixed extractant systems could present problems, but such systems appear to be used only in experimental studies where the need for analysis is not usually necessary.

The major analytical problems are then those faced in the determination of solvent components in raffinates. Probably the most pressing problem in this respect is the determination of the solubility of each of the solvent components in raffinates. Except for a few data on the solubility of extractants[12] nothing is known about the solubility of diluents and modifiers in solvent extraction processes. A knowledge of the solubility of each separate component in water is probably of little use, because in many cases the aqueous solutions involved in solvent extraction processes have high salt concentrations and are usually quite acidic, and also because it is unlikely that the solubility of each solvent component will be independent of the others.

It is also important to know whether the solubility of a reactive component of the solvent is a function only of its concentration in the solvent phase, a function of the concentrations of the other components of the solvent, or a combination of these. One instance of the solubility of an extractant increasing with increasing concentration in the solvent phase has been given for a carboxylic acid.[126] This aspect could be important if the use of extractant concentrations higher than those currently used were to be considered.

In a similar vein, it is important to know whether the extractant solubility in a given aqueous phase is a function only of the extractant, or is a function also of the formation of soluble metal–extractant complexes.

This approach appears to have been neglected in all studies of extractant solubility in raffinates, and could be of particular interest to those studying environmental effects of solvent extraction raffinates.

Obviously the analytical requirements in the areas indicated above will require, at least initially, modern analytical hardware and competent analysts. It might also mean that simple and inexpensive methods, suitable for plant control purposes, will not be forthcoming,

owing to the complexity and nature of the samples. However, this should not deter investigations into simple methods, or the use of unsophisticated equipment. For example, the use of atomic-absorption spectrophotometry is, today, a common method for the quantitative determination of metals in solution. Furthermore, these instruments are now quite cheap and suitable for use by plant technicians. Much the same can be said for gas chromatography, and the application of this approach could very well be the answer to some of the problems faced in the determination of organic materials in raffinates.

Concurrent with the development of methods of analysis must be the development of methods of sampling. Some of the problems involved in sampling have been discussed previously. Without an understanding of the problems associated with sampling, sample preparation, storage, adsorption of sample components on containers, and so on, the development of methods of analysis may be just an exercise in futility.

One area which also requires considerable thought is that of standards for calibration purposes. Since the extractants, diluents and modifiers used in solvent extraction processes are commercially produced, the composition of these reagents must be taken into account if they are used for purposes of calibration or standardization. A particular case in point is the use of the LIX extractants for calibration purposes. It is well known that these extractants contain some 40% v/v of an organic diluent, probably "Napoleum 470". Thus it is obvious that it is meaningless to use the commercial extractant as a standard without knowing exactly how much of the active reagent is present. Another complication in this particular case is the presence of two isomers of the active component, which could complicate methods which use the formation of an extractable metal complex as the means of determining the concentration of extractant.

Similar problems will arise with other extractants. Thus the commercially available Kelex 100 is only about 80% active reagent; tertiary amines contain primary and secondary amines, and so on. This problem can be alleviated if the particular method of analysis does not distinguish between similar components of the extractant, as is the case with most methods for the determination of amines which employ dyes as the chromophoric reagent.

As with all processes, maintenance of optimum operating conditions requires fast and accurate chemical analysis, both in the plant and in the laboratory. Control in the plant is generally limited to quick, routine methods suitable for use by plant operators, such as pH measurements, simple titrations, density measurements, and so on. Most of the analytical procedures are carried out in the plant laboratory, which again requires that these be fast, accurate and precise so that problems in the plant can be quickly diagnosed and corrected.

The choice of analytical methods is then of considerable importance, and is not usually an easy decision to make. In the selection of any control method the problem is one of deciding between accuracy and speed. As a general rule, the greater the reliability of the method the longer the time for analysis. Methods finally chosen involve a compromise between these two factors.

Another factor to be considered is the number of samples to be analysed. During bench-scale and pilot-plant studies a considerable number of samples, requiring several analyses on each, can be generated. This is the best time to assess methods of analysis for their accuracy, precision, speed and costs. Plant operations will normally involve fewer samples, especially after the initial plant problems have been overcome. But whichever methods are chosen will depend on the complexity of the samples, the number of analyses per sample, the available laboratory facilities, competence of the operators, and cost of analysis.

Undoubtedly, modern instrumentation can provide fast and accurate analysis. There are, of course, drawbacks to this approach, especially where a plant is situated in a remote area. For example, instrument failure could result in several weeks of down-time unless a back-up system were available. Most back-up systems are wet-chemical in nature. Sophisticated equipment also requires well-trained operators, not only to do the analyses, but also to maintain the equipment.

The analytical facilities, and analyses done, for a large pilot-plant operation for the separation of cobalt and nickel by solvent extraction, are given in Table 2 as an example of how this process was controlled analytically. The process used D2EHPA (as the

Table 2. Analytical requirements and methods of analysis used in a solvent extraction process for the separation of cobalt and nickel

Sample	Determination	Method
Aqueous feed	Co, Ni, Cu, Fe, As, Ca, Mg, Ag	XRF
	SO_4	Grav
	NO_3	Dist
	pH	
	Free acid	Vol
Solvent feed	D2EHPA	Vol
	D2EHPA (NH_4^+ salt)	Vol
Raffinate	Co, Ni	XRF
	D2EHPA	Color
	pH	
Scrub solution	Co, Ni	XRF
	pH	
	Free acid	Vol
Scrub raffinate	Co, Ni	XRF
	pH	
	Free acid	Vol
Loaded extract	Co, Ni, Ca	XRF
Scrubbed organic	Co, Ni	XRF
Strip solution	Free acid	Vol
Strip liquor	Co, Ni, As, Ca, Mg, Cu, Fe	XRF
	Free acid	Vol
	pH	
Nickel ammonium sulphate product from raffinate	Co, Ni, Cu, Fe, As, Ca, Mg, Ag	XRF
	SO_4	Grav
	NO_3	Dist
Cobalt oxide product	Co, Ni, Cu, Fe, As, Ca, Mg, Ag	XRF
	SO_4	Grav
	NO_3	Dist
Equilibrated solvent	D2EHPA	Vol
	D2EHPA (NH_4^+ salt)	Vol

XRF = X-ray fluorescence

ammonium salt) at pH 5–6 to extract cobalt from nickel, from a sulphate–nitrate solution.[127] The availability of X-ray fluorescence made analysis of the metal concentrations in the organic and aqueous phases fast and efficient. A similar scheme, used in a uranium solvent extraction plant in South Africa, has been described.[128]

In conclusion, there is much work to be done in the area of analytical chemistry associated with solvent extraction processing if this unit process is to achieve the success that many are predicting it will achieve. Analytical procedures are required that are simple, rapid, accurate, and precise, require little, or inexpensive, easily manipulated and maintained instrumentation, and are economic.

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MASSENSPEKTROMETRISCHE UNTERSUCHUNGEN ZUR ELEMENTARANALYSE ORGANISCHER VERBINDUNGEN—IV*

KINETIK DER VERBRENNUNG IM LEEREN ROHR†

OTTOKAR JAENICKE und WALTER WALISCH®

Organische und Instrumentelle Analytik, Universität des Saarlandes, 66 Saarbrücken, B.R.D.

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Zusammenfassung—Die in Teil III dieser Reihe beschriebene Meßanordnung gestattet durch gleichmäßiges Einleiten von Proben- und Trägergas (Sauerstoff) die Herstellung eines stationären Zustandes in einer Reaktionsstrecke und damit eine einfache Zuordnung der Länge l der Reaktionsstrecke zu einer Reaktionszeit t. Die bei l vorhandene Gaszusammensetzung wird stetig mittels einer beweglichen Einlaßsonde abgeschnüffelt, in etwa 80 ms ins Hochvakuum überführt, auf diese Weise "eingefroren" und sofort mit einem Massenspektrometer gemessen. Ist das Massenspektrometer auf einen für die zu beobachtende Komponente repräsentativen Peak eingestellt, so hat die registrierte Peakintensität $U(l)$ ihre Entsprechung in der kinetisch auswertbaren Kurve $U(t)$. Die Messung der thermischen Spaltung von Äthylacetat ergibt gute Übereinstimmung mit Literaturwerten. Orientierende Verbrennungsuntersuchungen an Wasserstoff, Kohlenmonoxid, Ammoniak und Methan zeigen, daß schon bei diesen einfachen Gasen das Verbrennungsgeschehen sehr komplex abläuft. Während Wasserstoff im Anschluß an eine Induktionsperiode gemäß einer Reaktion erster Ordnung bereits bei 928 K nahezu vollständig verbrennt, verläuft die Kohlenmonoxidoxidation bis 1150 K ziemlich langsam nach einem Geschwindigkeitsgesetz zweiter Ordnung. Ammoniak und Methan verbrennen wie Kohlenmonoxid je nach Reaktionstemperatur über andere Mechanismen, was sich in einer Änderung der Reaktionsordnung ausdrückt. Diese oft sprunghaften Änderungen erschweren, in Verbindung mit den Induktionsperioden, die kinetische Auswertung und beeinträchtigen die Genauigkeit der so gemessenen Geschwindigkeitskonstanten.

Die in Teil III[1] dieser Reihe beschriebenen Vorgänge der Verbrennung organischer Verbindungen, die im leeren Rohr beobachtet wurden, erlauben die Aufgliederung des Verbrennungsprozesses in eine oxidative Pyrolyse zu Molekül-Zwischenprodukten und deren anschließende Verbrennung zu Endprodukten. In den dargestellten Verbrennungs-Thermogrammen[1] ist die Temperaturabhängigkeit *beider* Schritte quantitativ erfaßt; u.a. ist daraus zu erkennen, daß mit steigender Temperatur die Verbrennung der Zwischenprodukte zur geschwindigkeitsbestimmenden Reaktion wird.

Eine Charakterisierung der Reaktionstypen, die dieser sekundären Verbrennung zugrunde liegen, wurde bisher nur über die Steigung der Umsatz-Temperaturkurven versucht und aus der maximalen Steilheit von 3%/Grad auf einen Radikal-Kettenmechanismus geschlossen. Eine genaue Kenntnis des *zeitlichen* Ablaufs der betreffenden Reaktionen und seiner Beeinflussung durch Partialdruck und Temperatur liefern zusätzliche Aussagen zum Mechanismus und erlauben eine Vorhersage des Reaktionsablaufs bei gegebenen Verbrennungsbedingungen. Ein gezieltes Eingreifen in den Verbrennungsprozeß wird nur so realisierbar.

Kinetische Untersuchungen der Verbrennungsreaktionen wurden bisher in der Regel unter Bedingungen[2–6] durchgeführt (Flamme, Stoßwellenrohr und statische Systeme), die mit den elementaranalytischen Gegebenheiten nicht vergleichbar sind. Lediglich in den Arbeiten von Pratt[7] sowie Burgoyne *et al.*[8] werden Meßbedingungen zugrunde gelegt, die gewisse Schlußfolgerungen auf elementaranalytische Verbrennungsprozesse zulassen. Ein Ergebnis dieser Arbeiten ist, daß sich der Reaktionsmechanismus mit der Temperatur, dem Summendruck und der Anfangskonzentration der Probe ändern kann. Weiterhin wurde ein Einfluß des Volumen-Oberflächenverhältnisses und des Gefäßmaterials festgestellt,[9] und es erscheint deshalb geboten, die Gesetzmäßigkeiten auch für den besonderen Fall der dynamischen Verbrennung im leeren Rohr experimentell zu bestimmen.

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Mit elementaranalytischen Verbrennungsprozessen haben sich erstmals Kainz und Mitarbb.[9,10] eingehender befaßt. Die von diesen Autoren eingesetzte "Pulsmethode" (einmalige impulsförmige Probenzugabe in den Trägergasstrom und Messung zu einem ausgesuchten Zeitpunkt nach Auslösen des Impulses) liefert jedoch immer nur einen Meßpunkt pro Probenimpuls, und für das Geschehen während der Verbrennung sind keine konstanten Bedingungen garantiert. Auf diese Weise können allenfalls Reaktionen 1. Ordnung erfaßt werden. Die Untersuchung des Zeitablaufs von Einstufen- und Mehrstufenreaktionen beliebiger Orgnung erfordert dagegen Bedingungen, unter denen Konzentrationsänderungen im strömenden System verfolgt werden können.

Durch fortlaufendes und gleichmäßiges Einleiten der Probe zum konstanten Trägergasstrom wird bei der Methode des stationären Zustandes[11,12] im Reaktionsrohr ein zeitinvarianter Zustand erreicht, der in einfacher Weise eine Zuordnung von Konzentration zu Reaktionszeiten zuläßt. Die früher verwendeten Analysensysteme[13,14] gestatten allerdings eine Variation der Reaktionszeit nur durch Veränderung des Trägergasstromes, so daß auch hier eine diskontinuierliche Messung unvermeidbar ist. Die weiterführende Methode der Bestimmung der Konzentration als Funktion der Länge der Reaktionsstrecke mittels einer Sonde[7] wird nicht voll ausgenutzt, da die sich anschließende chemische Analyse wieder diskontinuierlich gestaltet wird.

Das von uns mehrfach beschriebene viskose Einlaßsystem[1,15,16] für Massenspektrometer ermöglicht eine stetige Probennahme unter den extremen Bedingungen der Verbrennungsreaktionen, gewährleistet ein Einfrieren des Reaktionszustandes am Ort der Probennahme und bietet mit dem angeschlossenen Massenspektrometer die Möglichkeit, alle auftretenden Molekülarten qualitativ und quantitativ zu analysieren. Mit dieser in der Reaktionsstrecke verschiebbaren Einlaßsonde erfüllt die Kopplung von stationärem "Strömungsreaktor" und Massenspektrometer alle Voraussetzungen, die an eine Anordnung zur kinetischen Untersuchung von Verbrennungsvorgängen gestellt werden müssen.

MESSANORDNUNG

Die in Teil III dieser Reihe beschriebene Einrichtung kann in dem dort in Abb. 1 wiedergegebenen Aufbau unverändert auch zu kinetischen Untersuchungen herangezogen werden. Hierzu wird, wie bei der Aufnahme von Thermogrammen, die zu untersuchende Verbindung mit dem einstellbaren Probenstrom v' [mMol/s] dem Sauerstoffstrom v [mMol/s] zugesetzt. Das Sauerstoff–Probengemisch strömt in etwa 20 ms durch die Überbrückungskapillare ÜK in den Reaktionsraum RR und nimmt noch in der Überbrückungskapillare die Reaktionstemperatur T des Reaktionsraumes an.

Zur Messung des zeitlichen Ablaufs der Reaktion wird bei vorgegebenen Werten für v, v' und T die Reaktionsstrecke RS der Länge l (mm), die zwischen dem Eintritt der Überbrückungskapillaren in den Reaktionsraum und der Spitze der Einlaßsonde ES liegt, entweder von Hand auf bestimmte Werte eingestellt oder mittels eines Motors, der den Wagen verschiebt, auf dem die Anordnung montiert ist, stetig variiert. Die Reaktionszeit t ergibt sich mit ausreichender Genauigkeit aus Volumen und Temperatur der Reaktionsstrecke und dem Trägergasstrom v, solange $v' \ll v$ und damit die durch die Verbrennung zusätzlich entstehende Gasmenge vernachlässigbar ist. Der Probenpartialdruck p' ist durch Veränderung von v' bei konstantem v in gewissen Grenzen einstellbar, die Reaktionszeit t kann bei gleicher Reaktionsstrecke durch Veränderung von v variiert werden. Dabei ist in unserer Anordnung die Verweilzeit pro mm (spezifische Reaktionszeit t_s) etwa zwischen 0,01 und 0,1 s/mm wählbar, ohne daß die Grenzen der Methoden überschritten werden (bei 1000 K).

Am Ende der Reaktionsstrecke wird ein Teil des Reaktionsgemisches mit der Einlaßsonde abgeschnüffelt und in etwa 100 ms ins Hochvakuum überführt. Der so eingefrorene Reaktionszustand entspricht der Zeit $t = l \cdot t_s$ und wird massenspektrometrisch analysiert, indem eine für die Ausgangsverbindung oder ein Reaktionsprodukt repräsentative Peakintensität U' registriert wird. Da der isotherme Bereich der Reaktionsstrecke 250 mm beträgt und der Ofen mit dem Reaktionsrohr gegenüber der feststehenden Einlaßsonde auch um diese Strecke verschoben werden kann, beträgt der höchste zugängliche Reaktionsbereich 25 s. Bei maximal zulässigem Trägergasstrom kann ein kleinster Reaktionsbereich von 2,5 s noch hinreichend genau beobachtet werden. Damit besteht —in Verbindung mit dem großen Variationsbereich für die Reaktionstemperatur—ein ausreichender Spielraum für die beabsichtigten Untersuchungen.

Die Bestimmung des Faktors F'_T der "externen Partialdruckempfindlichkeit" gemäß $U' = F'_T \cdot p'$ erfolgt für jede Probe und jede Temperatur gesondert. Durch dynamische Hinzumischung[15] des jeweiligen Probengases erhält man sehr genau den gewünschten Eingangspartialdruck p'_0. In Stellung $l = 0$ bestimmt man die dazu gehörige Intensität U'_0 eines Peaks der Probe und damit den gesuchten Faktor F'_T. Anschließend stellt man eine genügend große Reaktionsstrecke ein, wählt einen für das zu beobachtende Endprodukt repräsentativen Peak, führt einen vollständigen Umsatz zu diesem Endprodukt durch Anhalten des Gasstromes herbei (stopped flow) und berechnet aus der gefundenen Peakintensität U'_u und der bekannten Stöchiometrie der Reaktion den gesuchten Faktor F'_T. Die entsprechenden externen Partialdruckempfindlichkeiten für andere Reaktionstemperaturen werden entweder in gleicher Weise gemessen oder nach Gleichung (7) in Teil I[15] berechnet (vergl. auch Tab. IV in Teil I). Wegen der ungenügenden Langzeitkonstanz der Faktoren werden die Eichmessungen häufig wiederholt.

KONTROLLUNTERSUCHUNGEN

Der nicht ganz genau definierbare Übergang von der Überbrückungskapillaren zum Reaktionsrohr sowie die Verweilzeit in der Überbrückungskapillaren und der Einlaßsonde gebieten eine Überprüfung des Nullpunktes der Reaktionsstrecke und damit der Zeitachse. Derartige Überprüfungen mit verschiedenen Gasphasenreaktionen ergaben, daß an der Stelle $l = 0$ bereits ein Reaktionsablauf angezeigt wird, der einer Reaktionszeit t_0 entspricht. Diese Null-Reaktionszeit ist über den aus der Überbrückungskapillaren herrührenden Anteil von v und T abhängig, während der durch die Einlaßsonde verursachte größere Teil im wesentlichen durch das Totvolumen der jeweiligen Sonde bestimmt wird, also nahezu konstant ist. Bei der eingesetzten Einlaßsonde liegt die Nullzeit je nach den Meßbedingungen zwischen 80 und 110 ms. Alle zukünftigen Zeitangaben sind um einen entsprechenden Betrag korrigiert.

Die Totzeit der Einlaßsonde im Vakuumteil beträgt etwa 0,2 s; die Einstellzeit (5–95%) des Massenspektrometers einschließlich des Elektrometerverstärkers liegt bei 0,3 s. Im Hinblick auf eine ausreichend genaue Zuordnung der Peakintensität U^i zur jeweiligen Länge l der Reaktionsstrecke ist demnach eine Vorschubgeschwindigkeit von 2 mm/s nicht zu überschreiten.

Im Gleichgewicht hätte die laminare Strömung bekanntlich die Ausbildung eines ausgeprägten Konzentrationsparaboloiden[17] zur Folge, wenn nicht die Diffusion für einen dauernden radialen Konzentrationsausgleich sorgte. Dieser Konzentrationsausgleich erfolgt offenbar unter den üblichen Reaktionsbedingungen so schnell, daß auch bei maximalem v-Wert kein radialer Konzentrationsgradient festgestellt werden kann, wenn man einen Rohrquerschnitt ($r = 4$ mm) abschnüffelt. Der Berechnung der Reaktionszeit t kann also die aus v und T berechnete, mittlere Strömungsgeschwindigkeit zugrunde gelegt werden.

Andererseits setzt die Strömungsmethode voraus, daß die Diffusion in axialer Richtung keine störende Vermischung bewirkt. Während die radiale Diffusion die Anwendbarkeit der Strömungsmethode bei hohen Strömungsgeschwindigkeiten begrenzt, setzt die axiale Diffusion bei niedrigen v-Werten eine Schranke. Nach Langmuir,[18] der sich ausführlich mit der Theorie des stationären Zustandes in einer Reaktionsstrecke befaßt hat, müßte unter unseren Meßbedingungen die axiale Diffusion vernachlässigt werden können.

Da es sich bei der Betrachtung von Langmuir um eine Näherung handelt, erscheint es angebracht, die Vernachlässigbarkeit der axialen Diffusion experimentell zu bestätigen. Eine direkte Überprüfung wie im Falle der radialen Verteilung ist nicht möglich. Deshalb wurde von uns durch Untersuchung der thermischen Spaltung von Äthylacetat ein Bezug zu Literaturwerten hergestellt. Diese Reaktion 1. Ordnung wurde von mehreren Autoren[13,19–21] mit verschiedenen Methoden eingehend untersucht. Eine Übereinstim-

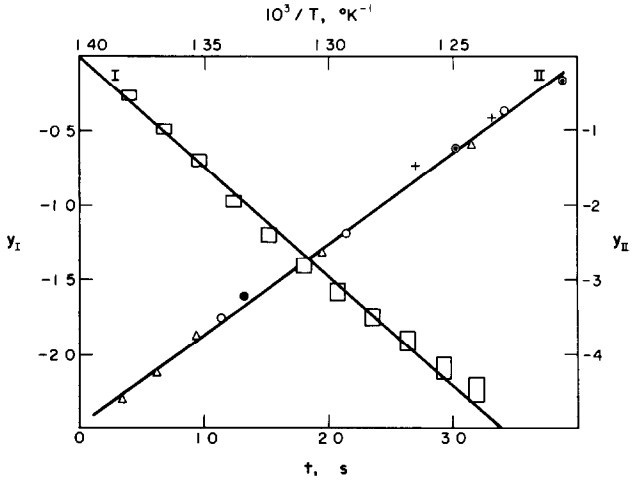

Abb. 1. Thermische Spaltung von Äthylacetat. I: $y = \ln(U_t^{61}/U_0^{61}) = f(t)$; $T = 829$ K. II: $y = \ln k_1 = f(1/T)$; Δ^{13}; $+^{19}$; ○ und ⊙ eigene Messung.

mung unserer Ergebnisse mit den andersartig bestimmten Werten würde sowohl die Vernachlässigbarkeit der axialen Diffusion als auch die Brauchbarkeit der gesamten Anordnung bestätigen.

Bezeichnen wir den Partialdruck von Äthylacetat an der Stelle l, der aufgrund der eingestellten Werte von v und T die Reaktionszeit t entspricht, mit p_t^l und an der Stelle $l = 0$ mit p_0^l, so gilt im Falle einer Reaktion 1. Ordnung:

$$\ln(p_t^l/p_0^l) = -k_1 t \text{ bzw. } \ln(U_t^l/U_0^l) = -k_1 t \qquad (1)$$

Es genügt also, das Massenspektrometer auf einen für die Ausgangsverbindung relevanten Peak einzustellen (bspw. den intensiven Peak bei Masse 61), den Motorvorschub des Reaktionssystems bei $l = 0$ beginnend einzuschalten und die Funktion $U_t^l(t)$ mittels eines Kompensationsschreibers zu registrieren. Eine Bestimmung der Partialdruckempfindlichkeit und des Wertes von p_0^l erübrigt sich. Das Äthylacetat wurde wie in Teil III für Feststoffe beschrieben verdampft.

In Abb. 1 ist das Ergebnis einer derartigen Messung wiedergegeben. Die Gesetzmäßigkeit der Gleichung (1) ist innerhalb der Fehlergrenzen $\Delta t = \pm 0{,}06$ s; $\Delta \ln U_t^l/U_0^l$ (wie in Abb. 1 eingezeichnet) voll erfüllt. Die aus dem Anstieg der Geraden I bestimmte Geschwindigkeitskonstante beträgt: $k_1 = 0{,}75 \pm 0{,}1$ (s^{-1}).

Zum besseren Vergleich mit Literaturwerten sind in Kurve II der Abb. 1 die von anderen Autoren[13,19] und uns bei verschiedenen Temperaturen gemessenen Geschwindigkeitskonstanten in der Form $\ln k_1 = f(1/T)$ aufgetragen. Alle Werte liegen auf *einer* Geraden. Damit ist die Eignung der Methode zur Bestimmung von Geschwindigkeitskonstanten und Aktivierungsgrößen bewiesen. Der große, zugängliche Temperaturbereich (wegen der Möglichkeit, die Reaktionszeit sowohl über die Reaktionslänge l als auch über den Trägergasstrom v zu variieren, können Geschwindigkeitskonstanten, die sich um einige Zehnerpotenzen unterscheiden, noch in zumutbaren Meßzeiten erfaßt werden) läßt eine eingehende Untersuchung der Aktivierungsgrößen von Gasphasenreaktionen auch bei hohen Temperaturen zu. Die stationäre Strömungsmethode mit massenspektrometrischer Detektion aller Reaktionskomponenten bietet also neben den qualitativen Aspekten[1] auch die Möglichkeit zu ausgiebigen, quantitativen kinetischen Untersuchungen.

MESSERGEBNISSE

Eine "vollständige Verbrennungskinetik" sollte eigentlich die Beobachtung der Bildung aller Primärprodukte und deren Übergang zu den Endprodukten beinhalten. Die in Teil III angeführten wenigen Beispiele lassen jedoch erkennen, daß das Verbrennungsgeschehen schon bei einfachen organischen Verbindungen so komplex sein kann, daß eine Aufklärung aller Schritte vorerst noch weit außerhalb unserer Möglichkeiten liegt. Die

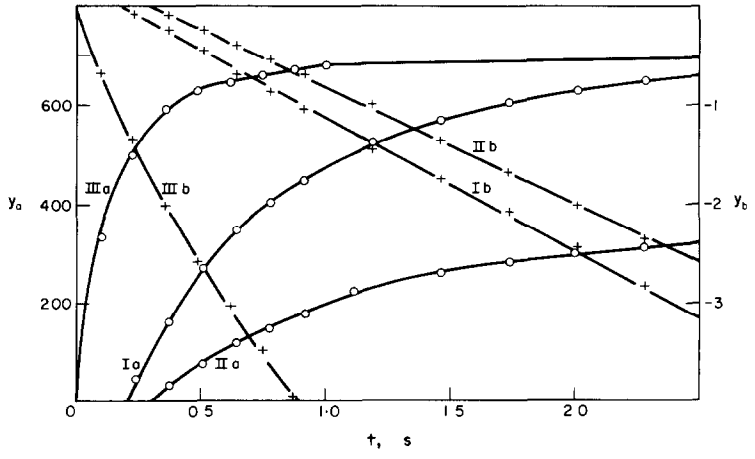

Abb. 2. Verbrennung von Wasserstoff. Ia: $y_a = U_t^{H_2O}$; $T = 928$ K; $p_0^{H_2} = 27{,}5$ mbar. IIa = Ia mit $p_0^{H_2} = 14{,}2$ mbar. IIIa ≡ Ia mit $T = 973$ K. Ib—IIIb: $y_b = \ln(1 - U_t^{H_2O}/U_u^{H_2O})$.

vorliegende orientierende Untersuchung beschränkt sich deshalb auf die Beobachtung des Übergangs der einfachsten Zwischenprodukte—Wasserstoff, Kohlenmonoxid, Ammoniak und Methan—in die entsprechenden Endprodukte. Obwohl wir Methan als Zwischenprodukt bisher nicht nachweisen konnten, haben wir es bei unseren Messungen berücksichtigt, da einerseits die Bedeutung von Methan als Zwischenprodukt immer wieder betont wird und andererseits[22] Meßergebnisse vorliegen, die unter vergleichbaren Bedingungen erarbeitet wurden.

In allen Fällen ist der Partialdruck der Probe so niedrig, daß die Veränderung der Reaktionsbedingungen hinsichtlich Temperatur und Sauerstoffpartialdruck durch die Reaktion selbst nicht berücksichtigt zu werden braucht, und der Sauerstoffpartialdruck, der in die beobachteten Reaktionen höchstens mit der Ordnung zwei eingeht,[2] wird in die Geschwindigkeitskonstante einbezogen.

Der Umfang des vorliegenden Zahlenmaterials läßt eine vollständige Wiedergabe nicht zu. Wir beschränken uns deshalb auf wenige aber typische Meßreihen, die zur besseren Übersicht in Form graphischer Darstellungen mitgeteilt werden.

Wasserstoffoxidation

Die Knallgasreaktion wurde schon früher[23–26] ausführlich untersucht. Sie verläuft in der Regel als durch und durch verzweigte Kettenreaktion,[4,5] und die Einflußgrößen Temperatur, Druck und Gefäßwand ändern nicht nur den Wert der Geschwindigkeitskonstanten, sondern oft auch den Reaktionsmechanismus und die Reaktionsordnung. Induktionsperioden und Zündungsphänomene spielen eine große Rolle.

Unsere Untersuchungen im leeren Rohr bestätigen weitgehend den bisherigen Erkenntnisstand. Wie aus Kurve Ia der Abb. 2 hervorgeht, setzt die Reaktion bei 928 K erst nach einer Induktionsperiode ein, die bei dem niedrigeren Eingangspartialdruck von 14,3 mbar in Kurve IIa noch ausgeprägter in Erscheinung tritt. Anschließend verläuft die Reaktion annähernd nach 1. Ordnung, wie die Geraden Ib und IIb beweisen, deren Extrapolation auf die Ordinate Null die deutlich verschiedenen Induktionszeiten $t_i = 0{,}17$ s bzw. $t_i = 0{,}30$ s ergibt. Dagegen wirkt sich bei dieser Temperatur der unterschiedliche Eingangspartialdruck auf die Geschwindigkeitskonstanten nur geringfügig aus ($k_1 = 1{,}38\ s^{-1}$ bei 27,6 mbar; $k_1 = 1{,}18\ s^{-1}$ bei 14,3 mbar).

Bei 973 K entfällt dagegen die Induktionsperiode völlig. Sowohl die Extrapolation der Kurve IIIa: $U_t^{18} = f(t)$ als auch der Kurve IIIb: $\ln(1 - U_t^{18}/U_u^{18}) = f(t)$ gehen durch den Zeitnullpunkt. An der leichten Krümmung der Kurve IIIb erkennt man, daß unter diesen Bedingungen das Zeitgesetz 1. Ordnung nicht mehr voll erfüllt wird. Stellt man zur Bestimmung der genauen Reaktionsordnung die Funktion $\ln(\Delta U/\Delta t) = f[\ln(U_u - U_t)]$graphisch dar, so ergibt sich aus dem Anstieg dieser Geraden die Reaktionsordnung $n = 1{,}2$. Aus

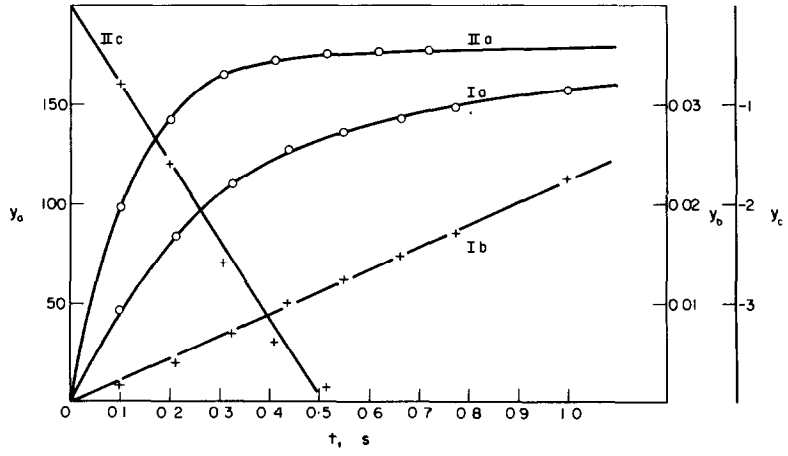

Abb. 3. Verbrennung von Kohlenmonoxid. Ia: $y_a = U_t^{CO_2}$; $T = 1123$ K; $p_0^{CO} = 13{,}8$ mbar. IIa ≡ Ia mit $T = 1223$ K. Ib: $y_b = (U_u^{CO_2} - U_t^{CO_2})^{-1} - (U_u^{CO_2})^{-1}$; sonst ≡ Ia. IIc: $y_c = \ln(1 - U_t^{CO_2}/U_u^{CO_2})$; sonst ≡ Ia mit $T = 1223$ K.

dem mittleren Anstieg der Kurve IIIb erhält man eine Geschwindigkeitskonstante $k_1 = 5{,}0\,s^{-1}$. Bemerkenswert ist weiterhin die außerordentlich große Änderung der Geschwindigkeitskonstanten zwischen 893 und 928 K von $k_1 = 0{,}055\,s^{-1}$ auf $k_1 = 1{,}3\,s^{-1}$, die nur mit Zündungsphänomenen erklärt werden kann (vergl. auch Abb. 2 in Teil III).

Kohlenmonoxidoxidation

Obwohl bereits sehr früh[27,28] erste Ansätze zur Aufklärung der CO-Verbrennung gemacht wurden, ist auch heute noch das Verständnis der sehr komplexen Vorgänge erheblich geringer, als im Falle der Wasserstoffoxidation.[4] Dies gilt besonders für die Verbrennung unter elementaranalytischen Bedingungen, wie u.a. die in Teil III dieser Reihe mitgeteilten Verbrennungsthermogramme zeigen.

Wie aus Abb. 3 hervorgeht, bewirkt eine Temperaturerhöhung von 1123 auf 1223 K offenbar eine grundsätzliche Änderung im Reaktionsgeschehen. Während die Meßwerte bei 1123 K (Kurve Ia) am besten mit einer Reaktion 2. Ordnung beschrieben werden können (Kurve Ib), ist bei der höheren Temperatur (Kurven IIa und IIc) das Geschwindigkeitsgesetz 1. Ordnung innerhalb der Fehlergrenzen erfüllt, und man erhält $k_1 = 7{,}9\,s^{-1}$. Eine Induktionsperiode wurde in beiden Fällen nicht beobachtet.

Bei 1123 K wurden weitere Meßreihen bei niedrigeren Eingangspartialdrucken durchgeführt. Auch die hierbei gefundenen Werte sind am ehesten mit der Reaktionsordnung $n = 2$ zu erklären. Die aus dem Anstieg der Geraden Ib ermittelten Geschwindigkeitskonstanten ($k_2 \# 0{,}32\,mbar^{-1} \cdot s^{-1}$) zeigen zwar keine systematische Konzentrationsabhängigkeit, sind aber andererseits auch nicht besonders gut reproduzierbar, was mit der sicher vorhandenen "Wandbeteiligung" erklärt werden kann. Ob der Wechsel in der Ordnung der Reaktion auf eine Veränderung des Kettenverzweigungsfaktors[29] zurückzuführen ist, bleibt vorerst genauso ungeklärt, wie die von uns bei 1098 K beobachtete extreme Verlangsamung der Reaktion, die nach einem Umsatz von 50% einsetzt, während bis zu diesem Zeitpunkt die Verbrennung grundsätzlich so verläuft, wie bei 1123 K.

Ammoniakoxidation

Bei der Verbrennung von Ammoniak entsteht nicht, wie bei den bisherigen Beispielen, ein einziges Endprodukt in einem Schritt, sondern es werden Wasser, Stickstoff und Stickstoffmonoxid gebildet. Möglicherweise ist dies die Ursache für den eigenartigen Verlauf der Ammoniakkurve Ia in Abb. 4, die über den NH-Peak bei der Masse 15 beobachtet wurde. Bei 973 K startet die Reaktion nach einer deutlichen Induktionsperiode von 0,3 s mit einer sehr steilen Abnahme des NH_3-Partialdrucks. Bei 0,6 s wird die Reaktionsgeschwindigkeit geringer und es beginnt eine Zone nahezu konstanter Reaktionsgeschwindigkeit, der ab 1,7 s (75% Umsatz) eine Zone abnehmender Reaktionsgeschwindigkeit folgt.

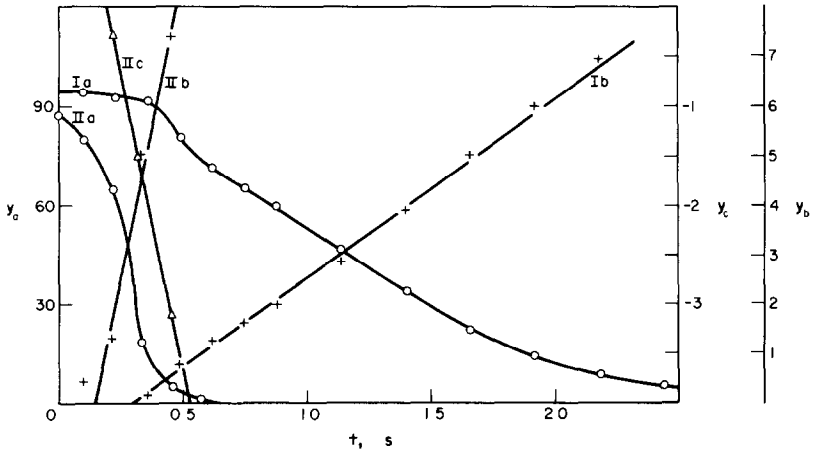

Abb. 4. Verbrennung von Ammoniak. Ia: $y_a = U_t^{NH}$; $T = 973\,K$; $p_0^{NH_3} = 21{,}6\,mbar$. IIa ≡ Ia mit $T = 1073\,K$. Ib: $y_b = \sqrt{U_0^{NH}} - \sqrt{U_t^{NH}}$; sonst ≡ Ia. IIb: $y_b = \sqrt{U_t^{NH}} - \sqrt{U_t^{NH}}$; sonst ≡ IIa. IIc: $y_c = \ln(U_t^{NH}/U_u^{NH})$; sonst ≡ IIa.

Für das Geschwindigkeitsmaximum bei 0,5 s und die anschließende Zone konstanter Geschwindigkeit haben wir vorerst keine Erklärung. Der eigenartige Verlauf ist reproduzierbar und tritt in gleicher Weise auch bei niedrigeren Eingangspartialdrucken (17,2 und 13,1 mbar) auf.

Wie aus Kurve Ib hervorgeht, beschreibt eine Geschwindigkeitsgleichung der Ordnung 1/2 das "mittlere Reaktionsgeschehen" in guter Näherung. Die mittels Ib extrapolierte Induktionszeit beträgt 0,30 s, während bei 1073 K (Gerade IIb) eine Induktionszeit von nur 0,15 s extrapoliert wird. Ob die gefundene mittlere Reaktionsordnung 1/2 tatsächlich aus einem einheitlichen Reaktionsgeschehen resultiert, oder ob sie das zufällige Ergebnis einer höheren Reaktionsordnung in der steilen Zündregion und einer niedrigeren Reaktionsordnung (Null) in der anschließenden Zone ist, bleibt noch definitiv zu klären. Wir neigen zu der zweiten Annahme.

Bei der Ammoniakverbrennung bei 1073 K (Kurve IIa) ist die sehr große Steilheit bei 0,28 s bemerkenswert; 50% der Reaktion erfolgen innerhalb 0,1 s, was einer Reaktionsstrecke von nur 4 mm entspricht. Damit ist bewiesen, daß extrem hohe axiale Konzentrationsgradienten im stationären Zustand bestehen und gemessen werden können, und die eingangs gemachte Annahme, daß eine störende, axiale Diffusion nicht stattfindet, erfährt hierdurch eine zusätzliche Bestätigung. Die Tatsache, daß die Gerade IIb auch in diesem Falle für eine Reaktionsordnung 1/2 spricht, darf keinesfalls überbewertet werden, wie aus der Geraden IIc ersichtlich ist, die $\ln(U_t^{1.5}/U_0^{1.5}) = f(t)$ darstellt. Auch sie ergibt innerhalb der Fehlergrenzen eine Gerade. Die räumliche und damit zeitliche Auflösung der Anordnung reicht für eine eindeutige Aussage über diese extrem schnelle Reaktion noch nicht aus.

Löst man das Gesamtgeschehen in seine Einzelbestandteile auf, indem man sowohl das Verschwinden von Ammoniak als auch das Entstehen von Wasser, Stickstoffmonoxid und Stickstoff in Abhängigkeit von der Länge der Reaktionsstrecke beobachtet, so erhält man eine Darstellung, die den Thermogrammen in Teil III nahe verwandt ist, und die bei der Verbrennung organischer Verbindungen—bei geeigneter Meßtemperatur—ebenfalls das ganze komplexe Reaktionsgeschehen sichtbar werden läßt.

Ein solches "Kinetogramm" ist in Abb. 5 für den sehr einfachen Fall der Verbrennung von Ammoniak wiedergegeben. Kurve I ist mit Kurve I in Abb. 4 identisch; es ist lediglich statt der Peakintensität U_t^{NH} der daraus berechnete Partialdruck $p_t^{NH_3}$ (mbar) aufgetragen. Da Wasser direkt und stochiometrisch aus Ammoniak entsteht, verläuft Kurve II erwartungsgemäß komplementär zu Kurve I. Dagegen ist das Verhältnis von Stickstoff zu Stickstoffmonoxid (Kurven III und IV) nicht konstant. Wie aus Kurve V $[y = p_t^{NO}/(p_0^{NH_3} p_t^{NH_3})]$ deutlich hervorgeht entsteht in der Induktionsperiode überwiegend Stickstoffmonoxid. In der Zündperiode (0,3–0,6 s) fällt der NO-Anteil sehr schnell auf 25% und sinkt dann in der Zone konstanter Geschwindigkeit (0,6–1,7 s) langsam auf 14%

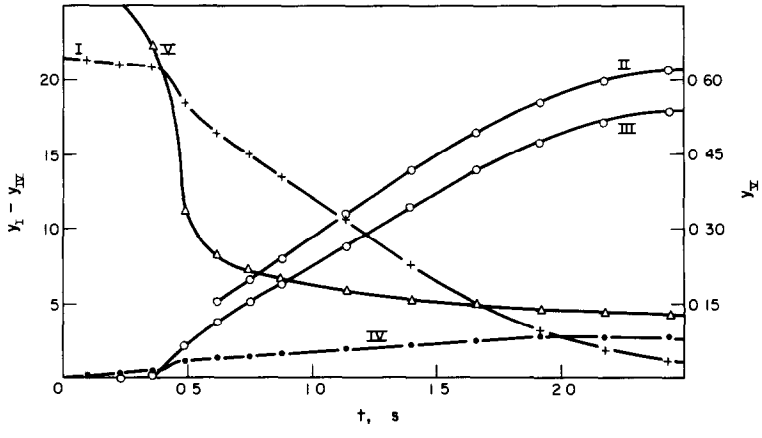

Abb. 5. $NO–N_2$ Verteilung bei der Verbrennung von Ammoniak ($T = 973$ K; $p_0^{NH_3} = 21{,}6$ mbar). I: $y = p_t^{NH_3}$ (mbar). II: $y = p_t^{H_2O}/1{,}5$ (mbar). III: $y = 2 \cdot p_t^{N_2}$ (mbar). IV: $y = p_t^{NO}$ (mbar). V: $y = p_t^{NO}/(p_0^{NH_3} p_t^{NH_3})$.

ab. Bis zum Reaktionsende erfolgt dann nur noch eine geringfügige Veränderung der NO–N_2 Verteilung. Diese Endverteilung—12% als NO und 88% als N_2—ist im leeren Rohr offenbar ammoniakspezifisch, da bei der Verbrennung anderer stickstoffhaltiger Verbindungen andere Endverteilungen von uns[1] beobachtet wurden.

Möglicherweise sind Sekundärreaktionen[30] zwischen gebildetem Stickstoffmonoxid und Ammoniak am Zustandekommen des eigenartigen Verhaltens wesentlich beteiligt. Daß mindestens teilweise eine konsekutive Reaktion stattfindet, ergibt sich aus dem von uns bei höheren Reaktionstemperaturen beobachteten, absoluten Partialdruckmaximum des Stickstoffmonoxids bei einem Umsatz von etwa 60%.

Methanoxidation

Wie bereits in Teil III dieser Reihe gezeigt (Abb. 3), entstehen bei der Verbrennung von Methan neben den Endprodukten CO_2 und H_2O mindestens noch die Zwischenprodukte Formaldehyd und Kohlenmonoxid. Wasserstoff und Wasserstoffperoxid, die unter anderen Bedingungen[7] gefunden wurden, konnten bisher von uns nicht nachgewiesen werden. Vielmehr scheint der im Methan enthaltene Wasserstoff fast vollständig (ein geringer Anteil wird über das Zwischenprodukt Formaldehyd verbrannt) unmittelbar in Wasser überführt zu werden, denn der reduzierte Wasserpartialdruck ($y = 0{,}5 \cdot p_t^{H_2O}$) verläuft, wie Kurve II in Abb. 6 zeigt, praktisch komplementär zum Methanzerfall der Kurve I. Dagegen entsteht CO_2 (Kurve IV) wegen der zwischenzeitlichen Bildung von CO stark verzögert. Kohlenmonoxid (Kurve III in Abb. 6) erreicht nach 0,9 s bei 80% Methanumsatz ein Maximum. Zu diesem Zeitpunkt sind erst 25% des verbrannten Kohlenstoffs in CO_2 umgewandelt. Erst nach dem CO-Maximum beginnt ein steiler Anstieg des Kohlendioxidpartialdruckes.

Einer einfachen kinetischen Auswertung zugänglich ist der Methanzerfall oder die diesem nahezu entsprechende Wasserentstehung. Wie Kurve V der Abb. 6 beweist, verläuft diese Reaktion bei 1023 K nach der Ordnung 1/2. Die Geschwindigkeitskonstante beträgt $8{,}4\ s^{-1} \cdot mbar^{0,5}$; die deutlich ausgeprägte Induktionszeit liegt bei 0,26 s. Führt man den gleichen Versuch bei niedrigeren Partialdrucken durch, dann wird die Reaktionsordnung 1/2 in allen Fällen bestätigt. Die Anstiege der entsprechenden Geraden nehmen jedoch —bei konstanter Induktionszeit—mit dem Eingangspartialdruck des Methans ab; bei $p_0^{CH_4} = 14{,}3$ mbar ist $k_{0,5} = 5{,}92\ s^{-1} \cdot mbar^{0,5}$ und bei 11,45 mbar findet man $k_{0,5} = 5{,}04\ s^{-1} \cdot mbar^{0,5}$. In erster Näherung ist also die Geschwindigkeitskonstante dem Eingangspartialdruck proportional und im untersuchten Druckbereich gilt: $k_{0,5} \# 0{,}4 \cdot p_0^{CH_4}\ s^{-1} \cdot mbar^{0,5}$.

Dagegen scheint bei der niedrigeren Temperatur von 973 K ein anderer Reaktionsmechanismus zu überwiegen. Während sich für den Reaktionsbeginn wie bei den höheren

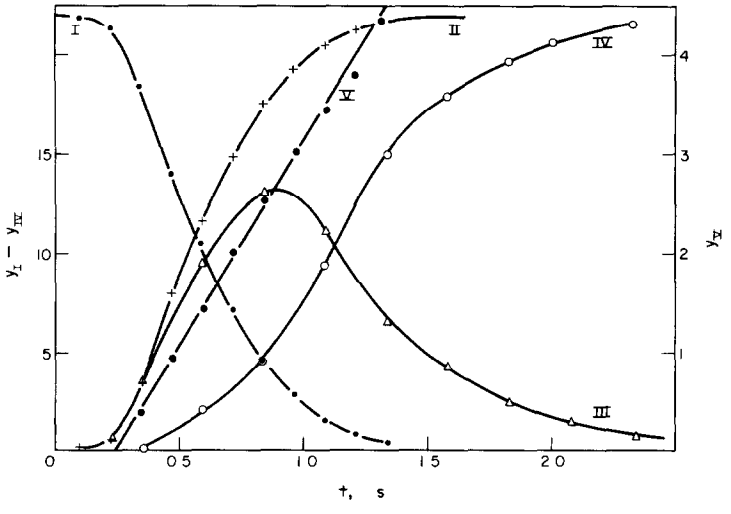

Abb. 6. Verbrennung von Methan ($T = 1023$ K, $p_0^{CH_4} = 22$ mbar). I: $y = p_t^{CH_4}$ (mbar), II: $y = 0{,}5 \cdot p_t^{H_2O}$ (mbar). III: $y = p_t^{CO}$ (mbar). IV: $y = p_t^{CO_2}$ (mbar) V: $y = \sqrt{p_0^{CH_4}} - \sqrt{p_t^{CH_4}}$ ($mbar^{1/2}$).

Temperaturen eine eindeutige Reaktionsordnung nicht fassen läßt, verläuft das Reaktionsgeschehen ab 40% Umsatz nicht nach der Ordnung 1/2, sondern nach zweiter Ordnung mit $k_2 = 0{,}05\ s^{-1} \cdot mbar^{-1}$. Bei 1073 K entfällt die Induktionsperiode völlig. Die wenigen Meßpunkte, die am Beginn der Reaktionsstrecke noch erfaßt werden können, lassen darauf schließen, daß am Reaktionsende eine Reaktion 1. Ordnung vorherrscht mit $k_1 = 7{,}2\ s^{-1}$.

DISKUSSION

Wie bereits aufgrund unserer qualitativen Untersuchungen in Teil III dieser Reihe erwartet werden konnte, ist auch der *zeitliche* Ablauf der Verbrennung im leeren Rohr überaus komplex. Sowohl Radikal-Kettenreaktionen mit den schwer faßbaren Einflußgrößen Oberfläche und Gaszusammensetzung als auch verzweigte Kettenreaktionen

Tabelle 1. Geschwindigkeitskonstanten der Verbrennung

Probe	T, K	t_I, s	n	k_n	$t_{0,5}$, s
Wasserstoff	893	1,7	1	$0{,}055\ s^{-1}$	13
	928	0,2	1	$1{,}3\ s^{-1}$	0,5
	973	—	1	$5{,}0\ s^{-1}$	0,15
Kohlenmonoxid	1123	—	2	$0{,}32\ s^{-1} \cdot mbar^{-1}$	0,31
	1223	—	1	$7{,}9\ s^{-1}$	0,1
Ammoniak	973	0,3	0,5	$3{,}5\ s^{-1} \cdot mbar^{0,5}$	0,52
	1073	0,15	?		
Methan	973	1	2	$0{,}05\ s^{-1} \cdot mbar^{-1}$	2,0
	1023	0,26	0,5	$5\ s^{-1} \cdot mbar^{0,5}$	0,37
	1078	—	1	$7\ s^{-1}$	0,1

Trägergas: Sauerstoff; Eingangsprobenpartialdruck $p_0 = 5$ bis 27 mbar; t_I = Induktionszeit; n = Reaktionsordnung; k_n = Geschwindigkeitskonstante der Ordnung n; $t_{0,5}$ = Halbwertszeit der Verbrennung bei $p_0 = 10$ mbar.

mit Zündungsphänomenen und Induktionsperioden sind offenbar maßgeblich beteiligt. Das bei der Verbrennung organischer Verbindungen unvermeidbare Auftreten vieler Zwischenprodukte[1] hat die gegenseitige Beeinflussung der gleichzeitig ablaufenden Kettenreaktionen zur Folge[6] und erschwert kinetische Untersuchungen und eindeutige Vorhersagen genauso, wie die als Folge geringfügiger Temperaturänderungen beobachteten Sprünge in den Reaktionsordnungen und Reaktionsmechanismen.

Möglicherweise wirken sich die beobachteten Induktionsperioden bei der Elementaranalyse nicht besonders störend aus, da durch die vorausgehende oxidative Pyrolyse eine ausreichende Konzentration an Radikal-Kettenstarter erzeugt wird. Andererseits muß damit gerechnet werden, daß, wie von uns im Falle von Harnstoff beobachtet, die oxidative Pyrolyse selbst eine Induktionsperiode und damit eine zusätzliche Reaktionsstrecke erfordert.

In Tabelle 1 sind die wichtigsten Meßergebnisse zusammengestellt. Die angeführten Werte für die Induktionszeit t_I, die Reaktionsordnung n, die Geschwindigkeitskonstante k_n sowie die Halbwertszeit $t_{0,5}$ sind mit der bei derartigen Reaktionen immer gebotenen Skepsis zu beurteilen. Die aus den gemessenen Geschwindigkeitskonstanten berechneten Halbwertszeiten erlauben aber, in Verbindung mit Trägergasstrom und Temperatur, eine grobe Abschätzung der zur vollständigen Verbrennung benötigten Reaktionsstrecke.

Wie erwartet, bestimmt Kohlenmonoxid Mindesttemperatur und Mindestlänge der Reaktionsstrecke, und bei der für elementaranalytische Verhältnisse sehr hohen Temperatur von 1123 K ist eine vollständige Verbrennung des CO nur bei sehr geringem Trägergasstrom gesichert. Allerdings ist in diesem Falle ($n = 2$) die benötigte Reaktionszeit umgekehrt proportional p_0^{CO}, so daß bei höheren Eingangspartialdrucken die vollständige Verbrennung eher erreicht wird. Es ergibt sich also die paradoxe Situation, daß Verbindungen mit geringem Kohlenstoffgehalt "schlechter" verbrennen, und daß eine langsame Verdampfung der Probe in den Verbrennungsraum (klassische Technik mit beweglichem Kurzbrenner) sich eher nachteilig auswirkt. Dieses überraschende Ergebnis erklärt auch, warum die explosionsartige "Pulsverbrennung",[31] bei der p_0 sicher sehr hohe Werte

annimmt, so erfolgreich verlaufen kann. Im übrigen sollte zur Bestimmung von Kohlenstoff, Wasserstoff und Stickstoff grundsätzlich nicht mit leerem Rohr, sondern mit einer kleinen Füllung von Platinwolle gearbeitet werden. Wie wir[1] gezeigt haben, wird dadurch der ungünstige homogene Reaktionstyp vermieden, und die Verbrennung ist auch bei erheblich niedrigeren Temperaturen vollständig.

Unsere bisherigen Verbrennungsuntersuchungen wurden fast ausschließlich mit einem kleinen 180° Massenspektrometer durchgeführt, das eine gleichzeitige Bestimmung der relevanten Zwischen- und Endprodukte nicht zuläßt. In der Zwischenzeit haben wir durch Verwendung von Mehrfängermassenspektrometer oder durch Einsatz eines Massenprogrammwählers die Simultanbestimmung realisiert. Wir erhoffen uns hiervon schnellere und genauere kinetische Daten und glauben, mindestens die grundlegenden Verbrennungsmechanismen in Bälde aufklären zu können.

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MASSENSPEKTROMETRISCHE UNTERSUCHUNGEN ZUR ELEMENTARANALYSE ORGANISCHER VERBINDUNGEN—V*

EINE STATISCHE METHODE ZUR BESTIMMUNG DES C–H–N-GEHALTES†

WALTER WALISCH® und ALBRECHT SIEWERT

Organische und Instrumentelle Analytik, Universität des Saarlandes, 66 Saarbrücken, B.R.D.

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Zusammenfassung—Basierend auf eigenen früheren Arbeiten wird eine Verbrennungsanordnung entwickelt, die es gestattet, die entstandenen Verbrennungsprodukte Kohlendioxid, Wasser und Stickstoff mittels eines kleinen, exponentiell abnehmenden Trägergasstromes in ein vorher evakuiertes Reservoir zu treiben und dort zu sammeln. Als Trägergas dient Helium mit einem Zusatz von 3% Sauerstoff. Der zur Verbrennung nicht benötigte Sauerstoff wird in einem Reduktionsrohr, in dem auch Stickoxide reduziert werden, zurückgehalten. Die das Reduktionsrohr mit dem Reservoir verbindende Kapillare ist so dimensioniert, daß das Reservoir mit einer Halbwertszeit von *ca.* 70 s gefüllt wird. Nach 8 Minuten ist der Enddruck erreicht, die Homogenität des Gasgemisches gewährleistet, und die Konzentration an Kohlendioxid, Wasser und Stickstoff wird mittels eines Massenspektrometers, das über ein viskoses Einlaßsystem mit dem Reservoir verbunden ist, durch Messung der Peakintensitäten bei den Massen 44, 28, 18 und 14 gemessen. Mit Einwaagen von etwa 300 μg können in einer Stunde fünf C–H–N-Bestimmungen durchgeführt werden.

In Teil II[1] dieser Reihe wurde gezeigt, daß bei dynamischer Gestaltung des Verbrennungsprozesses eine massenspektrometrische Bestimmung der Verbrennungsprodukte dadurch erfolgen kann, daß diese mit konstanter Geschwindigkeit an einem geeigneten Einlaßsystem[2] vorbei geführt werden und die Intensität eines für das gewählte Verbrennungsprodukt repräsentativen Peaks integriert wird. Das so gemessene zeitliche Peakintegral ist der jeweils entstandenen Menge des betreffenden Verbrennungsproduktes proportional und der gesuchte Prozentgehalt kann—bei Kenntnis der eingesetzten Probenmenge—aus diesem Peakintegral berechnet werden, wenn das gewählte Verbrennungsprodukt als einziges aus dem zu bestimmenden Element entsteht.

Diese dynamische Methode mit Peakintegration ist, wie auch van Leuwen[3,4] gezeigt hat, nur dann zur simultanen Mehrelementanalyse (bspw. C, H, N) einzusetzen, wenn ein Massenspektrometer mit mehreren Fängern und eine entsprechende Anzahl von Integratoren eingesetzt werden. Damit bleibt einerseits hinsichtlich der einsetzbaren Massenspektrometertypen kaum noch eine Auswahl und andererseits ist mit der Mehrfachintegration ein ziemlicher Aufwand verbunden. Die Vorteile eines Massenspektrometers, alle Komponenten eines Gemischs durch Aufnahme eines Gesamtspektrums bestimmen zu können, werden bei dieser Methode nicht genutzt.

Wie bereits angedeutet, erscheint eine Anordnung möglich, welche die prinzipiellen Vorteile dynamischer Methoden[5] mit den spezifischen Möglichkeiten eines Massenspektrometers dadurch optimal verbindet, daß zwar die Verbrennung dynamisch (flow-wise) gestaltet wird, daß aber die Messung selbst statisch (batch-wise) erfolgt. Hierzu werden die Verbrennungsabgase fortlaufend einem Reservoir zugeleitet und dort gesammelt. Nach dem beobachteten Ende der Verbrennung wird der Trägergasstrom abgeschaltet und normierte Werte für Druck und Temperatur eingestellt. Nachdem die Homogenität des Gemisches gewährleistet ist, wird der interessierende Massenbereich durchfahren, und man erhält in der Peakhöhe der gefundenen Massenpeaks ein Maß für die Konzentration der entstandenen Produkte. Die gesuchten Prozentgehalte können aus

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diesen Peakintensitäten und der eingesetzten Probenmenge (Einwaage) mittels Eichfaktoren berechnet werden. Die Eichfaktoren werden unter gleichen Bedingungen von Druck, Temperatur und Volumen des Reservoirs durch Verbrennung von Testverbindungen bestimmt.

Die hier skizzierte Methode hat vom Konzept her einige Gemeinsamkeiten mit der C–H–N-Apparatur von Simon *et al.*[6] und deren späteren kommerziellen Versionen. Auch dort werden die Verbrennungsprodukte mit einem Trägergas in ein Reservoir getrieben, und mit der Messung wird erst nach Beendigung der Verbrennung begonnen (bei Simon mit Wärmeleitfähigkeitsdetektoren). Wie Foissac[5] gezeigt hat, können einige Nachteile statischer Verfahren (Blindwerte, Memoryeffekte, Notwendigkeit einer genauen Normierung von Druck, Volumen und Temperatur, keine präzise Beobachtung des Verbrennungsprozesses) auf diese Weise nicht völlig beseitigt werden. Andererseits ist—bei massenspektrometrischer Detektion—eine Simultanbestimmung vieler Elemente möglich, und man kann sogar den Gehalt an verschiedenen Isotopen des gleichen Elementes in einem Arbeitsgang mitbestimmen.

Die Vor- und Nachteile der statischen Arbeitstechnik halten sich also bei massenspektrometrischer Bestimmung der Verbrennungsprodukte einigermaßen die Waage. Wenn es gelänge, die Störungen durch Blindwerte und adsorptionsbedingte Memoryeffekte genügend klein zu halten, könnten die Vorteile überwiegen, die darin bestehen, daß eine Vielfachelementaranalyse auf diese Weise mit einem kleinen Einfänger-Massenspektrometer durchgeführt werden kann. Ziel dieser Arbeit ist es, nach Wegen und Möglichkeiten zu suchen, welche die Vorteile der statischen Methode voll zum Tragen bringen, ohne daß die Nachteile allzusehr in Erscheinung treten.

MESSANORDNUNG

In Abb. 1 ist die letzte Version der entwickelten Meßanordnung schematisch wiedergegeben. Zur Verbrennung wählten wir die bewährten Bauelemente unseres CHN-Automaten,[7,8] für den inzwischen[9,10] Verbrennungstechniken für alle wichtigen Stoffklassen existieren, und der auch bei extrem kleinen Probenmengen noch gute Resultate liefert.[11] Wie in Teil II[1] dieser Reihe ausführlich dargelegt, wird das in der Druckflasche DF befindliche Trägergas—97% Helium und 3% Sauerstoff—über die Kapillare DK und das zur Gasreinigung erforderliche Absorptionsrohr AR dem Einfüllteil des Verbrennungsrohres VR zugeführt. Hier strömt ein Teil an der Einfüllöffnung EF vorbei über den Dreiwegehahn HE durch die Wassersäule DR ins Freie. Damit herrscht im geschlossenen Verbrennungsrohr immer der konstante Überdruck h, und atmosphärische Verunreinigungen, die durch Undichtigkeiten in diesen Teil des Verbrennungsrohres eindringen, werden über die Wassersäule ins Freie gespült.

An das Verbrennungsrohr, das mit Platinwolle, Kupferoxid und Silberwolle gefüllt ist, schließt sich ein mit Kupferstäbchen (reduziertes Kupferoxid) gefülltes Reduktionsrohr RR an. Dieses Reduktionsrohr ist kürzer (200 mm Länge) und dünner (12 mm Innendurchmesser) als die früher[7] beschriebene Version. Dadurch wird die sonst[9,12] gewünschte Bandenverbreiterung erheblich vermindert. Der Reflektor[8]-Verbrennungsofen VO hat die übliche Temperatur von 1150 K; im Reduktionsofen RO ist eine Temperatur von 750 K eingestellt. Das Reduktionsrohr endet in einem Dreiwegehahn HR, der das Reduktionsrohr entweder über die Spülkapillare SK mit der Atmosphäre verbindet oder über die Regelkapillare RK in das Reservoir RS führt. Dieses Reservoir wird durch den Ofen RSO auf 750 K geheizt und besitzt ein Volumen von 100 ml. Das Reservoir ist über die Einlaßkapillare EK mit dem Massenspektrometer MS sowie durch das Absaugrohr AR und den Hahn HP mit einer zwei

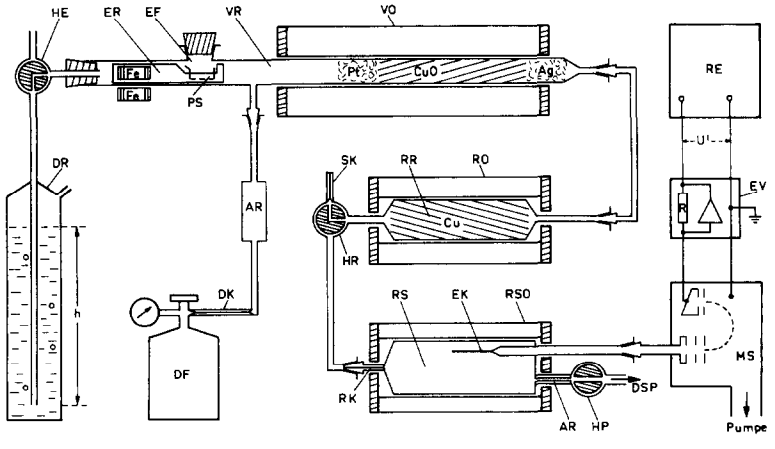

Abb. 1. Schema der Meßanordnung.

stufigen Drehschieberpumpe DSP verbunden. Die Regelkapillare RK ist so dimensioniert, daß das vorher evakuierte Reservoir, wenn es über den Dreiwegehahn HR mit dem Verbrennungsteil der Apparatur verbunden wird, mit einer Halbwertszeit von 68 s gefüllt wird und eine ausreichende Annäherung an den Enddruck nach 8 Minuten (7 Halbwertszeiten = 99,2%) erreicht ist.

Vor Beginn einer Verbrennung werden die beiden Dreiwegehähne HE und HR in Spülstellung (Verbindung zur Atmosphäre) gebracht, das Platinschiffchen PS mit der Probe in das Einschieberohr ER gestellt und die Einfüllöffnung EF mittels eines Stopfens wieder verschlossen. Nach einer Spülzeit von 10 s wird HE in Arbeitsstellung gebracht, und das Aufsteigen von Blasen in der Wassersäule zeigt an, wenn der Überdruck h (etwa 1200 mm Wassersäule) eingestellt ist und ein diesem Überdruck proportionaler Trägergasstrom von 10 ml/min über Verbrennungs- und Reduktionsrohr durch die Spülkapillare SK ins Freie tritt.

Während des Einfüllvorgangs, der insgesamt eine Minute erfordert, ist der Hahn HP geöffnet und das Reservoir wird auf einen Enddruck von etwa 0,5 mbar evakuiert. Nach Einstellen des Überdrucks h wird Hahn HR in Arbeitsstellung gedreht und das Reservoir bei einem Druck von 2 mbar mit reinem Helium gespült. Nach etwa einer Minute wird das Untergrundspektrum abgefragt, und die vom Elektrometerverstärker EV angezeigte Intensität der relevanten Peaks (44, 28, 18, 14) wird von der Registriereinrichtung RE festgehalten. Als Registriereinrichtung wird entweder ein schneller Kompensationsschreiber oder ein digitales Voltmeter mit Drucker eingesetzt. Nach Registrierung dieser Werte wird die Probe mittels der Magnetstäbe Fe in den heißen Teil des Verbrennungsrohres eingeschoben. Kurz bevor die ersten Verbrennungsprodukte das Reduktionsrohr verlassen (nach 20 s) wird der Hahn HP geschlossen, und alle Verbrennungsprodukte werden im Reservoir gesammelt. Der Trägergasstrom nimmt hierbei exponentiell ab (Anfangswert *ca.* 0,3 ml/s) und kommt nach 8 Minuten praktisch zur Ruhe. In dieser Zeit bleibt das Massenspektrometer auf der Masse 44 eingestellt, und das Fortschreiten der Verbrennung kann am Ansteigen des Kohlendioxidpeaks beobachtet werden.

Wie eingehende Voruntersuchungen gezeigt haben, ist bei fast allen Stoffklassen die Verbrennung nach wenigen Minuten beendet, und alle Verbrennungsprodukte befinden sich nach 8 Minuten im Reservoir. Wegen der hohen Temperatur (750 K) und des großen Durchmessers (20 mm) dieses Reservoirs erfordert die Einstellung der Homogenität durch Diffusion kaum zusätzliche Zeit, und die beobachtbare Konstanz des Kohlendioxidpeaks garantiert sowohl die Vollständigkeit der Verbrennung als auch den vollständigen Transport in das Reservoir sowie die Gleichverteilung in diesem. Eine Vergrößerung des Volumens des Reservoirs würde die Sicherheit erhöhen, daß wirklich *alle* Verbrennungsprodukte im Reservoir gesammelt sind. Andererseits würde hierdurch die Endkonzentration dieser Produkte entsprechend vermindert und der Einfluß der unvermeidbaren Blindwerte entsprechend erhöht. Die gefundene Lösung stellt einen Kompromiß dar, der hohe Endkonzentrationen und damit höhere Genauigkeit für die meisten Stoffklassen garantiert. Fehlmessungen bei langsamer verbrennenden Verbindungen sind als solche erkennbar, da in diesen Fällen die vorausgesetzte Konstanz des Kohlendioxidpeaks *nicht* erreicht wird. Ein Reservoir von nur 50 ml ist dagegen in fast allen Fällen zu klein, was sich darin dokumentiert, daß auch leicht verbrennbare Verbindungen wie Benzoesäure nicht mehr völlständig erfaßt werden.

Acht Minuten nach Einschieben der Probe wird die Intensität des Kohlendioxidpeaks U^{44} abgelesen und der Massenscan wird eingeschaltet. Bei Durchlaufen der Massen 28, 18 und 14 werden die entsprechenden Intensitäten U^{28}, U^{18} und U^{14} entweder vom Registrierpotentiometer RE registriert oder vom Drucker des digitalen Voltmeters ausgedruckt.

Vorversuche haben gezeigt, daß das Untergrundspektrum in allen relevanten Peaks niedriger ist, als das Spektrum, das man erhält, wenn man eine "Leerverbrennung" durchführt. Zur Ermittlung dieser Leerwerte wird der ganze Vorgang, wie eben beschrieben, durchgeführt, ohne daß eine Probe eingesetzt wird. Die hierbei erhaltenen Spannungen U_0^{14}, U_0^{18}, U_0^{28} und U_0^{44} bilden die echten Blindwerte, die von den bei Verbrennungen gefundenen Intensitäten subtrahiert werden müssen, um die gesuchten Werte zu erhalten. Aus der so bestimmten Differenz $W_C^{44} = U^{44} - U_0^{44}$ wird der C-Gehalt der eingesetzten Verbindung durch Division mit der Einwaage g und Multiplikation mit der Apparatekonstanten f_C berechnet. Analog hierzu ergibt sich der Gehalt an Wasserstoff aus U^{18}, f_H und g. Die Apparatekonstanten f_C und f_H werden durch Verbrennung von Testsubstanzen bestimmt.

Nimmt man zur Stickstoffbestimmung den Wert U^{14}, so kann in gleicher Weise verfahren werden. Dieser Peak ist jedoch nicht sehr intensiv, und wir untersuchten deshalb auch die Möglichkeit, den Molekülpeak bei der Masse 28, der aber zusätzlich durch das Kohlenmonoxidion belegt ist, zu verwenden. Die Intensität dieses Bruchstückions des Kohlendioxids ist unter konstanten Bedingungen der Intensität U^{44} proportional. Der Fragmentierungsgrad α_{28}^{44} kann durch Verbrennung einer stickstofffreien Verbindung bestimmt werden. Damit ergibt sich der Stickstoffgehalt zu: $f_N^{28} \cdot (U^{28} - \alpha_{28}^{44} \cdot U^{44} - U_0^{28})/g$.

KONTROLLERGEBNISSE

Die optimalen Versuchsbedingungen wurden in zahlreichen Voruntersuchungen erarbeitet. Besonderes Augenmerk galt dabei dem zeitlichen Einstellungsverhalten des massenspektrometrischen Detektors bei sprunghaften Änderungen der Konzentration eines möglichen Verbrennungsproduktes. Zur Beobachtung dieser Phänomene wurde ein Versuchsaufbau konzipiert, der es gestattet, Rechteckimpulse der fraglichen Verbrennungsprodukte—Kohlendioxid, Stickstoff und Wasser—im Trägergas Helium an der viskosen Einlaßsonde vorbei zu leiten.

Hierzu wird auf den Einlaßschliff ES (Abb. 2) des Massenspektrometers MS (Type CH 5 der Firma Varian-MAT) ein Einlaßrohr ER gesetzt, in dem sich die nadelförmige Einlaßkapillare EK befindet, deren Spitze fast bis zum Ende des Schliffkerns (NS 5) reicht, der das Einlaßrohr abschließt. Von diesem Schliff führt ein kleines mit Kupferoxid gefülltes Oxidationsrohr OR (Länge 80 mm, Innendurchmesser 8 mm), das durch eine Heizwicklung auf 750 K gehalten wird, zu einem Doppelhahn DH, der es gestattet, die Einlaßsonde entweder mit dem reinen Trägergas oder mit einem simulierten Probengas zu umspülen.

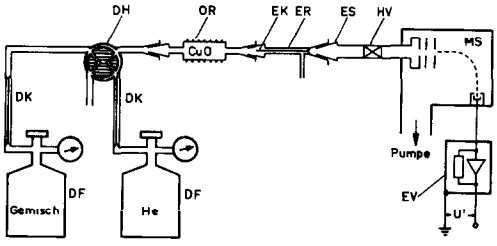

Abb. 2. Vorrichtung zur Messung von Einstellzeiten.

Die beiden Drosselkapillaren DK sind so gewählt, daß der Gasstrom aus beiden Druckflaschen DF je etwa 0,5 ml/s beträgt.

Nach dem Umschalten von Helium auf Gemisch (95% He, 2% CO_2, 2% N_2 und 1% H_2) beginnt der eingestellte Peak nach einer Totzeit von 4,0 s anzusteigen. Ist das Massenspektrometer auf die Masse 14 eingestellt, so steigt die vom Elektrometerverstärker EV abgegebene Spannung U^{14} sehr steil an, überschreitet nach 5,0 s den 90%-Wert und wird nach einer weiteren Sekunde stabil. Die Einstellzeit (0–99%) ist mit zwei Sekunden sehr gering. Beim erneuten Umschalten des Gasstromes auf Helium erfolgt, beginnend nach 4,0 s, ein ebenso steiler Abfall des U^{14}-Wertes.

Ist beim gleichen Versuch das Massenspektrometer auf den Kohlendioxid-Molekülpeak eingestellt, so bleibt die beobachtete Totzeit gleich, die Einstellzeit steigt dagegen erheblich an. Während der 60%-Wert von U^{44} in einem steilen Anstieg noch nach wenigen Sekunden erreicht wird, beginnt von da an ein sehr langsames Ansteigen des Signals. Erst nach zehn Minuten wird der Endwert erreicht. Der gleiche Vorgang wiederholt sich beim "Ausschalten" des Probengasstromes und Wiedereinschalten des Trägergases; nach sehr großer Anfangssteilheit wird der Abfall des Signals sehr stark verlangsamt, und die ursprüngliche Null-linie wird erst wieder zehn Minuten nach dem "Umschalten" erreicht. Stoppt man den Zustrom von Kohlendioxid zum Massenspektrometer durch Schließen des Hochvakuumventils HV, so dauert das Erreichen der Nullinie gleich lange. Die Ursache für diesen langen "Nachlauf" ist also im Massenspektrometer selbst zu suchen.

Die beobachteten Symptome lassen sich mit einer Kondensation des einströmenden Kohlendioxids an der Kühlfalle, die vor die Diffusionspumpe des Massenspektrometers geschaltet ist, erklären. In der Tat verschwindet der lange Nachlauf sofort, wenn die Kühlfalle nicht mit flüssigem Stickstoff gefüllt wird; der Kohlendioxidpeak wird, wie der Stickstoffpeak, mit einer Einstellzeit von wenigen Sekunden aufgebaut und—bei Ab schalten des Probengases—auch wieder abgebaut. Bei allen zukünftigen Messungen wird die Kühlfalle deshalb *nicht* gefüllt.

Der Massenpeak bei der Masse 28, dessen Plateau bei der eingestellten Auflösung von 250 sowohl vom Molekülion des Stickstoffs, als auch vom Bruchstückion Kohlenmonoxid gebildet wird, zeigt bei "eingeschalteter" Kühlfalle ebenfalls den langen Nachlauf; allerdings ist dieses Phänomen durch das Überwiegen der Stickstoffintensität stark gemildert. Bei ungefüllter Kühlfalle zeigen U^{14}, U^{28} und U^{44} den gleichen zeitlichen Verlauf, und das Massenspektrometer ist durchaus in der Lage, die gesuchten Konzentrationen in kürzester Zeit anzuzeigen.

Der Wasserpeak U^{18}, der als Folge der Reaktion des im Gemisch enthaltenen Wasserstoffs mit Kupferoxid ebenfalls als Rechteckbande auftreten sollte, benötigt auch bei ungefüllter Kühlfalle mehrere Minuten, bis der Endwert eingestellt ist. Aus dem zeitlichen Kurvenverlauf kann geschlossen werden, daß auch hier eine Kondensation an "kalten" Oberflächen den Nachlauf verursacht. Allerdings beginnen diese Kondensationsflächen offensichtlich bereits im Normaldruckbereich unmittelbar hinter dem Oxidationsrohr OR und erstrecken sich über die ganze Zuleitung zum Massenspektrometer vom Einfüllschliff beginnend über das Hochvakuumventil HV bis in die Ionenquelle. Erst wenn die gesamte Zuleitung zum Massenspektrometer und die Ionenquelle selbst auf 500 K geheizt werden, entsteht und verschwindet der Wasserpeak mit der noch erträglichen Einstellzeit von 20 s. Dementsprechend wird bei allen späteren Versuchen die Verbindung zwischen Reservoir und Massenspektrometer (Abb. 1) geheizt und die Ionenquellentemperatur auf den

Tabelle 1. Verbrennung von Benzoesäure

g, μg	U^{44}, mV	W_C^{44}, mV	U^{18}, mV	W_H^{18}, mV	W_C^{44}/g	W_H^{18}/g	%C	%H
0	19	—	56	—				
272,1	5250	5231	709	653	19,22	2,40	69,1	4,97
0	20	—	57	—				
255,8	4940	4920	666	609	19,23	2,38	69,2	4,93
0	20	—	54	—				
355,6	6810	6790	937	883	19,09	2,48	68,7	5,14
0	22	—	59	—				
169,6	3269	3247	433	374	19,15	2,21	68,9	4,58
0	19	—	48	—				
318,5	6080	6061	831	783	19,03	2,46	68,5	5,10

$W_C^{44} = U^{44} - U_0^{44}$; $W_H^{18} = U^{18} - U_0^{18}$.

genannten Wert eingestellt. Auch dann bleiben noch geringe Memoryeffekte im Wasserwert, und es empfiehlt sich, die erste Analyse einer Meßreihe zu verwerfen, da durch das vorherige lange Abpumpen andere Bedingungen entstanden sind, als sie im periodischen Betrieb (alle 12 Minuten eine Analyse) bestehen.

Unter den geschilderten Bedingungen erhält man mit Einwaagen zwischen 150 und 500 μg sehr brauchbare Kohlenstoff- und Wasserstoffwerte. In Tabelle 1 ist das Ergebnis einer solchen Testreihe wiedergegeben. Die bei zwischengeschobenen Leerverbrennungen gemessenen Blindwerte sind in die Tabelle mit aufgenommen. Sie zeigen eine erstaunliche Konstanz und werden deshalb zukünftig nur noch in größeren Abständen registriert.

Die in Tabelle 1 aufgeführten Werte lassen keinen systematischen Fehler erkennen. Unabhängig von der Größe der Einwaage schwanken die gefundenen C-Werte mit $\pm$ 0,3% um den theoretischen Wert (68,8%), und auch die H-Werte sind für ein statisches Verfahren erstaunlich gut.

Die Stickstoffbestimmung gelang dagegen mit dem eingesetzten Massenspektrometer nur unzulänglich. Einerseits war die Intensität des Bruchstückions U^{14} wider Erwarten gering. Während üblicherweise der Stickstoffpeak bei der Masse 14 mindestens 10% der Intensität des Molekülpeaks aufweist, konnten wir mit dem Massenspektrometer CH-5 allenfalls ein Intensitätsverhältnis von 4% realisieren, und der Blindwert U_0^{14} war fast so groß wie das Signal U^{14}. Andererseits zeigten auch die bei der Masse 28 gefundenen Stickstoffgehalte große Schwankungen. Offenbar führt die doppelte Korrektur um den Kohlenmonoxidanteil α_{28}^{44}. U^{44} und den Blindwert U_0^{28} in Verbindung mit hohen und wenig stabilen Blindwerten zu diesen großen Streuungen.

Während der Verbrennung wurde, wie eingangs beschrieben, die Intensität der Masse 44 registriert. Nach Durchlaufen eines Maximums nach 10 Minuten nahm diese Intensität wieder langsam ab. Diese leichte Abnahme ist auf den Gasverbrauch des Massenspektrometers zurückzuführen, der sich—in Spülstellung des Hahns HR—in einer entsprechenden Druckabnahme dokumentiert. Würden, ausgehend von der Masse 44, die anderen Massen mittels des stetigen Massenscans angesteuert, so könnte dies nur sehr langsam geschehen, denn der Elektrometerverstärker EV hat eine Einstellzeit (0–99%) von nahezu einer Sekunde, und die Auflösung kann nicht kleiner als 250 eingestellt werden. Wenn der Endwert jeweils erreicht werden soll, würde das Durchfahren des Massenbereichs von 44 bis 14 mindestens 3 Minuten in Anspruch nehmen. Wir zogen es deshalb vor, die gewünschten Massen jeweils von Hand einzustellen. Dieses Verfahren ist zeitsparend aber mühsam. Ein Massenprogrammwähler würde eine erhebliche Erleichterung bedeuten.

Zur Vermeidung der beiden im Massenspektrometertyp begründeten Mängel—zu geringe Stickstoffempfindlichkeit bei Masse 14 und zu große Scanzeit bzw. mühsame Masseneinstellung von Hand—setzten wir in einer letzten Version der Meßanordnung das Massenspektrometer M 3 der Firma Varian-MAT ein. Dieses für die Atemanalyse konzipierte Gerät besitzt ein 180°-Sektorfeld, das durch einen Permanentmagneten erzeugt wird und hat *vier* Ionenauffänger, die auf verschiedene Massen eingestellt werden können. Die

dazugehörenden vier Elektrometerverstärker können durch Einsatz entsprechender Arbeitswiderstände R der jeweiligen Meßaufgabe optimal angepaßt werden. Sie wurden von uns mit folgenden Werten bestückt: $R^{14} = 10^{11}\Omega$; $R^{18} = R^{28} = 3.10^{10}\Omega$; $R^{44} = 10^{10}\Omega$. Damit erhält man für N^{14} die gewünschte hohe Empfindlichkeit. Gleichzeitig ist bei diesem Massenspektrometertyp der Stickstoff-Ionenstrom der Masse 14 nur 10-mal kleiner als bei der Masse 28 und U_N^{14}/U_N^{28} liegt demnach bei 30% (4% im Falle des CH-5). Da zudem der Stickstoffblindwert bei der Masse 14 klein und stabil ist, sind alle Voraussetzungen für eine Stickstoffbestimmung besser.

Auch zur Bestimmung von Kohlenstoff und Wasserstoff ist das kleine Massenspektrometer* besser geeignet. Alle Ionenströme sind bei gleichen Partialdrucken im Massenspektrometer etwa um den Faktor 7 größer, so daß bei den intensiven Peaks die angegebenen kleineren Arbeitswiderstände, die kürzere Einstellzeiten, bessere Nullkonstanz und kleineres Rauschen bedingen, eingesetzt werden können.

Tabelle 2. Verbrennungsergebnisse bei Testverbindungen

Nr.	g, μg	U^{44}, mV	U^{18}, mV	U^{14}, mV	gefundene Werte %C	%H	%N	Fehler in abs. % ΔC	ΔH	ΔN
I	0	7	164	—	—	—	—	—	—	—
II	448,7	3698	3101	—	68,2	4,86	—	−0,6	−0,09	—
	347,2	2901	2532	—	69,1	5,06	—	+0,3	+0,11	—
	322,4	2694	2393	—	69,1	5,13	—	+0,3	+0,18	—
	250,1	2091	1803	—	69,1	4,85	—	+0,3	−0,10	—
	321,0	2670	2255	—	68,8	4,83	—	−0,1	−0,12	—
	260,3	2166	1911	—	68,8	4,97	—	−0,1	+0,02	—
III	361,7	1924	4570	—	44,0	9,06	—	−0,1	+0,18	—
	320,6	1718	4080	—	44,3	9,08	—	+0,2	+0,20	—
IV	219,6	1740	2021	—	65,4	6,27	—	+0,4	+0,20	—
V	273,9	2903	2509	—	87,7	6,35	—	0	0	—
I	0	5	185	41	—	—	—	—	—	—
VI	260,7	2293	2291	289	72,7	6,02	21,1	0	−0,08	0
	325,9	2856	2841	352	72,5	6,07	21,2	−0,2	−0,03	0
VII	219,9	973	1071	320	36,4	3,00	28,2	0	−0,05	−0,1
VIII	459,6	4380	3609	351	78,9	5,55	15,0	−0,2	+0,02	−0,4
IX	198,3	298	1169	517	12,2	3,70	53,2	+0,7	−0,17	−0,6
I	0	7	184	38	—	—	—	—	—	—

I = Leerwertmessung; II = Benzoesäure [68,84% C; 4,95% H]; III = Pentaerythrit [44,11; 8,88]; IV = Tropasäure [65,05; 6,07]; V = Triphenylcarbinol [87,66; 6,19]; VI = Methylbenzimidazol [72,70; 6,10; 21,19% N]; VII = 2,4-Dinitrophenylhydrazin [36,37; 3,05; 28,28]; VIII = Azobenzol [79,09; 5,53; 15,38]; IX = Nitroguanidin [11,54; 3,87; 53,84].

Die Verbrennung wird unverändert wie früher ausgeführt. Am Verstärker der Masse 44 ist als Registriereinheit RE ein digitales Voltmeter mit Drucker angeschlossen. Wenn U^{44} nach 8 Minuten stabil geworden ist, wird der anliegende Wert ausgedruckt. Über einen Tastenschalter werden dann nacheinander die Spannungen U^{28}, U^{18} und U^{14} an das Voltmeter gelegt und die anstehenden Werte ausgedruckt. Dieser Meßvorgang dauert nur wenige Sekunden. Anschließend wird wie oben beschrieben gespült, die neue Probe eingesetzt und die nächste Verbrennung gestartet. Bis zu sechs CHN-Analysen können so in einer Stunde durchgeführt werden.

Die in Tabelle 2 angeführten Ergebnisse zeigen die Brauchbarkeit dieser Anordnung. Die Blindwerte bei Leerverbrennungen sind ausreichend reproduzierbar und—verglichen mit den bei Proben gefundenen Ionenströmen—so niedrig, daß die unvermeidbaren Schwankungen das Endresultat nur wenig beeinflussen können. Im Falle des Kohlenstoffwertes können diese Blindwerte *nicht* die Ursache für die gefundenen Abweichungen vom theoretischen Wert sein. Die beobachtete Meßunsicherheit von etwa ± 0,3% im Kohlenstoffwert ist auch bei anderen Verfahren gleich groß, obwohl dort in der Regel erheblich größere Substanzmengen eingesetzt werden, wodurch Wägefehler weitgehend ausgeschaltet sind und obwohl bei anderen Verfahren der Zeitaufwand meistens erheblich größer ist.

* Das Gerät M 3 wurde uns von der Abteilung für Pneumologie, Universitätskliniken Homburg, dankenswerterweise zur Verfügung gestellt.

Daß die erste Vollanalyse mit $\Delta C = -0{,}6\%$ einen größeren Fehler zeigt, ist nicht außergewöhnlich und auch bei anderen Methoden im Bereich des Möglichen, wenn, wie hier, eine Reihe von Leerverbrennungen vorausgegangen sind. Unerklärlich bleibt vorerst der Fehler bei Nitroguanidin. Hier müßte in entsprechenden Untersuchungen erst festgestellt werden, ob es sich um eine systematische Abweichung handelt.

Die Genauigkeit der Wasserstoffwerte ist für ein statisches Verfahren frappierend. Die hohe Temperatur des massenspektrometrischen Detektors und die Beseitigung aller kalten Stellen in der übrigen Meßeinrichtung haben sich außerordentlich gut bewährt. Diese Erfahrung gibt uns die Hoffnung, daß der heimtückische Stoff "Wasser" auch im Zusammenhang mit anderen Analyseverfahren mittels eines massenspektrometrischen Detektors genügend genau bestimmt werden kann, und daß insbesondere eine Isotopenanalyse von ^{18}O auf diese Weise möglich ist.

Die aus U^{14} berechneten Stickstoffwerte sind akzeptabel, wenn man von dem leichten Ausrutscher bei Nitroguanidin absieht. Da hier auch der C-Wert etwas daneben lag, sollen vorerst daraus keine Schlußfolgerungen gezogen werden. Die Stickstoffgehalte wurden außerdem mittels des Peaks bei der Masse 28 bestimmt. Auch diese Werte waren durchaus brauchbar, und die Meßunsicherheit ist kaum größer als bei der Masse 14.

Die Proportionalitätsfaktoren f_C^{44} und f_H^{18} wurden aus den Verbrennungsresultaten der Benzoesäure berechnet. Der Stickstoff-aktor wurde mittels der Verbindung Nr. VI bestimmt. Die gute absolute Genauigkeit der CHN-Werte bei den anderen Verbindungen beweist, daß alle gemachten Prämissen erfüllt sind und zeigt erneut, daß unser viskoses Einlaßsystem[2] einwandfrei arbeitet.

Die Grenzen der Leistungsfähigkeit der beschriebenen Apparatur werden aber sehr schnell überschritten, wenn schwer verbrennbare Stoffklassen eingesetzt werden und die Verbrennung der Probe sich über mehrere Minuten erstreckt. Dann werden nämlich die Verbrennungsprodukte nicht mehr vollständig in das kleine Reservoir überführt. Dieses müßte vielmehr ein erheblich größeres Volumen erhalten, und damit wäre eine entsprechende Verminderung der Endkonzentration verbunden. Bei gleichbleibenden Blindwerten hätte das aber einen Verlust an Genauigkeit zur Folge. Die Verwendung höherer Einwaagen könnte einen Teil der Konzentrationsminderung wettmachen; andererseits ist bekannt, daß schwer verbrennbare Stoffklassen noch am ehesten im Ultramikrobereich erfolgreich analysiert werden können.

Insgesamt gesehen stellt die beschriebene statische Methode eine brauchbare Ergänzung des dynamischen Verfahrens[1] dar. Sie gestattet bei Verwendung kleiner Massenspektrometer mit hoher Partialdruckempfindlichkeit, kleinem Eigenvolumen, geringer Auflösung und großem Proportionalitätsbereich insbesondere dann eine gleichzeitige Bestimmung vieler Elemente auch mit einem Ionenauffänger, wenn das Massenspektrometer Hochspannungsscan besitzt, damit die relevanten Peaks mittels eines schnellen Massenprogrammwählers abgefragt werden können.

Eine besonders interessante und schwierige Vielfachelementaranalyse ist die Bestimmung des Gehalts an Isotopen bei angereicherten organischen Verbindungen. Für derartige Bestimmungen kommen insbesondere ^{13}C, ^{2}H, ^{15}N und ^{18}O infrage, für die es derzeit kaum brauchbare elementaranalytische Verfahren gibt. Die beschriebene Apparatur ist durchaus in der Lage, solche Aufgaben zu lösen. Eine diesbezügliche Arbeit ist in Vorbereitung und wird demnächst innerhalb dieser Reihe erscheinen.

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TOTAL SYSTEMATIC ERROR IN REDOX TITRATIONS WITH VISUAL INDICATORS—I

BASIC PRINCIPLES

ADAM HULANICKI and STANISŁAW GŁĄB
Institute of Fundamental Problems in Chemistry, University, Warsaw, Poland

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Summary—The following factors contribute to the total error in redox titrations with visual indicators: the end-point error (ΔV_T), which arises from the difference between the potential of the equivalence point and that of the actual end-point determined by a given indicator; the indicator consumption error (ΔV_I), which arises from the amount of indicator oxidized (or reduced) by the titrant; the irreversibility error, which is in fact a part of the indicator consumption error, arising from the generally uncontrolled processes connected with the irreversibility of the redox processes, decomposition of the reaction products, *etc.* The first two factors can be evaluated on the basis of the physicochemical characteristics of all the systems involved. They contribute to the total systematic error. The third, being not strictly controlled, in general increases the positive indicator consumption error, depending on such parameters as rate of titrant addition, stirring, effect of decomposition products on the potential, *etc.*

The end-point error has been treated in the literature[1,2] to some extent. In this paper a single equation is given which is a common expression for both oxidimetric and reductimetric titrations. It is presented for symmetrical reactions of the titrant and of the titrand, *i.e.*, the stoichiometric coefficients for the reduced and oxidized species of each half-reaction should be the same. Therefore the treatment is not strictly valid for such couples as $Cr_2O_7^{2-}/Cr^{3+}$ or I_2/I^-.

The indicator consumption error has not previously been treated in detail, but only the sum of the two contributions to it; it is extremely difficult, if indeed possible, to calculate an indicator correction in redox titrations even for reversible systems.

SYMBOLS USED

V_x, V_T	volumes of the titrand and titrant, respectively.
C_x, C_T	molar concentrations of titrand and titrant, respectively.
[Ox], [Red]	actual concentrations of oxidized and reduced forms respectively, of the species indicated by subscripts.
E°_x, E°_T	formal redox potentials of titrand and titrant, respectively.
E°_{ind}	formal redox potential of the indicator.
E	potential of the titration end-point, equal to the transition potential of the indicator.
C_{ind}	molar concentration of the indicator at the end-point.
A	for a one-colour indicator, the minimal absorbance of the solution, at which a colour is just visible in a layer of thickness l (end-point absorbance at which titration is ceased, when the initial indicator form is colourless).
A'	for a one-colour indicator, the maximum absorbance at which no colour is visible in a solution of layer thickness l (end-point absorbance at which titration is ceased, when the initial indicator form is coloured).
M, N	for a two-colour indicator, the ratio of absorbance of the post-end-point form to the absorbance of the pre-end-point form of the indicator for oxidimetric and reductimetric titrations, respectively. This ratio is often assumed to be equal to 10.
ϵ_{Red}, ϵ_{Ox}	molar absorptivities of the reduced and oxidized forms of the indicator, respectively.
ΔV_T, δ_T	absolute and relative end-point errors, respectively.
ΔV_I	absolute indicator consumption error.
ΔV	total absolute titration error.

END-POINT ERROR

Using a treatment similar to that given by Brinkmann,[2] the end-point error may be calculated as follows. For oxidimetric titrations the following reactions may be written:

$$\begin{array}{l} Red_x - n_x e \rightleftharpoons Ox_x \text{ (titrand)} \\ Ox_T + n_T e \rightleftharpoons Red_T \text{ (titrant)} \\ \hline n_T Red_x + n_x Ox_T \rightleftharpoons n_T Ox_x + n_x Red_T \end{array} \quad (1)$$

In reductimetric titrations the following reactions occur:

$$\begin{aligned} Ox_x + n_x e &\rightleftharpoons Red_x \text{ (titrand)} \\ Red_T - n_T e &\rightleftharpoons Ox_T \text{ (titrant)} \end{aligned}$$

$$n_T Ox_x + n_x Red_T \rightleftharpoons n_T Red_x + n_x Ox_T \tag{2}$$

For the first case [reaction (1)] the absolute systematic end-point error in gram-equivalents of titrant is equal to the difference between the amount of the titrand and the amount of titrant added, in the total volume $(V_T + V_x)$. Because from the stoichiometry

$$[Red_T]\, n_T = [Ox_x] n_x \tag{3}$$

then

$$C_T n_T \Delta V_T = \{[Ox_T] n_T - [Red_x]\, n_x\}\, (V_T + V_x) \tag{4}$$

Thus the relative error is given by

$$\sigma_T = \frac{\Delta V_T}{V_T} = \frac{(V_T + V_x)}{C_T n_T V_T} \{[Ox_T] n_T - [Red_x] n_x\} \tag{5}$$

In this equation the actual concentrations of Ox_T and Red_x may be expressed as a function of the potentials which characterize the system. From the mass-balance equation for the titrand

$$([Ox_x] + [Red_x])(V_T + V_x) = C_x V_x \tag{6}$$

and the exponential form of the Nernst equation (for 25°)

$$\frac{[Ox_x]}{[Red_x]} = 10^{n_x(E - E_x^0)/0.059} \tag{7}$$

the concentration of the reduced form of the titrand is given by

$$[Red_x] = \frac{C_x V_x}{V_T + V_x} (1 + 10^{n_x(E - E_x^0)/0.059})^{-1} \tag{8}$$

From the Nernst equation for the titrant

$$\frac{[Ox_T]}{[Red_T]} = 10^{n_T(E - E_T^0)/0.059} \tag{9}$$

and equations (3) and (7) we obtain an expression for the concentration of the oxidized form of the titrant:

$$[Ox_T] = \frac{n_x C_x V_x}{n_T (V_T + V_x)} \cdot 10^{n_x(E - E_x^0)/0.059} \cdot 10^{n_T(E - E_T^0)/0.059} (1 + 10^{n_x(E - E_x^0)/0.059})^{-1} \tag{10}$$

When the expressions (8) and (10) are inserted in equation (5), assuming that $n_x C_x V_x = n_T C_T V_T$ we obtain finally:

$$\sigma_T = [10^{n_T(E - E_T^0)/0.059} - 10^{-n_x(E - E_x^0)/0.059}][1 + 10^{-n_x(E - E_x^0)/0.059}]^{-1} \tag{11}$$

In a similar way an equation can be derived for a relative systematic end-point error in a reductimetric titration [reaction (2)]:

$$\sigma_T = [10^{-n_T(E - E_T^0)/0.059} - 10^{n_x(E - E_x^0)/0.059}][1 + 10^{n_x(E - E_x^0)/0.059}]^{-1} \tag{12}$$

When in equations (11) and (12) the numbers of electrons n_T and n_x are taken with the sign given in the corresponding half-reactions written in the direction in which they proceed, then a common expression is obtained:

$$\sigma_T = [10^{n_T(E - E_T^0)/0.059} - 10^{n_x(E - E_x^0)/0.059}][1 + 10^{n_x(E - E_x^0)/0.059}]^{-1} \tag{13}$$

which is equivalent to the two equations given by Brinkman.[2]

Indicator	Form of added indicator	General equation	Simplified equation for $a = b = 1$
one-colour (Ind_{Ox} coloured)	Red	$E = E^0_{Ind} + \frac{0{\cdot}059}{n_{Ind}} \log \frac{a^b A^a (l\epsilon_{Ox})^{b-a}}{(alC_{Ind}\epsilon_{Ox} - bA)^b}$	$E = E^0_{Ind} + \frac{0{\cdot}059}{n_{Ind}} \log \frac{A}{lC_{Ind}\epsilon_{Ox} - A}$
one-colour (Ind_{Ox} coloured)	Ox	$E = E^0_{Ind} + \frac{0{\cdot}059}{n_{Ind}} \log \frac{a^b A^a (l\epsilon_{Ox})^{b-a}}{b^b (lC_{Ind}\epsilon_{Ox} - A)^b}$	
one-colour (Ind_{Red} coloured)	Red	$E = E^0_{Ind} + \frac{0{\cdot}059}{n_{Ind}} \log \frac{a^a (lC_{Ind}\epsilon_{Red} - A')^a}{b^a A^b (l\epsilon_{Red})^{a-b}}$	$E = E^0_{Ind} + \frac{0{\cdot}059}{n_{Ind}} \log \frac{lC_{Ind}\epsilon_{Red} - A'}{A'}$
one-colour (Ind_{Red} coloured)	Ox	$E = E^0_{Ind} + \frac{0{\cdot}059}{n_{Ind}} \log \frac{(blC_{Ind}\epsilon_{Red} - aA')^a}{b^a A'^b (l\epsilon_{Red})^{a-b}}$	
two-colour	Red	$E = E^0_{Ind} + \frac{0{\cdot}059}{n_{Ind}} \log \frac{\epsilon^a_{Red} (aC_{Ind})^{a-b} M^a}{\epsilon^b_{Ox} (a\epsilon_{Ox} + bM\epsilon_{Red})^{a-b}}$	$E = E^0_{Ind} + \frac{0{\cdot}059}{n_{Ind}} \log \frac{\epsilon_{Red} M}{\epsilon_{Ox}}$
two-colour	Ox	$E = E^0_{Ind} + \frac{0{\cdot}059}{n_{Ind}} \log \frac{\epsilon^a_{Red} (bC_{Ind})^{a-b} M^a}{\epsilon^b_{Ox} (a\epsilon_{Ox} + bM\epsilon_{Red})^{a-b}}$	

Table 2. The transition potentials for reductometric titrations

Indicator	Form of added indicator	General equation	Simplified equation for $a = b = 1$
one-colour (Ind_{Ox} coloured)	Red	$E = E^0_{Ind} + \frac{0{\cdot}059}{n_{Ind}} \log \frac{a^b A'^a (l\epsilon_{Ox})^{b-a}}{(alC_{Ind}\epsilon_{Ox} - bA')^b}$	$E = E^0_{Ind} + \frac{0{\cdot}059}{n_{Ind}} \log \frac{A'}{lC_{Ind}\epsilon_{Ox} - A'}$
one-colour (Ind_{Ox} coloured)	Ox	$E = E^0_{Ind} + \frac{0{\cdot}059}{n_{Ind}} \log \frac{a^b A'^a (l\epsilon_{Ox})^{b-a}}{(blC_{Ind}\epsilon_{Ox} - bA')^b}$	
one-colour (Ind_{Red} coloured)	Red	$E = E^0_{Ind} + \frac{0{\cdot}059}{n_{Ind}} \log \frac{(alC_{Ind}\epsilon_{Red} - aA)^a (l\epsilon_{Red})^{b-a}}{b^a A^b}$	$E = E^0_{Ind} + \frac{0{\cdot}059}{n_{Ind}} \log \frac{lC_{Ind}\epsilon_{Red} - A}{A}$
one-colour (Ind_{Red} coloured)	Ox	$E = E^0_{Ind} + \frac{0{\cdot}059}{n_{Ind}} \log \frac{(blC_{Ind}\epsilon_{Red} - aA)^a}{b^a A^b (l\epsilon_{Red})^{a-b}}$	
two-colour	Red	$E = E^0_{Ind} + \frac{0{\cdot}059}{n_{Ind}} \log \frac{\epsilon^a_{Red} (aC_{Ind})^{a-b}}{\epsilon^b_{Ox} (b\epsilon_{Red} + aN\epsilon_{Ox})^{a-b} N^b}$	$E = E^0_{Ind} + \frac{0{\cdot}059}{n_{Ind}} \log \frac{\epsilon_{Red}}{\epsilon_{Ox} N}$
two-colour	Ox	$E = E^0_{Ind} + \frac{0{\cdot}059}{n_{Ind}} \log \frac{\epsilon^a_{Red} (bC_{Ind})^{a-b}}{\epsilon^b_{Ox} (b\epsilon_{Red} + aN\epsilon_{Ox})^{a-b} N^b}$	

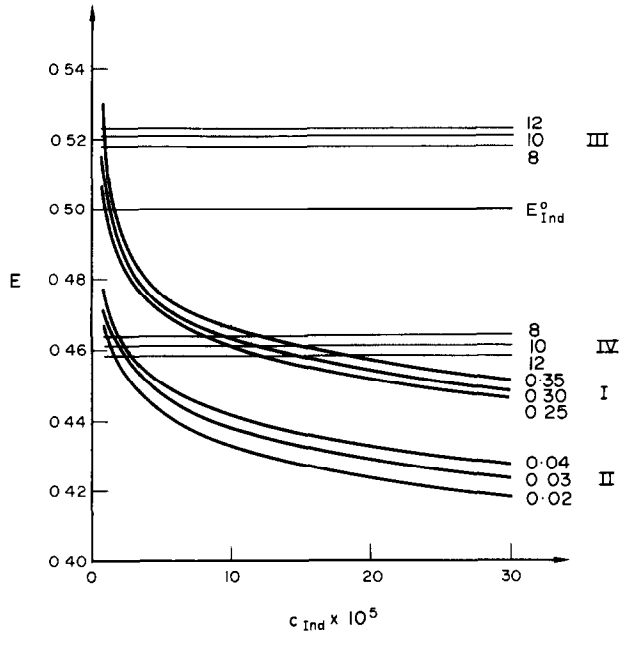

Fig. 1. The relationship between the transition potential of one-colour (I, II) and two-colour (III, IV) indicators and the indicator concentration in the final solution. Curves I and III correspond to symmetrical oxidimetric titrations, curves II and IV to symmetrical reductimetric titrations. The M and N values, as well as the A and A' values, are indicated and were chosen as close to real values observed in titrations. E° is the formal potential of the reversible indicator undergoing a two-electron reaction. The molar absorptivities were assumed to be $\epsilon_{ox} = 10^4$ l. mole^{-1} cm^{-1} for the one-colour indicator and $\epsilon_{ox} = 10^4$; $\epsilon_{Red} = 5 \times 10^3$ for the two-colour indicator. The depth of the coloured solution was taken as 5 cm.

The potential E in equation (13) corresponds to the transition potential of an indicator which reacts according to the equation:

$$a\ \mathrm{Ind_{Ox}} + n_{\mathrm{Ind}}\ \mathrm{e} \rightleftharpoons b\ \mathrm{Ind_{Red}} \tag{14}$$

The transition potential can be connected with the physical characteristics of the indicator, namely with the molar absorptivities, ratio of absorbances (M or N) at this particular point of the colour change, the thickness of the solution layer and stoichiometric coefficients.[3] The detailed form of such expressions depends on the type of indicator, the form of it used in the titration, and the type of titration. In Tables 1 and 2 the corresponding expressions are given for oxidimetric and reductimetric titrations respectively. When $a = b = 1$, they are significantly simplified, and for a two-colour indicator the transition potential does not depend on the indicator concentration. The graphical presentation of these relationships is given in Fig. 1 for a two-colour indicator, assuming several values of M (8, 10, 12), and for a one-colour indicator, assuming several values of the minimal observable absorbance A. Because most practical indicators may be considered as of the one-colour type, the transition potential, and therefore the end-point potential in redox titrations depends on the indicator concentration in the titrated solution. This is especially significant when small concentrations of indicators are used. However this effect does not contribute significantly to the end-point error when the differences between transition potential (*i.e.*, end-point potential) and the formal potentials of titrant and titrand are large. Obviously this corresponds to the case where the potential change in the titration is large and the transition potential is significantly different from both formal potentials in the system. The magnitude of the error may be simply found from a diagram (Fig. 2).[4] On this diagram the error is indicated as a function of $n_x(E - E^\circ_x)/0{\cdot}059$ and $n_T(E - E^\circ_T)/0{\cdot}059$. When both values are more negative than -3 the systematic end-point error always falls in the range $\pm 0{\cdot}1\%$.

The same diagram may also be used for simple calculation of the transition potential necessary to keep the error low in a given titration. For example when $E^\circ_T = 1{\cdot}00$ V

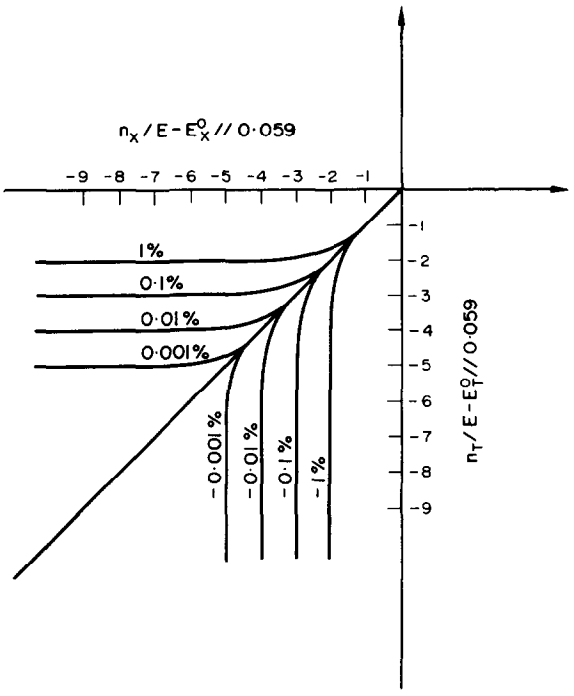

Fig. 2. The dependence of the systematic error of the end-point in redox titrations on the potentials of the systems.

($VO_2^+ + e \rightleftharpoons VO^{2+}$) and $E^o_x = 0{\cdot}46$ V ($Fe^{2+} \rightleftharpoons Fe^{3+} + e$, in H_3PO_4), the error will be below 0·1% when for the titrant

$$n_T(E - E^o_T)/0{\cdot}059 < -3, \textit{ i.e.}, E < 0{\cdot}82 \text{ V}$$

and for the titrand

$$n_x(E - E^o_x)/0{\cdot}059 < -3, \textit{ i.e.}, E > 0{\cdot}64\ V$$

This corresponds to the transition-potential condition

$$0{\cdot}64 < E < 0{\cdot}82$$

Thus diphenylaminesulphonic acid may be used in this titration, because its transition potential is 0·81 V.

INDICATOR CONSUMPTION ERROR

This error results from the fact that if the indicator is added in the same redox form as the titrand, it consumes an amount of titrant equivalent to the quantity of indicator that must react to reach the end-point of the titration. When the indicator is added in the same form as the titrant it reacts with the titrand in amount equivalent to its total quantity, but only a fraction of it is converted back into its original form at the end-point. Considering all possibilities, six cases each for oxidimetric and reductimetric titrations may be distinguished. The final equations are given in Tables 3 and 4, and the basis for their derivation is shown in the Appendix. The value of the indicator consumption error may be positive or negative. When it depends on the indicator concentration, the relationship is linear.

TOTAL SYSTEMATIC TITRATION ERROR

The total systematic error, being the sum of both contributions, is given by

$$\Delta V = \Delta V_T + \Delta V_I \qquad (15)$$

and in all instances depends on the indicator concentration. Only for two-colour indicators for which $a = b$ is the dependence of the total systematic error on the concentration

Table 3. The reagent consumption error for oxidimetric titrations

Indicator	Form of added indicator	ΔV_I	
		General equation	Simplified equation for $a = b = 1$
one-colour (Ind_{Ox} coloured)	Red	$B\frac{A}{al\epsilon_{Ox}}$	$B\frac{A}{l\epsilon_{Ox}}$
one-colour (Ind_{Ox} coloured)	Ox	$B\frac{1}{a}\left(\frac{A}{l\epsilon_{Ox}} - C_{Ind}\right)$	$B\left(\frac{A}{l\epsilon_{Ox}} - C_{Ind}\right)$
one-colour (Ind_{Red} coloured)	Red	$B\frac{1}{b}\left(C_{Ind} - \frac{A'}{l\epsilon_{Red}}\right)$	$B\left(C_{Ind} - \frac{A'}{l\epsilon_{Red}}\right)$
one-colour (Ind_{Red} coloured)	Ox	$-B\frac{1}{b}\frac{A'}{l\epsilon_{Red}}$	$-B\frac{A'}{l\epsilon_{Red}}$
two-colour	Red	$B\frac{M\epsilon_{Red}C_{Ind}}{a\epsilon_{Ox} + bM\epsilon_{Red}}$	$B\frac{M\epsilon_{Red}C_{Ind}}{\epsilon_{Ox} + M\epsilon_{Red}}$
two-colour	Ox	$B\frac{1}{a}\left(\frac{bM\epsilon_{Red}C_{Ind}}{a\epsilon_{Ox} + bM\epsilon_{Red}} - C_{Ind}\right)$	$B\left(\frac{M\epsilon_{Red}C_{Ind}}{\epsilon_{Ox} + M\epsilon_{Red}} - C_{Ind}\right)$

$$B = \frac{(V_T + V_X)n_{Ind}}{C_T n_T}$$

of the indicator linear. In the other cases the correlation is more complex. The total error may be decreased even to zero when the proper type and concentration of indicator are used, and the indicator E° value is correctly matched to the titrand–titrant system. Some examples of graphical presentation of ΔV_T, ΔV_I and ΔV as functions of the indicator concentration are shown in Fig. 3. All this is strictly valid only when a reversible indicator is considered, however. In the case of pseudo-reversible and irreversible indicators the error is as a rule greater than the calculated error. This follows from the fact that a certain quantity of the titrant reacts with the indicator to give products that do not contribute to the end-point detection. This quantity depends on the kinetics of the indicator oxidation compared with that of the main redox titration reaction, the mixing of the solutions, the temperature, the rate of decomposition of the oxidized form of the indicator, *etc.*

Table 4. The reagent consumption error for reductimetric titrations

Indicator	Form of added indicator	ΔV_I	
		General equation	Simplified equation for $a = b = 1$
one-colour (Ind_{Ox} coloured)	Red	$-B\frac{1}{a}\left(\frac{A'}{l\epsilon_{Ox}}\right)$	$-B\frac{A'}{l\epsilon_{Ox}}$
one-colour (Ind_{Ox} coloured)	Ox	$B\frac{1}{a}\left(C_{Ind} - \frac{A'}{l\epsilon_{Ox}}\right)$	$B\left(C_{Ind} - \frac{A'}{l\epsilon_{Ox}}\right)$
one-colour (Ind_{Red} coloured)	Red	$B\frac{1}{b}\left(\frac{A}{l\epsilon_{Red}} - C_{Ind}\right)$	$B\left(\frac{A}{l\epsilon_{Red}} - C_{Ind}\right)$
one-colour (Ind_{Red} coloured)	Ox	$B\frac{1}{b}\left(\frac{A}{l\epsilon_{Red}}\right)$	$B\frac{A}{l\epsilon_{Red}}$
two-colour	Red	$B\frac{1}{b}\left(\frac{aN\epsilon_{Ox}C_{Ind}}{b\epsilon_{Red} + aN\epsilon_{Ox}} - C_{Ind}\right)$	$B\left(\frac{N\epsilon_{Ox}C_{Ind}}{\epsilon_{Red} + N\epsilon_{Ox}} - C_{Ind}\right)$
two-colour	Ox	$B\frac{N\epsilon_{Ox}C_{Ind}}{b\epsilon_{Red} + aN\epsilon_{Ox}}$	$B\frac{N\epsilon_{Ox}C_{Ind}}{\epsilon_{Red} + N\epsilon_{Ox}}$

$$B = \frac{(V_T + V_X)n_{Ind}}{C_T n_T}$$

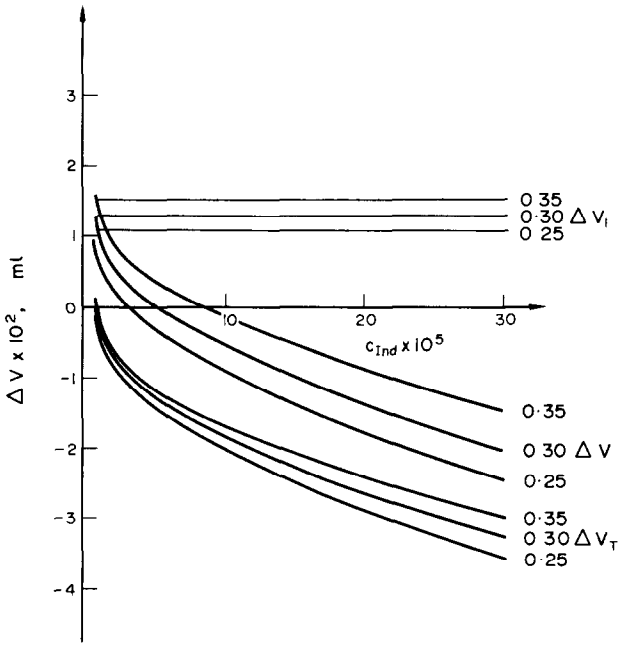

Fig. 3. The calculated relationship between the error contributions in oxidimetric titrations and the concentration of the indicator in the final solution. $E^0_{Ind} = 0{\cdot}50$ V, $E^0_X = 0{\cdot}30$ V, $E^0_T = 0{\cdot}75$ V, $n_T = n_x = 1$, $n_{Ind} = 2$, $\epsilon_{ox} = 10^4$ l. mole^{-1} cm^{-1}, $l = 5$ cm. The sets of curves correspond to various absorbances (as indicated) of a one-colour indicator. $\Delta V = \Delta V_T + \Delta V_I$.

APPENDIX

The basis of derivation of the equation for the indicator consumption error is given below for oxidimetric titrations. For reductimetric titrations the procedure is similar, being based on the same principle.

a. One-colour indicator, coloured form Ox_{Ind}, added in the reduced form. When the minimal observed absorbance is A, the oxidized form concentration is $[Ox_{Ind}] = A/l\epsilon_{ox}$. Thus the error is

$$\Delta V_I = \frac{(V_T + V_x)}{C_T n_T} \cdot \frac{n}{a} \cdot \frac{A}{l\epsilon_{ox}}$$

b. One-colour indicator, coloured form Ox_{Ind}, added in the oxidized form. Of the initially reduced indicator, only a part is reoxidized, the concentration of the oxidized form being the same as in case *a*. Therefore the error is negative, being the difference between the amount of oxidized form and the initial total amount of indicator.

$$\Delta V_I = \frac{(V_T + V_x)}{C_T n_T} \cdot \frac{n}{a} \cdot \left(\frac{A}{l\epsilon_{ox}} - C_{Ind} \right)$$

c. One-colour indicator, coloured form Red_{Ind}, added in the reduced form. At the end-point the solution apparently becomes colourless, the absorbance being in fact A'; the concentration of unoxidized indicator is $[Red_{Ind}] = A'/l\epsilon_{Red}$, whereas that of the oxidized form is $[Ox_{Ind}] = a/b(C_{Ind} - A'/l\epsilon_{Red})$. This gives the magnitude of the error as

$$\Delta V_I = \frac{(V_T + V_x)}{C_T n_T} \frac{n}{b} \left(C_{Ind} - \frac{A'}{l\epsilon_{Red}} \right)$$

d. One-colour indicator, coloured form Red_{Ind}, added in the oxidized form. The concentration of the reoxidized indicator is equal to that in case *c*. Because the indicator is first reduced the error is the difference between this and the total concentration of the indicator. Thus the error is

$$\Delta V_I = -\frac{(V_T + V_x)}{C_T n_T} \frac{n}{b} \frac{A'}{l\epsilon_{Red}}$$

e. Two-colour indicator, added in the reduced form. For the end-point the absorbance of the oxidized indicator is M times that of the reduced form

$$M[Red_{Ind}]\epsilon_{Red} = [Ox_{Ind}]\epsilon_{ox}$$

Since the total concentration of the indicator is the sum of both forms, the error is

$$\Delta V_I = \frac{(V_T + V_x)}{C_T n_T} \cdot \frac{nM\epsilon_{Red} C_{Ind}}{(a\epsilon_{ox} + bM\epsilon_{Red})}$$

f. Two-colour indicator, added in the oxidized form. With a similar assumption as in case *e*, the oxidized form concentration is given by

$$[\mathrm{Ox_{Ind}}] = \frac{bM\epsilon_{\mathrm{Red}}C_{\mathrm{Ind}}}{a\epsilon_{\mathrm{ox}} + bM\epsilon_{\mathrm{Red}}}$$

Since the whole amount of indicator reacted initially with the titrand,

$$\Delta V_{\mathrm{I}} = \frac{(V_{\mathrm{T}} + V_{\mathrm{x}})}{C_{\mathrm{T}}n_{\mathrm{T}}}\frac{n}{a}\left(\frac{bM\epsilon_{\mathrm{Red}}C_{\mathrm{Ind}}}{a\epsilon_{\mathrm{ox}} + bM\epsilon_{\mathrm{Red}}} - C_{\mathrm{Ind}}\right)$$

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ADVANTAGES OF STATISTICAL DESIGN IN THE INVESTIGATION OF TITRIMETRIC METHODS, AS EXEMPLIFIED BY A FACTORIAL-EXPERIMENT STUDY OF THE FERRIC IRON–ASCORBIC ACID TITRATION SYSTEM

LESLIE DAVIES

The Ramage Laboratories, Department of Chemistry and Applied Chemistry, University of Salford, Salford, England

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Summary—An example is outlined of the application of factorial experiment-design to the development of a titrimetric method, and the usefulness of such designs to analytical chemistry is discussed.

Principles of statistical mathematics are commonly used in investigations of the effects of experimental variables on the behaviour of chemical systems, and numerous textbooks are available, those by Davies[1] and by Duckworth[2] being well-known examples. Statistically-designed investigations are valued because they yield a relatively large amount of information for a given amount of effort. They give more estimates of the effects of individual variables than do conventional (change-one-variable-at-a-time) procedures, for the same amount of work, and additionally give estimates of the effects of interactions between variables (which conventional methods do not). Statistical designs are therefore commonly used in attempts to optimize yield and/or purity in synthetic operations at all levels of scale.

This being so, it seems surprising that apparently little attention has been paid to such designs in optimizing experimental procedures for analytical determinations. After all, chemical analyses involve essentially quantitative synthesis, of whatever complexity, and the results of physical analyses are also susceptible to the influence of variables. Statistical techniques which have proved valuable outside the analytical laboratory should therefore at least be worthy of investigation within it.

The standard deviation of a set of results is a measure of variation observed when a given procedure is replicated. In common practice, its origin is left virtually undefined as "experimental error." That is to say, there is always some variation the source(s) of which cannot in practice be identified. It arises from unrecognized variations in sampling, in sample preparation or determination technique, in impurities present in samples and reagents, in speed of working, and so on. The standard deviation is a function of any, some or all of these.

It may be, however, that a relatively small variation in *e.g.*, sample acidity will make a greater difference to the results than some other variables taken together. The analyst's real difficulty arises when, nonetheless, the variation due to acidity is small compared with the magnitude of the experimental results. It may be a long time before the influence of the acidity becomes apparent. In general, unless experimental variables likely to be of importance are carefully listed and the sensitivity of the proposed procedure to variations in them is carefully assessed, the results obtained may be "wrong" to a measurable degree.

Since a statistically-designed "factorial experiment" affords such an opportunity of listing variables and examining their influence, in a systematic and revealing way, such a procedure has been applied to an investigation of a titration system of moderate complexity, to obtain an indication of the usefulness of such experiments in the selection of titrimetric conditions. The intermediate degree of complexity arises because, while the mechanism of reduction of ferric iron is relatively simple, rapid, and pH-independent under the conditions used, that of oxidation of ascorbic acid involves more than one step, is relatively slow,

and is pH-dependent. The determination chosen may therefore be expected to be more sensitive to variables (and to more variables) than, say, the iron(III)/vanadium(II) reaction but less sensitive (and easier to interpret) than reactions in which both reactants have complicated mechanistic pathways. Doubtless, however, statistical design would be of extra value in unravelling the latter type of system. The design used in this investigation was essentially simple, involving three variables each at two values (levels). Standard texts indicate ways in which the number of variables and/or levels may usefully be increased; notes on these are appended to this paper.

THE FERRIC IRON–ASCORBIC ACID SYSTEM

A number of authors have examined the determination of ferric iron by titration with standard ascorbic acid solution,[3–10] and a number of applications have been suggested.[11–14] The reverse titration, that is the determination of ascorbic acid with standard ferric solution has also been investigated,[15] but apparently to a much less extent. The latter might be of more interest than the former, for two reasons. The first is that ferric iron would be a cheap substitute for the iodine which is commonly used for the titrimetric determination of ascorbic acid. The second is that ascorbic acid solution must either be frequently restandardized or stored in absence of air,[4] and air-stable mercurous solutions[16] may be preferred for the reductimetric determination of ferric iron.

Erdey and Bodor[4] investigated the titration of ferric iron with 0·05*M* ascorbic acid, with potassium thiocyanate as indicator, comparing the results with those of three other titrimetric methods and one gravimetric method, and assessing the precision of the procedure. They concluded (for the titration of 0·1*M* ferric chloride with 0·05*M* ascorbic acid) that the results were the same at 60° and "in the cold," and were independent of whether ferric solution or ascorbic acid solution was in the burette. To prevent measurable reaction of dehydroascorbic acid (which is produced by the ferric–ascorbic reaction) with further ferric ions, the authors recommended that the temperature be not above 60°, that the acidity be at least 0·1*M* H^+, and that the titration time be not greater than 5 minutes. However, they did not indicate the degree of error introduced by divergence from these conditions. The recommended procedure as stated by Erdey and Bodor[4] provides for initial heating to 60° and a titration time of less than 5 minutes, but is not sufficiently specific to guarantee an acidity of at least 0·1*M* H^+. The effect of acid concentrations above 0·5*M* H^+ was apparently not assessed; it was only stated that no change in end-point was noted when the concentration of acid was less than this value.

EXPERIMENTAL

In order to assess the importance of temperature, initial mineral acidity and initial reagent concentration in the determination of ascorbic acid by titration with ferric solution, and to extend the investigation of Erdey and Bodor into the effect of these variables on the opposite procedure, 2^3 factorial experiments with triplication[1a,2a] have been carried out with the conditions shown in Table 1. Individual titrations were done in random order[1b] in each of the triplicate runs, and the work was divided randomly between two operators (who did not communicate results to one another during the work) in order to minimize systematic errors of operators and materials, and also any tendency to subjectivity on the part of the operators.

Table 1. Experimental conditions investigated for the ferric iron–ascorbic acid system

	Variables investigated		
	A initial temp. °C	B initial mineral acidity in flask, [HCl], *M*	C nominal initial reagent concentration in flask, *M*
Low level	40	0·1	0·05
High level	80	0·8	0·075

The titrant was either 0·05*M* ascorbic acid or 0·1*M* ferric alum, and 0·1 ml of 0·5*M* potassium thiocyanate was used as indicator; 25-ml portions were titrated. The rate of reaction was observed qualitatively, in addition to the recording of titration volumes. The titration was carried out three times for each combination of variables, and the results summed for each combination. The sums were then analysed by Yates's table technique.[1c,2b] The results and analysis of variance are presented in Tables 2–5. The ascorbic acid solution was made up freshly

Table 2. Experimental results and Yates analysis: titration of ascorbic acid with Fe(III)

Experimental conditions, A/B/C levels	Sum of 3 titrations, *ml*	(1)	(2)	(3)	(3)/4 × 3 = effect	$(3)^2/4 \times 3 \times 2$ = mean square	Mean square / residual (approx.)
low/low/low	74·27	0·79	0·83	2·08	—	—	—
high/low/low	74·52	0·04	1·25	0·42	0·035	0·00735	1·1
low/high/low	73·97	0·90	0·35	−1·30	−0·108	0·0741	10·6
high/high/low	74·07	0·35	0·07	−0·08	−0·0067	0·000266	1·1
low/low/high	74·45	0·25	−0·75	0·42	0·035	0·00735	0·04
high/low/high	74·45	0·10	−0·55	−0·28	−0·0233	0·00327	0·5
low/high/high	74·14	0·00	−0·15	0·20	0·0167	0·00167	0·25
high/high/high	74·21	0·07	0·07	0·22	0·0183	0·00202	0·28
	code: deduct 74·00						

Titrations converted to ml of 0·1*M* Fe(III) *vs.* 25 ml of 0·05*M* ascorbic acid.

Table 3. Ascorbic acid in flask: calculation of residual variance and of mean square/residual ratios

		Sum of squares	Degrees of freedom (ϕ)	Mean square	Mean sq. / residual (approx.)
main effect	A	0·00735	1		1·1
main effect	B	0·0741	1		10·6 significant at 1% level
main effect	C	0·00735	1		1·1
two-factor interaction	AB	0·000266	1	as sums of squares	0·04
two-factor interaction	AC	0·00327	1		0·5
two-factor interaction	BC	0·00167			0·25
three-factor interaction	ABC	0·00202	1		0·28
	Sum	0·09603	7		
Remainder = "error"		0·1112	16	0·00695 (="residual variance" σ_0^2)	
	Total	0·2072	23		

Table 4. Experimental results and Yates analysis: titration of Fe(III) with ascorbic acid

Experimental conditions A/B/C levels	Sum of 3 titrations, *ml*	(1)	(2)	(3)	(3)/4 × 3 = effect	$(3)^2/4 \times 3 \times 2$ = mean square	Mean square / residual (approx.)
low/low/low	75·22	1·35	3·60	8·29	—	—	—
high/low/low	74·13	2·25	4·69	−3·01	−0·2508	0·3775	11·0
low/high/low	75·52	2·08	−1·88	1·43	0·1191	0·0852	2·48
high/high/low	74·73	2·61	−1·13	0·17	0·0141	0·0012	1·35
low/low/high	75·29	−1·09	0·90	1·09	0·0908	0·0466	0·03
high/low/high	74·79	−0·79	0·53	0·75	0·0625	0·0234	0·67
low/high/high	75·62	−0·50	0·30	−0·37	0·0308	0·0057	0·17
high/high/high	74·99	−0·63	−0·13	−0·43	0·0358	0·0077	0·22
	code: deduct 74·00						

Titrations converted to ml of 0·05*M* ascorbic acid *vs.* 25 ml of 0·1*M* Fe(III).

Table 5. Fe(III) in flask: calculation of residual variance and of mean square/residual ratios

		Sum of squares (ϕ = 1)	Mean square	Mean square residual (approx.)
main effect	A	0·3775	0·3775	11·0 Significant at 1% level
main effect	B	0·0852	0·0852	2·48
main effect	C	0·0012	0·0012	1·35
two-factor interaction	AB	0·0466	0·0466	0·03
two-factor interaction	AC	0·0234	0·0234	0·67
two-factor interaction	BC	0·0057	0·0057	0·17
three-factor interaction	ABC	0·0077	0·0077	0·22
	Sum	0·5473 (ϕ = 7)		
Remainder		0·5511 (ϕ = 16)	0·0344 (= residual variance σ_0^2)	
	Total	1·0984 (ϕ = 23)		

for each of the triplicate runs, and standardized with potassium ferricyanide.[17] The ferric alum solution was standardized gravimetrically.

The mean square/residual variance ratios shown in the right-hand columns of Tables 2–5 were tested for significance of the experimental variables examined, by Fisher's variance ratio (F) test.[2c]

DISCUSSION OF RESULTS

The investigation indicates, with better than 99% confidence, that

(*a*) in the titration of ascorbic acid with ferric chloride, the effect of increase of acidity from 0·1 to 0·8*M* H^+ (in the flask at the commencement of titration) is significant; it decreases the volume of Fe(III) required;

(*b*) in the titration of ferric chloride with ascorbic acid, the effect of increase of temperature from 40° to 80° is significant; it decreases the volume of ascorbic acid required.

Some additional observations may also be made:

(*c*) no other variable or interaction of variables gave a significant variation in results:

(*d*) the titration values show that in these experiments 25 ml of 0·05*M* ascorbic acid were on average equivalent to

(*i*) 24·76 ml of 0·1*M* Fe(III) when ascorbic acid was in the flask;

(*ii*) 24·99 ml of 0·1*M* Fe(III) when the latter was in the titration flask;

(*e*) by observation, the increase of acidity in (*a*) reduced the reaction rate, while the increase of temperature in (*b*) increased it.

These results can be discussed in terms of an outline mechanism of reaction as follows. Let A = ascorbic acid, B = Fe(III), C = dehydroascorbic acid, D = some further oxidation product(s) from dehydroascorbic acid, and consider the two cases I: titration of Fe(III) with ascorbic acid, II: titration of ascorbic acid with Fe(III).

In I, during the titration, small amounts of A are added to (except near the end-point) relatively much B, so:

$$\text{a little A} + \text{much B} \rightarrow \text{a little C (plus much B remaining)}$$

$$\text{C may react further with B} \rightarrow \text{D.}$$

That is to say, in the titration of Fe(III), the further oxidation of dehydroascorbic acid may readily be envisaged.

In II, the situation is essentially different:

$$\text{a little B} + \text{much A} \rightarrow \text{a little C}$$

but there is now negligible B present; C remains. Hence in the titration of ascorbic acid, further oxidation of its dehydro-derivative is unlikely.

This model agrees with the average results in (*d*) (*i*) and (*ii*) above, since these show that a given amount of ascorbic acid reduced more Fe(III) when further oxidation was more likely (scheme I) than when it was less likely (scheme II). The same results indicate that (on average over the experimental conditions investigated) the thiocyanate end-point gives

good stoichiometric equivalence when ferric iron is titrated with ascorbic acid. But this may be somewhat fortuitous, being compounded of incomplete oxidation of ascorbic acid to the dehydro-derivative together with some further oxidation of the latter [compare the results in (*d*) (*i*) and (*ii*)].

The same model agrees with the significance of temperature variation in the titration of Fe(III). Increase of temperature would speed up the further oxidation step, and thus at the higher temperature a fixed amount of Fe(III) would be reduced by less ascorbic acid, (as observed). In the other titration, the further oxidation step would be much less likely, and temperature increase would not, on the basis of the model, vary the quantitative amount of reduction (as observed). Additionally, in the titration of ascorbic acid, increase of acidity decreased the volume of Fe(III) required, and slowed the reaction down. These observations may be interpreted in terms of competing equilibria and reaction rates as follows. The slowing of reaction indicates that the ascorbic acid species involved in the rate-determining step is reduced in concentration at higher acidities. Although the mechanism of oxidation of ascorbic acid species has not been fully worked out,[17] if the concentration of the oxidizable species has been reduced, then the point at which there is a tendency for ferric ions to remain unreduced for sufficiently long for the titration to appear complete, will be reached earlier. Hence the end-point will be earlier (as observed).

The lack of dependence on acidity in the titration of Fe(III) is presumably because the ascorbic acid concentration will always be low anyway (up to the end-point), so the point at which the ferric iron apparently remains unreduced will be independent of acidity.

Overall, the investigation bears out the recommendations of Erdey and Bodor[4] for the titration of ferric iron, in that an initial temperature of 60° and an initial mineral acid concentration of about 0·5*M* in the flask (mean 0·45*M* in this investigation) gives good stoichiometry. However, it does not confirm their report of consistent titration values from one form of the titration to the other; the same temperature and acidity conditions appear to lead to only about 99% titration of ascorbic acid at the visual end-point. The statistical analysis reveals a clear change of significant variable from one titration form to the other, not reported by Erdey and Bodor. The behaviour can be interpreted by a simple reaction scheme.

ADVANTAGES OF STATISTICALLY-DESIGNED INVESTIGATIONS OF TITRIMETRIC SYSTEMS

The economy of statistically-designed experiments may be demonstrated by reference to Table 6, which represents the eight different experiments ("treatment combinations") of a 2^3 design, with the corresponding results ("response") x_1–x_8.

Estimates of the effect on the response due to varying A from low to high level are given by (x_2-x_1), (x_4-x_3), (x_6-x_5), (x_8-x_7). Therefore, a 2^3 design triplicated (24 titrations) gives *twelve* estimates of the effect of varying A from one level to the other (eff_A).

Now, in a conventional investigation 24 titrations would be needed to give 12 estimates of the effect of variable A, and (since the other variables would be kept constant over all twenty-four titrations) this is all the information which could be gathered. But in the statistically-designed work, the *same* 24 titrations also give 12 estimates of eff_B: (x_3-x_1), (x_4-x_2), (x_7-x_5), (x_8-x_6), each triplicated, and 12 estimates of eff_C: (x_5-x_1), (x_6-x_2), (x_7-x_3), (x_8-x_4), also each triplicated.

These latter effect-estimates therefore represent additional information from a given amount of work, compared with conventional operations. It may additionally be shown[1d,2d] that still further information is obtainable, about the effect that the level of one variable has on the effect of another (interactions). It therefore follows that research by

Table 6.

Treatment combination	lll	hll	lhl	hhl	llh	hlh	lhh	hhh
Response	x_1	x_2	x_3	x_4	x_5	x_6	x_7	x_8

l = low level, h = high level; quoted in the order of variables A, B, C.

the statistical design approach is far more productive of information than is work done in the conventional way.

Since the technique summarized in this paper has been applied so extensively to systems in which yields will inevitably be only partial (as in organic synthesis), the particular advantage of statistical design and analysis for the analytical chemist has apparently gone unrecognized. This arises because the analyst is concerned with even very small failure to give quantitative response, and is therefore looking for variables which will be important even though their proportional influence on the result is only small. In moving from one experiment to another, he is looking for small differences between large magnitudes.

The construction of the Yates analysis table[1c,2b] is such that the value −0·108 in the "effect" column of Table 2 represents the average reduction in titration volume (ml) on raising the initial acidity. This change is relatively small (0·43%), but as it is the mean of twelve estimates, considerable confidence can be reposed in it. The *F*-test shows that this systematic effect of acidity is significantly bigger than the "residual error", which is the "experimental error" referred to earlier, and is in fact a measure of the influence of any uncontrolled variables, including variability due to the operator. Variations in results which are comparatively small (but not insignificant to the analyst) may therefore be assessed with confidence, provided the variables chosen for study include all those which are significant, and the operator variance is relatively insignificant. A relatively large residual variance will indicate an unidentified significant variable and/or an imprecise operator.

It is suggested that factorial experiments may advantageously be used in designing analytical procedures.

Notes

The design used in the present study used the minimum number of levels, on the assumption that any variation of response would be monotonic between the levels. A more generally desirable procedure is to examine at three levels (3^n design[1e]), to give the possibility of detecting any maxima or minima in the effects of factors within the range of levels examined. In the present case of three examined variables ($n = 3$), there would be a set of twenty-seven treatment combinations. Triplication of the design would have led to a total of 81 titrations.

In addition, it may often be decided that there are more than three possibly significant variables to be investigated. With increase of variables, the number of treatment combinations rises exponentially. In general, factorial designs with replications lead to rapidly-increasing numbers of determinations as the numbers of factors and levels increase. Difficulties of this kind may be reduced in two ways, (*i*) by carrying out only a known fraction of the total design (fractional factorials), and/or (*ii*) by omission of replication.

The statistical function of replication is to provide a residual ("experimental") error against which the magnitudes of the systematic effects of variables may be measured. If this method of comparison is not available, owing to lack of replication, the effects of the individual factors (and of lower-order interactions in some designs) may be assessed as follows.

The order of an interaction may be viewed as the number of factors which must change *together* in order that a particular significant variation in response occurs. It appears that chemically-significant variations rarely involve the simultaneous change of several variables (*i.e.*, are rarely truly due to high-order interactions). It thus becomes acceptable to assume that effects ascribed to such interactions are in fact due to experimental error. Hence, in the absence of replication, the mean effect of the higher (or highest) interactions is used as the residual variance of the *F*-test.[1f,2e] Conversely, this technique is used to avoid the need for replication.

Fractional-factorial designs[1g,2f] similarly can markedly reduce the number of determinations required, at the expense only of loss of ability to measure high-order interactions. Inevitably, if only a fraction of a complete experiment is carried out, some knowledge must be lost, but optimal choice of design will minimize the chance of loss of signifi-

cant information. The subject is too large to outline here, but the references given above provide a detailed account of the procedure.

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A STABLE d.c. CAPILLARY ARC PLASMA FOR SOLUTION ANALYSIS

H. DENTON, B. L. SHARP and T. S. WEST

Chemistry Department, Imperial College, London SW7, England

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Summary—The analytical capability of a d.c. capillary arc plasma, operating on argon, is described. Solutions containing Cd, Pb, Hg, I, As and Zn are introduced into the plasma from a tantalum-filament atomizer. Signals are observed from both the arc and the tail-flame. The problem of sample rejection by the hot plasma is illustrated and discussed.

Many workers have used d.c. transferred plasmas for spectrochemical analysis of solutions, notably Margoshes and Scribner[1] and Korelov and Vainshtein.[2] These workers used conventional pneumatic nebulizers to introduce the samples into the plasmas, which operated at between 15 and 20 A. However, these plasmas were rather unstable and Owen[3] modified the design by stabilization with a tungsten electrode maintained at the same potential as the cathode ring. Later, Margoshes and Scribner modified the Owen design.[4] The "Spectra Jet" described by Elliot[5] had the cathode positioned to the side of the central column axis, so that the tail-flame, where greater line-to-background ratios should be obtainable, could be viewed separately. Yamamoto[6] introduced another version of the plasma jet, in which he used a copper anode and a thoriated tungsten cathode. One disadvantage of this plasma was that it operated at currents in the range 200–500 A with a 23-V voltage drop. Kranz[7,8] described a transferred plasma in which the plasma was ejected perpendicular to the arc axis. The plasma operated on nitrogen at flow-rates between 5 and 12 l./min and at arc currents from 20 to 60 A. A stable laminar plasma about 15 cm long was obtained. Valente and Schrenk[9] have described a similar plasma that gave excellent detection limits and was also economical because the total flow-rate of argon was only 2·5 l./min. The capillary arc to be described in this paper is a further development of the transferred plasma.

EXPERIMENTAL

The d.c. capillary arc plasma

The plasma unit (Applied Research Laboratories Ltd., Luton, U.K.) consists of four main parts: (*i*) a cathode block, (*ii*) a tantalum electrode and boron nitride insulator, (*iii*) a boron nitride plasma channel, and (*iv*) an anode block. Both the anode and cathode blocks are made of copper and water-cooled (1 l./min). The arc operates at between 5 and 15 A, but instability is often encountered at below 8 A. When the arc is operating at 10 A a 50-V drop occurs across the arc. The anode is operated at ground potential. The arc is initiated by a short 25-kV spark from a Tesla high-frequency coil built into the power supply. The cathode consists of a piece of tantalum wire (2·5 mm thick) sharpened to a point with an angle of *ca.* 30°. This electrode is held in place in the cathode block inside a screw-in boron nitride electrode holder. The electrode is held at right angles to the main plasma

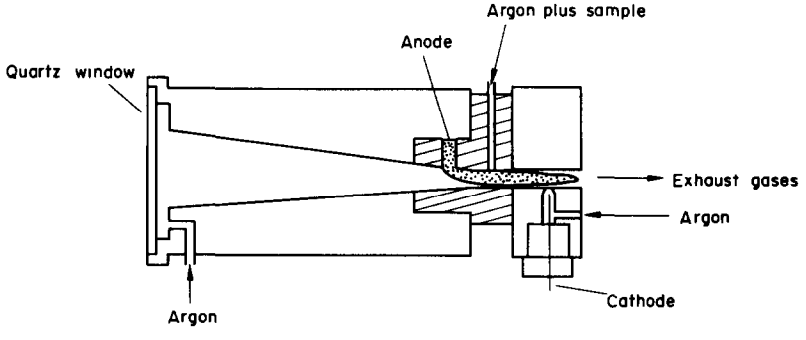

Fig. 1. The capillary arc plasma.

column and the electrode chamber is flushed with argon to prevent excessive electrode wear. The anode contact is made with the copper body of the anode block through a 2-mm hole in the boron nitride plasma channel.

The plasma can be viewed through the core *via* a quartz window. When the tail-flame is viewed at right angles to the plasma core a special brass cut-away cathode block is used. The plasma unit is shown in Fig. 1.

Flow-rates

The arc was designed to operate on a total argon flow-rate of *ca.* 2·5 l. min. There are three gas flows involved: (*i*) the cathode flush which operates at *ca.* 0·12 l./min, (*ii*) the main plasma flow, *ca.* 1·1 l./min, and (*iii*) the tangential sample introduction, *ca.* 1·4 l./min. The plasma can be operated with or without the sample flow. The effect of varying the flow-rates on the stability of the plasma is discussed later.

RESULTS AND DISCUSSION

Sample introduction

Commercial pneumatic nebulizers were found to be unsuitable for sample introduction because they operate at relatively high flow-rates (about 3 l./min of argon). In order to investigate the use of the plasma for analytical emission spectrometry, it was decided to use a one-shot method for sample introduction. This method has been used previously in this department for a microwave plasma.[10] The borosilicate glass cell that was used is shown in Fig. 2. A serum cap was used to seal the sample introduction port, and the heating/atomizer coil was made from tantalum (1½ turns of 0·25-mm diameter Ta wire). The tantalum was spot-welded onto two 1-mm diameter tungsten electrodes, held in a PTFE plug.

Platinum and tungsten were also used for heating/atomizer coils, but platinum could only be heated to about 1500° before it became deformed, and it melts at 1769°. Tungsten has a high melting point but it is easily oxidized and becomes brittle. Tantalum was chosen because of its high melting point (2996°) and its resistance to oxidation. The tantalum coil employed in these studies lasted for thousands of samples.

The sample cell was connected to the tangential sample-introduction port with a short piece of nylon tubing. To operate this system the serum cap was removed from the sample cell and a 5-μl aqueous sample was placed onto the tantalum coil from an Eppendorf pipette. A small current from a "Variac" transformer was passed through the tantalum coil to remove the water, followed by a larger current to atomize the sample into the argon stream of the plasma.

Signal measurement

The plasma was viewed by focusing an image of the tail-flame, or the arc-core, onto the slit of a modified Unicam SP900 spectrophotometer, as described elsewhere.[10,11] Transient signals were measured on a storage oscilloscope (Telequipment Type DM53A) damped with a 0·047-μF capacitor. Photon-counting measurements were made as before[11] and integration of the transient signals was performed with a stable d.c. analogue integrator.

Plasma stability

In order to assess the stability of the plasma, its core was viewed through the quartz window. The wavelength of viewing was chosen at the 253·6-nm mercury line, with a

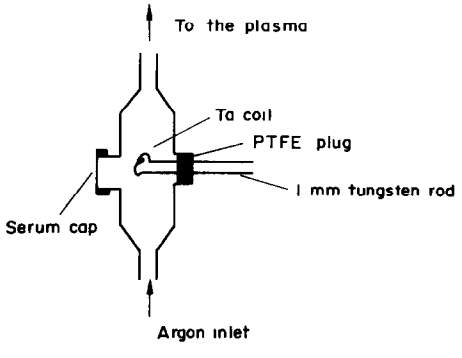

Fig. 2. Sample cell.

Table 1. Effect of argon flow-rate on precision of measurement

Sample flow-rate, *l./min*	1·42	1·65	1·85	2·1	2·4	2·7	2·8
Rel. std. devn., %	0·32	0·23	0·51	0·54	1·4	1·3	1·0

spectrometer slit-width of 0·05 mm; (*i.e.*, a band-width of *ca.* 0·22 nm). Ten-second photon counts were measured over a period of several hours. The results of 79 photon counts showed that the maximum drift over 30 min was only 2·3%. From one photon count to the next the maximum drift was 1·5%. The relative standard deviation on the 79 counts taken was found to be 0·8%. From one photon count to the next the average "noise" on the signal was 0·55%. Longer operating times of up to 5 hr showed that the plasma emission did not drift more than about 2%.

Effect of argon flow-rates on plasma stability

The cathode flush flow-rate did not seem to affect the arc stability, and the arc operated stably as long as the flush was operated at about 0·1 l./min. It was observed that high sample-introduction flow-rates were responsible for plasma instability. To study the effect of varying the sample flow, the main plasma flow-rate was fixed at 1·06 l./min and the cathode flush at 0·125 l./min. The arc was viewed through the quartz window and sixteen 10-sec photon counts were taken for several different sample flow-rates. The relative standard deviations for each set of photon counts are shown in Table 1.

From the table, it can be seen that the arc was more stable when the sample flow-rate was kept below 1·7 l./min. At above 2 l./min the plasma could be heard to become more unstable, and was pushed over to one side of the boron nitride insulator.

Electrode wear

Cathode wear was found to be about 1/16 in. after a whole day's operation, and the plasma was easily ignited when the cathode was sharpened before ignition. Most of the cathode wear seemed to occur during the ignition and stabilization of the plasma, which normally took about 3 min.

Optimal operating conditions

Cadmium was chosen to optimize the plasma operating conditions, because it was easily volatilized off the tantalum coil, and also because it has strong emission lines in the low-background region of the plasma (resonance line at 228·8 nm). Initially, the arc was viewed by focusing an unmagnified image onto the spectrometer slit which, set to 0·1 mm, gave a spectral bandpass of 0·3 nm.

Sample flow-rate

The effect of sample flow-rate on the transient signal from 5 μl of 1-ppm cadmium sulphate solution was investigated by varying the argon flow-rate from 1·38 to 0·4 l./min. All

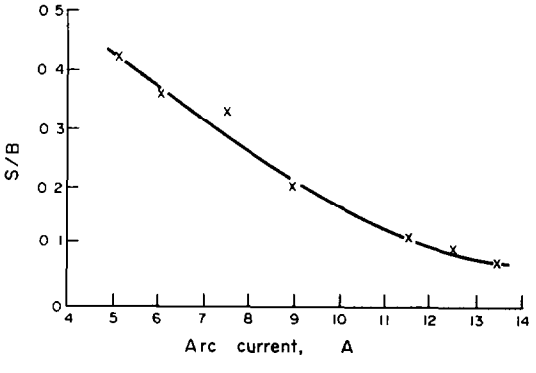

Fig. 3. Graph of signal/background *vs.* arc current for 1 ppm cadmium solution.

other operating parameters were held constant. The peak height of the signal on the oscilloscope was not greatly affected except at low flow-rates below 0·6 l./min, when multiple emission peaks were obtained.

Main plasma flow

Variation of the main plasma flow between 0·4 and 1·5 l./min did not significantly affect the signal from 1 ppm of cadmium.

The arc current was optimized by using the gas flow-rates previously determined; 5-μl samples of 1-ppm cadmium solutions were introduced at various arc currents between 5 and 12 A. The signal to arc-background ratio for the 228·8-nm line was measured and plotted against arc current (Fig. 3). The graph suggested that better signals were obtained at lower arc currents, but the noise and instability of the arc became a problem at currents below 8 A. The best signal-to-noise ratios were obtained at arc currents of 10 A or more. It was observed that the signal from the cadmium did not vary much over the whole range of currents used, the increase in background emission at high currents being responsible for the shape of the graph.

Heating rate of the tantalum sampling coil

The height of the transient signal from cadmium was found to increase when faster heating rates were used. The time for full-scale response of the damped oscilloscope was about 0·1 sec. A heating rate to give the maximum of the peak signal after about 0·3 sec was therefore chosen. For the 1-ppm cadmium sample, the total signal duration was about 1 sec.

Calibration graph

A calibration graph for 0–25 ppm of cadmium (at 228·8 nm) was plotted from the peak heights of the signals on the oscilloscope. The curve was slightly convex up to about 20 ppm and much more so at higher concentrations, probably owing to the combined effects of self-absorption and the increase in the duration of the signal. Signals from 20-ppm Cd solutions were found to have a total duration of 2 sec whereas those from 2-ppm solutions had a duration of only 1 sec.

Precision and detection limit

The detection limit for Cd at 228·8 nm was found to be 0·01 ppm for a 5-μl sample (5×10^{-11} g absolute). The detection limit calculated from signal-to-noise measurements was 0·008 ppm ($S/N = 2$). Precision measurements were made on 1-ppm and 0·1-ppm solutions. The relative standard deviations on 40 samples were 6·5% and 11·1% respectively.

Observation at other wavelengths

The 361·0- and 326·1-nm lines were viewed, but no signal could be seen for 1000 ppm of cadmium. The signal was lost in the high background of the plasma.

Observation of the tail-flame

To observe the tail-flame at 90° to the plasma flow, the brass cut-away cathode was used. An unmagnified inverted image of the tail-flame was focused onto the spectrometer slit; the visible part of the tail-flame was about 0·5 cm long and 0·35 cm in diameter at its base. Cadmium samples were introduced into the plasma and the centre of the tail-flame was viewed. No emission at 228·8 nm was seen. It was soon realized that signals could only be observed near the edge or higher up in the tail-flame. The signal was also very dependent upon the sample flow-rate. Figure 4 shows the changing signal/background ratio (from 10-ppm cadmium solution) obtained by scanning across the plasma with a narrow vertical slit. It can be seen that the sample entered only one side of the plasma. Figure 5 shows a plot of the signal/background ratio against height. It can be seen that large signal/background ratios were observed at heights of 11 mm above the base of the tail-flame. However, at this height in the plasma the flicker noise becomes quite large. The signal/noise ratio from 10-ppm cadmium solution, high in the tail-flame, was less than the signal/noise ratio when the edge was viewed with the vertical slit.

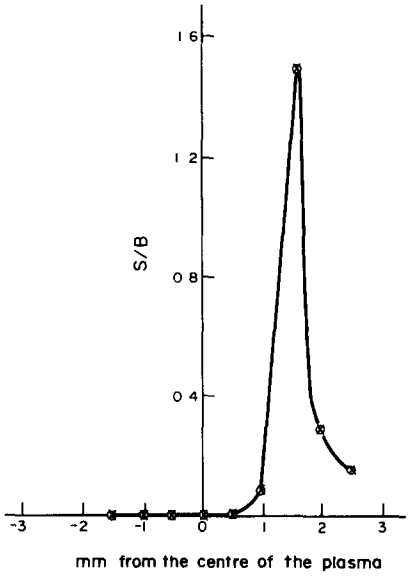

Fig. 4. Graph of signal/background for Cd *vs.* position of viewing.

Flow-rate optimization

Figures 6 and 7 show the variation in the signal/background ratio for 10-ppm cadmium solution when the flow-rates were varied. The tail-flame was viewed 1·5 mm from its centre with a spectrometer slit of 0·15 mm. At low and high sample flow-rates no signal could be observed. It was mentioned previously that at high sample flow-rates the plasma was pushed over to one side of the channel. To show that the loss in signal at high flow-rates was not due to this effect, the tail-flame was viewed at several positions across the plasma, but still a signal could not be observed.

The best viewing position for cadmium emission at 228·8 nm, using a 0·1-mm spectrometer slit, was 1·5 mm from the centre of the plasma and 4 mm above the base of the tail-flame. Here the best signal/background ratios were observed and a detection limit of 0·01 ppm was obtained.

Arc current

The arc current was varied from 8 to 12·5 A and Cd was introduced. At higher currents better signal/background ratios were observed, and also the signal/noise ratio was improved.

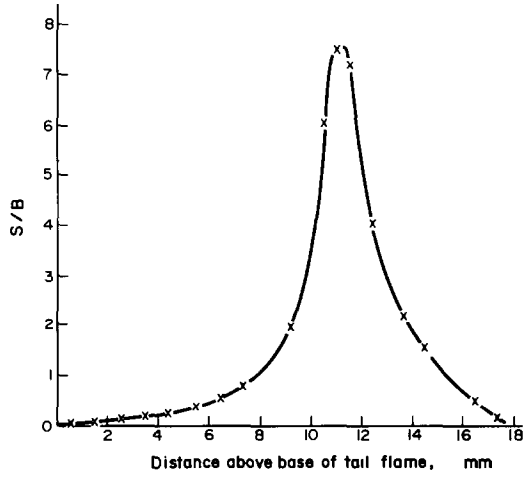

Fig. 5. Graph of signal/background *vs.* height of observation in the plasma.

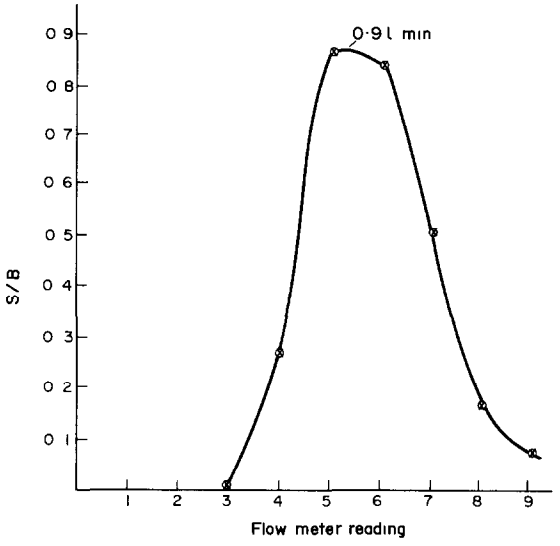

Fig. 6. Graph of signal/background (10 ppm Cd) *vs.* sample flow-rate.

Operation of the arc on the sample-flow

Figure 4 indicates that the sample is rejected by the hot expanding plasma gas. In an attempt to overcome this problem, the plasma was operated on the sample and cathode-flush flows only; 10-ppm cadmium solution was introduced into the plasma, but only small signals were recorded.

Analysis at 326·1 and 361·0 nm

The signal from 1-ppm cadmium solution could easily be seen at 326·1 and 361·0 nm. The detection limits for 5-μl samples were 0·1 and 0·05 ppm respectively. Observation of the analytical signal in the tail-flame was considered preferable to observation through the arc core, because of the considerably lower continuum emission in the spectral region at wavelengths greater than 300 nm.

Calibration graph for tail-flame observation

A calibration graph for cadmium at 228·8 nm was plotted from 0·1 to 30 ppm. The graph was similar in shape to the arc-core calibration curve, but the convexity became very pronounced at about 10 ppm of cadmium. Another graph was constructed for results obtained with the transient signal integrator, which was capable of integrating the signal without effect from the plasma's background emission. The output from the integrator was fed into a potentiometric recorder. An analytically useful curve was obtained for the range from 0 to 500 ppm Cd, with markedly less curvature, the small amount of curvature probably

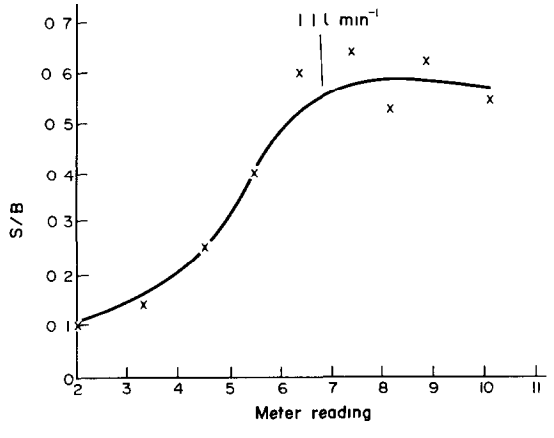

Fig. 7. Graph of signal/background (10 ppm Cd) *vs.* plasma flow-rate.

Table 2. Effect of 100-ppm concentrations of various ions on the signal for cadmium (1 ppm) at 228·8 nm

	Oscilloscope measurement		Integration measurement	
Interferent	Interference, %	Comment	Interference, %	Comment
Fe as $FeCl_3$	600	—	300	—
NO_3 as HNO_3	0	—	0	—
BO_3 as H_3BO_3	0	—	0	—
As as $NaAsO_4$	2000	—	1400	—
Sb as $SbCl_3$	400	—	200	—
SiO_4 as Na_4SiO_4	−30	Broader peaks	−20	Variable signal
PO_4 as H_3PO_4	0	—	0	—
V as NH_4VO_3	0	Narrow peaks	−40	Variable signal
Cl as HCl	−25	—	0	—
SO_4 as H_2SO_4	−25	—	0	—
Na as NaCl	0	Broader peaks	60	—
Al as $Al_2(SO_4)_3$	−30	Broader peaks	0	—

being due to self-absorption. The precision of this method signal measurement was established by using a 1-ppm cadmium solution, and the relative standard deviation for 20 samples was 5·3%.

Interferences

Signals from 1-ppm cadmium solution in the presence of 100-fold amounts of various interferents were measured by using the peak-height shown on the oscilloscope. Table 2 shows the interference effects along with any comments on peak shape. The positive deviations caused by arsenic and antimony were due to spectral line overlap. The negative deviations caused by sodium silicate, aluminium sulphate and chloride were probably due to changes in the rate of volatilization from the tantalum coil. This is indicated by broader signals. The interference from iron cannot be explained in terms of spectral interference.

It was thought that any interference effects due to different rates of volatilization from the tantalum coil would be eliminated by use of the integrator. In the case of the interferences due to aluminium sulphate this was found to be so (see Table 2). The effect of sodium silicate was somewhat reduced, but the behaviour of sodium chloride and hydrochloric and sulphuric acids is not yet understood.

Determination of other elements

The other elements investigated were arsenic, zinc, lead, mercury and iodine. The position of viewing the tail-flame for each of these elements was optimized, and detection limits were measured. Theoretical detection limits were calculated from signal/noise ratios. Table 3 shows the detection limits, position of viewing the tail-flame and theoretical detection limits.

Other methods of sample injection

To try to overcome the sample-rejection problem a high-velocity sample input was created by inserting a 20-gauge stainless-steel tube (0·6 mm bore) into the tangential sample-introduction port. The stainless-steel tube was connected to the sample cell and samples were introduced in the normal way. However, it was found that the sample did not enter the central regions of the plasma.

Table 3. Analytical data for various elements in the plasma

Element	Wavelength, *nm*	Detection limit, *ppm* (5 μl sample)	Theoretical det. lim., *ppm*	Position of viewing, *mm*
As	228·8	0·25	0·25	1·5 and above
Zn	213·8	0·25	0·2	1·5 and above
Pb	261·41	1·5	0·7	4 and above
Hg	253·7	1	0·7	1·5 and above
I	206·1	50	14	1 and above

An alternative method for high-velocity sample-introduction involved injecting the sample along the axis of the plasma. This was performed by removing the quartz window and inserting a "Tufnol" plastic plate fitted with a copper sleeve, to allow introduction of the stainless-steel injection tube. The tube was then raised to within 3 mm of the plasma anode. Unfortunately the tube melted at the tip. The melting problem was overcome by using alumina tubing cemented to the end of a piece of 17-gauge stainless-steel tubing. It was possible to move this alumina tubing to within 1 mm of the plasma anode, without any damage being done to the injection orifice. Various tube sizes from 0·2 to 0·86 mm bore were tried and the 0·38-mm tube was found to be the best for sample injection, at a flow-rate of 0·4 l./min. The detection limit for cadmium with this tube was about 0·005 ppm. The results, however, tended to be erratic from day to day. This was thought to be due to movement of the injection tube. In order to overcome this problem, a precision racking device which allowed the capillary tube to be moved up and down inside the plasma channel and also across the base of the plasma, was constructed. This did not, however, increase the reliability of the sample injection and the best position for viewing the cadmium emission was still at one edge of the plasma. The shape of the plasma may have been responsible for this difficulty. The sample was shown to enter only the side of the plasma opposite the anode. It was usually observed that sample injection was reproducible during a given run, even though not efficient. However, on restarting the arc following switch-off, realignment of the sample introduction tube was necessary on every occasion.

Conclusions

The plasma was found to be very stable and it operated for several hours with only slight cathode wear and negligible anode wear. Sample introduction with commercial nebulizers was unsuccessful because they operated at flow-rates too high for the plasma. The plasma tail-flame was found to be superior to the arc-core for analysis because the background emission was much lower. Integration of the transient emission signals produced more linear calibration graphs, and also solved some of the interference problems that were due to the varying rates of volatilization of the sample from the tantalum filament. Sample rejection by the plasma was thought to be responsible for the poor sensitivity. Several attempts to inject the sample into the centre of the plasma met with limited success.

Future work

A nebulizer/desolvation system has been constructed to permit continuous sample introduction. A detailed study of the arc has shown that continuous sample introduction does not, however, overcome the sample-rejection problem. Work is now in hand to modify the arc so that the exhaust gases may be subjected to microwave excitation to obtain a stable microwave plasma. Preliminary studies have been made on volatile elements such as Zn, Hg, As and Cd. Initial results show that the detection limits are comparable to those for the flame atomic-absorption technique. It is intended to extend the range of elements studied, to include those that are known to form thermally stable compounds when vaporized from aqueous solution. This work will be reported in a subsequent publication.

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MICROANALYTICAL DETERMINATION OF TIN IN ORGANOTIN COMPOUNDS

I. L. MARR

Chemistry Department, The University, Old Aberdeen, Scotland

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Summary—Existing procedures for the determination of tin in organotin compounds are reviewed, and a new procedure is described which can be used for the rapid microanalysis of most organotin compounds. Wet oxidation with sulphuric acid and 30% hydrogen peroxide is followed by spectrophotometric determination of the extracted ternary tin(IV)–chloride–oxine complex in chloroform. Time for a single determination is 20 min, and the relative standard deviation is 0·7% for 1–5 mg of tin. On account of their volatility, methyltin compounds must be subjected to a sealed-tube wet oxidation in sulphuric–nitric acid mixture. Addition of sulphamic acid after boiling to remove most of the nitric acid makes this compatible with the solvent extraction step. Tin present as organotin stabilizer in PVC samples can also be determined by this method, after destruction of the organic matter with sulphuric acid and 50% hydrogen peroxide.

The interests of a group of workers in this department, all concerned with various aspects of tin chemistry, both inorganic and organometallic, led to the need for a rapid micro method for the determination of tin in a wide variety of compounds. None of the existing methods described in the literature seemed to meet these requirements.

Tin in inorganic compounds is probably best determined titrimetrically with iodate after reduction to tin(II) with aluminium metal under a protective atmosphere.[1] This oxidimetric method takes time but gives very good results on reasonably large samples. The obvious interferences are all those ions which undergo similar redox reactions. This method was not tried on the micro scale.

Gravimetric methods for tin generally yield SnO_2 as the final product,[2] but the precipitate used may be a chelate with a suitable organic reagent such as cupferron.[3] Limited experience of such methods even on a 100-mg scale showed them to be slow and difficult. For milligram amounts a gravimetric finish is not particularly convenient, and only an experienced operator can get good results.

The complexometric titration is subject to several difficulties.[4] Tin(II) forms more than one complex, and tin(IV) hydrolyses more rapidly than it forms complexes, even around pH 2. Back-titrations must be used, with the EDTA in excess being added to the acid solution of tin(IV) before adjustment of the pH, but even then care must be taken over the neutralization stage.

Spectrophotometry on the other hand seemed to be a more attractive solution to the problem. A number of reagents form coloured complexes with tin and can be used for its estimation over a wide range of concentrations. The "Metallic Impurities in Organic Matter" sub-committee of the SAC, reporting in 1967, recommended Catechol Violet for the determination of up to 30 μg of tin, and toluene-3,4-dithiol for the range 30–150 μg.[5] A recent critical investigation by Engberg[6] compared the spectrophotometric determination using quercitin, suitable for the range 30–300 μg of tin, with the atomic-absorption (AAS) method using the hydrogen–air flame, which was slightly less sensitive. He concluded that for smaller amounts of tin the quercitin method was to be preferred, but for larger amounts the two methods were equally good.

The use of reagents such as those mentioned has been criticized because they are not specific for tin, and a preliminary separation step is therefore needed.[7] The separation step is also desirable before the AAS determination as this is also susceptible to a number of interferences.[6] As most of the interest has centred on the determination of trace amounts of tin, usually in foodstuffs, the separation step, often involving extraction of SnI_4 into toluene from a strongly acidic iodide solution, offers an additional preconcentration of the tin, and is no disadvantage.

Oxine has also been criticized because of its reactivity with so many metallic ions, but it has a number of features which make it worthy of consideration: it is readily available in a high state of purity, its aqueous solutions are reasonably stable, the chelates are formed rapidly and are stable for long periods of time, and are usually readily extracted. In some cases pH-control and the use of suitable masking reagents can improve the selectivity markedly. Finally, the chelates absorb light at different wavelengths from the reagent itself in non-ionizing solvents, and make possible a photometric determination of the extracted metal ion. Eberle and Lerner took advantage of these features to determine small amounts of molybdenum and tin in a wide variety of steels and alloys,[8] by first extracting the molybdenum (at pH 0·7 where scarcely anything else is extracted) and then adding chloride to facilitate the extraction of tin as a ternary complex, probably $SnCl_2Ox_2$, at the same pH. Amounts of tin up to 50 μg were handled by the standard procedure, with 20 ml of chloroform and measurement of the absorbance at 385 nm in a 4-cm cell.

This method offers satisfactory precision and more than adequate sensitivity for the determination of tin in milligram amounts of tin compounds, and is therefore adopted for the determination step. The second part of the present problem involves the choice of a method of decomposition for the organotin compounds.

Oxygen-flask combustion has been used for the analysis of organotin compounds,[9] but a lengthy and involved treatment was necessary to get the tin, 80% of which was thought to be present as rather inert SnO_2, into solution for subsequent titration. Morsches and Tölg[10] observed that recoveries of tin in an ultramicro procedure for combustion in oxygen were distinctly low, and experience in this laboratory showed that very little tin was to be found in the absorption solution, even an acidic one, after combustion in the oxygen flask.

Wet oxidation by various combinations of sulphuric acid with nitric acid,[11–14] perchloric acid,[1,15] hydrogen peroxide (30%[16] or 50%[17,18]) or potassium sulphate[19] have been advocated by many authors for the destruction of organic matter before the determination of tin. Goss[11] in 1917 used sulphuric–nitric acid mixtures for the destruction of such large quantities of fruit solid matter as to make possible a gravimetric finish for ppm levels of tin. Kirk and Pocklington mentioned difficulties encountered when larger amounts of tin were present,[14] suggesting some loss of tin by precipitation of SnO_2, which occurs more readily when nitric acid is present. Losses of tin by adsorption onto incompletely oxidized organic matter were investigated by Manicke and Lauth[16] who found both sulphuric–nitric acid and potassium chlorate–hydrochloric acid mixtures to be less than satisfactory. They recommended the use of sulphuric acid with hydrogen peroxide, with which complete oxidation to yield a clear solution was possible, and the tin was recovered quantitatively. They showed that the addition of nitric acid to the sulphuric acid–hydrogen peroxide mixture did not have any deleterious effect. This is in agreement with Gorsuch's conclusion[20] that the presence of nitric acid does not necessarily mean that tin will be precipitated as metastannic acid.

Down and Gorsuch[17] investigated the recovery of trace elements after wet oxidation with sulphuric acid and 50% hydrogen peroxide. Their results showed that tin was quantitatively recovered from mixtures of cocoa and sodium chloride, *i.e.*, that there was no loss by volatilization of $SnCl_4$ from the sulphuric acid solution, a possibility that had often been previously suggested.[21] It was pointed out that the ^{113}Sn had been added as tin(II), and that the chloride could possibly have been lost before the tin was oxidized. The suggestion that the oxidation of compounds containing covalently bound chlorine be studied in this connection has been followed up in the present work, as has that concerning the use of perchloric acid.

Macdonald and Sirichanya[22] recommended the wet-oxidation of organometallic compounds with sulphuric acid and hydrogen peroxide (30%) for cases where the metal is likely to form insoluble oxides in the oxygen-flask combustion, but did not mention organotin compounds.

A recent chapter "Analysis of Organotin Compounds"[23] dismissed wet analysis in a few lines, saying that tin is usually determined as tin(IV) oxide after heating to dryness with concentrated sulphuric acid, and that the redox titrimetric method can also be used. The

gravimetric method described by Gilman and King in 1929,[24] in which a preliminary oxidation with bromine in carbon tetrachloride was carried out to avoid losses of volatile organotin decomposition products, seems to have remained the method of choice, though many years later[25] Gilman described a simplification in which gentle heating in concentrated sulphuric acid without the bromine pretreatment gave satisfactory results even for volatile compounds. The disadvantage is of course that the method requires large samples—200 mg is suggested.

A fairly recent paper by Heimes and Braun[15] mentions some of the difficulties encountered with the old method of Farnsworth and Pekola, and describes their solution to the problem—wet oxidation in a mixture of sulphuric, nitric and perchloric acids, followed by a complexometric titration. Their procedure (mainly the decomposition) takes quite a long time, and a number of factors, such as sulphate concentration and pH, have to be carefully controlled if accurate results are to be obtained. They point out that chloride no longer prevents hydrolysis of tin(IV) at pH 2, and precipitation can occur as soon as this pH is reached.

It thus seemed that the sulphuric acid–hydrogen peroxide wet oxidation in a micro Kjeldahl tube would be convenient and efficient for milligram samples, and that simple dilution with addition of chloride would then enable the ternary complex to be extracted: this proved to be the case.

EXPERIMENTAL

Reagents

Sulphuric acid, concentrated.
Hydrogen peroxide, 30% (100-volume).
Ammonium chloride, 20% solution, aqueous.
8-*Hydroxyquinoline* solution, 1% aqueous with sufficient hydrochloric acid present to maintain solution.
Chloroform.
Tin metal, granulated.

Apparatus

Micro Kjeldahl tubes, bulb capacity 7–8 ml, and glass beads. Spectrophotometer (SP 600, Unicam) and glass cells (1-cm).

Procedure

Weigh out 5–8 mg of sample (to $\pm 0{\cdot}01$ mg) and transfer to a micro Kjeldahl tube. Add 1 ml of concentrated sulphuric acid, 1 ml of 30% hydrogen peroxide, two small glass beads, and shake gently to mix. Heat gently till boiling, then boil for about 5 min, *i.e.*, till all the hydrogen peroxide and water has been lost. The acid should be colourless. Let cool, then add about 1 ml of water and rinse with a few ml of 20% ammonium chloride solution into a 50-ml standard flask already containing 5 ml of ammonium chloride solution. Make up to the mark.

Transfer an aliquot containing not more than 500 μg of tin to a 100-ml separating funnel containing 5 ml of ammonium chloride solution and 25 ml of 1% oxine solution. Add 20 ml of chloroform and shake vigorously for 1 min. Separate the chloroform layer and filter into a 25-ml standard flask (to remove droplets of water). Make up to the mark, mix, and measure the absorbance at 385 nm in a 1-cm cell against chloroform as a blank.

Calibration

Pieces of tin metal weighing 2–5 mg are taken through the whole procedure and a calibration curve plotted. It is linear with an intercept of between 0·01 and 0·02 absorbance units, though the reagent blank does not give the same value. For routine use it is preferable to calculate the best straight line by regression analysis[26] and then to calculate all tin values directly from the absorbance readings.

RESULTS AND DISCUSSION

Standards and calibration

Stock solutions of tin can be prepared from larger amounts of tin metal but must be kept in 25% sulphuric acid to prevent hydrolysis and precipitation.[6] As the reagent and the extracted species are stable and the reproducibility of the procedure are good, it is not necessary to repeat standards regularly once a working calibration has been established. The liberal use of ammonium chloride solution is to ensure that the tin is kept in solution when the acidity is lowered. If too much sulphuric acid has been lost during the wet oxidation, the acidity may not be sufficient to keep the tin in solution in spite of the ammonium chloride, and within 30 min of dilution a cloudiness will be observed.

The oxine concentration used is lower than that recommended by Eberle and Lerner, mainly so as to minimize the reagent blank. However, because the volume of aqueous phase taken for the extraction is smaller in this method than in the original one, the extraction is still quantitative in one stage, and a double extraction would only increase the blank.

For the calibration based on thirteen tin samples weighing between 2 and 5 mg, regression analysis gave a relative standard deviation of the slope of 0·71%. For samples weighed on a semimicro balance, and a spectrophotometric finish, this value would seem acceptable, and it is improved by working only at the upper end of the calibration range.

A range of organotin compounds, some also containing halogens or sulphur, was analysed by this procedure. All were decomposed quickly and cleanly and gave acceptable results. Compounds containing bromine or iodine were of interest as the former could have suffered some losses through volatilization of $SnBr_4$ and the latter could have given slightly high absorbances if the corresponding iodide ternary complex were preferentially extracted.[8] The iodine was not always lost in the wet oxidation, but the large excess of chloride present clearly swamped any possible interference. Amounts of iodide added immediately before the extraction step, corresponding to I:Sn mole ratios of 1:1–3:1 caused no significant variation from the value obtained in the absence of iodide.

The effect of pH, and the blank

Eberle and Lerner chose pH 0·7 for the extraction of molybdenum and of tin, but stated that higher values could be used, though iron(III) would then also be extracted. The procedure described here gives a final pH of 0·85–1·1 in the aqueous phase, which is quite suitable, and eliminates the need for any further pH control. Though in this study the pH was always measured, this is not necessary for routine analysis.

A small amount of oxine is extracted even at pH 1, depending on the pH and hence on the original volume of sulphuric acid or the size of the aliquot extracted. The effect of varying the volume of acid is shown in Table 1. Over the pH range used, the variation in the blank is not significant.

Application of regression analysis to results for tin metal standards, and simple extrapolation of an apparently linear graphical plot, both yielded intercepts (*i.e.*, blanks) of around 0·015, for several sets of results collected at different times and at different laboratory temperatures. In all analyses the calculated intercept was used and the variation with pH was assumed to be that shown in Table 1.

As a final check, 10-ml aliquots of three tin solutions were taken and the recoveries were 99·7, 100·2, and 100·0%. The variation in pH produced by the procedure seems to have no significant effect on the accuracy of the results.

Interferences

The results in Table 2 indicate that most of the commoner hetero-elements present in organometallic compounds are without effect on the procedure. Fluoride is said to interfere in the extraction step,[8] but samples of tin metal (5 mg) with solid sodium fluoride (about 15 mg) taken through the full procedure gave satisfactory results provided the acid was boiled for a few minutes longer than normal, to dispel all the hydrogen fluoride. The Kjeldahl tubes were of course badly attacked.

Table 1. The absorbance blank in the absence of tin

Sulphuric acid, *ml*	pH of aqueous phase after extraction	Absorbance at 385 nm 4-cm cell	1-cm cell
1	1·05	0·031	0·008
2	0·89	0·027	0·007
3	0·81	0·024	0·006
4	0·76	0·022	$0·005_5$

5-ml aliquots were taken from 50 ml after dilution.

Table 2. Tin determinations with wet oxidation by sulphuric acid–hydrogen peroxide (30%) mixture

	Theory, %	Found, %				
		Mean	Range	Std. devn. Rel.	Std. devn. Abs.	No. of detns.
Tin metal	100·0	—	0·9	$0·6_3$	$0·6_3$	13
Triphenylvinyltin	31·5	31·5	0·25	$0·1_9$	0·6	6
Tetraphenyltin	27·8	27·5	0·3	$0·1_7$	0·6	5
Triphenylstannyl iodomethane	24·2	24·4	0·4	$0·3_2$	1·3	6
"Hexaphenylditin"*	33·9	31·4	0·2	$0·1_4$	0·5	4
Triphenyltin chloride	30·8	30·6	0·4	$0·4_2$	1·5	6
Ph_3SnS  But	23·0	22·7	0·3	$0·2_1$	1·0	6
Tin(II) acetate, sublimed	50·1	49·9	0·7	0·5	1·0	5

* Also found, C = 63·3%, H = 4·9%, total = 99·6%.

Phosphate cannot be removed by heating with concentrated sulphuric acid, and does interfere in the extraction step. Addition of 15 mg of disodium hydrogen phosphate to a 5-mg sample of tin caused 50% hold-back at pH 1·0.

Germanium does not interfere.

Organotin compounds

A range of solid organotin compounds yielded the results shown in Table 2. The higher standard deviations for some compounds would suggest some degree of inhomogeneity in these samples. The sample of triphenyltin chloride answers Gorsuch's query about covalently bound chlorine—there is no loss of tin.

Methyltin compounds

As methyltin compounds are in general rather volatile, it was to be expected that serious losses might arise during the wet oxidation. This was found to be so, but the variation in behaviour between compounds is considerable. Thus Me_3Sn  OMe gave 44·3 and 43·5% tin (calc. 43·8%), as well as some very low results, when the sample was put through the standard procedure, whereas Me_3Sn  Me gave values ranging from 9·5 to 21·5% (calc. 46·6%). This latter compound was chosen for a number of trials involving various oxidation procedures. It is a viscous liquid of low volatility, and was weighed onto pieces of filter paper from a glass capillary. Prior oxidation with bromine in carbon tetrachloride[24] was not successful, and recourse had to be made to heating with mixed sulphuric and nitric acids in a sealed tube at 150° for a few hours, which was entirely satisfactory. The results are presented in Table 3.

Table 3. Determination of tin in trimethyltin compounds

Compound	Theory, %	Found, %		
		H_2SO_4/H_2O_2	H_2SO_4/HNO_3, sealed tube without sulphamic acid	H_2SO_4/HNO_3, sealed tube with sulphamic acid
Me_3Sn  Me*	46·6	14·5 9·5	46·3 47·6	45·7
		21·4 10·4	47·8	46·0
Me_3Sn  OMe†	43·8	44·3 11·2	49·9	43·9
		17·2 43·5	50·4	44·1

* Also found, C = 47·7%, H = 6·9%, with Sn = 45·8%, total = 100·4%.
† Also found, C = 44·6%, H = 6·5%, Sn = 44·0%. Calculated C = 44·3%, H = 5·9%, Sn = 43·8%.

A dimethyl compound—in fact an impure sample of $Me_2Sn(S$ $Br)_2$—gave only slightly low results by the standard procedure compared with those obtained by the sealed-tube method and by open-tube oxidation with sulphuric–nitric acid mixture.

Table 4. Oxidation with sulphuric–nitric acid mixture

	Sn, %				
	Theory	H_2SO_4/H_2O_2 (Table 2)	H_2SO_4/HNO_3 open-tube	H_2SO_4/HNO_3 sealed-tube	$H_2SO_4/HNO_3/NH_2SO_3H$ open-tube
Triphenylvinyltin	31·5	31·5	28·4		31·5 (4)
Tetraphenyltin	27·8	27·5	28·1 27·7		
Triphenylstannyl iodomethane	24·2	24·4	24·3 23·8		24·2 (4)
Triphenyltin chloride	30·8	30·6	29·1 30·5		
Ph_3SnS⬡But	23·0	22·7	22·5 22·9		
Tin(II) acetate	50·1	49·9	49·3 49·5		
Methyltin compounds					
$Me_2Sn(S$⬡$Br)_2$*	—	19·8	20·3	20·4	
$Me_2Sn(S$⬡$Me)_2$	30·0	30·0			
$Me_2Sn(S$⬡$Br)_2$	22·6	5·0	22·2	22·6	
$Me_2Sn(S$⬡$But)_2$†	24·7	24·7 22·3	25·3 26·0		24·0

* Also found, C = 29·1%, H = 3·5%, S = 12·7%, Br = 30·4%; with Sn = 20·4% total = 96·1%. Calc. C = 32·1%, H = 2·4%, S = 12·2%, Br = 30·5%; with Sn = 22·7%.
† Also found. C = 55·8%, H = 7·2%, S = 13·6%; with Sn = 24·0%, total = 100·6%

Oxidation with mixed sulphuric–nitric acids

This combination effectively and rapidly oxidized all the organotin compounds investigated, but boiling for up to 30 or even 45 min was required to remove the excess of nitric acid and get a colourless sulphuric acid solution of the tin. A calibration based on individual pieces of tin metal showed a relative standard deviation of the slope of 1·7%. As these samples had been digested on one day and finished on the following, a second set was run without the delay—to minimize the possibility of any hydrolysis or precipitation of the tin. The relative standard deviation, for 8 samples, was then 1·5%, and the slope was less than for the standard sulphuric acid–hydrogen peroxide procedure. The same compounds which had been used for the earlier work were also tried with this mixed acid, the appropriate calibration data being used. The spread was worse, and the results were not acceptable (Table 4).

It then seemed likely that residual oxides of nitrogen were responsible for the errors, which was confirmed by adding substantial amounts of nitrate to some solutions just before the extraction step, and finding no interference at all. The addition of sulphamic acid to the partly diluted sulphuric acid after the boil-up was found to solve the problem. The calibration slope under those conditions was the same as that for the sulphuric acid–hydrogen peroxide oxidation, and good reproducibility was obtained on the better organotin standards. A method was thus available for the wet oxidation with sulphuric–nitric acid mixture, which was compatible with the solvent-extraction step, and could be used for the sealed-tube oxidation of the methyltin compounds.

Procedure for methyltin compounds

Weigh the sample (2–5 mg), onto a piece of filter paper if it is a liquid, and transfer to a thick-walled test-tube, 25 cm × 18 mm diameter. Add 1 ml of concentrated sulphuric acid and 1 ml of concentrated nitric acid, cooling briefly as the acids mix, and then two small glass beads. Draw the top of the tube down to a capillary as described by Steyermark[27] and seal off. Place in an oven at 150° for a few hours and then allow to cool. This is conveniently done batchwise overnight, switching off at midnight. Release the pressure by heating the side of the sealed capillary with a fine-tipped flame,[27] then cut off the top and boil the contents till the yellow oxides of nitrogen are no longer visible in the tube. Cool, add a little water, a few ml of ammonium chloride solution, and rinse the contents into a 50-ml standard flask containing 5 ml of the latter solution and 5 ml of 10% sulphamic acid solution. Make up to the mark, mix, and take a suitable aliquot for extraction as before

Other oxidants

Sulphuric acid with perchloric acid as an additional oxidant was also tried for the wet oxidation. Perchloric acid alone precipitates the tin. Calibrations based on the mixed acid gave a slope about 5% lower than for the standard procedure. The two good organotin standards gave reasonable results when heated in sealed tubes with sulphuric and perchloric acids, but only after boiling up with a drop or two of peroxide to decolorize the solution. One may conclude that this combination is not ideal.

Table 5. Determination of tin in PVC samples—additives at 1% level (samples ~ 100 mg)

Additive	Tin added, %	Tin found, % other method*	this method (mean)	Rel. std. devn., %	No. of detns.
Dioctylthiotin	0·152	0·15 0·16	$0·13_0$	0·009	9
Dibutylthiotin	0·152	0·16 0·16	$0·13_0$	0·014	6
Butyltin maleate	0·159	0·14 0·15	$0·14_5$	0·008	7

* Decomposition in H_2SO_4/HNO_3, determination by plasma-torch method.

Organotin additives in PVC plastics

Taubinger and Wilson[28] described the sucessful destruction of various plastics by heating with concentrated sulphuric acid to its boiling point, and then adding 50% hydrogen peroxide dropwise, and the procedure has received subsequent recommendation.[17,18] Such a procedure would appear entirely compatible with the extraction–determination steps used in this work. Moreover, for reasons of their low aqueous solubility and toxicity, organotin compounds with long alkyl chains rather than short ones (typically butyl or octyl) are frequently added as stabilizers to PVC, and these compounds may be dealt with by the simple open-tube sulphuric acid–hydrogen peroxide decomposition without risk of loss of tin by volatilization. Only the rather high chlorine content relative to the tin content might give some cause for concern. By courtesy of Messrs. Albright & Wilson, three samples of PVC, each containing a different additive at around the 1% level, were made available. Because of the low tin levels, somewhat larger samples had to be taken, but up to 100 mg of plastic chips could be completely decomposed by this method in 1 ml of concentrated sulphuric acid (with dropwise addition of 50% hydrogen peroxide) in about 10 min. The results are shown in Table 5. As phosphate would interfere, its absence was first confirmed by a molybdenum-blue determination. Unfortunately, since phosphate esters are sometimes used as plasticizers for PVC, this method for determining tin cannot be recommended as generally applicable for such samples.

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SEPARATION OF MOLYBDENUM AND TECHNETIUM ON DI-2-ETHYLHEXYLPHOSPHORIC ACID (D-2-EHPA)–KIESELGUHR

W. D'OLIESLAGER, J. INDESTEEGE and M. D'HONT

Laboratory for Radiochemistry, Katholieke Universiteit Leuven, Celestijnenlaan 200F, 3030 Heverlee, Belgium

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Summary—The distribution ratio of Mo(VI) and Tc(VII) in different acid media on D-2-EHPA–kieselguhr was studied in batch experiments. From these data a separation procedure for Mo–Tc is proposed, which consists in the selective elution of Tc(VII) and Mo(VI) by reverse-phase partition chromatography. The D-2-EHPA–kieselguhr column can also be used as a solid phase for a ^{99m}Tc generator.

Element 43 (technetium) was discovered by Perrier and Segré in 1937 (isotopes ^{95}Tc and ^{97}Tc) by deuteron irradiation of molybdenum.[1] At present nearly all technetium is obtained by separation of the element from irradiated nuclear fuel solutions as the isotope ^{99}Tc ($t_{1/2} = 2{\cdot}12 \times 10^5$ y) or by neutron irradiation of molybdenum in a high-flux reactor, as the isotope ^{99m}Tc ($t_{1/2} = 6{\cdot}0$ hr).

The analytical work on this element has been largely based on procedures for the extraction of ^{99}Tc from high-level radioactive waste. The main procedures for the separation of ^{99}Tc are based on a series of sulphide precipitations and the distillation of technetium heptoxide,[2] or on the precipitation of Tc as tetraphenylarsonium pertechnetate.[3] Solvent extraction with trilaurylamine[4] or with trioctylphosphine in cyclohexane[5] and anion-exchange on Amberlite IRA 400[6] have also been used for the recovery of fission technetium.

The isotope ^{99m}Tc is produced mainly for application in medical diagnosis and as a convenient tracer for research. ^{99m}Tc generators have been described, based on the sorption of ^{99}Mo as molybdate on ferric oxide,[7] manganese dioxide,[8] alumina[9] and pertitanic acid[10] columns from which the technetium can readily be separated. As the half-life of this isotope is rather short ($t_{1/2} = 6$ hr) separation techniques for the ^{99}Mo–^{99m}Tc system must be rapid.

EXPERIMENTAL

Reagents

All reagents used in this work were of commercially available analytical grade. Stock solutions of acids were prepared by dilution of the commercial product, and the concentration of the acid was determined by potentiometric titration with standard alkali. The di-2-ethylhexylphosphoric acid was purified by Peppard's method,[11] and its purity (>99·5%) checked by potentiometric titration with alkali. ^{99}Mo ($t_{1/2} = 67$ hr) was obtained as sodium molybdate from the nuclear centre at Mol (S.C.K.-C.E.N.). Its radiochemical purity was checked by γ-spectrometry with an NaI(Tl) scintillator and a Nuclear Data multichannel analyser. ^{99m}Tc was obtained by eluting it from a ^{99m}Tc generator (Philips–Duphar) with a 0·5% sodium chloride solution.

Preparation of D-2-EHPA–kieselguhr

Kieselguhr (120–130 mesh) was washed several times with 4*M* hydrochloric acid. After being rinsed thoroughly with doubly distilled water and dried at 100° (24 hr) the kieselguhr was treated with dimethyldichlorosilane in a desiccator (4 days). Subsequently di-2-ethylhexylphosphoric acid (D-2-EHPA) (30% w/w with respect to the kieselguhr) dissolved in chloroform was added to the kieselguhr. The chloroform was evaporated under continuous stirring so as to yield a homogeneous distribution. The powder thus obtained was dried for 48 hr at 80° to eliminate any traces of chloroform.

Batch experiments

The distribution ratios (D) of Mo(VI) between aqueous solutions and D-2-EHPA–kieselguhr were obtained by equilibrating 300 mg of the solid phase with 20 ml of the appropriate Mo(VI) solution, with ^{99}Mo as tracer. After equilibrium was reached the solid phase was separated by centrifugation and a known amount (*e.g.*, 2 ml)

Table 1. Influence of the equilibration time on the distribution ratio D of Mo(VI) in different acid media on D-2-EHPA–kieselguhr

Equilibration time, *hr*	Log D				
	H_2O	0·1*M* $HClO_4$	0·1*M* HNO_3	0·1*M* HCl	0·1*M* H_2SO_4
0·25	2·298			2·609	
0·5	2·228			2·701	
1	2·407	2·451	2·468	2·739	2·464
2	2·494	2 546	2·511	2·773	2·503
4	2·738	2·742	2·935	2·813	2·726
6	2·860			2·811	
8	2·895	2·783	2·904	2·944	2·782
16	2·975	2·812	2·893	2·928	2·815
24	2·992	2·813	2·887	2·950	2·872
48			2·908		2·962

of the liquid phase taken for γ-counting. A similar volume of the initial Mo(VI) solution was used for determining the total molybdenum content.

Column runs

Chromatographic columns (diameter 0·4 cm, height 14 cm) were prepared by evenly packing a known amount of D-2-EHPA–kieselguhr, and equilibrated before use by means of the appropriate solutions (*e.g.*, 5% sodium chloride, hydrochloric acid or nitric acid). The sample to be separated (Mo–Tc) was adsorbed in a small volume on top of the column and eluted with the appropriate solution; fractions (5 drops) were collected in counting cups for γ-counting.

γ-Counting

^{99m}Tc was determined by counting its 141-keV γ-ray photopeak on a 3 × 3 in. NaI(Tl) scintillator coupled to a linear amplifier, a single-channel analyser and a timer scaler ^{99}Mo was counted in the same way after radiochemical equilibrium of ^{99}Mo–^{99m}Tc had been reached (48 hr).

RESULTS AND DISCUSSION

Batch experiments

The distribution of Mo(VI) between acid solutions and D-2-EHPA–kieselguhr was studied in different acid media: perchloric, nitric, hydrochloric and sulphuric acids. Table 1 shows the variation of the distribution ratio as a function of the equilibration time for the four acids as well as for an Mo(VI) solution in doubly distilled water. It may be concluded that equilibrium is reached after 8 hr in perchloric and nitric acid media and after 16 hr in water and hydrochloric acid media. In sulphuric acid even after 2 days equilibration time there is still a small increase in the distribution ratio. As Mo(VI) is known to form polymolybdate ions the slow adsorption of Mo(VI) on D-2-EHPA–kieselguhr may be explained by the slow depolymerization of polymolybdates.

The influence of the acid concentration on the distribution ratio of Mo(VI) (24-hr equilibration) depends on the nature of the acid, as shown in Table 2. At relatively low acid concentrations ($[H^+] < 2M$) the distribution ratio decreases very rapidly with increasing acid concentration. At acid concentrations above 2*M* the distribution ratio continues to

Table 2. Influence of concentration and nature of the acid on the distribution ratio (D) of Mo(VI) on D-2-EHPA–kieselguhr

Acid concentration, *M*	D			
	$HClO_4$	HNO_3	HCl	H_2SO_4
0·1	649	769	849	660
0·5	375	546	374	902
1	290	258	245	413
2	278	187	171	226
3	364		141	136
4	606	207	58	83
6	2950		7	61
7		384		
8			4	

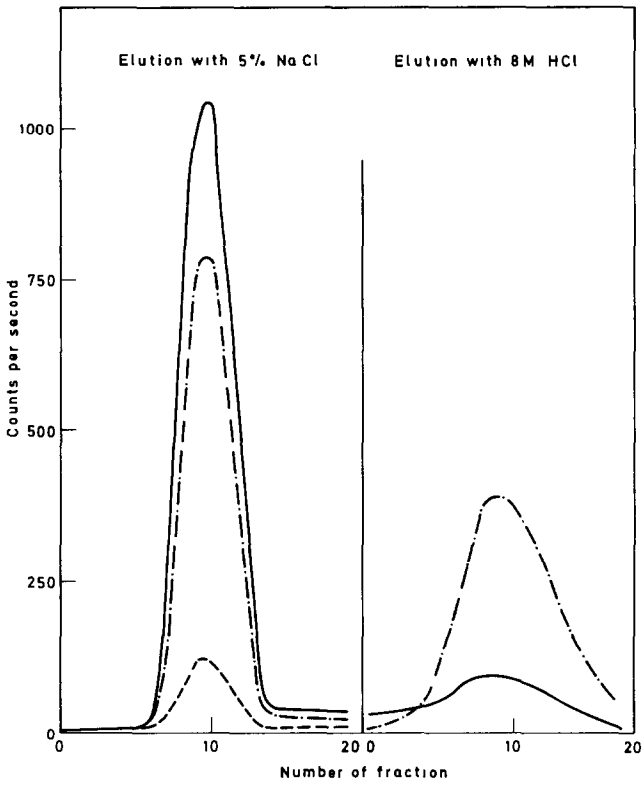

Fig. 1. Separation of Mo–Tc mixture on a D-2-EHPA–kieselguhr column (diameter 0·4 cm, height 14 cm): elution with 5% NaCl [Tc(VII)] and with 9*M* HCl [Mo(VI)]. γ-counting: (——) immediately after collecting the sample (5 drops); (–·–·–) after 2·5 hr; (– – –) after 19 hr.

fall for hydrochloric and sulphuric acid media, while in nitric acid solutions there is a moderate and in perchloric acid a marked increase in these values.

The increase of the *D* values at high nitric and perchloric acid concentrations is caused by the influence of these acids on the protonation and depolymerization equilibria of polymeric oxy-cations, *e.g.*, $Mo_2O_5^{2+}$, $Mo_3O_8^{2+}$, while the steady decrease in *D* for hydrochloric and sulphuric acid media can be explained by the formation of non-extractable anionic complexes of the molybdenyl ion (MoO_2^{2+}) with Cl^- or HSO_4^-.[11–15]

Batch experiments on the adsorption of pertechnetate on D-2-EHPA–kieselguhr showed that there was no adsorption of technetium under the same experimental conditions.

Column separation of Mo and Tc

From the data obtained in batch experiments it may be concluded that it should be possible to separate a mixture of Mo and Tc on D-2-EHPA–kieselguhr columns by selective elution of both ions. The experimental procedure is as follows. A small sample (0·5 ml) of a ^{99}Mo–^{99m}Tc tagged solution of Mo(VI) in 0·1*M* hydrochloric acid is adsorbed on top of a D-2-EHPA–kieselguhr column. The column is eluted successively with 3 ml of 5% sodium chloride solution and with 8*M* hydrochloric acid.

Fractions (5 drops) are counted immediately after collection. The results given in Fig. 1 show two peaks corresponding to the selective elution of Tc and Mo. As the γ-activity of the first peak (elution with 5% sodium chloride solution) decreases on recounting the samples 2·5 and 19 hr after elution, this peak can be identified with the elution of Tc(VII). The increase of the γ-activity of the second peak (elution with 8*M* hydrochloric acid) corresponds to the growth of ^{99m}Tc by the β decay of ^{99}Mo in these fractions. This agrees with the distribution data obtained in the batch experiments.

The radiochemical purity of the pertechnetate fractions was checked by following the radioactive decay curve of the ^{99m}Tc isotope. The half-life of ^{99m}Tc obtained by least-squares analysis was 6·07 hr, which agrees very well with the literature value.

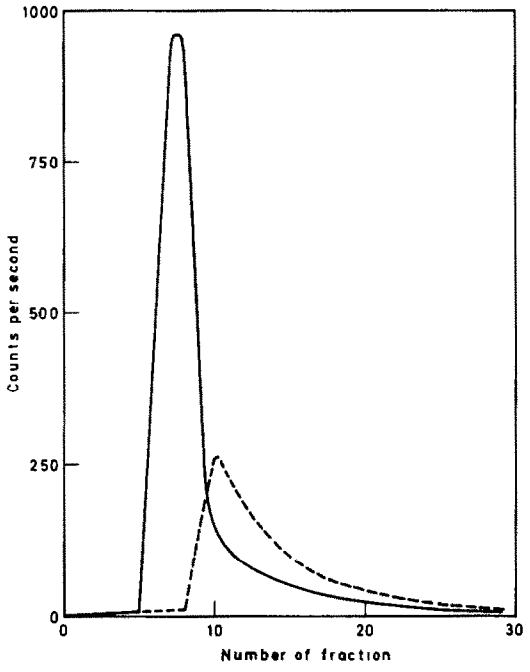

Fig. 2. Sorption of Mo–Tc on a D-2-EHPA–kieselguhr column (diameter 0·4 cm, height 14 cm) and elution with 0·1*M* citric acid. γ-counting: (——) immediately after elution; (– – –) after 2 days.

The separation of Mo–Tc mixtures, adsorbed on D-2-EHPA–kieselguhr columns with other eluting agents such as nitric, perchloric, sulphuric and hydrochloric acids at concentrations up to 3*M*, was studied. In these cases Tc(VII) is eluted in a very small volume (~ 1 ml) while Mo(VI) stays on the column. The same result is obtained in eluting with 0·5*M* phosphoric acid.

The adsorption of Mo–Tc from 0·1*M* hydrochloric acid on D-2-EHPA–kieselguhr and elution with citric acid (0·1–1*M*) results in incomplete separation. The data in Fig. 2, obtained by counting immediately after separation (solid curve), show that Tc(VII) is easily eluted although the curve has a long tail. This corresponds to fractions containing some Mo(VI), the elution of which overlaps that of Tc(VII). This break-through of Mo(VI) was proved by recounting the sample 2 days after the elution: the peak corresponding to pure ^{99m}Tc disappeared, and a new peak corresponding to the ^{99}Mo appeared.

Adsorption of Mo–Tc on the column and elution with 0·5*M* ammonium hydrogen phosphate results in a single peak, containing both Mo(VI) and Tc(VII).

D-2-EHPA–kieselguhr should be a suitable column material for a ^{99m}Tc generator.

CONCLUSION

The batch experiments on the adsorption of ^{99}Mo-tagged Mo(VI) on D-2-EHPA–kieselguhr have shown the distribution ratio to be dependent on the nature and the concentration of the acid solution. The increase in the *D* values in fairly concentrated perchloric and nitric acid media ([H^+] 2*M*) is explained by the influence of the proton in the depolymerization of polymolybdic acid. In concentrated hydrochloric and sulphuric acid media the formation of molybdenyl chloride and molybdenyl bisulphate or sulphate complexes results in a steady decrease of the distribution ratio.

The experiments with Tc(VII) have shown that this element is not absorbed on D-2-EHPA–kieselguhr under the same experimental conditions as Mo(VI).

The column runs have shown that D-2-EHPA–kieselguhr can be used for an easy and rapid separation of Mo and Tc. It may be concluded that D-2-EHPA–kieselguhr can be considered as an appropriate column material for a ^{99m}Tc generator.

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CATALYSIS OF THE ARSENIC(III)–POTASSIUM BROMATE REACTION—II

CATALYTIC DETERMINATION OF OSMIUM

A. E. BURGESS and J. M. OTTAWAY

Department of Pure and Applied Chemistry, University of Strathclyde, Cathedral Street, Glasgow G1 1XL, Scotland

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Summary—A simple visual titrimetric procedure is proposed for the catalytic determination of osmium, based on the arsenic(III)–bromate reaction. A detailed kinetic study of the catalytic reaction allows a mechanism to be proposed and optimum conditions for analysis to be selected. The analytical method has a detection limit of 10^{-4} ppm osmium and possesses a higher degree of freedom from interference by ruthenium than other similar systems.

Although the analytical determination of osmium is not a common problem, it is required in a number of industries for the analysis of ores, concentrates and metal alloys, *etc.* Since osmium is usually present in such materials at low concentrations, methods with reasonable or high sensitivity are required. In addition, osmium is usually present in association with other platinum metals and in this case, methods are also required to have high selectivity. The poor selectivity of many existing techniques has necessitated the development of adequate separation procedures. Osmium and ruthenium are quite easily separated from other metals, since both form volatile tetroxides which can be distilled into suitable collecting solutions from solutions containing one of a number of oxidizing agents. It is also possible to separate osmium from ruthenium by selective oxidation/distillation procedures.[1] Separation of osmium from other noble metals, particularly ruthenium, is an essential pre-requisite of all spectrophotometric methods.[1] The available spectrophotometric methods are also not very sensitive; few published methods have detection limits lower than about 0·5 ppm. Determination of osmium at even the 1–10 ppm level in solid materials will, therefore, usually require preconcentration as well as separation of the osmium. Newer techniques such as atomic-absorption spectrometry also lack sensitivity for osmium and are by no means free from interference.

The disadvantages of other techniques have led to the development of a number of catalytic procedures for the determination of osmium, and the available methods have recently been reviewed.[2] Catalytic methods are very sensitive,[3,4] methods for osmium often attaining detection limits of the order of 10^{-4}–10^{-5} ppm.[2] The most commonly described method for the catalytic determination of osmium is based on its catalysis of the cerium (IV)–arsenic(III) reaction.[5–7] The only other catalysts for this reaction are iodide and ruthenium, and the effect of iodide can be easily masked with mercury(II).[7] Ruthenium, however, remains a serious source of interference, since on a molar basis it is five times more active as a catalyst than osmium.[8,9] In developing a method for the determination of ruthenium, based on this reaction, Surasiti and Sandell[8] described methods for separating ruthenium from osmium, based on distillation of the tetroxides.

In attempting the determination of osmium and ruthenium in mixtures by use of catalytic methods without prior separation of the elements, two approaches are possible. The kinetic rate equations of the ruthenium and osmium-catalysed arsenic(III)–cerium(IV) reactions exhibit different dependencies on reagent concentrations.[8,9] It was pointed out by Habig *et al.*[9] that the catalytic activities of osmium and ruthenium would vary in a different way with variation in reaction conditions. It is therefore possible to determine osmium and ruthenium in mixtures by carrying out measurements under two sets of conditions and computing the analytical results from a knowledge of the kinetic parameters.

Such a procedure was subsequently described by Worthington and Pardue.[10] The second approach involves the use of one reaction exhibiting greater selectivity towards osmium and a different reaction with greater selectivity for ruthenium. In Part I of this series[11] it was reported that osmium tetroxide was a highly effective catalyst for the reaction of arsenic(III) with potassium bromate and that a number of other species, including ruthenium, showed no catalytic effect during a titration of arsenic(III) with potassium bromate. In the arsenic(III)–bromate reaction, no reactant or product species can be conveniently monitored spectrophotometrically and a polarographic procedure was developed[12] to follow the reaction for the catalytic determination of osmium. Polarography is not a particularly convenient or simple method for carrying out such an analysis and we have now established a simple kinetic technique, based on visual titration, for carrying out a highly selective determination of osmium by using the arsenic(III)–bromate reaction. The proposed technique is described in this paper, together with a kinetic investigation of the reaction, which allowed the selection of the most suitable analytical conditions and also provided some useful data for comparison with the analogous osmium–catalysed cerium(IV)–arsenic(III) reaction.

EXPERIMENTAL

Reagents

All reagents were of analytical-reagent grade and were used without further purification. The following stock solutions were prepared.

Osmic acid, $7{\cdot}8 \times 10^{-3}M$ in 2·0*M* perchloric acid.
Arsenious oxide, 0·01*M*.
Potassium bromate, 0·1*M*.
Potassium hydrogen carbonate, 1*M*.
Iodine, approx. 0·001*M*, in aqueous potassium iodide solution.
Sulphuric acid, 2·0*M*.
Perchloric acid, 2·0*M*.
Sodium perchlorate, 1·0*M*.
BDH iodine indicator.

Osmic acid, arsenic(III) and potassium bromate solutions were prepared and standardized as described previously.[11,13] Acid solutions were standardized by titration with sodium carbonate, and sodium perchlorate solution was standardized by drying an aliquot to constant weight. Iodine solutions were standardized with the arsenic solution in a blank experiment, as will be described.

Procedures

Kinetic investigations. The osmium-catalysed arsenic(III)–bromate reaction was followed by adaptation of a method used previously,[13] which consisted of quenching an aliquot of the reaction mixture in bicarbonate buffer and titrating with iodine the arsenic(III) remaining.

Glass tubes of about 200 ml capacity were used as reaction vessels. In one tube were placed 100 ml of solution containing the required amounts of arsenic(III), osmium(VIII), perchloric acid and sodium perchlorate. In a second tube was placed 25 ml of solution containing the required amount of potassium bromate. The tubes were maintained at 25·00 ± 0·05° in a water-bath for 10 min, and then the reaction was started by rapid mixing of the contents of the tubes. Transfer from one tube to the other three times ensured thorough mixing. Zero time was taken to be the time of first transfer. Aliquots (10 ml) of the reaction mixture were removed at 0·5 or 1·0-min intervals as required, by using a fixed-delivery plunger-driven dispenser of grade-A precision. The aliquots were dispensed into separate tubes containing 10 ml of bicarbonate quenching solution. Each aliquot was then titrated with iodine solution (BDH iodine indicator), to determine the residual arsenic(III). Zero-time conditions were simulated by using a blank reaction mixture containing no osmium, and a corresponding iodine titration value obtained.

Determination of osmium. The kinetic investigations to be described indicated the most suitable conditions for the routine determination of osmium. Provided that the initial concentration of bromate ion is greater than or equal to the concentration of arsenic(III) and a working pH of between 2 and 3 is chosen, then a simple fixed-time quenching and titration procedure can be used to give a linear calibration for osmium at the $10^{-8}M$ level. Under these conditions the rate of reaction is independent of bromate ion concentration and, for practical purposes, is insensitive to small changes in hydrogen ion concentration. The only reagent which has to be added in precisely controlled amounts is therefore arsenic(III). For the analytical method, sulphuric acid was substituted for perchloric acid for pH control. The procedure adopted was as follows.

Dilute, where necessary, the stock reagent solutions to the following concentrations: potassium bromate, 0·1*M*; sulphuric acid, 0·3*M*; osmic acid, $1{\cdot}25 \times 10^{-7}M$; arsenic(III), $2{\cdot}0 \times 10^{-3}M$; iodine $\sim 5 \times 10^{-4}M$; potassium bicarbonate, 1*M*.

Transfer 2 ml of potassium bromate solution, 2 ml of sulphuric acid and an appropriate aliquot of osmic acid solution to a 50-ml standard flask, dilute to the mark with distilled water and mix. Pipette 10 ml of this solution into a clean dry boiling-tube, and into a similar tube pipette 10 ml of arsenic(III) solution. Maintain both tubes in a temperature-controlled water-bath at 25·00 ± 0·05° for 10 min. Mix the reactants by carefully pouring the contents of one tube into the other and back again twice to ensure thorough mixing. Replace both tubes in the water-bath. Exactly 3 min (or longer if required) after mixing, dispense 5 ml of bicarbonate quenching solution into each tube. Rinse the contents of both tubes into a 250-ml conical flask, add iodine indicator, and titrate

with iodine. Carry out a blank determination with osmium absent and obtain the iodine volume, V_B, for the uncatalysed reaction mixture. Let the volume of iodine needed in the presence of osmium be V_C; plot a calibration curve of $\log(V_B/V_C)$ *vs.* osmium concentration, *i.e.*, the usual calibration curve for the fixed-time method using pseudo first-order reactions.[14] The blank titration allows the use of iodine solution concentrations of any value near the recommended value without standardization.

RESULTS AND DISCUSSION

Kinetic studies

The stoichiometry of the reaction between bromate and arsenic(III) can be represented by

$$BrO_3^- + 3As(III) + 6H^+ \rightarrow Br^- + 3As(V) + 3H_2O \quad (1)$$

It was pointed out in Part I[11] that, in the absence of catalysts, this reaction is extremely slow. However, provided that the pH is below 3·5, very small amounts of osmic acid bring about a considerable increase in the rate of reaction. It is well known[13] that chloride and bromide also act as catalysts for reaction (1) by the intermediate generation of bromine or chlorine:

$$BrO_3^- + 6H^+ + 5Br^- \rightarrow 3Br_2 + 3H_2O \quad (2)$$

$$As(III) + Br_2 \rightarrow As(V) + 2Br^- \quad (3)$$

The rate of this two stage oxidation of arsenic(III) is controlled by the rate of generation of bromine by reaction (2), and the rate law is then of the form[13]

$$\frac{-d[As(III)]}{dt} = \frac{d[Br_2]}{dt} = k_2[BrO_3^-][H^+]^2[Br^-] \quad (4)$$

The rate of this reaction above pH 1 is too slow for titration purposes and appears to be insignificant above pH 2 owing to the dependence on the square of the hydrogen-ion concentration.

In the osmium-catalysed arsenic(III)–bromate reaction, bromide ions will be produced according to the stoichiometry of reaction (1) and will also catalyse the reaction at a rate given by equation (4). This, however, will only be significant below pH 2. In studying the osmium-catalysed reaction we have therefore identified two separate conditions under which different overall rate equations apply, one for which bromide makes a significant and increasing contribution to the rate of reaction (pH < 2), and the other for which bromide makes no effective contribution (pH > 2).

Rate equation at pH < 2. In all the kinetic studies, bromate was taken in large excess over the arsenic(III), and at pH < 2 the concentrations of both bromate and hydrogen ion remain effectively constant during the reaction. The stoichiometry of reaction (1) indicates that for every three moles of arsenic(III) oxidized, one mole of bromide is produced. If $[As(III)]_0$ is the initial concentration of arsenic(III) at $t = 0$ and $[As(III)]_t$ is the concentration at any time t, then the bromide concentration at time t will be given by

$$[Br^-]_t = \frac{[As(III)]_0 - [As(III)]_t}{3} \quad (5)$$

Even though extra bromide is subsequently produced from reduction of bromate by reactions (2) and (3), the stoichiometry is such that equation (5) is still obeyed. The rate of the bromide-catalysed reaction will, therefore, be given by equation (4), in which $[Br^-]$ is substituted according to equation (5). If it is assumed that the osmium-catalysed reaction is first order in arsenic(III) and first order in osmium, then the overall rate of reaction at any time t, at pH < 2, will be given by

$$\frac{-d[As(III)]}{dt} = k_1[As(III)]_t[Os] + k_2[BrO_3^-][H^+]^2\left(\frac{[As(III)]_0 - [As(III)]_t}{3}\right) \quad (6)$$

The form of the second term in this rate equation is well established[13] and a value for k_2 of 2·72 l^3. $mole^{-3}$. sec^{-1} was obtained under the conditions used in this study at 25°. The form of the first term is, however, assumed and can be tested by investigation of equation (6) under a wide variation of conditions of arsenic(III), bromate, hydrogen ion and osmium concentrations.

Table 1. Values of k_1 at 25 ± 0·05°C, calculated from equation (7) (k_2 = 2·72 l^3.mole^{-3} sec^{-1} at 25°C)

Initial concentrations of reagents, M				k_1,
Bromate × 10^2	Arsenic(III) × 10^3	Perchloric acid, × 10	Osmium(VIII) × 10^8	$l.mole^{-1}.sec^{-1}$ × 10^{-5}
*2·0	*1·28	*0·64	*1·63	1·88
1·6	1·28	0·64	1·63	1·80
1·0	1·28	0·64	1·63	1 74
0·8	1·28	0·64	1·63	1·92
2·0	2·56	0·64	1·63	1·98
2 0	1·92	0·64	1·63	1 90
2·0	0·96	0·64	1 63	1·85
2·0	0·64	0·64	1·63	1·81
2·0	1·28	1·92	1·63	1·97
2·0	1·28	1·28	1·63	1·79
2·0	1·28	0·96	1·63	1·88
2·0	1·28	0·32	1·63	1·75
2·0	1·28	0·64	3·26	2·00
2 0	1·28	0·64	2·44	1·86
2·0	1·28	0·64	1 22	1 99
2·0	1·28	0·64	0·82	1·81

Typical results under conditions marked * above:

t, sec	60	90	120	150	180	210	240	300	360	420
$k_1 \times 10^{-5}$, $l.mole^{-1}.sec^{-1}$	1·80	1·79	1·84	1·82	1·81	1·99	1·90	1·98	1·92	1·96

If a single rate-determining step in the osmium-catalysed reaction is assumed, then the available concentration of osmium will be constant and equal to the total concentration of osmium present. The concentrations of bromate and hydrogen ion are also constant, as is $[As(III)]_0$ during any specific experiment. $[As(III)]_t$ is, therefore, the only variable, and equation (6) can be integrated to yield

$$t = \frac{2{\cdot}303}{1/3k_2[BrO_3^-][H^+]^2 - k_1[Os]} \log\left(\frac{k_2[BrO_3^-][H^+]^2}{3k_1[Os]} \frac{([As(III)]_0 - [As(III)]_t)}{[As(III)]_0} + \frac{[As(III)]_t}{[As(III)]_0}\right) \quad (7)$$

Values of $[As(III)]_t$ were measured at various times t during the reaction, by use of the simple titration procedure described in the experimental section. Since the values of all other terms are known, values of k_1 can be calculated by computer. Values of k_1 obtained for a wide range of reaction conditions are given in Table 1, as also are a set of values from a single experiment to give some idea of the precision of the measurement. Values of k_1 under the different conditions are an average of ten titration results for samples taken at different times during the reaction. Values of k_1 were consistent under all reaction conditions, confirming the rate equation for the osmium reaction assumed in equation (6). An average value for k_1 of 1·87 × 10^5 l.mole^{-1}.sec^{-1} is obtained from the results in Table 1.

Rate equation at pH > 2. At pH > 2, the effect of bromide is insignificant and the rate equation simplifies to

$$\frac{-d[As(III)]}{dt} = k_1[As(III)][Os] \quad (8)$$

Integration of this equation between $t = 0$ where $[As(III)] = [As(III)]_0$ and $t = t(\neq 0)$ where $[As(III)] = [As(III)]_t$ yields

$$\log\left(\frac{[As(III)]_0}{[As(III)]_t}\right) = \frac{k_1 t[Os]}{2{\cdot}303} \quad (9)$$

If $[As(III)]_0$ is determined from a titration of a blank solution containing no osmium

(blank titration V_B), and $[As(III)]_t$ from a titration of a quenched reaction solution (reaction titration V_C), then equation (9) can be transformed into equation (10):

$$k_1 = \frac{2{\cdot}303}{t[Os]} \log\left(\frac{V_B}{V_C}\right) \tag{10}$$

and there is no necessity for the iodine solution to be accurately standardized. By use of this equation, the values of k_1 in Table 2 were obtained and these are consistent for all the conditions investigated, and also in good agreement with the values in Table 1, obtained by using equation (7). An average value for k_1 of $1{\cdot}88 \times 10^5$ $1.mole^{-1}.sec^{-1}$ is obtained from the results in Table 2.

A working pH range of 2–3 was used in this investigation, as below pH 2 equation (7) applies and above pH 3·5 the catalyst becomes ineffective, owing to hydrolysis of one of the active osmium species. At higher concentrations of osmium a black precipitate can be observed at pH > 3·5. Variations in ionic strength, brought about by adding sodium perchlorate or by changes in the reagent concentration, had no apparent effect on the value of k_1. Values of k_1 measured over the temperature range 20–50° gave a linear Arrhenius plot and a value for the activation energy of 7·89 kcal/mole.

Table 2. Values of k_1 at 25 ± 0·05°C, calculated from equation (10)

Initial concentrations of reagents, *M*				Quench time, *sec*	$\log(V_B/V_C)$			k_1, *l mole*$^{-1}$ *sec*$^{-1}$ × 10^{-5}
Bromate × 10^3	Arsenic(III) × 10^3	Perchloric acid, × 10^3	Osmium(VIII) × 10^8		1	2	Average	
2·0	1·00	6·0	2·0	180	0·0993	0·0976	0·0983	2·03
				240	0·1245	0·1255	0·1250	1·94
				300	0·1590	0·1599	0·1595	1·98
				360	0·1953	0·1931	0·1942	2·00
2·0	1·00	6·0	0·78	180	0·1086	0·1086	0·1086	1·78
				240	0·1480	0·1471	0·1475	1·82
				300	0·1847	0·1856	0·1852	1·82
				360	0·2156	0·2167	0·2162	1·77
2·0	1·00	6·0	1·25	180	0·1910	0·1929	0·1919	1·96
				240	0·2534	0·2545	0·2540	1·95
				300	0·3060	0·3060	0·3060	1·88
				360	0·3757	0·3744	0·3751	1·92
2·0	1·00	6·0	1·56	180	0·2174	0·2164	0·2169	1·78
				240	0·3059	0·3059	0·3059	1·88
				300	0·3895	0·3910	0·3902	1·92
				360	0·4400	0·4383	0·4394	1·80
2·0	1·00	6·0	1·87	120	0·1952	0·1942	0·1947	2·00
				180	0·2897	0·2920	0·2908	1·99
				240	0·3722	0·3722	0·3722	1·91
				300	0·4741	0·4705	0·4723	1·94
2·0	1·00	6·0	1·95	120	0·1844	0·1855	0·1849	1·82
				180	0·2711	0·2711	0·2711	1·78
				240	0·3860	0·3860	0·3860	1·90
				300	0·4551	0·4533	0·4547	1·79
2·0	1·00	6·0	2·50	120	0·2335	0·2313	0·2324	1·78
				180	0·3856	0·3872	0·3864	1·98
				240	0·4752	0·4771	0·4761	1·83
2·0	1·00	6·0	3·12	120	0·3104	0·3104	0·3104	1·91
				180	0·4859	0·4859	0·4859	1·99
2·0	0·50	6·0	1·87	120	0·1858	0·1870	0·1864	1·91
				180	0·2903	0·2885	0·2894	1·98
				240	0·3890	0·3890	0·3890	2·00
2·0	1·50	6·0	1·87	120	0·1937	0·1937	0·1937	1·99
				180	0·2799	0·2788	0·2794	1·91
				240	0·3640	0·3640	0·3640	1·87
2·0	2·00	6·0	1·87	120	0·1752	0·1755	0·1754	1·80
				180	0·2622	0·2613	0·2618	1·79
				240	0·3701	0·3701	0·3701	1·90
4·0	1·00	6·0	1·87	120	0·1801	0·1801	0·1801	1·85
				180	0·2749	0·2749	0·2749	1·88
				240	0·3434	0·3412	0·3473	1·76
6·0	1·00	6·0	1·87	120	0·1956	0·1942	0·1949	2·00
				180	0·2869	0·2869	0·2869	1·96
				240	0·3905	0·3905	0·3905	2·00
8·0	1·00	6·0	1·87	120	0·1861	0·1838	0·1850	1·90
				180	0·2878	0·2878	0·2878	1·97
				240	0·3562	0·3552	0·3558	1·83
2·00	1·00	12·0	1·87	120	0·1729	0·1735	0·1732	1·78
				180	0·2737	0·2728	0·2733	1·87
				240	0·3519	0·3519	0·3519	1·81
2·00	1·00	9·00	1·87	120	0·1738	0·1723	0·1732	1·78
				180	0·2648	0·2648	0·2648	1·81
				240	0·3583	0·3583	0·3583	1·84

Reaction mechanism

The rate equation for the osmium-catalysed bromate oxidation of arsenic(III) shows a rate-determining step which is first order in osmium and first order in arsenic(III). Since bromate does not appear in the rate equation, the most plausible mechanism is that the reduction of osmium(VIII) by arsenic(III) is slow and is followed by rapid reoxidation of the reduced osmium by the excess of bromate present. By analogy with the osmium-catalysed arsenic(III)–cerium(IV) reaction,[9] the following mechanism could be assumed.

$$\text{As(III)} + \text{Os(VIII)} \xrightarrow{k_1} \text{As(V)} + \text{Os(VI)} \tag{11}$$

$$\text{Os(VI)} + \text{BrO}_3^- (+ 2\text{H}^+) \xrightarrow{\text{fast}} \text{Os(VIII)} + \text{BrO}_2^- (+ \text{H}_2\text{O}) \tag{12}$$

with BrO_2^- rapidly reduced to Br^- in the following steps:

$$\text{As(III)} + \text{BrO}_2^- (+2\text{H}^+) \xrightarrow{\text{fast}} \text{As(V)} + \text{BrO}^- (+ \text{H}_2\text{O}) \tag{13}$$

$$\text{As(III)} + \text{BrO}^- (+2\text{H}^+) \xrightarrow{\text{fast}} \text{As(V)} + \text{Br}^- (+\text{H}_2\text{O}) \tag{14}$$

At pH < 2, the bromide generated would then further react with bromate according to equations (2) and (3). Reactions (12)–(14) are only one possible sequence for the conversion of bromate into bromide and are in no way confirmed by the results above. Reduction products of bromate (except bromide) are known to be highly reactive, however, and either this sequence or some other equivalent set of reactions must occur. The catalytic sequence in reactions (11) and (12) might be replaced by reactions involving osmium in oxidation states (VI) and (IV) rather than (VIII) and (VI) but this seems unlikely in the presence of a large excess of bromate. In the osmium-catalysed arsenic(III)–cerium(IV) reaction, a computed value of k_1 of $8{\cdot}0 \times 10^4$ $1.\text{mole}^{-1}.\text{sec}^{-1}$ was obtained[9] for 2*M* sulphuric acid medium, and is reasonably close to the value of $1{\cdot}87 \times 10^5$ $1.\text{mole}^{-1}.\text{sec}^{-1}$ obtained in the present work.

Catalytic determination of osmium

The kinetic studies above are concerned with the catalysed reaction and conditions were chosen such that the uncatalysed reaction proceeded to a negligible extent during the measurements. In the analytical application of this reaction we attempted to measure the detection limit, and it became clear that with lower osmium concentrations and longer reaction times the uncatalysed reaction was no longer insignificant. Analytical calibration curves were still constructed from a plot of $\log(V_B/V_C)$ *vs.* the concentration of osmium but it was no longer true to assume that $[\text{As(III)}]_0 \propto V_B$, as was assumed in the derivation of equation (10). It can be shown as follows that equation (10) remains valid, however, under these conditions. If the uncatalysed reaction, which may be formulated

$$\text{As(III)} + \text{BrO}_3^- \rightarrow \text{Products} \tag{15}$$

is assumed to be first order in arsenic(III), with all other possible reactants, bromate, hydrogen ion present at much higher and therefore constant concentrations, the rate equation can be written

$$\frac{-\text{d[As(III)]}}{\text{d}t} = k_B\,[\text{As(III)}] \tag{16}$$

where k_B is the rate constant for the uncatalysed reaction and includes terms for bromate, *etc.* Integration of this equation from $t = 0$ when $[\text{As(III)}] = [\text{As(III)}]_0$ and $t = t$ when $[\text{As(III)}] = [\text{As(III)}]_{B,t}$ gives

$$\log[\text{As(III)}]_0 - \log[\text{As(III)}]_{B,t} = \frac{k_B t}{2{\cdot}303}. \tag{17}$$

In the presence of the catalyst, osmium, the rate of reaction will now be the sum of the rates of the uncatalysed and catalysed reactions, *i.e.*,

$$\frac{-\text{d[As(III)]}}{\text{d}t} = k_B\,[\text{As(III)}] + k_1\,[\text{As(III)}]\,[\text{Os}] \tag{18}$$

Integration of this rate equation within the same limits gives

$$\log [\text{As(III)}]_0 - \log [\text{As(III)}]_{C,t} = \frac{(k_B + k_1[\text{Os}])t}{2{\cdot}303} \tag{19}$$

where subscript C refers to the total reaction. Subtraction of equation (17) from equation (19) gives

$$\log [\text{As(III)}]_{B,t} - \log [\text{As(III)}]_{C,t} = \frac{k_1[\text{Os}]t}{2{\cdot}303} \tag{20}$$

which is equivalent to

$$\log\left(\frac{V_B}{V_C}\right) = \frac{k_1[\text{Os}]t}{2{\cdot}303} \tag{21}$$

which is the same as equation (10). This equation was used in the contruction of all calibration graphs, typical examples of which are shown in Fig. 1. As expected from equation (21), the sensitivity of the method increases with increase in the fixed time for which the reaction is allowed to proceed. Linear calibration curves were obtained in the range 8×10^{-10}–$10^{-7}M$ osmium, although $10^{-7}M$ may not represent the upper limit of linearity, as this was not determined. The slopes of all the calibration curves in this region give values for the rate constant, k_1, in precise agreement with the values obtained in the kinetic studies. As can be seen in Fig. 1, the curves at all reaction times exhibit non-linearity below about $8 \times 10^{-10}M$ osmium and the occurrence of curvature was confirmed by a series of experiments at the 10-min reaction time at low concentrations of osmium. Extrapolation of the linear portions to $\log(V_B/V_C)$ equal to zero shows that all curves cross the osmium concentration axis at 3–4 $\times$ $10^{-10}M$. No explanation can at present be offered for this phenomenon but it does appear that some of the osmium added to each reaction mixture is ineffective as a catalyst and that the amount is consistent in all experiments. Two possible explanations were investigated, *i.e.*, complexation of catalyst by trace organic complexing agents from the reagents or demineralized water used, or adsorption onto the glass walls of the reaction tubes. With $3 \times 10^{-10}M$ osmium and under the same conditions as those used for the results in Fig. 1, an iodine titration of 32·20 $\pm$ 0·10 ml was obtained after a 10-min reaction. Zinc sulphate was used at $2 \times 10^{-4}M$ concentration in an attempt to remove possible complexing agents and titrations of 32·10 ml and 32·20 ml were obtained. When all the solutions were prepared in doubly distilled water, two

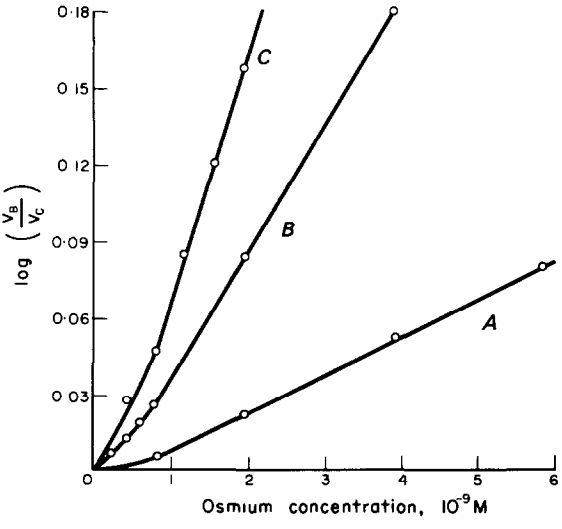

Fig. 1. Calibration graphs for the determination of osmium concentrations up to $6 \times 10^{-9}M$ after reaction times of (*A*) 3 min, (*B*) 10 min, (*C*) 20 min. Reaction conditions; bromate, $2 \times 10^{-3}M$; arsenic(III), $1{\cdot}1 \times 10^{-3}M$; perchloric acid, $1{\cdot}84 \times 10^{-2}M$; temperature 25°C.

Table 3. Detection limits of the method at different reaction times

[Os], *M*	Reaction time, *min*	No. of detns.	Average titn., *ml*	Std. devn., *ml*	Detection limit, [Os], *M*
0	3	10	36·85	0·04	2×10^{-10}
$7{\cdot}8 \times 10^{-10}$	3	10	36·40	0·04	
0	10	10	36·10	0·21	1×10^{-10}
$7{\cdot}8 \times 10^{-10}$	10	10	34·00	0·07	
0	20	6	34·05	0·10	$0{\cdot}5 \times 10^{-10}$
$7{\cdot}8 \times 10^{-10}$	20	6	30·65	0·09	

titrations of 32·30 ml were obtained. To test the adsorption hypothesis, a quantity of glass beads was added to the reaction mixture but a titration of 32·20 ml was still obtained. No positive evidence in favour of either explanation can therefore be advanced.

The detection limit of the method is reduced at longer reaction times. The detection limit was determined as the concentration of osmium equivalent to the blank reading plus two

Table 4. Interferences in the determination of $1{\cdot}51 \times 10^{-8}M$ osmium. Values of V_C/V_{CI} where V_C is the titration value without test interferent and V_{CI} is the value with test interferent present. (Reaction conditions: $[BrO_3^-]$, $2 \times 10^{-3}M$; [As(III)], $1 \times 10^{-3}M$; $[H_2SO_4]$, $6{\cdot}0 \times 10^{-3}M$)

Test interferent	Concentration, *M*						
	10^{-1}	10^{-2}	10^{-3}	10^{-4}	10^{-5}	10^{-6}	10^{-7}
EDTA	—	—	0·79	0·94	0·97	1·00	1·00
Potassium hydrogen tartrate	—	—	0·65	0·80	0·93	0·95	1·00
potassium chloride	0·83	0·97	1·00	1·00	1·00	1·00	1·00
potassium sulphate	—	0·95	1·00	1·00	1·00	1·00	1·00
magnesium sulphate	—	0·92	1·00	1·00	1·00	1·00	1·00
zinc sulphate	—	1·06	1·00	1·00	1·00	1·00	1·00
manganese sulphate	—	0·97	1·00	1·00	1·00	1·00	1·00
cobalt sulphate	—	0·95	1·00	1·00	1·00	1·00	1·00
nickel sulphate	—	0·95	1·00	1·00	1·00	1·00	1·00
copper sulphate	—	1·00	1·00	1·00	1·00	1·00	1·00
potassium nitrate	—	0·98	1·00	1·00	1·00	1 00	1·00
ferric nitrate	—	1·5	1·07	0·99	1·00	1·00	1·00
chromic nitrate	—	—	1·00	1·00	1·00	1·00	1·00
ammonium sulphate	0·65	0·86	0·98	0 98	1·00	1·00	1·00
sodium sulphate	—	0·94	1·00	1·00	1·00	1·00	1·00
cadmium sulphate	—	—	0·99	1·00	1·00	1·00	1·00
mercuric nitrate	—	—	0·5	0·91	0·96	1·00	1·00
ruthenium(III) chloride	—	—	—	—	1·09	1·03	1·00
silver nitrate	—	—	0·78	0·79	0·81	0·99	1·00
sodium perchlorate	0·97	1·00	1·00	1·00	1·00	1·00	1·00
potassium bromide	—	1·00	0·99	1·00	1·00	1·00	1·00
lead nitrate	—	0·97	1·00	1·00	1·00	1·00	1 00
potassium iodate	—	∝	∝	1·20	1·16	1·00	1 00
potassium iodide	—	—	1·13	1·16	1·19	1·15	1·14
palladium(II)	—	—	—	1·10	1·03	1·00	1·10
gold(III)	—	—	—	1·16	1·00	1 00	1·00
platinum(II)	—	—	—		1·08	1 01	1·00
iridium(III)	—	—	—	1·13	1·02	1·00	1 00
sodium tungstate	—	1·3	0·90	1·00	1·00	1·00	1 00
potassium fluoride	—	0·73	0·99	1·00	1·00	1·00	1·00
potassium cyanide	—	—	—	<0·5	0·52	0·90	0·98
ammonium thiocyanate	—	—	—	<0·5	0·74	0·98	1·00
uranyl nitrate	—	—	1·00	1·00	1·00	1·00	1·00
ammonium molybdate	—	—	<0·7	0·86	1·00	1·00	1·00
sodium metavanadate	—	—	0·98	1·00	1·00	1·00	1·00
rhodium(III) chloride	—	1·00	1·00	1·00	1·00	1·00	1·00
phosphoric acid	—	1·02	1·00	1·00	1·00	1·00	1·00
barium chloride	—	—	1·08	1·00	1·00	1·00	1·00
calcium chloride	—	—	1·00	1·00	1·00	1·00	1·00
strontium chloride	—	—	1 00	1·00	1·00	1·00	1·00
aluminium sulphate	—	—	0·99	1·00	1·00	1·00	1·00
lithium chloride	—	—	1·00	1·00	1·00	1 00	1·00
thallous nitrate	—	—	0·8	0·94	1·00	1·00	1·00
caesium sulphate	—	—	0·63	1·00	1·00	1·00	1·00
cerium sulphate	—	—	0·80	0·99	1·00	1·00	1·00

standard deviations of either the blank reading or the reading at $0{\cdot}78 \times 10^{-9}M$ osmium. The results are shown in Table 3.

The detection limit of $0{\cdot}5 \times 10^{-10}M$ at 20-min reaction time is equivalent to 10^{-4} ppm osmium. As there is little to gain from increased reaction time, a reaction time of 3 or perhaps 5 min would probably be adequate for determinations of osmium with calibration in the range $0{\cdot}5$–$100 \times 10^{-9}M$ osmium.

A detailed study of possible interferences was carried out and the results are shown in Table 4. If a substance is considered to interfere with the method when the value of V_C/V_{CI} falls outside the range 0·95–1·05, then the only serious interferences in the $10^{-6}M$ concentration range are from iodide and cyanide. Chloride and bromide, which might be expected to catalyse the reaction, give no interference up to $10^{-2}M$. Cyanide and thiocyanate apparently cause interference with the titration rather than with the osmium catalysis of the reaction. Iodide gave no interference at the $10^{-8}M$ level and its effect could no doubt be masked at levels up to $10^{-6}M$ by addition of mercury(II). Ruthenium only begins to interfere at between 10^{-6} and $10^{-5}M$ and the interference at the $10^{-5}M$ level could probably be tolerated. Other noble metals do not interfere with the determination at similar levels. This reaction thus possesses considerable selectivity for osmium over other noble metals which could be very useful when the non-selectivity of other methods of analysis, both catalytic methods and other techniques, is taken into account.

The method described thus offers several advantages for the determination of osmium. It is simple to use, and no solutions, including the iodine solution, need to be standardized or purified. The apparatus required is simple and cheap. The reaction itself is highly sensitive and selective towards osmium. Owing to the method of calibration, results on different days fit the same calibration graph although the reagent concentrations must then be similar. Since all the reagent solutions are highly stable, *e.g.*, the bromate and arsenic(III), large quantities of stock solutions can be prepared to facilitate the use of the same calibration graphs over an extended period.

We have recently discovered a paper describing the use of the arsenic(III)–bromate reaction for the determination of osmium in complex materials.[15] The method and kinetic conditions are quite different from those proposed in the present paper but the results given confirm the selectivity of this reaction for osmium in the presence of ruthenium and other metals. Using either procedure, this reaction should, therefore, be more suitable than the cerium(IV)–arsenic(III) reaction for the determination of osmium.

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DETERMINATION OF RUTHENIUM AND IRIDIUM IN ANODE COATINGS BY ATOMIC-ABSORPTION SPECTROSCOPY

D. E. HARRINGTON and W. R. BRAMSTEDT

Diamond Shamrock Corporation, Painesville, Ohio 44077, U.S.A.

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Summary—A method is described for the determination of ruthenium and iridium coated on an electrode surface. The coating is chemically removed from the electrode by fusion with alkali, and the resulting solution prepared for analysis. Interelement interferences are eliminated by using a titanium–potassium matrix solution as a releasing agent. Recovery and precision data are given for ruthenium and iridium. The AAS determination of ruthenium compares favourably with a standard colorimetric method.

Dimensionally stable anodes, used in chlorine–caustic cells, are prepared by consecutively baking layers of a coating solution on to a titanium substrate. The coating solutions contain one or more of the following elements as major constituents: ruthenium, iridium, and titanium.

Analysis of the anode coating requires removal of the coating from the titanium substrate and preparation of the resulting solution for atomic-absorption analysis. Removal is accomplished by dissolving the coating and a small portion of the titanium substrate in a molten mixture of potassium hydroxide and potassium nitrate. The resulting solution is acidified and digested. Aliquots of this solution can be used to determine ruthenium, iridium, and titanium by atomic-absorption spectroscopy. Previously, these elements were determined by time-consuming colorimetric or gravimetric procedures.

Atomic-absorption spectroscopy (AAS) methods using an air–acetylene flame were described for ruthenium by Allan,[1] and iridium by Mulford.[2] Amos and Willis reported the sensitivity for titanium was improved by using a nitrous oxide–acetylene flame.[3] For samples containing high salt concentrations, an extraction procedure has been reported which uses ammonium pyrrolidinedithiocarbamate (APCD) as a complexing agent and methyl isobutyl ketone (MIBK) as the extracting medium.[4,5] In our work, the APDC and MIBK system was used successfully for ruthenium chloride hydrate; however, the chlororuthenate species from the anode solutions was extracted non-reproducibly. It was necessary, therefore, to determine ruthenium, iridium, and titanium directly in the salt solution.

Other investigators have devised methods for the direct determination of precious metals in solutions with high salt concentrations. The use of uranium to mask interferences has been investigated by Scarborough.[6] The enhancement effect of lanthanum was suggested by others.[7,8] The complexity of possible interferences in the determination of precious metals by AAS was summarized by Mallett and co-workers.[9] These procedures required the addition of salts to the solution to eliminate interferences. Previous work conducted in this laboratory[10] showed that the presence of titanium had a beneficial effect in the elimination of interferences in the determination of ruthenium. The AAS determination of iridium is subject to a number of chemical interferences. Investigators have found a number of spectro chemical buffers that eliminate these problems. Lanthanum,[11,12] strontium,[11] and a mixture of copper and sodium sulphates have been successfully used as spectrochemical buffers for the determination of iridium.[13,14]

EXPERIMENTAL

Apparatus

Perkin–Elmer Models 303 and 403 Atomic Absorption Spectrometers were used. Representative operating conditions for the Model 303 are presented overleaf.

	Iridium	Ruthenium	Titanium
Wavelength, *Å*	2850	3499	3643
Lamp current, *mA*	45	30	40
Slit setting	3	3	3
Burner	Boling	Boling	N_2O
Flame	Lean	Lean	Adjust with standard
Oxidant and flow, *l./min*	Air, 23	Air, 23	N_2O, 21
Acetylene flow, *l./min*	4	4	8
Scale expansion	5×	1×	1×
Response time, *sec*	1	1	1·5

The colorimetric measurements were done with a Beckman Model B spectrophotometer.

Reagents

Standard solutions of ruthenium and iridium. Prepared by weighing 250 mg of ruthenium and 100 mg of iridium as the pure metals, fusing each metal in a nickel crucible with 45 g of potassium hydroxide and two 5-g portions of potassium nitrate as described in the procedure. Keep the melt near the boiling point for 10 min, then at a lower temperature (to keep it liquid) for 30–45 min. Cool the melt to room temperature, dissolve it in 400 ml of water, and acidify with 90 ml of concentrated hydrochloric acid. Digest the solutions on a steam-bath and dilute them to appropriate volumes.

Spectroscopic buffer solution. Prepared by dissolving 1·6 g of titanium metal in 150 ml of concentrated hydrochloric acid, digesting, and diluting to 200 ml with 20% w/v hydrochloric acid. To 100 ml of this solution add 37 ml of concentrated hydrochloric acid and 10 g of potassium nitrate, followed by a solution containing 45 g of potassium hydroxide, and dilute the mixture to 1 litre in a standard flask.

Procedure

The precious metal coating is stripped from the electrode in a nickel pan of sufficient size to contain the sample. Potassium hydroxide pellets (45 g) are first placed in the pan and heated with a Méker burner until a clear liquid is obtained. Then 5 g of potassium nitrate are dissolved in the melt. The coated electrode is immersed in the melt and heated until hydrogen is evolved. A second 5-g portion of potassium nitrate is added, and the melt is kept near boiling for 3–5 min. The electrode is then removed, air-cooled, washed, and dried, and the wash-water is kept. To ensure dissolution of the precious metals, the melt is digested at a low temperature for 35–45 min. The melt is cooled and dissolved in the water used to wash the anode. This solution is cautiously acidified with concentrated hydrochloric acid, digested for one hour on a steam-bath, and diluted to 1 litre in a standard flask. If a precipitate remains, it must be collected, re-fused, and added to the sample before the final dilution. If dark areas of stains are observed on the electrode, a second stripping is necessary.

The ruthenium, iridium, and titanium are then determined by AAS. An aliquot (25 ml or less) containing not more than 750 μg of ruthenium is diluted to 25 ml with 10% w/v hydrochloric acid and mixed with 25 ml of spectroscopic buffer solution. For iridium an aliquot containing up to 3000 μg of iridium is similarly treated. For titanium an aliquot is diluted to suitable volume with 10% w/v hydrochloric acid.

RESULTS AND DISCUSSION

Calibration data

The calibration data for ruthenium, iridium, and titanium are summarized in Table 1.

Table 1. Calibration data for ruthenium, iridium, and titanium

Ruthenium,*		Iridium,*		Titanium,†	
ppm	Absorbance	*ppm*	Absorbance	*ppm*	Absorbance
0	0	0	0	0	0
5	0·036	8	0·006	40	0·125
10	0·067	20	0·014	80	0·221
15	0·096	30	0·021	120	0·316
		40	0·026	160	0·396
		60	0·040	240	0·526

* Dilutions were made with titanium matrix solution.

† Dilutions were made with a salt matrix of 6% w/v KCl and 1% w/v KNO_3 in 0·4*M* HCl.

Interferences

A major problem encountered when determining precious metals by the atomic-absorption method is the existence of interelement interferences. When binary combinations of the various elements of interest were examined in 10% hydrochloric acid solution, a variety of enhancements and depressions of the analyte absorption were observed, Table 2. Spectrochemical buffers for individual metals have been reported; in this study, a complex

buffer solution was developed that allowed the determination of all precious metal analytes contained in the stripped-anode solution. A comparison of results obtained for analytes in a 10% w/v hydrochloric acid matrix and the titanium-matrix spectrochemical buffer solution is presented in Table 2.

Table 2. Ruthenium and iridium interference studies—binary combinations

Element added (10 ppm)	Absorbance (Ru 10 ppm)		Element added (40 ppm)	Absorbance (Ir 40 ppm)	
	10% HCl matrix	Titanium matrix		10% HCl matrix	Titanium matrix
Au	0·065	0·094	Au	0·059	0·059
Bi	0·083	0·095	Bi	0·065	0·069
Co	0·084	0·099	Co	0·065	0·068
Cu	0·086	0·101	Cu	0·065	0·067
Ir	0·081	0·097	Ni	0·062	0·066
Ni	0·079	0·097	Pb	0·059	0·067
Pb	0·064	0·095	Pd	0·057	0·058
Pd	0·086	0·098	Pt	0·064	0·064
Pt	0·088	0·093	Rh	0·062	0·064
Rh	0·088	0·098	Ru	0·060	0·065
Sb	0·077	0·100	Sb	0·064	0·067
Sn	0·071	0·100	Sn	0·061	0·067
—	0·064	0·097	—	0·061	0·066
Blank	0·000	0·002	Blank	0·000	0·007

Further investigation of the properties of this spectrochemical buffer solution indicated that titanium was the effective buffer for ruthenium, and potassium functioned well for iridium. When various concentrations of titanium were added to ruthenium solutions, an enhancement was observed; however, a plateau was reached at a w/w ratio of 24:1 for Ti:Ru (Table 3).

Table 3. Enhancement of ruthenium absorbance by titanium

Ti added, *ppm*	Absorbance (Ru 10 ppm)	Ti added, *ppm*	Absorbance (Ru 10 ppm)
0	0·035	180	0·068
30	0·042	210	0·072
60	0·051	240	0·077
120	0·061	270	0·077
150	0·065		

The enhancement of the ruthenium absorption in the presence of titanium appears to be due to an increase in the dissociation of ruthenium rather than to spectral interference. A 4000-ppm solution of titanium, when aspirated into the flame, showed zero absorption at the wavelength setting of 3499 Å used for ruthenium. An enhancement of the ruthenium absorption by titanium was also noted at ruthenium's second strongest absorption line of 3637 Å with zero absorption by a 4000-ppm titanium solution alone.

The high concentration of solids resulting from the dissolution procedure depresses the ruthenium absorption by a factor of three, relative to that of an aqueous solution containing only ruthenium. However, this depression is nearly cancelled by the 2·2-fold increase in absorption due to titanium enhancement.

In the case of iridium, potassium is the effective component of the complex buffer solution as indicated in Table 4.

Table 4. Iridium determination—effect of various levels of potassium

K added, *ppm*	Absorbance (Ir 20 ppm)	K added, *ppm*	Absorbance (Ir 20 ppm)
0	0·012	200	0·024
40	0·018	300	0·023
100	0·021	400	0·021
140	0·023		

The titanium determination was free from any interference by iridium, ruthenium, or nickel and influenced slightly by the bulk matrix effect from the high salt concentration in solution.

Method evaluation

Recovery of pure ruthenium and iridium by the procedures outlined was tested (Table 5) and found satisfactory.

Table 5. Recovery of iridium and ruthenium metals

Taken, *mg*	Iridium found, *mg*	Found, %	Taken, *mg*	Ruthenium found, *mg*	Found, %
23·0	22·4	97·4			
11·8	11·6	98·3	11·0	11·1	100·9
25·1	24·7	98·2	19·6	19·6	100·0
25·4	24·8	97·6	22·5	22·3	99·1
	Average	97·9		Average	100·0

The accuracy of the titanium method was verified by determining titanium in the iridium–ruthenium matrix solution. The solution was spiked with 768 ppm of titanium, and the result obtained was 763 ppm. The relative error of 0·7% and the absolute error of 5 ppm are within the usual precision expected of the method.

Precision data for various analyte concentrations are presented in Table. 6.

Table 6. Precision data for Ru, Ir, and Ti*

Element†	Concentration, *ppm*	Scale expansion	Coefficient of variation, %
Ru	5	1×	0·7
Ru	5	2×	0·7
Ru	15	1×	0·3
Ru	15	2×	0·5
Ir	20	5×	0·5
Ir	60	5×	0·6
Ti	80	1×	0·7
Ti	240	1×	1·4

* The sensitivity for 1% absorption for Ru, Ir, and Ti was 0·5, 5, and 2 ppm, respectively.

† Six replicates were measured at each concentration.

To evaluate the AAS method for ruthenium, samples were cross-checked by spectrophotometry,[15] and the results are included in Table 7.

The determination of titanium in the sample solutions is not normally necessary, but two cases arise where it is convenient to determine it. If the ruthenium content is less than 2 ppm and the titanium content is at least 50 ppm the spectroscopic buffer can be omitted and the ruthenium determined in the strip solution without dilution. When the ruthenium

Table 7. Comparison of AAS and spectrophotometric results

Sample	AAS Ru, *mg*	Distillation colorimetric, Ru, *mg*	Sample	AAS Ru, *mg*	Distillation colorimetric, Ru, *mg*
A	9·2	9·4	K	49·8	50·0
B	13·1	13·5	L	60·0	60·0
C	13·7	15·0	M	9·0	9·2
D	11·9	11·7	N	15·3	15·8
E	11·8	10·9	O	15·8	16·8
F	42·0	40·0	P	32·4	33·6
G	36·9	37·5, 36·7	Q	18·8, 18·8	18·8
H	21·0	19·5, 19·5	R	18·3	18·3
I	58·5	54·5, 55·5	S	59·0, 59·0	58·4
J	54·0	53·4			

is not distributed evenly on the titanium substrate, large amounts of titanium will dissolve before all the ruthenium is stripped, and if the titanium content of the strip solution is then sufficiently high, addition of the spectroscopic buffer is superfluous.

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METAL AND METALLOID INDICATOR ELECTRODES FOR THE NON-AQUEOUS POTENTIOMETRIC TITRATION OF WEAK ACIDS

COMPARATIVE EVALUATION OF GROUP III, IV AND V MAIN-GROUP ELEMENTS

E. J. GREENHOW and B. F. AL-MUDARRIS

Department of Chemistry, Chelsea College, University of London, Manresa Road, London, SW3 6LX, England

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Summary—Indicator electrodes constructed from aluminium, gallium, indium, thallium, carbon, silicon, germanium, tin, lead, arsenic, antimony and bismuth have been evaluated for the potentiometric titration of solutions of benzoic acid in dimethylformamide and 4-methyl-2-pentanone. The aluminium, gallium, silicon and arsenic electrodes have also been evaluated for the determination of 3,5-xylenol in the same two solvents. Aluminium, gallium, indium, silicon, germanium, antimony and bismuth electrodes are superior to, or compare favourably with, a glass electrode for the determination of benzoic acid, when the criterion of efficiency is the sharpness of the end-point inflexion. In non-aqueous titrations of 3,5-xylenol, aluminium and gallium electrodes are similar in efficiency to the glass electrode for determinations in dimethylformamide solution, while the gallium electrode is superior to the glass electrode when 4-methyl-2-pentanone is the solvent. Possible relationships between the properties of the electrode element and the end-point sharpness when it is used as an indicator electrode are briefly considered.

Glass electrodes are widely used as indicator electrodes in non-aqueous as well as aqueous titrations. However, in non-aqueous media, these electrodes show certain undesirable features. For example, they tend to behave variably and their behaviour depends on the nature and extent of pretreatment or "conditioning" of the electrode. In addition, the electrodes have a limited useful life when employed in non-aqueous titration because the solvents dehydrate the glass membrane, thereby reducing its affinity for, or response to, hydrogen ions.

As an alternative to glass electrodes, metal and metalloid indicator electrodes are superior in two respects: they do not require conditioning in the titration solvent and the electrode surface can easily be cleaned when the electrode loses its sensitivity. Metals and metalloids that have been reported as being suitable for use as indicator electrodes in non-aqueous potentiometric titration include aluminium, titanium, iron, nickel, copper, molybdenum, rhodium, palladium, silver, antimony, tungsten, platinum, gold and bismuth.[1–5] Carbon, although not a metal, conducts electricity and has also been used successfully as an indicator electrode.[5]

Antimony and platinum appear to be the most widely used of the metal indicator electrodes. Both have been found to be suitable for determination of the end-point in titrations of carboxylic acids dissolved in neutral solvents such as mixtures of benzene and methanol and in basic solvents such as ethylenediamine, pyridine and dimethylformamide.[6]

Jasinski and Kwiatowski[3] and Pražák and Grimmer[4] have evaluated bismuth and aluminium indicator electrodes, respectively, for the potentiometric titration of weak acids, and it is claimed that for this purpose both metals are superior to antimony in terms of the end-point sharpness obtained.

The calomel and silver/silver chloride reference electrodes used in aqueous systems require modification for use in non-aqueous potentiometric titration to prevent contamination of the solvent by water from the reference half-cell. Usually the water is replaced by methanol or a non-aqueous salt bridge is employed. Convenient alternatives to these reference half-cells are the in-stream reference electrodes,[7–9] in which an inert metal such as platinum is immersed in the titrant and electrical contact between the titrant and titrand

is made either by allowing the burette tip to dip into the titrand solution or by having a membrane between the two solutions.

No attempts appear to have been made to study systematically the efficacies of chemical elements as indicator electrodes. The present paper reports on a preliminary evaluation (a more detailed investigation will be made later) of the relationships between the properties of elements of the main groups III, IV and V of the periodic table and the potential changes that occur when these elements are used as indicator electrodes in the non-aqueous titration of weak acids. The potential changes in the region of the end-point have been taken as being a quantitative measure of the efficiency of the indicator electrode. An in-stream reference electrode has been used in all determinations. With this, the only contamination possible from the reference electrode is by the titrant, and no fluctuations in the magnitude of the potential changes occurring during titrations can possibly be attributed to this electrode.

EXPERIMENTAL

Reagents

Dimethylformamide and 4-methyl-2-pentanone were ≥99% pure and were dried over activated alumina, type H, before use. The solvents contained about 0·1% of water after drying.

Tetra-n-butylammonium hydroxide (laboratory-reagent grade) 0·1*M* solution in toluene–methanol (3:1 v/v), was standardized against an aqueous solution of potassium hydrogen phthalate, with phenolphthalein as indicator.

Indicator electrodes

The nominal purities of the elements used for the construction of the electrodes were as follows: aluminium, gallium, indium, thallium, silicon and arsenic ≥99·999%; lead ≥99·97%; germanium ≥99·95%; tin ≥99·92%; graphite ≥99·5%; bismuth ≥99%; antimony ≥98·5%.

The thallium and graphite were obtained as rods of diameters 8 and 5 mm, respectively, and the aluminium was obtained as 1-mm diameter wire. All three were mounted in PTFE holders shaped to fit into a B14 socket.

Tin, lead, antimony and bismuth were formed into rods of diameter 6 mm and length 15 mm by pouring the molten metal into Pyrex glass tubes sealed at one end and, after inserting a copper lead into the molten metal, cooling the glass tube and breaking the glass away from the lower 10 mm of the rod.

Rods of arsenic, m.p. 817°, and germanium, m.p. 937·4°, were prepared in a similar manner except that the electrical contact was made through a mercury pool on top of the cooled rod.

Electrodes of gallium, m.p. 29·8°, and indium, m.p. 156·6°, were prepared by pouring the molten metal into glass J-tubes (Fig. 1).

The silicon electrode was a fragment of silicon, about 5 mm wide, fused onto the flat-ground end of a length of silica tubing. A mercury-pool contact was used.

The glass electrode was an Activion Screened Glass Electrode type 003-11-101, and was conditioned in the appropriate solvent for 90 hr before use.

Apparatus

The apparatus (Fig. 2) was essentially that of Brooks and Maher[10] and consisted of a 50-ml titration cell with ground-glass sockets to accommodate the indicator electrode, the combined 10-ml titration burette and in-stream reference electrode, and an inlet and outlet for inert gas. A magnetic stirrer was used and the cell was screened with earthed aluminium foil.

The reference electrode was a platinum wire sealed into the extension to the burette and immersed in the titrant, and electrical contact with the titrand was made through a tube connected to the burette and terminated with a flamed* porosity-4 sintered-glass membrane. Potentials were measured with an E.I.L. Vibron Electrometer, type 33B.2.

Fig. 1. J-tube electrode.

* The sinter is flamed carefully until it will support a 6-in. head of solvent for more than 2 hr without detectable diffusion, while still giving an acceptable total cell resistance when incorporated in a cell with a metal indicator electrode.

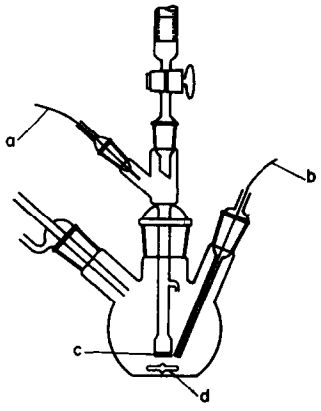

Fig. 2. Titration apparatus. *a*, reference electrode (Pt); *b*, indicator electrode; *c*, flamed porosity-4 glass sinter; *d*, magnetic stirrer.

Procedure

For the comparative evaluation studies, a weighed sample of benzoic acid or 3,5-xylenol, about 0·1 meq, was dissolved in 25 ml of the solvent, containing 0·4 g of tetra-n-butylammonium iodide, in the titration cell. The cell was then purged for about 5 min with dry nitrogen and the flow of nitrogen was continued during the course of the titration.

The solution was then titrated potentiometrically by adding 0·1-ml increments of 0·1*M* tetra-n-butylammonium hydroxide and measuring the potential immediately before the addition of each increment. Potential measurements were made at 2-min intervals at the beginning of the titration and at 4-min intervals in the region within ±0·3 ml of the end-point. Increments of 0·1 ml were the minimum that could reasonably be reproduced with the burette used. The precision is clearly critical in determination of end-point sharpness.

After each titration the electrode was replaced or its surface was renewed. A fresh length of aluminium wire was used for each determination. The thallium, germanium, tin, lead, arsenic, antimony and bismuth electrodes were resurfaced by slicing a thin layer from the end of the rods, and the graphite rod was cleaned by scraping with a knife. The surfaces of the gallium and indium electrodes were renewed by immersing the J-tubes in hot water and hot oil, respectively, to melt the elements, and then wiping off any dross with a tissue; the silicon electrode was cleaned by immersing it in hydrofluoric acid. The cleaned electrodes were exposed to the air for 2 hr before being used again.

For the "full-scale" titrations, 1 meq of benzoic acid and 0·8 g of tetra-n-butylammonium iodide were dissolved in 10 ml of dimethylformamide in the titration cell, and the latter purged with nitrogen as above. The 0·1*M* tetra-n-butylammonium hydroxide was added in 1-ml increments until 9 ml had been added, then in 0·1-ml increments until the first small potential rise occurred and, finally, in 0·04-ml increments until the titration curve "rounded off". All the increments were added at 3-min intervals and the potential was measured immediately before each addition.

RESULTS AND DISCUSSION

Precision

The end-point inflexions of the various titration curves obtained are shown in Figs. 3–5. Tables 1 and 2 summarize the information given by these curves in terms of both the end-point sharpness, *i.e.*, the change in potential in the region of the end-point, and the potential change from 0·5 ml before the end-point to 0·5 ml after it (given because it is difficult in practice to measure the maximum overall potential change when, as sometimes happens, a steady potential drift continues even after the addition of a considerable excess of titrant).

The glass electrode used for comparison measurements was conditioned for 90 hr in the solvent to be used in the determination. A shorter conditioning time—17 hr—led to significantly less sharp end-point inflexions in the determination of benzoic acid (Table 1).

With the aluminium, gallium, silicon, antimony and bismuth indicator electrodes, the end-point sharpness is about the same for dimethylformamide and 4-methyl-2-pentanone as the solvent for benzoic acid. However, with the arsenic, carbon, germanium, tin and lead electrodes, the end-point is considerably sharper with 4-methyl-2-pentanone, but with indium the sharpness is slightly, but significantly, poorer. Thallium is rather useless as the indicator electrode.

In terms of end-point sharpness over the ±0·05-ml range, and in order of decreasing sensitivity, the gallium, aluminium, antimony and bismuth electrodes are superior to the glass electrode for the titration of benzoic acid in either solvent. The indium and silicon

Table 1. Effect of the indicator electrode on potential changes during the titration of benzoic acid in solution in dimethylformamide and 4-methyl-2-pentanone

	Al	Ga	In	Tl	C	Si	Ge	Sn	Pb	As	Sb	Bi	Glass*	Glass†
Potential change in the region of the end-point, *mV*						*Dimethylformamide solvent*								
±0·05 ml	317	325	287	43	134	284	212	113	116	80	298	297	222	142
±0·10 ml	368	380	332	64	166	328	252	146	136	134	346	344	246	210
±0·15 ml	420	438	378	84	201	372	294	180	156	186	393	393	270	276
±0·50 ml	533	525	448	119	248	446	345	208	188	334	433	467	368	345
Potential change in the region of the end-point, *mV*						*4-Methyl-2-pentanone solvent*								
±0·05 ml	300	329	253	7	286	286	303	198	254	154	315	306	288	
±0·10 ml	384	344	288	7	328	310	318	204	262	212	346	348	352	
±0·15 ml	468	360	321	7	369	333	333	210	270	270	375	390	417	
±0·50 ml	572	392	373	19	427	388	362	290	304	401	437	452	506	

The values tabulated are the mean of two determinations.
* Conditioned for 90 hr
† Conditioned for 17 hr.

electrodes are also more sensitive than the glass electrode for the titrations in dimethylformamide, while germanium is slightly the more sensitive electrode for the titrations in 4-methyl-2-pentanone. The carbon, silicon and glass electrodes all show similar sensitivities in the latter solvent.

Of the four element-electrodes investigated for the titration of 3,5-xylenol, only the gallium one is superior to the glass electrode for the determination in 4-methyl-2-pentanone solution, and in dimethylformamide solution the gallium, aluminium and glass electrodes behave similarly with respect to end-point sharpness.

The gallium indicator electrode is the most sensitive of those evaluated, but the aluminium, antimony and bismuth electrodes are similar to it in sensitivity. In practice, all four electrodes would be satisfactory for determining the end-point in the non-aqueous titration of weak acids. The experimental results obtained in this limited screening investigation suggest that bismuth offers no advantages over antimony as an indicator electrode, at least for the determination of carboxylic acids (*cf.* ref. 3). Gallium and aluminium electrodes have some practical advantages over these last two electrodes in that the gallium electrode can be resurfaced by melting in hot water and the aluminium electrode is readily made in rod or wire form.

The application of the aluminium, gallium and silicon electrodes to real analytical determinations was tested by titrating 1-meq amounts of benzoic acid in solution in dimethylformamide. The volumes of nominally 0·1*M* tetra-n-butylammonium hydroxide required were 9·66 ± 0·05 ml (Al electrode), 9·60 ± 0·08 ml (Ga) and 9·74 ± 0·07 ml (Si). With these 10-ml titrations the composition of the solvent mixture at the end-point differs quantitatively from that in the comparative-evaluation experiments in which dimethylformamide was always in considerable excess. As a consequence of this the end-point sharpnesses are different also.

Table 2. Effect of the indicator electrode on the potential changes occurring during the titration of 3,5-xylenol in solution in dimethylformamide and 4-methyl-2-pentanone

Potential change in the region of the end-point, *mV*	Dimethylformamide						4-Methyl-2-pentanone				
	Al	Ga	Si	As	Glass*	Glass†	Al	Ga	Si	As	Glass*
±0·05 ml	53	53	27	21	59	38	41	69	24	19	56
±0·10 ml	96	92	42	38	88	63	74	100	38	30	70
±0·15 ml	138	132	57	54	117	87	108	129	54	39	84
±0·50 ml	332	238	90	140	180	160	293	188	137	92	135

The values tabulated are the mean of two determinations.
* Conditioned for 90 hr.
† Conditioned for 17 hr.

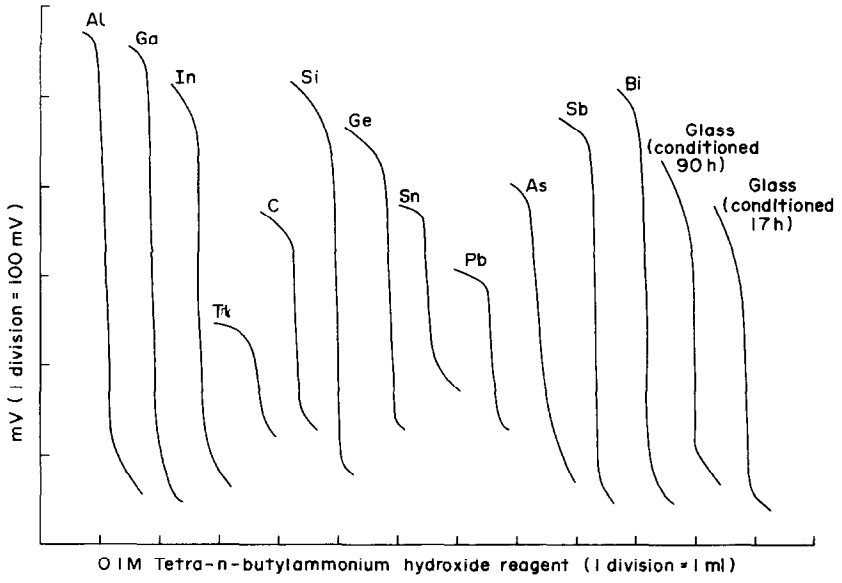

Fig. 3. The effect of the indicator electrode on the shape of the end-point inflexion in the potentiometric titration of benzoic acid in dimethylformamide solution.

Position in the Periodic Table

If the end-point sharpness in the determination of benzoic acid is related to the position of the electrode elements in the Periodic Table, some trends are apparent. Thus, in both solvents there is a decrease in end-point sharpness from gallium to thallium in Group III and, in dimethylformamide only, from silicon to tin in Group IV. Carbon, the first element of Group IV, does not fit into this trend. In Group V, only three elements can be fabricated into electrodes; the end-point sharpness when the arsenic electrode is used is much less than that obtained with the antimony and bismuth electrodes, which yield very similar titration curves.

There is some evidence of trends in end-point sharpness if the elements are considered according to their horizontal relationships in the Periodic Table, *i.e.*, according to the period. Thus, in the third period, aluminium gives a sharper end-point than silicon, and

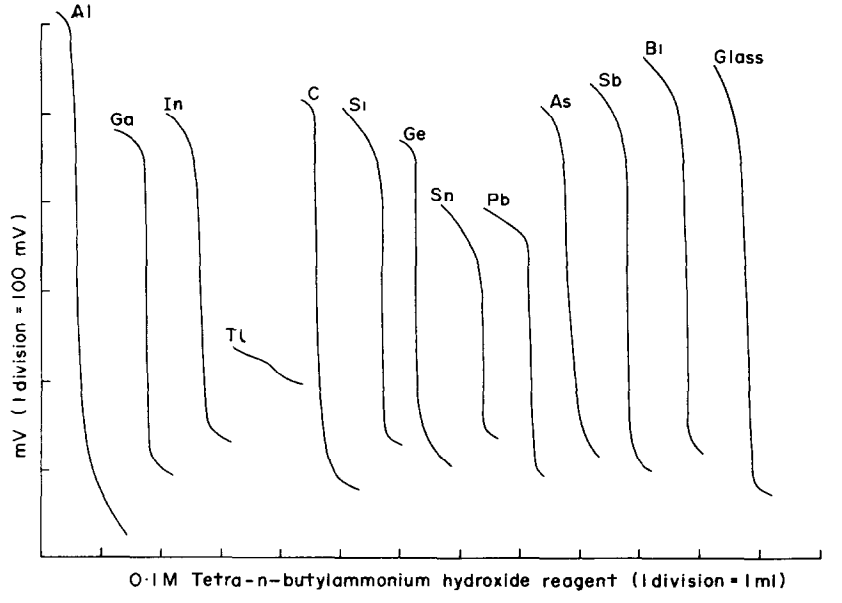

Fig. 4. The effect of the indicator electrode on the shape of the end-point inflexion in the potentiometric titration of benzoic acid in 4-methyl-2-pentanone solution.

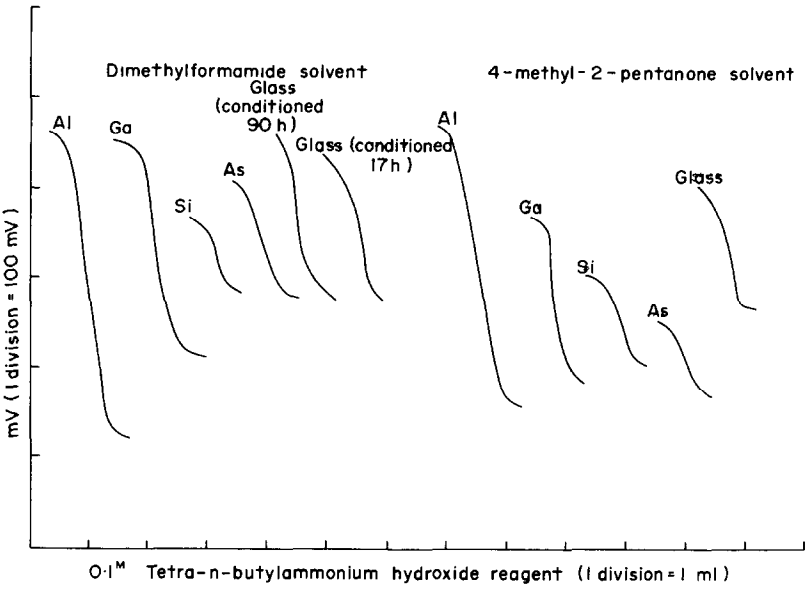

Fig. 5. The effect of the indicator electrode on the shape of the end-point inflexion in the potentiometric titration of 3,5-xylenol in solution in dimethylformamide and 4-methyl-2-pentanone

in the fourth period the end-point sharpness decreases from gallium to arsenic. In the sixth period the trend is in the reverse direction, from bismuth to thallium. In the fifth period there is no trend but tin shows a minimum value.

It can be seen that the least effective electrode elements, thallium and arsenic, are at the ends of one of the diagonals of the block of elements tested while the most effective ones, gallium (~aluminium) and bismuth (~antimony) are at the ends of the other diagonal. Thallium and arsenic represent the chemical extremes of the metal and metalloid elements investigated. Thallium resembles in some respects the strongly basic alkali metals while arsenic is the most electronegative of all the elements investigated with the exception of the non-metal, carbon.

The different potential changes occurring in the region of the end-point when the different metal and metalloid indicator electrodes are used, *i.e.*, the non-Nernstian effects, are probably caused by differences in the chemical and physical properties of the electrode elements, in so much as these affect the solubility and reactivity of the element and its oxide film.

The small overall potential change and the exceptionally small potential change at the end-point obtained when thallium is used as the indicator electrode are probably a result of the unusual chemical characteristics of this element, compared to those of the other elements evaluated as indicator electrodes. Thallium differs from the other elements of Main Group III in its ability to form stable salts of its singly-charged ion. These thallous salts resemble those of the alkali metals and it is probable that the oxide film on the thallium electrode is soluble in the mixture of titrand and titrant.

Metal/metal oxide electrode processes of the type discussed could not take place if the oxide film were removed in this way.

Mechanism

The electrode processes responsible for the potential changes occurring during these non-aqueous titrations may be assumed to be of the same type as that postulated for the antimony electrode in aqueous solution and represented by the redox equation:[11]

$$Sb_2O_3 + 6H^+ + 6e \rightleftharpoons 2Sb + 3H_2O$$

provided that the activities of the electrode element and the oxide film which forms on its surface remain substantially constant. This requirement would be met with most of the electrodes used because the non-aqueous solutions of the weak acids would be unlikely to attack or dissolve the element or its surface oxide.

The mechanism of electrode reactions with oxidized antimony electrodes in aqueous solution has been investigated thoroughly. Much of this work is mentioned in a detailed study carried out by Bishop and Short.[12] The important role of the oxygen dissolved in the electrolyte in aqueous systems has been emphasized. In contrast, in non-aqueous titration in which the antimony and other oxide-type electrodes are used, the usual practice is to avoid the introduction of oxygen and often to provide a dry nitrogen atmosphere above the sample solution. Molecular oxygen can undergo reaction with many of the non-aqueous solvents used and the organic compounds determined. Its presence is particularly undesirable in the titration of phenols. We have therefore used a nitrogen atmosphere for all our titrations and this, no doubt, will accentuate any differences in mechanism.

If the electrode reactions were reversible, as shown in the equation above, then the Nernst equation might then apply. In dilute aqueous solution the activity of the water would be constant, but if the Nernst equation applied in non-aqueous solution the potential developed would be related to the activities of both the hydrogen ion and the water:[3]

$$E = E_0 + RT/F \ln [a_{H^+}/(a_{H_2O})^{\frac{1}{2}}]$$

When solutions of quaternary ammonium hydroxides in non-aqueous solvents are used as titrants, water is formed during the neutralization of the acid sample, and the potential changes are not simply related to the activity of the hydrogen ion only. However, since the concentration of the water increases during the titration and that of the acid decreases, the potential change should be greater than the corresponding one when the water concentration remains constant. Theoretical values for this increase in the potential change can be calculated by inserting the appropriate data into the Nernst equation. For example, if concentrations are assumed to be equivalent to activities, then the potential change will be 14% greater when water is formed during the reduction of the hydrogen ion concentration from 10^{-1} to $10^{-2}M$ than when the water content remains constant, if the initial water content is 0·18% w/v (*i.e.*, 0·1*M*). The theoretical relationship between E.M.F. and pH is non-linear when the water content does not remain constant, and the improvement in the potential change is greater the higher the initial hydrogen ion concentration and the lower the initial water content. It is important then, for comparative evaluation studies, that the sample size and the initial water content of the solvent should be the same in all determinations.

The use of metal/metal oxide indicator electrodes has been criticized on the grounds of inadequate reproducibility of potential measurements[6,11,13,14] and the slowness with which the theoretical potential is attained.[15] However, it is claimed that reproducible potentials and end-points can be obtained with an antimony/antimony oxide indicator electrode if the electrode is cleaned efficiently before each titration.[14]

The systematic investigation, of which this evaluation study forms a part, is concerned mainly with changes in, as distinct from absolute values of, the electrode potential. The lack of reproducibility of individual potential measurements when metal/metal oxide indicator electrodes are used is not, therefore, of over-riding importance.

Acknowledgement—Mr. S. F. George is thanked for constructing the electrodes and the titration apparatus.

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THIOMERCURIMETRIC DETERMINATION OF CARBON DISULPHIDE, CARBONYL SULPHIDE, THIOLS AND HYDROGEN SULPHIDE BY USE OF 1,3-DIAMINOPROPANE AND TRIBUTYLTIN CHLORIDE

MIECZYSŁAW WROŃSKI

Department of Chemical Technology, University of Łódź, Nowotki 18, Łódź, Poland

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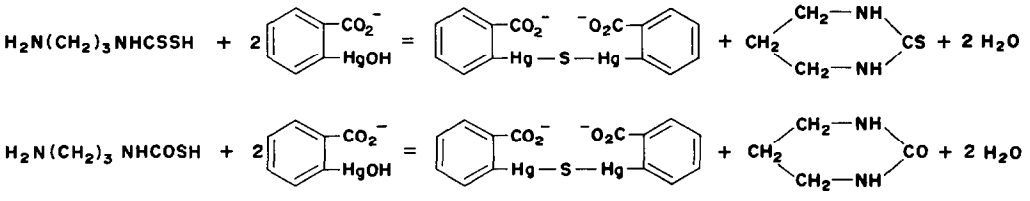
Summary—A new approach to the determination of carbon disulphide and carbonyl sulphide in the presence of each other is based on the reaction with 1,3-diaminopropane (DAP), and titration with *o*-hydroxymercurybenzoic acid (HMB) before and after the selective decomposition of the COS-derivative at pH 4. Determination of hydrogen sulphide, thiols, carbon disulphide and carbonyl sulphide in the presence of each other in hydrocarbon solvents involves four titrations with HMB, *viz.* of all compounds after conversion of CS_2 and COS with DAP, of thiols plus H_2S, of the thiols alone after removal of H_2S by extraction, and of CS_2 alone after removal of other compounds by shaking with aqueous alkali. For selective trapping of H_2S, HCN, RSH, CO_2 and CS_2 + COS, the sample gas is passed successively through a potassium antimonyl tartrate filter, a nickel carbonate filter, a tributyltin chloride filter, a bubbler containing 40% potassium hydroxide solution and a bubbler containing a benzene solution of DAP. The analysis is completed by titration with HMB with dithizone or dithiofluorescein as indicator.

Rapid, simple and reproducible methods for determination of sulphur compounds occurring in gases and hydrocarbon solvents are of vital importance. Although the development of gas chromatography employing new types of detector for sulphur compounds has opened the way for interesting investigations, the practical difficulties in dealing with very complicated mixtures may appear formidable. In spite of a rather extensive literature on the determination of sulphur compounds,[1] no one method deserves to be recommended for analysis of hydrocarbon solvents and fuel gases containing hydrogen sulphide, thiols, carbon disulphide and carbonyl sulphide. It is attempted in this paper to demonstrate the usefulness of a new approach to analysis of sulphur compounds, based on the application of the reagents, new for this purpose, 1,3-diaminopropane and tributyltin chloride. The former is soluble in aromatic and mixed hydrocarbons and reacts very rapidly with carbon disulphide and carbonyl sulphide to give the derivatives, 1-amino-3-propyldithiocarbamate and 1-amino-3-propylmonothiocarbamate, which can conveniently be determined by titration with *o*-hydroxymercurybenzoic acid (HMB). Taking into account that one mole of either carbon disulphide or carbonyl sulphide produces one mole of hydrogen sulphide, and that cyclic thioureas are indifferent towards HMB in alkaline solution,[2] the only possible course of the reactions is given by the equations



It has been found that in acid solution the derivative of COS is rapidly decomposed to COS and DAP, whereas the derivative of CS_2 is relatively stable. In 5 min at 20° the COS derivative is 100, 99·5 and 7% decomposed at pH 3·5, 4 and 5, respectively. The corresponding values for the CS_2 derivative are 0·6, 0·2 and 0·0%. Consequently the decomposition at pH 4 is the most suitable for the determination of both derivatives in the presence of each other. This approach has proved to be more convenient than methods based on

selective hydrolysis of carbonyl sulphide[3] or on spectrophotometric determination of the derivatives.[4]

A benzene solution of DAP can be used for trapping carbon disulphide and carbonyl sulphide. The tributyltin chloride filter has been used with success for trapping thiols in absence of hydrogen sulphide and hydrogen cyanide, which must be removed beforehand. The thiols retained can be simply washed out and determined by titration with HMB. For trapping hydrogen sulphide a filter containing potassium antimonyl tartrate has proved the most suitable. The antimonyl sulphide formed can be dissolved in sodium hydroxide and titrated with HMB. For selective removal of hydrogen cyanide from H_2S-free gas a nickel carbonate filter can be recommended.

EXPERIMENTAL

Reagents

The preparation of the solution of HMB in 50% v/v aqueous propyl alcohol, and of the solutions of dithiofluorescein and dithizone is described in an earlier paper.[5]

1,3-Diaminopropane and tributyltin chloride were supplied by EGA Chemie KG (7924 Steinheim bei Heidenheim/Brenz, West Germany).

Solution *A* is 0·05*M* in potassium carbonate and 0·025*M* in borax in saturated sodium chloride solution. The extraction coefficient for the system toluene–solution *A* is 0·074 for H_2S, 72 for CH_3SH, and 40 for thiophenol.

Solution *B* is *M* in phosphoric acid and 0·5*M* in tartaric acid.

Reagents for impregnating filters

Filter A *for trapping hydrogen sulphide.* Whatman CF 11 cellulose (10 g) mixed with 12 ml of a solution containing 30 g of potassium antimonyl tartrate, 50 g of disodium tartrate, 10 g of disodium EDTA and 4 g of potassium carbonate per litre.

Filter B *for trapping hydrogen cyanide.* Solutions of 2·5 g of nickel chloride hexahydrate in 7·5 ml of water and 1·5 g of potassium carbonate in 2·5 ml of water are mixed and added to 10 g of cellulose.

Filter C for trapping thiols. Tributyltin chloride (10 ml of 0·5*M* solution in 2-ethylhexanol) mixed with 0·4 ml of triethanolamine and 10 g of cellulose.

Filter D *for trapping carbon disulphide and carbonyl sulphide.* Tributyltin chloride (1 ml), 1,3-diaminopropane (3 ml) and 2-ethylhexanol (10 ml) are mixed with 10 g of Woelm column-chromatography polyamide.

Analysis of solvents

Determination of carbon disulphide and carbonyl sulphide, procedure 1 *a.* Place in a dry 15-mm diameter test-tube 0·05 ml of DAP, add 2 ml of sample solvent, placing the jet of the pipette at the bottom in order to avoid any loss of COS, wait 2 min, add 2 ml of propanol, 0·15 ml of 2*M* potassium hydroxide and titrate with $10^{-3}M$ HMB, using dithiofluorescein as indicator. Wait 3–5 min and titrate to the final end-point. During the titration add ethanol in amounts just enough to clear the emulsion produced.

The method is directly applicable to aromatic hydrocarbons; aliphatic hydrocarbons should first be diluted 1:1 with sulphur-free benzene. With alcohols as samples the reaction is not so rapid; a wait of about 10 min is needed before the titration.

Procedure 1 *b.* Place 0·05 ml of DAP in a separating funnel and add slowly, keeping the jet of the pipette at the bottom, 10 ml of the sample, mix, wait 2 min, add 2 ml of 0·3*M* potassium hydroxide containing 1 g of EDTA per litre, shake for 5 min, let the phases separate, take 1·5 ml of the aqueous phase, add 2 ml of ethanol and 0·1 ml of 4*M* potassium hydroxide, and titrate in a test-tube with 10^{-4}–$10^{-3}M$ HMB, using dithizone as indicator, to a permanent purple colour. Dithiofluorescein can be used as well but dithizone is preferable. In titration with $10^{-4}M$ HMB a blank comparison solution containing dithizone and HMB must be used, the titration being continued until the colours of the both solutions match. The result multiplied by the ratio 2·05/1·5 (because DAP increases the volume of the aqueous phase) corresponds to the whole sample. If an aliquot of the aqueous phase is titrated after 5 min decomposition at pH 4, as described later, the COS and CS_2 content can be calculated.

Procedure 1b can be used for analysis of aromatic hydrocarbons, aliphatic hydrocarbons diluted with benzene and for halogen derivatives such as carbon tetrachloride.

Procedure 1 *c.* This applies to determination of CS_2 and COS in water. In this case the use of ethylenediamine is preferable. Heat in a test-tube 0·5 ml of ethylenediamine and add slowly 1–5 ml of water sample, keeping the jet of the pipette at the bottom. Do not mix. The ethylenediamine should form an upper layer, Place the test-tube in boiling water for 2 min, then mix and titrate with $10^{-3}M$ HMB in the presence of dithiofluorescein.

Procedure 2. This applies to determination of hydrogen sulphide and thiols in the presence of carbon disulphide and carbonyl sulphide. Carbonyl sulphide interferes with the titration in alkaline solution but does not in slight alkaline solution. On the other hand a remarkable loss of hydrogen sulphide can be observed during titration in slight alkaline solution. Good results can, however, be obtained by using a reverse titration: a definite volume of HMB is diluted with ethanol and titrated with the sample, added from a graduated pipette with the jet kept at the bottom of the HMB solution, in the presence of dithiofluorescein as indicator, until the solution turns blue. The content of CS_2 and COS can be calculated by difference from the results of this procedure (H_2S + RSH) and of procedure 1a (H_2S + RSH + CS_2 + COS).

Procedure 3. This applies to determination of small amounts of thiols in the presence of an excess of hydrogen sulphide, carbon disulphide and carbonyl sulphide. Place 10 ml of sample in a separating funnel and extract four times with 4 ml of solution A and finally with 2 ml of water. Add 5 ml of propanol and titrate the thiols remaining in the organic phase with $10^{-3}M$ HMB in the presence of dithiofluorescein.

Procedure 4. This applies to determination of small amounts of carbon disulphide in the presence of an excess of hydrogen sulphide, carbonyl sulphide and thiols. Remove the interfering compounds by shaking 10 ml of sample twice for 1 min with 5 ml of 2*M* potassium hydroxide, for 30 min with another 5 ml (to complete the hydrolysis of carbonyl sulphide) and finally twice for 1 min with 2 ml portions of alkali. Determine the carbon disulphide remaining, according to procedure 1b. Only about 0·1% CS_2 is lost by hydrolysis.

Analysis of gases

For preparation of the filters use 10-mm diameter 100-mm long tubes, packed for a length of 0·5–2 cm with slight pressure from a glass rod. On both sides of the packing place wads of cotton-wool, (except for filter *D*). The gas or air sample is aspirated at a rate of 0·1 l./min through the trapping filters and solutions in the following order, 1-cm filter *A*, 0·5-cm filter *B*, 1·5-cm filter *C*, 10-mm diameter U-tube containing 10 ml of 40% w/w potassium hydroxide solution (to remove carbon dioxide which at high concentration interferes with trapping of carbon disulphide and carbonyl sulphide), 20-ml conical gas bubbler containing 4 ml of 2·5% v/v solution of DAP in benzene or toluene. When only the CS_2 and COS content are to be determined the gas is passed through 40% potassium hydroxide solution and the DAP bubbler. When no distinction between CS_2 and COS is necessary, filter *D* may be used instead of the DAP bubbler.

After the sample, pass a stream of pure inert gas or air for 5 min and determine the separated constituents as described below.

Determination of hydrogen sulphide. Place in a 14-mm diameter 180-mm long test-tube a glass rod of 8-mm diameter and 140-mm long, push out filter *A* onto it and wash the filter (in a vertical position) with 2 ml of 1*M* sodium hydroxide and 2 ml of water, using air pressure on the upper part of the filter tube to accelerate the flow. The solution passes the filter and flows down along the glass rod to the bottom of the test-tube. Remove the filter and glass rod (rinsed with a few drops of water) and titrate the solution with 10^{-4}–$10^{-3}M$ HMB in the presence of dithizone.

Determination of thiols. Wash filter *C* twice with 2 ml of ethanol as described above, add dithiofluorescein and 1*M* sodium hydroxide dropwise till the solution just turns blue. Titrate with $10^{-3}M$ HMB until the blue colour disappears.

Determination of carbon disulphide and carbonyl sulphide. Add to the DAP bubbler 4 ml of 0·3*M* potassium hydroxide (containing 1 g of EDTA per litre) and stir vigorously with an air stream for 5 min to transfer the product into the aqueous phase. Let the phases separate, and take 1 ml of the aqueous phase, add 0·2 ml of 4*M* potassium hydroxide, dilute with ethanol and titrate with 10^{-4}–$10^{-3}M$ HMB, using dithizone as indicator, (V_1 ml). In another bubbler (prepared from a test-tube) place 2 ml of the aqueous phase and add enough of solution *B* (as determined in a blank test) to make the pH 3·5–4·0, or add solution *B* dropwise till Methyl Red added as indicator just changes to red. Pass an air-stream for 5 min to remove the carbonyl sulphide produced, add the same volume of 4*M* potassium hydroxide as of solution *B*, dilute with ethanol and titrate with $10^{-3}M$ HMB in the presence of dithizone as indicator, (V_2 ml). Calculate the concentration (mg/l.) as follows:

$$[CS_2] = \frac{38 \times 1{\cdot}05 \times 2{\cdot}05 \times V_2 \times M_{HMB}}{V_g}$$

$$[COS] = \frac{1{\cdot}05(4{\cdot}10V_1 - 2{\cdot}05V_2)30M_{HMB}}{V_g}$$

where V_g is the volume of gas taken and 1·05 is an empirical coefficient.

Another approach is based on using filter *D*. After trapping of CS_2 and COS by a 2-cm filter *D*, the filter is pushed out into a test-tube, ethanol and 0·2 ml of 4*M* potassium hydroxide are added and the sample is titrated with HMB, with dithizone as indicator.

RESULTS AND DISCUSSION

Samples containing known amounts of test substances were prepared or produced as follows.

Carbon disulphide solutions were prepared by weighing and gas mixture by acid decomposition of an aqueous solution of sodium diethyldithiocarbamate, the concentration of

Table 1. Determination of carbon disulphide and carbonyl sulphide in benzene and in water

Procedure	Taken, *μeq* CS_2	Taken, *μeq* COS	Rel. std. devn. %	Mean recovery* (6 titrations), %
1 a	23·5	—	0·3	99·7
1 a	2·35	—	0·5	96·4
1 a	4·55	—	0·5	97·2
1 a	—	2·02	0·6	96·8
1 a	—	4·04	0·8	97·6
1 b	2·35	—	0·8	98·4
1 b	0·42	—	4·1	94·3
1 b	0·74	—	3·3	97·0
1 b	0·04	—	13	93·6
1 b	—	2·02	0·6	97·5
1 c	8·70	—	0·7	98·3

* Without correction.

Table 2. Determination of methanethiol in benzene in the presence of hydrogen sulphide, carbon disulphide and carbonyl sulphide (100 μeq of each) (procedure 3)

Taken, μeq	Found, μeq
1·02	0·98, 0·99, 0·99
2·04	2·01, 1·98, 2·00
3·06	3·00, 3·05, 3·03

Table 3. Determination of carbon disulphide in benzene in the presence of methanethiol, hydrogen sulphide and carbonyl sulphide (100 μeq of each) (procedure 4)

Taken, μeq	Found, μeq
1·50	1·47, 1·54, 1·48
3·00	3·02, 2·96, 2·99

which was determined *via* $BaSO_4$. Known amounts of carbonyl sulphide, hydrogen sulphide and methanethiol were produced by acid decomposition, in a stream of nitrogen, of aqueous solutions of DAP–COS, of soluble starch–zinc sulphide[6] and of a solution of methanethiol in 2*M* potassium hydroxide. The solutions were analysed by titration with HMB, and decomposed by 1*M* sulphuric acid.

Table 4. Determination of hydrogen sulphide and methanethiol in the presence of each other in nitrogen, by using filters *A*, *B* and *C*

Taken, μeq		Found, μeq	
H_2S	CH_3SH	H_2S	CH_3SH
0·44	1·30	0·44, 0·43, 0·41	1·25, 1·27, 1·25
1·76	3·90	1·73, 1·75, 1·70	3·88, 3·90, 3·92
0·044	3·90	0·040, 0·041	3·88, 3·86

As shown by Tables 1–5, the results are satisfactory and the suggested methods can be recommended for general use. Method 1b has a lower limit of 0·1 ppm and is very suitable for trace determination of carbon disulphide in such solvents as benzene or carbon tetrachloride. By use of procedures 1a, 2, 3 and 4, a solvent containing carbon disulphide, carbonyl sulphide, hydrogen sulphide and thiols can easily be analysed. The results are not influenced by thioethers and disulphides, but free sulphur interferes with the procedures for CS_2 and COS. In the presence of hydrogen cyanide a few drops of 5% formaldehyde solution must be added.

Table 5. Determination of carbon disulphide and carbonyl sulphide in the presence of each other in nitrogen after passage through filters *A*, *B*, *C* and potassium hydroxide bubbler. Results are corrected by a factor of 1·05

Taken, μeq		Found, μeq	
CS_2	COS	CS_2	COS
1·16	42·5	1·15	41·7
55·8	2·18	56·0	2·22
11·6	4·25	11·3	4·23
6·10	0	5·90	0·10
6·10	1·80	5·95	1·84
0	7·25	0·05	7·10

The use of filters *A* and *C* for trapping hydrogen and thiols and of filter *D* for trapping carbon disulphide can be recommended for air analysis as the products are very resistant to air oxidation.

In order to make a correction for low recovery of CS_2 and for loss of COS during passage through the 40% potassium hydroxide solution, the use of an empirical coefficient, 1·05, is suggested.

The average CS_2 and COS content in the town gas in Łodz, as determined by the suggested method, amounted to 0·077 and 0·103 mg/l. respectively.

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DIRECT GRAVIMETRIC DETERMINATION OF MOLYBDENUM(VI) IN PRESENCE OF OTHER IONS AND ITS APPLICATION TO ALLOY STEEL

SYAMAL CHATTOPADHYAY, BIJOLI KANTI PAL and BIRENDRA KUMAR MITRA

Department of Chemistry, Jadavpur University, Calcutta-700032,

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Summary—*N-o*-Toluoyl-*N-o*-tolylhydroxylamine has been synthesized and employed successfully as a gravimetric reagent for direct determination of molybdenum(VI). The dried complex (110–120°) has definite composition, $MoO_2(C_{15}H_{14}O_2N)_2$. The method is quite simple, rapid, sensitive and gives reproducible results. The precipitation is quantitative at room temperature over a wide range of acidity. The reagent is highly selective and the method is satisfactory for analysing alloy steels.

Comparatively few gravimetric methods exist for determination of molybdenum(VI). Those involving ignition of Mo-complexes to MoO_3 are time-consuming and require strict control of a narrow range of temperature (500–550°) because of the appreciable volatility of MoO_3 at higher temperature. The 8-hydroxyquinoline method[1] is less tedious and more reproducible than the lead molybdate method[2] but restricted in application by the non-selective nature of oxine (even in presence of EDTA certain other components of alloy steels will be precipitated). The *N*-benzoyl-*N*-phenylhydroxylamine (BPHA) method[3] calls for a digestion for 1 hr and is neither selective nor sensitive. According to data given by Majumdar[4] Nb, Ta, Ti(IV), Zr, Hf, Sn(IV), W(VI), Ge and other ions would interfere under the prescribed acid conditions, which restricts the application of the BPHA method.

The use of *N*-salicylhydroxamic acid, an analogue of BPHA, has also been recommended[5] but although relatively quicker the method has hardly any advantage over the BPHA method, so far as selectivity is concerned. Since the cations mentioned above are common constituents of many industrial alloys and steels, attempts have been made to synthesize a new reagent which will be effective for direct determination of Mo(VI) in presence of these interfering ions.

The present paper describes a simple, rapid, highly selective method for Mo(VI) over a wide range of acidity and at room temperature, using a newly synthesized reagent, viz. *N-o*-toluoyl-*N-o*-tolylhydroxylamine (OTOTHA). The method is sensitive, molybdenum(VI) being determined with reasonable accuracy at concentrations as low as 25 mg/l. The method works satisfactorily for determining molybdenum in alloy steels.

EXPERIMENTAL

General procedure

From Table 1 it is clear that precipitation is quantitative over a wide range of acidity but 1–4*M* mineral acid medium is recommended for better selectivity.

An aliquot of standard molybdenum solution was diluted to 100–150 ml in a 250-ml beaker and the acidity adjusted to 1–4*N* with respect to hydrochloric or sulphuric acid, and 1% reagent solution added at room temperature with stirring until precipitation was complete. After 10–15 min the precipitate was filtered off on a weighed porosity-3 sintered-glass crucible, washed with 0·05% wash solution until free from sulphate or chloride and finally with 5–10 ml of 0·01% wash solution, then dried at 110° and weighed. The conversion factor to molybdenum is 0·1576.

The standard solution of molybdenum(VI) was prepared by dissolving a known weight of analytical-grade ammonium molybdate in dilute ammonia solution, diluting to known volume with distilled water, and standardizing by the oxine method. Standard solutions of niobium, tantalum, titanium, zirconium and hafnium were prepared by fusing their "Specpure" (Johnson–Matthey) oxides with potassium bisulphate and dissolving the cooled clear melts with 5% tartaric acid solution. The niobium and tantalum solutions were standardized by the method of Majumdar and Pal[6] and the titanium, zirconium and hafnium solutions with cupferron.[7]

For solutions of other cations, their corresponding nitrates, chlorides and sulphates were used. Tartaric or oxalic acid was added to the solutions of those metal ions (*e.g.*, As, Bi, Sb) which hydrolyse.

Table 1. Effect of acidity and pH (a = H_2SO_4, b = HCl)

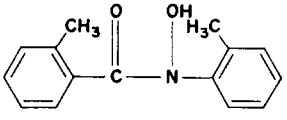
Acidity		Mo taken, mg	Mo complex, mg	Mo found, mg
1*N*	*a*	13·80, 13·37	87·7, 84·6	13·82, 13·34
	b	13·80, 13·37	87·5, 84·8	13·79, 13·37
2*N*	*a*	13·80	87·5, 87·7	13·79, 13·82
	b	13·80	87·7	13·82
3*N*	*a*	13·80	87·3	13·75
	b	14·03	89·4	14·06
4*N*	*a*	14·03, 13·37	89·2, 84·6	14·05, 13·34
	b	13·80	87·4	13·77
6*N*	*a*	14·03	90·2	14·21
	b	13·80	84·0	13·23
8*N*	*a*	14·03	90·6	14·27
		13·37	ignition	13·39
	b	13·80	no precipitation	
pH 1		13·80	87·6	13·80
pH 2		13·80	87·5	13·79
pH 3		14·03	88·6	13·95
pH 4·5		14·03	88·7	13·98
pH 5		14·03	88·9	14·01
pH 6·2		13·80	58·0	9·14

Preparation and properties of chelating reagent (OTOTHA)

First *o*-toluoyl chloride was prepared by treatment of *o*-toluic acid with a slight excess of thionyl chloride under reflux for 2–3 hr on a water-bath; when the reaction was over, 20–30 ml of benzene were added and the solvent and excess of thionyl chloride were removed under reduced pressure. The liquid remaining in the flask was *o*-toluoyl chloride.

An ethereal solution of *o*-tolylhydroxylamine, prepared after the method of Majumdar and Pal,[6] was transferred to a 600-ml beaker and about 300 ml of water were added. It was rendered slightly alkaline by addition of solid sodium bicarbonate and kept in an ice-bath. An appropriate amount of *o*-toluoyl chloride was added very slowly from a dropping funnel, the solution being thoroughly stirred mechanically. Sodium bicarbonate was added from time to time to keep the reaction mixture slightly alkaline throughout the process. The acid chloride addition was continued until the reaction mixture failed to blacken Tollen's reagent. The addition was then stopped and stirring was continued for another 30 min. The yellow-reddish semi-solid mass thus obtained was separated by decantation and triturated with 10% sodium bicarbonate solution to remove the entrapped and adhering acid chloride. Finally it was washed with water, then extracted with ammonia solution 3 or 4 times, and the extract filtered through glass wool. The filtrate was added slowly to ice-cold 4*M* hydrochloric acid with stirring, and *N*-*o*-toluoyl-*N*-*o*-tolylhydroxylamine separated out. It was filtered off, washed with water and recrystallized from aqueous alcohol to give white needle-shaped crystals, m.p. 87–88°. Analysis gave C 75·0%, H 6·2%, N 5·9% (calculated for $C_{15}H_{15}O_2N$: C74·68%, H6·22%, N 5·80%).

The structural formula is



The reagent is highly soluble in glacial acetic acid; a 1% solution in this acid, diluted 20-fold with water, is stable between pH 4·0 and an acidity of 4*N* sulphuric or hydrochloric acid. At higher sulphuric acid concentration the solution becomes turbid owing to separation of free reagent, and at pH 4·5–7·0, the free reagent is also precipitated. In this pH range, however, a 1% alcohol solution of the reagent shows no turbidity. The reagent is soluble in most organic solvents and in hot water.

A 1% alcohol solution was used as precipitant at pH values higher than 3·0 and for more acid media a 1% solution in glacial acetic acid was used.

Initial washing of the precipitate was done with 0·05% reagent solution prepared by dissolving 50 mg of reagent in about 10 ml of alcohol and diluting to 100 ml with water. Final washing was done with 0·01% reagent solution.

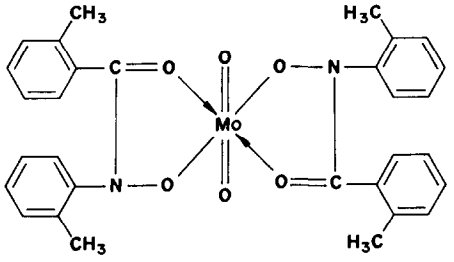
RESULTS AND DISCUSSION

Effect of acidity and pH

At low acidity (pH < 1) the solution needed heating to 70° in presence of a little ammonium chloride (100 mg) for quicker coagulation of the precipitate. The positive errors obtained with > 4*N* sulphuric acid were due to the separation of free reagent, but ignition of the complex showed the precipitation to be quantitative even from 8*N* sulphuric acid.

Composition of the complex

The dried complex was analysed for molybdenum by ignition of a weighed portion to molybdenum trioxide and by the oxine method after decomposition of a weighed portion of the complex with a mixture of concentrated nitric, sulphuric and perchloric acids. The carbon, hydrogen and nitrogen contents were estimated by the usual combustion methods. Found: Mo 15·8, 15·9%, C 59·7%, H 5·1%, N 4·8%; $MoO_2(C_{15}H_{14}O_2N)_2$ requires Mo 15·76%, C 59·20%, H 4·64%, N 4·60%. The structure is probably



Thermal analysis showed that the molybdenum complex is perfectly stable up to 200°.

The freshly precipitated complex is perfectly white and crystalline, becoming cream coloured when dried. It is insoluble in water, dilute acetic acid and aqueous alcohol (1 : 10) but highly soluble in chloroform, benzene and acetone.

Effect of diverse ions

In 1–2*N* acid, a considerable number of cations and anions were found not to interfere (Table 2). In certain cases masking agents were added. The figures in parentheses in Table

Table 2. Effect of diverse ions in 1–2*N* acid medium

Ions (*mg*)	Mo taken, *mg*	Complexing agent added, *mg*	Mo complex, *mg*	Mo found, *mg*
Cu(II)(65), Co(II)(60)	13·57	—	85·8	13·51
Cu(II) (100), Co(II) (100), Ni(100), Mn(II) (100)	13·80	—	87·5	13·79
Cu(II) (100), Co(II) (100)	13·37	—	84·9	13·39
Ni (85), Mn(II) (100)	13·37	—	84·7	13·36
Fe(III) (50), V(V) (50)	13·57	Ascorbic acid (200)	86·3	13·60
Cr(III) (100), U(VI) (100)	13·80	—	87·5	13·79
Cr(III) (100), U(VI) (100)	13·37	—	85·2	13·43
Ti(IV) (50)	13·80	NH_4HF_2 (200)	—	13·86
Zr(100), Hf(100)	13·80	Oxalic acid (500)	88·1	13·88
Sn(IV) (100), Zr(100)	13·37	NH_4HF_2 (500)	—	13·30
Nb(V) (50)	13·80	NH_4HF_2 (200)	—	13·86
Ga(150), Sc(100)	13·80	—	87·8	13·83
Re(VII) (30)	13·80	—	87·4	13·77
Re(VII) (100)	13·37	—	84·8	13·37
As(III) (80)	13·80	—	88·0	13·87
Bi(50)	13·80	—	87·7	13·82
Be(50)	13·80	—	87·3	13·75
Ce(IV) (30)	13·80	—	88·3	13·91
Ce(III) (150)	13·37	—	85·3	13·43
Al(50), Mg(50)	13·80	—	87·8	13·83
Th(50), La(100)	13·80	—	87·5	13·79
Tl(I) (200), Se(IV) (150)	13·37	—	84·9	13·39
Zn(100), Hg(II) (100), Cd(100)	13·37	—	84·8	13·37
EDTA, tartrate, oxalate, citrate, phosphate (500 each)	13·80	—	88·0	13·87
SCN^-(100)	13·80	—	87·2	13·74
F^-(200)	13·80	—	—	13·82

2 represent the amounts of ions added and not the amounts tolerable. The fluoride ion in acidic media attacks the glass crucibles used and hence in these cases collection on paper and ignition of the complex at 500–550° is necessary.

Estimation of molybdenum in presence of tungsten

Aliquots of standard solutions of molybdenum(VI) and tungsten(VI) were mixed and diluted to 100–150 ml with water. After the addition of a little ammonium chloride and 5–10 ml of 5% tartaric acid solution the pH was adjusted to 1–1·5. The solution was heated to about 70° on the water-bath and 1% reagent solution added with stirring until no more precipitate formed; stirring was continued for some time. The precipitate was collected, washed and dried as before. Recovery was 99·9%.

Estimation of molybdenum in presence of tantalum

Aliquots of standard molybdenum(VI) and tantalum oxalate solutions were mixed and diluted to 100 ml and the tantalum precipitated with dilute ammonia solution in presence of ammonium chloride, filtered off and washed thoroughly with water. The acidity of the filtrate was adjusted to 1–4*N* and the molybdenum precipitated as before. Recovery was 99·9%.

If tartrate is present the precipitation of tantalum hydroxide fails, and in that case both tantalum and molybdenum are precipitated with OTOTHA, then ignited to the mixed oxides, which are dissolved and the tantalum is then precipitated from oxalate medium as the hydroxide, as above.

Direct determination of molybdenum in steels

About 0·3 g of steel was accurately weighed into a 250-ml beaker and treated carefully with 15 ml of *aqua regia*, the beaker being covered with a watch-glass. After completion of the brisk reaction the contents were heated gently over a hot-plate, evaporated to small volume, and cooled. Then 5 ml of concentrated sulphuric acid were added and heated to fumes to drive off nitric acid. To the cold pasty mass about 100 ml of water were added and heated for a while to dissolve the soluble salts. About 1 g of tartaric acid was added and the solution rendered slightly ammoniacal to dissolve any precipitated MoO_3 or WO_3 as their ammonium salts. Any insoluble matter was filtered off and the solution was then rendered neutral by boiling, diluted with 100 ml of water, cooled and made 1-4*N* with respect to sulphuric acid (by addition of 8*N* sulphuric acid). Then 1 g of ascorbic acid was added and molybdenum precipitated as already described.

Since tungsten can be masked with tartaric acid only at pH 1–1·5, if it is present it will be precipitated along with the molybdenum. Therefore for tungsten steels the combined tungsten and molybdenum precipitate is collected on paper, washed well with reagent solution and ignited at 500–550°. The oxides are then dissolved in dilute ammonia solution and filtered free from insolubles, then 500 mg of tartaric acid are added and the molybdenum precipitated at pH 1–1·5. Typical results are shown in Table 3.

Table 3.

Sample	Mo, certified value, %	Mo found, %
(1) British Chemical Standard Nb-Mo '18/12' stainless steel No. 246. (Mo 2·89%, Nb 0·82%, Cr 18·8%, Ni 12·1%, W 0·22% Cu 0·13% and Sn less than 0·01%)	2·89	2·78, 2·96
(2) British Chemical Standard Sample No. 64B. (Mo 4·95%, V 1·99%, W 7·05% and Cr 4·55%)	4·95	5·10, 4·78, 5·09

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THE INTERFERENCE OF HETERONUCLEAR CHROMIUM(III) TARTRATE COMPLEXES IN THE EDTA TITRATION OF COBALT(II), COPPER(II), ZINC(II) AND CADMIUM(II)

C. G. RAMSAY and B. TAMHINA*

Department of Chemistry, University of Aberdeen, Old Aberdeen, Scotland

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Summary—When present together in solution, chromium(III) and tartrate can interfere seriously in the titration of Co(II), Cu(II), Zn(II) and Cd(II) with EDTA. Ternary (heteronuclear) tartrate complexes containing Cr(III) and bivalent metal ion in the ratio 1:1 are formed. The conditions for the formation of these complexes have been investigated. Cadmium(II) can be determined without interference by employing potentiometric end-point detection.

It is known that certain bivalent metal ions [such as cobalt(II), copper(II), zinc(II) and cadmium(II)] can be determined by EDTA titration in weakly acidic media (pH 5–6) with Xylenol Orange as metallochromic indicator.[1,2] Chromium(III) does not interfere in such titrations at room temperature.[2] Neither does tartrate interfere in the photometric titration of Co(II), Cu(II), Zn(II) and Cd(II). However, when Cr(III) and tartrate are present together, significant amounts of these metal ions are masked owing to formation of ternary heteronuclear complexes of the bivalent metal ion, chromium and tartrate.

The formation of ternary complexes of oxyacids (*e.g.*, tartaric, citric, malic and lactic acids) and two different metal ions has been previously recognized in several systems.[3–21] In particular, chromium(III) has been shown to form a heteronuclear complex with tartaric acid and tin[12] or indium.[9,12]

This paper describes the interference of chromium(III) and tartrate in the photometric and potentiometric EDTA titrations of Co(II), Cu(II), Zn(II) and Cd(II), and the characteristics of the heteronuclear complexes causing the interference.

EXPERIMENTAL

Reagents

EDTA (disodium salt). A stock 0·2*M* aqueous solution was prepared from the analytical-grade reagent and standardized by titration against zinc.

Stock solutions of bivalent metal ions, 0·05*M*. Prepared from the analytical-grade nitrate, sulphate, or chloride salts, and standardized against EDTA.

Chromium(III) nitrate, 0·05*M*. Laboratory-reagent grade.

Potassium sodium tartrate, 0·4*M*. Laboratory-reagent grade.

Hg(II)-EDTA, 0·001*M*. Prepared daily from equivalent volumes of mercury(II) nitrate and 0·01*M* EDTA.

All other reagents used were of laboratory-reagent grade. Distilled water was used throughout.

Procedure

Solutions were prepared by mixing the required volumes of chromium(III) nitrate solution (0·05*M*), bivalent metal ion solution (0·05*M*), potassium sodium tartrate solution (0·4*M*) and water. After adjustment of the pH with dilute sodium hydroxide solution or nitric acid, the solutions were heated in a boiling water-bath, cooled to room temperature (20 ± 2°), transferred quantitatively to 50-ml volumetric flasks, and diluted to the mark with water. The change in pH during heating was less than 0·2 units.

Aliquots (5 ml) of the solutions were diluted to about 20 ml and titrated photometrically or potentiometrically at pH 5·0–5·5 with EDTA added from a 0·5-ml Agla micrometer-syringe burette. In the photometric titrations, solid Xylenol Orange and hexamine were added as indicator and buffer respectively. An EEL photometric titrator, with Unigalvo galvanometer and filter with maximum transmittance at 580 nm, was employed.

In the potentiometric titrations, saturated calomel and J-type mercury-drop electrodes[2] connected to a Honeywell VT100 digital voltmeter were used to monitor the potential. Before the titration, mercury-EDTA (1 ml of 0·001*M* solution) was added, and nitrogen was bubbled through the solution to remove dissolved oxygen. The pH was adjusted to 5·5 with dilute nitric acid or sodium hydroxide solution at the start of the titration, the buffering capacity of the tartrate being sufficient to prevent the pH falling below 5·0 by the time

* On leave from the Laboratory of Analytical Chemistry, Faculty of Science, Strossmayerov trg 14, Zagreb, Yugoslavia.

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the end-point was reached. Since chloride interferes with the mercury indicator electrode, nitrates or sulphates of the bivalent metal ions were employed in systems which were titrated potentiometrically

RESULTS

General observations

Equilibria were attained rapidly during EDTA titration of the binary bivalent metal ion–tartrate systems. Although the presence of tartrate necessitated intrumental end-point detection, the intersections of the linear portions of the photometric titration curves were very sharp. When chromium(III) was present, however, the intersections in the titration curves were less sharp and equilibrium was attained less rapidly owing to slow dissociation of the heteronuclear complexes. Titrations of Cu(II) or Cd(II) in the ternary systems were relatively fast, equilibrium being attained in less than 1 min, but equilibrium in the corresponding Zn(II) and Co(II) systems was only attained after 4 and 10 min, respectively.

Hexamine buffer did not affect the heteronuclear complexes: identical photometric titration results were obtained when the pH was maintained at 5·5 by addition of dilute sodium hydroxide solution during the titration, and when the pH was controlled by the addition of hexamine.

The end-points in potentiometric titrations of tartrate solutions of Cu(II), Zn(II) and Cd(II) were indicated by potential breaks of 50–100 mV, but only a gradual decrease in potential throughout the titration was observed for Co(II) tartrate systems. Neither did a potential break occur during the titration of Zn(II) when Cr(III) was present.

Only in the case of copper(II) was it possible to titrate the same aliquot of solution both photometrically and potentiometrically. Otherwise, the Xylenol Orange in the combined titration system was masked in a stable yellow complex also containing mercury(II) and tartrate. Copper(II) demasked the Xylenol Orange to form the characteristically red-violet metal–indicator complex, but cobalt(II), zinc(II) and cadmium(II) did not. Consequently, photometric and potentiometric titrations of the latter metals were performed separately.

The results of the titrations are expressed as the "% masked" which is defined as

$$100(1 - A/B)$$

where A is the volume of EDTA required when Cr(III) is present, and B is the corresponding volume when Cr(III) is absent. Since the results for the ternary systems are very dependent on the experimental conditions, and since only the relative values of the titrations are of general importance, no calculation of errors or precision has been made, but each result is the average of at least two determinations.

Effect of pH

The effect of pH on heteronuclear complex formation was investigated by photometric EDTA titration of aliquots of solutions heated for 2 hr and containing 0·01*M* Cr(III),

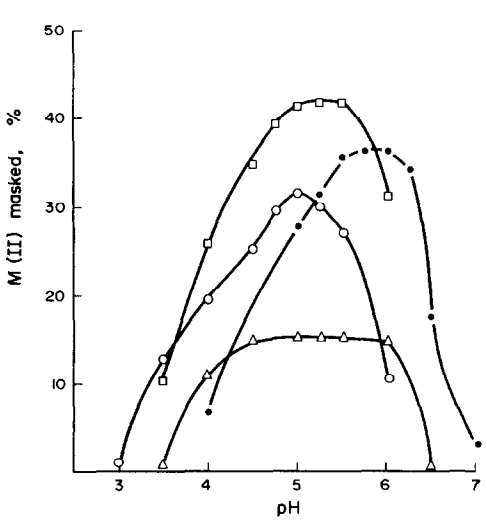

Fig. 1. Effect of pH on heteronuclear complex formation with Cr(III), tartrate and Co(○), Cu(●), Zn(□) or Cd(△).

0·01*M* bivalent metal ion and 0·16*M* tartrate, and corresponding solutions without chromium. The results (Fig. 1) indicate that the optimal pH values for heteronuclear complex formation for Co(II), Cu(II), Zn(II) and Cd(II) are 5·0, 5·8, 5·2 and 5·2, respectively. All subsequent solutions were prepared at these pH values.

Effect of heating time

Solutions containing 0·01*M* Cr(III), 0·01*M* bivalent metal ion and 0·16*M* tartrate were heated in a boiling water-bath for various times. Comparison of the results (Fig. 2) for photometric titration of aliquots of these solutions with blanks containing no Cr(III) indicates that the amount of Cr(III) heteronuclear complex formation with Co(II), Zn(II) or Cd(II) remains constant for between 10 and 120 min heating. In the case of Cu(II), however, the amount of heteronuclear complex formed increases significantly throughout the time range investigated. Heating of Cu(II) solutions for longer than 120 min resulted in the precipitation of a red powder containing Cu(II). Unless otherwise stated, subsequent solutions were heated for 2 hr.

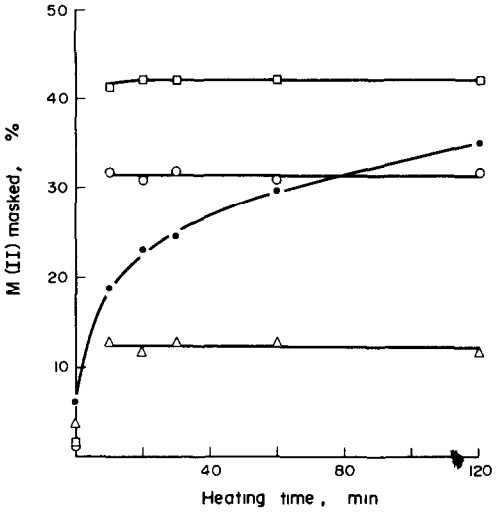

Fig. 2. Effect of heating time on heteronuclear complex formation with Cr(III), tartrate and Co(○), Cu(●), Zn(□) or Cd(△).

Effect of tartrate concentration

Photometric titration results for solutions containing 0·01*M* Cr(III), 0·01*M* bivalent metal ion (M), and various concentrations of tartrate were compared with those for solutions containing 0·01 *M* bivalent metal ion and correspondingly halved tartrate concentrations. The amounts of bivalent metal ion masked (Fig. 3) are independent of the concentration ratio of tartrate to total metals between the values 3:1 and 10:1. Hydrolysis of the metal ions occurred at low ratios. No conclusions are drawn as to the ratios of tartrate to metal ions in the heteronuclear complexes since the systems are complicated by the presence of binary tartrate complexes. That the curves in Fig. 3 reach plateaux at such low concentrations of tartrate, however, illustrates the considerable stability of the heteronuclear complexes. Most other experimental work was carried out at a tartrate:total metals ratio of 8:1.

Chromium(III):bivalent metal ion ratio

The ratios of Cr(III):bivalent metal ion in the heteronuclear complexes were evaluated as 1:1 for each of the bivalent metal ions by both the mole-ratio method and by Job's method (Figs. 4 and 5).

For the mole-ratio work, aliquots of solutions 0·01*M* in bivalent metal ion, 0·16*M* in tartrate and containing the requisite concentrations of Cr(III) were titrated photometrically. For Job plots, aliquots of solutions in which the tartrate concentration was 0·08*M* and

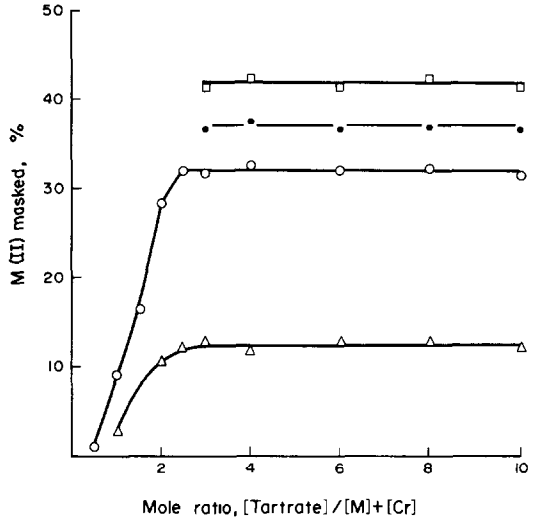

Fig. 3. Effect of tartrate concentration on heteronuclear complex formation with Cr(III), tartrate and Co(○), Cu(●), Zn(□) or Cd(△). Hydrolysis occurred at concentration ratios below the minimum values plotted.

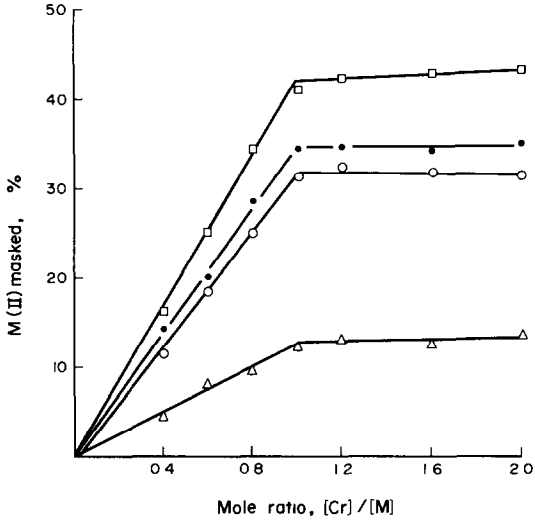

Fig. 4. Mole-ratio plot for heteronuclear complexes of Cr(III), tartrate and Co(○), Cu(●), Zn(□) or Cd(△).

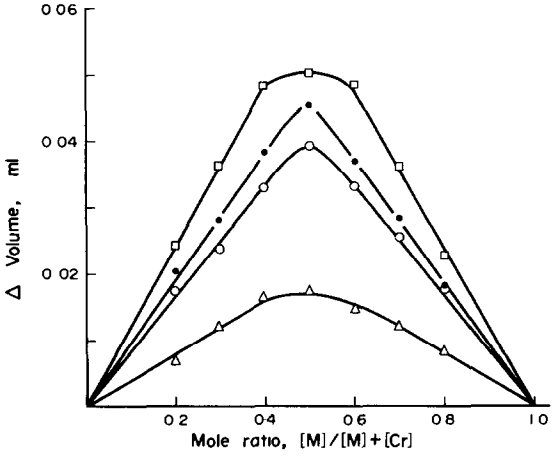

Fig. 5. Job plot for heteronuclear complexes of Cr(III), tartrate and Co(○), Cu(●), Zn(□) or Cd(△). △ volume is the reduction in the volume of EDTA required to titrate the bivalent metals in tartrate solutions when Cr(III) is present.

the total concentration of Cr(III) plus bivalent metal ion was 0·01*M* were titrated similarly. Titrations of corresponding solutions containing no Cr(III) yielded linear calibration graphs.

Storage effects

The change with time in the amounts of Co(II), Cu(II), Zn(II) and Cd(II) masked was investigated over 14 days both for solutions which had not been heated and for solutions which had been heated for 2 hr on day zero and then stored at room temperature. The results of photometric titrations of aliquots of solutions 0·01*M* in Cr(III), 0·01*M* in bivalent metal ion and 0·16*M* in tartrate are listed in Table 1.

Table 1. Change with time in the amount of bivalent metal masked as a heteronuclear chromium(III) tartrate complex

Storage time, *days*	% Masked			
	Co(II)	Cu(II)	Zn(II)	Cd(II)
0*	0·8	6·0	1·2	3·6
1	3·3 (31·8†)	7·6 (35·6†)	6·6 (42·0†)	6·3 (12·4†)
2	11·4	8·0	8·5	8·0
5	17·9	8·4	19·2	14·0
7	25·6	9·2	20·7	15·2
14	29·3 (32·0†)	17·7 (35·2†)	42·9 (42·8†)	22·2 (21·5†)

* Titrations on day zero were completed less than 1 hr after mixing the reagents.
† These results are for heated solutions; the other results are for unheated solutions.

Heteronuclear complex formation proceeds relatively slowly at room temperature, but after 14 days only in the case of Cu(II) does the amount of bivalent metal ion masked in unheated systems differ greatly from that masked in heated systems. The Co(II), Cu(II) and Zn(II) heated systems are stable for at least 14 days. In contrast, the heated Cd(II) system shows a large increase in the amount of cadmium masked. This increase is puzzling since there is no difference in the amount of cadmium masked after 10 min heating and after 120 min heating (Fig. 2).

Potentiometric titrations

Aliquots of solutions 0·01*M* in Cr(III), 0·01*M* in bivalent metal ion and 0·16*M* in tartrate were titrated both potentiometrically and photometrically. The results in Table 2 show that the formation of heteronuclear complexes does not interfere in the potentiometric EDTA titration of cadmium: the value −0·2% masked reflects the titration error. Hence, potentiometric end-point detection is recommended when Cd(II) is determined by EDTA titration in systems containing tartrate and Cr(III). As in the photometric titrations, the accurate potentiometric EDTA titration of Co(II), Cu(II) or Zn(II) is not possible when Cr(III) and tartrate are present.

Table 2. Amounts of bivalent metal masked in potentiometric and photometric EDTA titrations of previously heated solutions containing 0·01*M* Cr(III), 0·01*M* M(II) and 0·16*M* tartrate

M(II)	% M(II) masked	
	Potentiometric titration	Photometric titration
Co	NPB	28·6
Cu	21·6	23·3
Zn	NPB	33·3
Cd	−0·2	14·6

NPB—No potential break observed.

DISCUSSION

Heteronuclear complexes of considerable stability are formed by Cr(III), tartrate and the bivalent metal ions Co(II), Cu(II), Zn(II) and Cd(II). Consideration of the thermodynamic stability of these complexes is complicated by the high kinetic stability of Cr(III) complexes. Remembering this qualification, however, it may be concluded that all four bivalent metal ions investigated form heteronuclear complexes of greater stability than the corresponding metal–Xylenol Orange complexes. Whereas the cadmium(II) heteronuclear complex is less stable than the Cd(II)–EDTA complex (since no cadmium is masked in potentiometric EDTA titrations), the analogous copper(II) complex is more stable than the Cu(II)–EDTA complex.

Although heteronuclear complex formation proceeds more rapidly at higher temperatures, significant quantities of the bivalent metals are masked at 20° within the time taken to mix the reagents and perform the titrations (about 1 hr). Much greater interferences occur when the systems are heated, as in most decompositions preceding analysis, or when the systems are stored for several days. Since the masking is not quantitative, no immediate analytical use can be made of these particular systems, but the effect must be regarded as a major source of possible error in EDTA titrations. The titration results, however, imply only that the interplay of equilibria during the titrations is such as to mask various amounts of bivalent metal ions; they do not prove that the heteronuclear complex formation in solution is non-quantitative.

This work, combined with the growing amount of published data on heteronuclear hydroxycarboxylate complexes, emphasizes the necessity for caution when hydroxycarboxylic acids in particular (and polydentate ligands in general) are employed in analytical procedures.

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AN INVESTIGATION OF THE POTENTIAL USES OF IODINE MONOCHLORIDE AS A TITRANT IN THERMOMETRIC TITRIMETRY

L. S. BARK and J. K. GRIME*

Department of Chemistry and Applied Chemistry, University of Salford, Salford M5 4WT, England

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Summary—An investigation has been made of the potential uses of iodine monochloride as a titrant in thermometric titrimetry. A series of substances, inorganic and organic, has been selected so that a range of stoichiometries and of various types of reaction products result from the oxidation. It has been found to be necessary to prevent the formation of iodine formed by oxidation of the iodide produced by the reduction of iodine monochloride. This is successfully accomplished by using mercury(II) to mask the iodide in a mercury(II)–iodide complex. However, the evolution of gaseous products tends to give curvature of the enthalpogram near the equivalence point and the method is not recommended for the determination of compounds such as thiosemicarbazide. For many other systems, iodine monochloride used in the presence of mercury(II) has analytical potential as a thermometric titrant.

For a compound to be accepted as a titrant in thermometric analysis, it is necessary that it not only meets the requirements of classical titrimetry, but also has a relatively high solubility (since concentrated titrants are always used) and that the kinetics of the reaction at the equivalence point are sufficiently favourable for there to be no "dragging" of the endpoint, which would produce marked curvature of the enthalpogram.[1] The overall enthalpy change of the reaction must also be fairly high (> 16 kJ/mole) so that an acceptable sensitivity may be obtained when simple apparatus is used.[2]

The enthalpy changes associated with oxidation–reduction reactions are often relatively large.[1] In addition to this many redox systems have favourable kinetics, and the rates of reaction are often quite high.

We have examined several oxidizing titrants including chloramine-T, *N*-bromosuccinimide, potassium hexacyanoferrate(III) and iodine monochloride for use in thermometric titrations. Of these, only iodine monochloride showed any promise, the others failing to meet one or more of the requirements, especially at room temperature and in aqueous solutions of sufficient concentration to be used in the manner required.

Iodine monochloride has been used as an oxidimetric titrant both in direct titrations[3,4] and in indirect titrations.[5,6] It has also been used for substitution and addition reactions in the titrimetric determination of organic compounds in functional group analysis.[7] It has found some use as a catalyst in the reaction between arsenic(III) and cerium(IV).[8]

The direct titration of reducing agents with iodine monochloride can be done with the aid of visual indicators, in either acidic or weakly alkaline solutions. Since the iodine monochloride titrant needs to be prepared in hydrochloric acid medium, it is not convenient to use the titrant for weakly alkaline media in thermometric titrimetry, since the heat of neutralization tends to mask the equivalence point for the redox system. It is thus preferable to use oxidations in acidic conditions.

In acidic conditions there are two possible mechanisms of oxidation–reduction involving iodine monochloride.[9] If the standard potential of the titrand is less than +0·4 V, the iodine monochloride titrant is reduced to iodide. When no more titrand remains to be oxidized, the titrant may oxidize the iodide to elemental iodine. These two successive reactions are quite discrete and if followed potentiometrically, the change from one reaction to the other is observed as a discontinuity in the record.

If the standard potential of the titrand is much greater than +0·4 V, then the iodine monochloride titrant is reduced directly to elemental iodine.

* Present address: Department of Chemistry, Pennsylvania State University, State College, Pa, USA.

The calculated standard potentials for these reactions are $E^{\circ}_{I^+/I^-} = 0{\cdot}795$ V,[9] and $E^{\circ}_{I^+/I^-} = 1{\cdot}06$ V.[10]

We have previously reported[11] that in the titration of ascorbic acid with iodine monochloride, it is necessary to add an excess of mercury(II) to the solution if only one point of discontinuity is to be seen on the enthalpogram. The action of the mercury(II) is to mask the iodide by the formation of a stable mercury–iodide complex, and this masking action prevents the oxidation of the iodide by the iodine monochloride. There is thus a sharp indication of the end of the redox reaction involving the original titrand.

A series of substances has been selected to investigate the effect of different stoichiometrics, gaseous reaction products and different end-products of the iodine monochloride.

The compounds contain typical functional groups that can be determined by oxidation, *e.g.*, hydroquinone and hydrazides, or are inorganic ions capable of being oxidized by I^+, *e.g.*, Sb(III) and As(III).

It is considered that these compounds are typical of the possible problems and cover both possible electrode potential ranges.

EXPERIMENTAL

Apparatus and reagents

The circuit for the basic bridge system and the details of the titration assembly have been reported previously.[2] All the compounds used were analytical-reagent grade and were assayed by the appropriate standard method.[12]

The standard solution of iodine monochloride is prepared by the oxidation of iodide with iodate in the presence of concentrated hydrochloric acid. The amounts used are in accordance with the stoichiometry of the reaction:

$$2I^- + IO_3^- + 6H^+ = 3I^+ + 3H_2O$$

The experimental details of this preparation and the subsequent standardization procedure have been previously reported.[11] The free hydrochloric acid concentration should be adjusted to 2*M* to avoid heat of dilution effects.

Procedure

Dissolve the sample in 2*M* hydrochloric acid, transfer the solution to the reaction cell and make up to 10 ml with 2*M* hydrochloric acid. Immerse the tip of the burette below the surface of the titrand and position the thermistor so that local temperature effects are avoided. Activate the temperature-sensing circuit and stir at a constant rate until thermal equilibrium is achieved (as shown by the trace on the recorder chart). When thermal equilibrium is obtained titrate the sample with iodine monochloride solution (which should also be 2*M* with respect to hydrochloric acid in order to avoid any heat of dilution effect).

When the effect of mercury(II) is to be investigated, then the solution in the reaction vessel should be approximately 0·1*M* with respect to mercury(II) chloride and 2*M* with respect to hydrochloric acid.

RESULTS AND DISCUSSION

Some examples of the types of enthalpograms obtained are shown in Figs. 1 and 2. Some typical results are shown in Table 1. All the results quoted were obtained from sample solutions containing an excess of mercury(II).

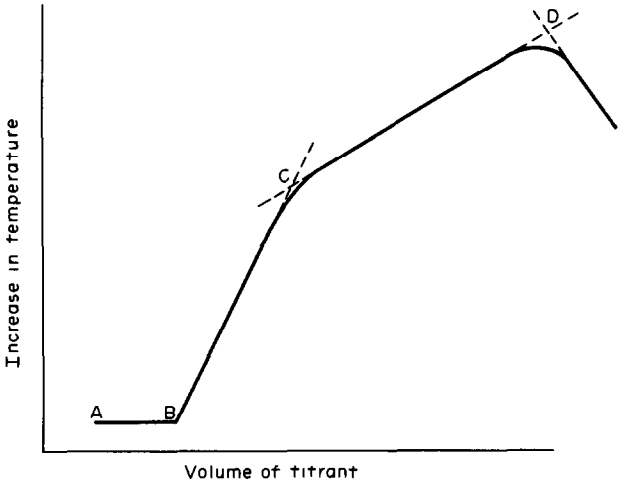

Fig. 1. Iodine monochloride titration of As(III) in absence of $HgCl_2$.

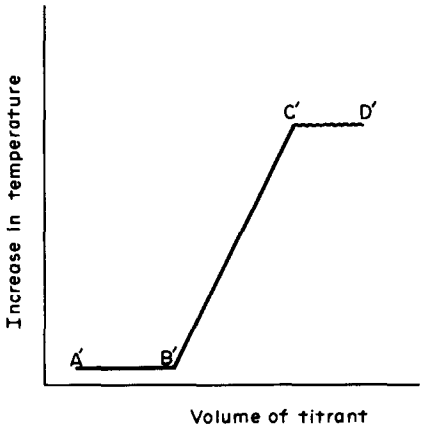

Fig. 2. Iodine monochloride titration of As(III) in presence of excess of $HgCl_2$.

The reactions for the compounds investigated have all been previously reported. It is of interest to note that when one or more of the reaction products is gaseous and hydrogen ions are also produced, that some curvature of the enthalpogram at or about the equivalence point is produced, *viz.*, for hydrazine ($N_2 + 4H^+$), phenylhydrazine ($N_2 + 3H^+$), semicarbazide ($N_2 + CO_2 + 3H^+$) and thiosemicarbazide ($N_2 + SO_2 + CO_2 + 9H^+$).

It is considered likely that the conditions are not favourable at the equivalence point, because the exothermic production of protons is offset by the endothermic loss of gaseous products from the system is generally an endothermic process and result in

Table 1.

Compound	Weight taken, *mg**	Weight found, *mg*†	Error, %
Hydrazine sulphate‡	11·7	11·7	0·0
	28·3	28·2	−0·4
	40·0	40·0	0·0
	55·6	56·5	+1·6
Hydroquinone§	2·49	2·48	−0·4
	4·99	4·96	−0·6
	7·44	7·90	+6·2
	9·92	10·70	+7·8
Phenylhydrazine hydrochloride‖	5·8	5·8	0·0
	15·0	14·9	−0·6
	19·8	19·6	−1·0
	33·3	33·1	−0·6
Potassium antimonyl tartrate‡	30·7	31·0	+1·0
	40·2	40·4	+0·5
	50·5	50·5	0·0
Sodium arsenite‡	10·1	10·1	0·0
	13·5	13·4	−0·8
	15·4	15·3	−0·7
	32·0	32·2	+0·6
Semicarbazide hydrochloride§	8·0	8·3	+3·8
	15·0	15·1	+0·7
	18·5	18·3	−1·5
Ascorbic acid‡	5·3	5·25	−1·0
	10·6	10·45	−1·2
	20·5	20·3	−1·5
Thiosemicarbazide	The amount of curvature near the equivalence point make accurate extrapolation very difficult. The error is analytically unacceptable.		

* At least 3 aliquots of a freshly prepared solution used for each weight.
† The worst result for each weight used.
‡ Well defined equivalence point.
§ Considerable curvature in the region of the equivalence point. (Especially for sample weights of hydroquinone greater than 5 mg.)
‖ Slight curvature in the region of equivalence point.

the enthalpogram being curved. The amount of distortion produced in the hydrazine sulphate reaction is small and the sharpness of the end-point is acceptable for the precision required.

In the case of phenylhydrazine hydrochloride the equivalence point can be located accurately by extrapolation of the slopes before and after the maximum point of curvature.

Attempts to obtain more acceptable enthalpograms for semicarbazide and thiosemicarbazide by heating the system to 30° and hence increasing the rate of the reaction, did not produce acceptable curves; the rate of loss of the gaseous products is also increased and the possible beneficial effects produced by increasing the temperature of the system are apparently cancelled by this increase.

In the reaction where the iodine monochloride is reduced directly to elemental iodine, *i.e.*, the reduction using hydroquinone, it is possible to obtain good results only over a small range. This is again caused by the loss of gaseous reaction product, in this case I_2. The evolution of purple vapours of I_2 is noticeable at the end of the titration. It is for this reason, that in those reactions where the iodine monochloride is first reduced to iodide ion, that we recommend the masking of the iodide ion with mercury(II), in order to prevent the oxidation of the iodide to elementary iodine by the iodine monochloride. In such cases the results are generally within 1·5% of those expected.

Thus we may interpret the enthalpograms produced in the presence and in the absence of mercury(II) in the following manner. When no mercury(II) is present (Fig. 1) the line BC represents the exothermic reduction of iodine monochloride, and the line CD represents the heat of oxidation of the iodide ions by iodine monochloride. This is confirmed by the fact that the volumes of titrant consumed over the ranges corresponding to BC and CD are approximately equal. Furthermore the endothermic and visible evolution of iodine vapour is observed as a decrease in temperature on the enthalpogram, after D.

An excess of mercury(II) complexes the iodide as it is formed, and only one equivalence point is observed with increased sharpness (Fig. 2).

Thus from the compounds examined and the various classes of reactions which are found, we recommend that iodine monochloride be used in thermometric analysis in such conditions that the evolution of iodine is prevented by the masking with mercury(II) of the iodide produced in the preliminary reduction of I^+.

The direct determination of hydrazinium functional groups in organic compounds which react to give relatively large amounts of gaseous products, is not recommended.

However the heat of reaction and the kinetics for other reactions indicate the analytical potential of the oxidant.

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ION-EXCHANGE INVESTIGATION OF THE ARSENAZO III–URANYL SYSTEM

CONFIRMATION OF THE PHYSICAL EXISTENCE OF A WEAK M_2L-TYPE NEW COMPLEX COMPOUND

J. A. PÉREZ-BUSTAMANTE

Departamento de Química Analítica, Facultad de Ciencias y C.S.I.C., Universidad Complutense, Ciudad Universitaria, Madrid-3, Spain

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Summary—Ion-exchange experiments have proved the physical existence in the arsenazo III–uranyl system of an M_2L complex species in addition to the well-known ML complex. The emerald-green M_2L complex exhibits a very low stability which permits the preparation of pure stoichiometric bluish ML complex solutions by percolation of the former through a cation-exchanger in the sodium form. Both complexes exhibit a similar visible spectrum with maxima located at 605 and 655 nm, the maximum absorptivity of M_2L being slightly greater ($\epsilon_{655} \sim 5{\cdot}8 \times 10^4$ $l.mole^{-1}.cm^{-1}$) than that of ML ($\epsilon_{655} = 5{\cdot}0 \pm 0{\cdot}3 \times 10^4$). The complexes have a net negative charge which depends strongly on the particular washing conditions used for the complexes sorbed on chloride-form anion-exchange resins.

The question posed by the mono- or bifunctionality of the arsenazo III reagent has given rise to a number of contradictory hypotheses.[1] As a rule, arsenazo III forms ML, ML_2 and even ML_3 complexes with a number of elements, especially the transition elements,[2] in which arsenazo III acts as a typical monofunctional analytical reagent.

The ability of this reagent to form M_2L-type binuclear complexes has been demonstrated[3] with complex systems involving Pd(II). The common explanation of the factual monofunctionality of this reagent is based mainly on the strong deactivation of the second azo group, which arises from the electronic transfer processes which take place upon the complexation of a metal cation by the first azo group of the symmetrical arsenazo III molecule.[2] The most logical explanation furnished so far to account for the bifunctionality of the reagent with Pd(II) and some other typically "soft" acids involves the participation of the cation *d*-electrons in a pi-bond with the deactivated second azo group.[2] However, no complex of this type has been reported so far for the uranyl ion, despite its *f*-electron system. This is rather understandable since this cation can be considered as a typical "hard" acid[4] unable to participate in π-back-bonding.

By material balance experiments using ion-exchange resins we have been able to demonstrate the physical existence of such a type of M_2L compound for the uranyl–arsenazo III system. It is of very low stability and exhibits spectral properties closely approaching those exhibited by the "common" ML-type complex.[5–7]

EXPERIMENTAL

Apparatus

Ion-exchange columns. Simple and combined two-body glass-fitted columns of 8–10 mm internal diameter and 100–250 mm overall length.

Reagents

Arsenazo III stock solutions, 0·1%.
Uranyl nitrate solution 0·020*M*.

Ion-exchange resins

Dowex 50 W cation-exchange and Dowex 2 × 8 anion-exchange resins, 50–100 mesh, originally in the sodium and chloride forms respectively.

RESULTS AND DISCUSSION

Initial work on the monochloroacetic acid/sodium monochloroacetate/arsenazo III/uranyl system showed only compounds of ML stoichiometry,[6] but further examination has shown the possibility of M_2L species. These have now been investigated by ion-exchange.

Preliminary ion-exchange experiments

Two complex solutions (pH 2·3 ± 0·2) were submitted to ion-exchange experiments, one having M : L = 5 (emerald-green) and the other L : M = 5 (red-pinkish). The results are summarized in Table 1.

The results for the resin in the sodium form may be connected with the decomposition of a green labile M_2L complex to form a bluish ML complex:

$$2\,\text{R–Na} + \underset{\text{(green)}}{M_2L} \rightleftharpoons \underset{\text{(bluish)}}{R_2\text{–}UO_2} + ML \qquad (1)$$

followed (anionic sorption) by the reaction (anionic resin):

$$p\text{R–Cl} + ML^{p-} \rightleftharpoons R_p\text{–}ML + p\text{Cl}^- \qquad (2)$$

To test this hypothesis a spectrophotometric study was undertaken. Spectra were recorded, starting with pure bluish effluent solutions (from an R–Na layer fed with green solution) to which varying amounts of U(VI) were added (Fig. 1). An isosbestic point was found at 575 nm, which can be related to the establishment of the equilibrium

$$ML + UO_2^{2+} \rightleftharpoons M_2L \qquad (3)$$

Table 1. Investigation of the ion-exchange properties of uranyl–arsenazo III complex solutions

Resin system	Remarks: Green solution ($C_M = 5C_L$)	Remarks: Pinkish-red solution ($C_L = 5C_M$)
R–H	Quick decomposition of the complex; quantitative sorption of U(VI) on the exchanger; red-crimson effluent of free arsenazo III solution	Same phenomena as for the green system
R–Na	Bluish effluent solution; sorption of excess of U(VI) on the exchanger. The effluent solution was shown to rebuild the green feed solution upon addition of excess U(VI). A material balance carried out with the feed effluent solutions, together with the yellow colour of the exchanging layer showed that no complex sorption takes place on the resin layer	No sorption of either U(VI) or arsenazo III on the resin layer was observed. The effluent solution leaves the resin column quite unchanged
R–OH	Both types of feed solution become quantitatively sorbed on the resin which becomes intensely dark coloured. The effluent solutions exhibit a very slight alkalinity indicating that all complexes, excess of uranyl ion and excess of ligand are taken up by the anionic resin	
R–Cl	Similar results as for the preceding case for both feed solutions. In this case, however, the effluent for the green feed solution contained free uranyl (arsenazo III test) but that of the pinkish red solution did not. In both cases considerable amounts of Cl^- were set free from the resins into the effluent. Upon thorough washing the sorbed complex species of the green solution evidenced a much stronger tendency towards hydrolysis than the sorbate complex resulting from the other feed solution. Consequently arsenazo III tests carried out on the wash-liquors of the complex sorbed from the green solution showed the presence of appreciable amounts of hydrolysed U(VI) in contrast to the other column which did not show such a hydrolytic process	
R–Na/R–Cl	Sorption of excess of U(VI) on the cationic layer. Quantitative sorption of bluish effluent solution of the cationic layer on the anionic layer. Considerable amounts of Cl^- were detected in the effluent from the anionic layer. Washing of the anionic layer showed a certain tendency of U(VI) to hydrolyse (arsenazo III test)	No sorption of any species was noticed on the cationic layer. Similar results as for the preceding case (R–Cl system) were obtained in connection with the sorption process on the anionic resin
	In both cases the effluents of the two-body column system were quite clear	

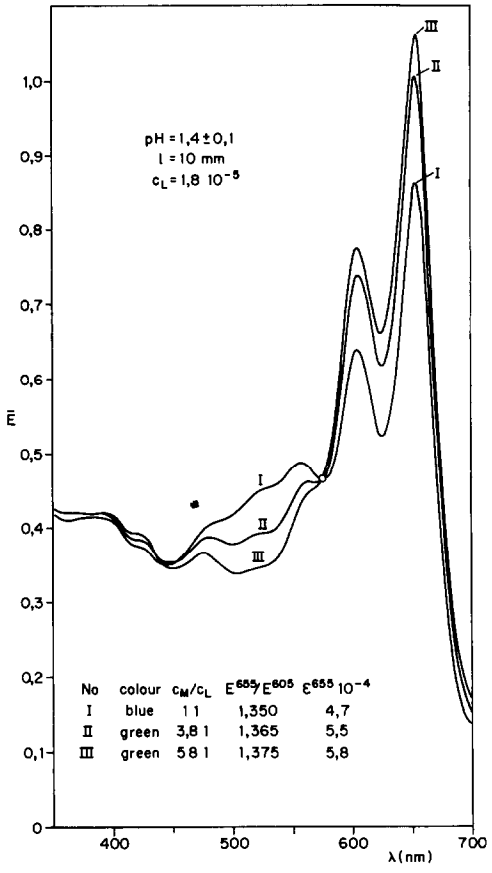

Fig. 1. Spectral characteristics of the arsenazo III–uranyl complex system as a function of the cation: ligand molar ratio.

However, all the spectra are similar, making it difficult to extract any confirmation of the individuality of the two complexes. It is, however, interesting to note that the molar absorptivity of the green species increases steadily with increasing cation: ligand ratio, thereby proving the weak character of the presumed M_2L complex (a metal:ligand ratio of 120 increases the molar absorptivity to about 2% over the value shown in curve III).

It was deduced (*a*) the bluish solution corresponds practically to a stoichiometric ML complex, (*b*) the green solution corresponds to a mixture of both M_2L and ML complexes, more of the M_2L species being present as the U(VI):arsenazo III ratio is raised, (*c*) the molar absorptivity of the M_2L compound is higher than that of the ML species although the spectra of both systems are practically identical.

Confirmatory ion-exchange experiments

Two 25-ml portions of a green solution (pH 2·1; $C_M = 2{\cdot}4 \times 10^{-3}M$; $C_L = 5{\cdot}5 \times 10^{-4}M$) were prepared by addition of a $1{\cdot}25 \times 10^{-3}M$ arsenazo III (H_8L pure acid form) solution to a 0·020*M* acid-free aged (6–7 yr) uranyl nitrate solution. One portion was percolated slowly (0·1 ml/min) through a combined R–Na/R–Cl two-body column and the other was percolated through an R–Cl layer. In the first system the effluent ML complex from the R–Na was absorbed by the R–Cl layer while in the second the sorption of the ML complex was attempted. About 0·0139 mmole of each type of complex should theoretically have been retained on the corresponding R–Cl layers.

Both column systems were then washed with water and the effluent collected in 100-ml standard flasks. Completeness of washing and hydrolysis of U(VI) were tested for qualitatively with arsenazo III. No U(VI) could be detected in the effluent from the ML layer, thereby proving the quantitative sorption of the complex by the resin as well as the absence of hydrolysis.

Excess of U(VI) not sorbed by the anionic resin was detected from the column with the M_2L complex, and hydrolysis with release of some U(VI) was observed upon prolonged washing of the column. The two layers were washed until the effluent solutions gave a negative test with arsenazo III, then the solutions were made up to the mark with water, carefully mixed and the U(VI) was determined by spectrophotometry with arsenazo III.[6] The uranium on the columns was determined by difference.

In order to check the material balance, the U(VI) sorbed on both layers was determined upon complete desorption and elution of both complexes with concentrated perchloric acid (70%). The elution had to be carried out discontinuously with 10–25 ml batches of perchloric acid every 4–24 hr. Batch fractions of this kind, collected over a week, proved necessary to obtain a virtually quantitative elution of the two complexes. The uranium in the collected effluent was determined by fluorimetry. The results are shown in Table 2.

Table 2. Uranium analysis based on the material balance of anion-exchange sorption of green and bluish arsenazo III–U(VI) complex solutions (absolute amount of arsenazo III sorbed in both cases: 0·0139 mmole)

	Uranium found, *mmole*			
	Green feed solution		Bluish feed solution	
Resin system	direct method eluate (fluorimetry)	indirect method (uranyl balance)	direct method (fluorimetry) eluate	indirect method (uranyl balance)
R–Cl	0·0192	0·0238	—	—
R–Na/R–Cl	—	—	$0{\cdot}139_5$	$0{\cdot}138_6$

The results indicate the validity of the hypothesis that M_2L and ML uranyl–arsenazo III complexes exist. As might be expected, the U(VI) analysis by the indirect mass balance gives more accurate results ($C_M : C_L = 1{\cdot}71$) than the direct fluorimetric approach based on the elution of the sorbed complex ($C_M : C_L = 1{\cdot}38$), because of the losses of U(VI) by hydrolysis in the latter determination.

Despite the imprecision of the results it seems safe to conclude that the M_2L complex has a real existence.

Ion-exchange experiments for the determination of the net anionic charge and inner-sphere composition of the ML complex

The anionic complex ion has the general formula $UO_2H_n(H_mL)^{(2+n)-(8-m)}$, where H_8L is arsenazo III. An attempt was made to determine n and m by ion-exchange experiments. The same resin types and green feed solutions used in the preliminary experiments were used again. The results are shown in Table 3. There were a number of unavoidable experimental inconsistencies which are summarized below.

(*i*) The purity of the arsenazo III cannot be established with sufficient certainty, because different methods of analysis give rather large discrepancies. It was therefore assumed to be 100% pure.

(*ii*) Though freshly-prepared acid-free uranyl nitrate solutions give normal ion-exchange with Na^+ and Cl^- ions, corresponding aged (several years) solutions have been shown to undergo an anomalous cation-exchange process whereby an "apparent" charge of $\pm(3{\cdot}7 \pm 0{\cdot}1)$ is observed.[8]

(*iii*) Excess of U(VI) present in the green M_2L complex feed solution undergoes exchange with Na^+ ions on the R–Na column when giving rise to the bluish ML solution. The sorption of Na^+ ions plus anionic ML complex onto a second R–OH exchanger layer does not, however proceed normally, since instead of equivalent exchange of the ML complex (setting free the corresponding amount of OH^- while Na^+ percolates unchanged into the effluent solutions together with OH^- ions) insoluble sodium uranates are formed on the R-OH layer. Thus it is impossible to establish satisfactorily any mass balance.

(*iv*) The anomalies connected with the inconsistent cation-exchange of aged acid-free uranyl solutions seem to constitute a general phenomenon.

Table 3. The determination of the net ionic charge and composition of the M_2L and ML uranyl–arsenazo III complexes

Resin system[a]	Feed solution[b] Volume, *ml*	Arsenazo III, *mmole*	U(VI), *mmole*	NO_3^-, *mmole*	Sorbed species	Consumption of titrant[c] Reagent	*N*	*ml*	*mmole*	Apparent charge[d]	Complex inner-sphere type
R–Cl	25	0·0225	0·070	0·14	M_2L	$AgNO_3$	0·100	2·35	0·235	−4·2	$(UO_2)_2L^{4-}$
R–Cl	25	0·0225	0·070	0·14	M_2L	$AgNO_3$	0·100	2·44	0·244	−4·6	$(UO_2)_2(OH)L^{5-}$
R–Na[e]	15	0·0134	0·042	0·084	U(VI)	flame photometric determination of sodium ion effluent			0·152	−2·0[e]	$(UO_2)(H_4L)^{2-}$
R–Na/R–OH	50	0·045	0·14	0·28	—[f]	HCl	0·100	0·52	0·052	—[f]	insoluble uranates sorbed on the R–OH resin
R–Na/R–Cl	50	0·045	0·14	0·28	ML	$AgNO_3$	0·100	5·65	0·565	−6·3	$(UO_2)L^{6-}$
R–Na/R–Cl	50	0·045	0·14	0·28	ML	$AgNO_3$	0·100	6·68	0·668	−8·6	$UO_2(OH)_2L^{8-}$
R–Na/R–Cl	50	0·045	0·14	0·28	ML	$AgNO_3$	0·100	6·02	0·602	−7·1	$UO_2(OH)L^{7-}$
						flame photometric determination of Na^+			0·664	−5·0	$UO_2(HL)^{5-}$

[a] Dowex 2 × 8 (anionic resin); Dowex 50W (cationic resin). Both resins 50–100 mesh.

[b] pH = 2·1; $C_M = 2{\cdot}4 \times 10^{-3} M$; $C_L = 5{\cdot}5 \times 10^{-4} M$.

[c] Titration of effluent plus washings.

[d] Problematic values as derived from inconsistencies associated with the anomalous cation-exchange behaviour of aged acid-free uranyl nitrate solutions.[8]

[e] The anomalous +3·7 apparent charge of uranyl stated earlier[8] is confirmed (aged acid-free uranyl solution). Assuming this anomalous value a net charge of −2 is calculated for the complex, while a value of −5 is calculated assuming a normal +2 charge for the uranyl ion.

[f] The extremely low OH^- concentration in the effluent indicates the practically quantitative hydrolysis of U(VI)[8] on the R–OH layer together with the quantitative sorption of the anionic complexes.

[g] Different results and interpretations are obtained depending on whether the calculations are based on the Cl^- or Na^+ effluent concentrations, thereby indicating further inconsistencies associated with the assumptions of normal equivalent ion-exchange processes.

(*v*) A further important problem is the real nature of the green complex feed solution since on long standing a dark-green precipitate is produced. Dilution of this solution minimized but did not prevent the precipitation. It is possible that this problem could be circumvented by resorting to much greater dilutions but this approach was not attempted for practical reasons. On the other hand it is hard to be sure whether the main soluble green compound of the feed solutions behaves semicolloidally or as a true ionic compound.

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SEPARATION OF PLATINUM AND PALLADIUM WITH SILICONE-RUBBER FOAM TREATED WITH DIMETHYLGLYOXIME

D. C. GREGOIRE and A. CHOW
Department of Chemistry, University of Manitoba, Winnipeg, Manitoba, R3T 2N2, Canada

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Summary—Open-pore silicone-rubber foam is shown to be a good inert solid support for column separations. Foams treated with dimethylglyoxime were studied for their adsorption of platinum and palladium from solution. The separation of platinum and palladium was achieved in solutions containing as little as 1·0 ppm.

The use of porous polymeric materials as rigid supports in chromatography was first reported by Hollis[1] who used polystyrene in gas chromatographic columns. Open-pore polyurethane foam gas-chromatographic columns[2] have also been prepared by placing a mixture of the polymer precursors in the column and allowing the foaming process to take place.

Bowen[3] introduced the use of open-pore polyurethane foams for the extraction of metals from solution as well as the removal of some organic compounds in low concentration from aqueous solution. These foams have also been used for the extraction and concentration of polychlorinated biphenyls[4] and other pesticides[5] from aqueous media as well as the recovery of gold[6] from thiourea solutions.

Specially treated polyurethane foams[7] have been developed for use in the separation of palladium and nickel by reverse-phase partition chromatography. A novel method for the extraction of mercury from aqueous solutions with sulphide-treated polyurethane foam has been reported.[8]

Techniques for the production of ion-exchange foams[9] and redox foams[10] as well as investigations into the nature[11] of the chemical reactions taking place in these foams have been reported by Braun *et al.*

Reports on the use of support-bonded silicones[12] for the extraction of organochlorines from water and the chemical properties of some aminoalkyl polysiloxanes[13] used as stationary phases in gas chromatography have appeared in the recent literature. However, none have appeared describing the use of silicone foams as an inert support for chromatographic separations.

Many techniques[14] have been developed for the separation of platinum and palladium in aqueous media. Anion-exchange [15,16] has been used to achieve a quantitative separation of the two metals by the use of Dowex-1 resin. Solvent extraction[17,18] also has extensive application for the separation of the noble metals. Methods of separating platinum and palladium by partition chromatography on cellulose columns[19,20] have been reported, but since only macro amounts of metal can be separated, these techniques have found only limited application in analytical chemistry. Separation schemes based on paper chromatography,[21,22] however, can separate easily microgram quantities of the metals. Separations at the microgram level have also been achieved on columns packed with Poracil C[23] and Daiflon.[24]

Separation of the two metals by selective precipitation of the hydrous oxides from hot bromate solutions has been reported.[25] Many oxime reagents have also been used for this separation.[26] Dimethylglyoxime[27] has been used successfully for the separation of the two metals in solutions containing concentrations of metal as low as 5 ppm.

TAL 22/4–I

This paper reports a study of the separation of platinum and palladium by dimethylglyoxime-treated silicone-rubber foam. The separation of platinum and palladium in solutions containing from 10 to 100 ppm platinum and from 1 to 10 ppm palladium is discussed.

EXPERIMENTAL

Apparatus and reagents

Perkin–Elmer model 306 atomic-absorption spectrophotometer.
Varian–Techtron hollow-cathode lamps.
Fisher Accumet model 520 digital pH-meter.
Soxhlet extraction apparatus.
Dow Corning S-5370 RTV silicone rubber foam.
All chemicals used were of reagent grade. The water was distilled twice and then demineralized.

Preparation of standard and sample solutions

Stock 1000-ppm Pd(II) solution was prepared by dissolving $PdCl_2 . 2H_2O$ (Johnson Matthey) in 0·1*M* hydrochloric acid. Stock 1000-ppm Pt(IV) solution was prepared by dissolving $H_2PtCl_6 . 6H_2O$ (Baker Platinum of Canada) in 0·1*M* hydrochloric acid. More dilute solutions were obtained by dilution with 0·1*M* hydrochloric acid. Sample solutions were brought to the desired pH with sodium hydroxide or hydrochloric acid.

Preparation of silicone-rubber foam

The silicone-rubber foam was produced from a Dow Corning product called Silastic S—5370 RTV. The kit consisted of a clear liquid catalyst (stannous octoate) and a more viscous brown foam-base mixture. The foam base was found to contain polydimethylsiloxane and powdered silica used as an inert filler. A solution was made of foam base and carbon tetrachloride (1:1 v/v). To every 500 ml of this solution were added 5·0 g of activated carbon, which served as a decolorizing agent. This mixture was left to stand for 5 hr after which it was passed, with suction, through a bed of finely divided silica gel. The clear solution that resulted was then rotary-evaporated at steam temperature until the then opaque solution contained about 5% v/v carbon tetrachloride. The purified foam-base solution was now ready to be used in the production of silicone rubber foams, by mixing 6 parts by weight of the catalyst with every 100 parts by weight of prepared foam base. The foaming chamber consisted of a glass cylinder 30 mm in diameter and 125 mm in length, the inner surface of which was coated with a film of poly(vinyl chloride). One end of the cylinder was stoppered by means of a rubber plug also coated with poly(vinyl chloride). The plastic film prevented the foam from sticking to the walls of the glass cylinder while itself being separable from the finished foam.

Into the foaming chamber were placed 5·0 g of foam base and the appropriate amount of stannous octoate catalyst. After thorough mixing of the two components with a stirring rod for 15 sec, the foam was allowed to cure for 1 hr before being removed from the mould. After 24 hr of additional curing at room temperature, the foam was cut into 4·6-cm lengths and stored in a covered glass beaker.

Cleaning of foams

It was observed that the catalyst (stannous octoate) would cause the reduction and precipitation of palladium by itself; thus before the foams could be expected to give reproducible results, the catalyst that remained trapped in the polymer matrix had to be removed. To accomplish this, the unwashed silicone rubber foams were placed in *aqua regia* and allowed to soak for 30 min. The foams were saturated with the solution by squeezing out the trapped air bubbles with the base of a measuring cylinder. After soaking, the foams were removed from the *aqua regia* and washed several times with demineralized doubly distilled water. The foams, which had become brown, were extracted with acetone in a soxhlet extractor for 1 hr. The white foams which resulted were pressed free from excess of acetone, air-dried for 12 hr and then stored in a covered glass beaker. The foams produced by this method were pure white and had a pore size of between 0·5 and 1·0 mm. The average density of the foam changed from 0·109 g/cm^3 before washing to 0·163 g/cm^3 after the cleaning process. The washing procedure caused a 13% shrinkage, thus reducing the length from 4·6 to 4·0 cm and the width from 3·0 to 2·7 cm.

Separation procedure

A dimethylglyoxime-treated silicone-rubber foam was placed in a 2·4-cm diameter glass column so that the foam fitted tightly at the base of the column. Ten ml of hydrochloric acid of appropriate concentration were pipetted onto the column. A slight vacuum was applied to the mouth of the column and released when no more air bubbles could be seen rising to the surface.

To minimize dilution of the test solution on its addition to the column, the hydrochloric acid was drained to the level of the top of the foam. Fifty ml of test solution were then pipetted into the column and allowed to flow through the foam. An investigation of palladium adsorption by the treated foam as a function of flow-rate indicated that maximum adsorption could be achieved at a flow-rate of 0·35 ml/min. Once the level of the test solution reached the top of the foam, an additional 10·0 ml of hydrochloric acid was added and allowed to flow through the column. A slight air-pressure was then applied to the column to force any residual solution from the foam into the sample flask

Effect of pH

A cleaned silicone-rubber foam was placed in a beaker containing 50 ml of a saturated solution of dimethylglyoxime in acetone. Trapped air bubbles were expelled from the foam as before. After 6 hr, the foam was removed from the solution and pressed between two sheets of filter paper to expel excess of dimethylglyoxime solution, and then air-dried for 24 hr.

Loose particles of dimethylglyoxime were removed by washing five times with 20-ml portions of demineralized doubly distilled water. The foam was dried for 24 hr, and stored in a sealed polythene bag.

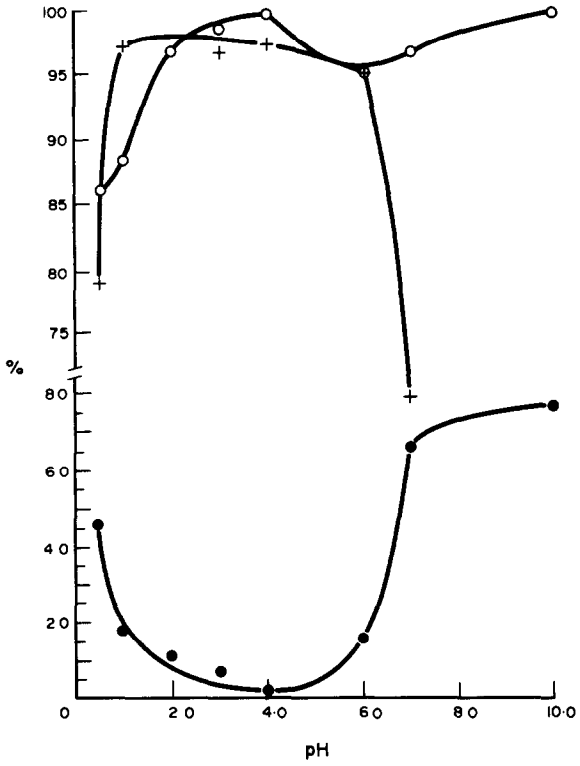

Fig. 1. Adsorption of platinum and palladium by dimethylglyoxime-treated silicone-rubber foam *vs.* pH of solution (+ palladium retained, %; O platinum retained, %; ● palladium leached, %).

For each pH studied, the sample and rinse solutions were brought to the same pH. All test solutions consisted of 50·0 ml of 9·85 ppm palladium and 10·0 ppm platinum in hydrochloric acid. The flow-rate was kept at 2·0 ml/min.

The fraction of palladium adsorbed onto the foam was determined in each case by measuring the concentration of palladium remaining in the test solution. The fraction of platinum recovered was taken to be the sum of the fraction retained in the test solution and the fraction recovered from the foam by the wash solution. Wash solutions consisted of 100·0 ml of hydrochloric acid of appropriate concentration. The fraction of palladium leached from the loaded foam was also measured by estimating the amount of palladium in the 100·0 ml of wash solution, and comparing this with the amount of palladium adsorbed onto the foam.

Figure 1 shows that in all three cases, for palladium extraction, palladium leached by the wash solution, and for platinum recovery, a pH of 4·0 provides an optimum operating pH for the complete separation of platinum and palladium.

When 50·0 ml of a test solution containing 10·0 ppm platinum in 0·01*M* hydrochloric acid are passed through a dimethylglyoxime-treated silicone-rubber foam, a small amount (3–7%) of the metal is absorbed onto the foam. To recover this platinum from the foam, 100·0 ml of hydrochloric acid of the appropriate concentration are passed through the foam at a flow-rate of 1·0 ml/min. The amount of platinum recovered is reported as the sum of the platinum found in the test solution and that found in the wash solution.

The sample solutions were analysed for metal content by direct aspiration into the air–acetylene flame of an atomic-absorption spectrophotometer. Concentrations of the sample solutions were determined by comparison against several standard solutions of known concentration. The matrix of all standard and blank solutions was matched as closely as possible to the matrix of the sample solution. All experiments were run in triplicate and the results reported as an average of these together with the average deviation.

Separation of platinum and palladium

Solutions containing various concentrations of platinum and palladium were passed through dimethylglyoxime-treated silicone-rubber foams. Each experiment consisted of a single pass through the foam at a flow-rate of 0·35 ml/min. All solutions were made up in $10^{-4}M$ hydrochloric acid.

Table 1 shows that good palladium retention was obtained in every case when 50·0 ml of test solution were used. Although results were low when the platinum/palladium concentration ratio was 10:1, retention was quantitative when this ratio was 100:1. The concentration of platinum in the solution does not seem to effect the adsorption of palladium onto the foam.

When 1·0 litre of 0·1-ppm palladium solution was passed through a foam, a low extraction of only 13·7% resulted. This was probably due to the large volume of solution used, which dissolved much of the dimethylglyoxime out of the foam, making the foam inert towards palladium after some of the solution had been eluted.

Recovery of platinum was quantitative (>99%) in every case with the exception of those solutions containing 100·0 ppm platinum.

Table 1. Separation of platinum and palladium by dimethylglyoxime-treated silicone-rubber foam

Total volume of test solution, *ml*	Palladium concentration, *ppm*	Platinum concentration, *ppm*	Palladium retained, %	Platinum recovered, %
50·0	9·85	100·0	97·6 ± 0·8	98·1 ± 1·5
50·0	9·85	30·0	98·0 ± 0·7	99·6 ± 1·2
50·0	9·85	10 0	99·7 ± 0·2	99·6 ± 1 1
50·0	1·0	100·0	100·0 ± 0 0	97 1 ± 1·1
1000·0	0·1	1·0	13·7 ± 1 0	102 6 ± 1 6

The palladium adsorbed onto the foam could be easily recovered with 200·0 ml of 8*M* nitric acid passed through the foam at a flow-rate of 10·0 ml/min. Table 2 shows that recovery is quantitative when the acid solution is kept at 50°.

Effect of other ions on the adsorption of palladium

The metal ions investigated were those thought to occur most commonly with palladium, notably other noble metals and some base metals.

Solutions already containing 9·85 ppm palladium and 10·0 ppm platinum were made up to contain additionally 100- and 1000-ppm concentrations of the foreign metal ion. All foreign metal solutions were made up from 10,000-ppm stock solutions of the metal chloride, with the exception of silver (the nitrate was used)

Fifty ml of each of these solutions were passed through a dimethylgloxime-treated silicone-rubber foam in the usual manner. All solutions were made up in $10^{-4}M$ hydrochloric acid with the exception of iron which were made up in 0·01*M* acid to avoid precipitation of the hydroxide, and silver for which 0·01*M* nitric acid was used Platinum could not be included in a solution of nitric acid since the nitrate of platinum does not exist under normal conditions and precipitation occurs. Palladium nitrate was produced by evaporating to dryness several times a solution of palladium chloride in 8*M* nitric acid.

Table 2. Recovery of palladium from loaded dimethylglyoxime silicone-rubber foam with 8*M* nitric acid at 25° and 50°

Volume of 8*M* nitric acid, *ml*	Temperature, °C	Palladium recovered %
50·0	25	88·5 ± 2·5
50·0	50	88·0 ± 0·1
100·0	25	94·9 ± 1·8
100·0	50	94·6 ± 0·2
150·0	25	97·7 ± 1·4
150·0	50	98·2 ± 0·2
200·0	25	97·9 ± 1·5
200·0	50	100·9 ± 0·4

Table 3. Effect of various metal ions on the adsorption of palladium by dimethylglyoxime-treated silicone-rubber foam

Metal ion	Concentration, *ppm*	*pH*	Palladium retained, %
—	—	4·0	99·7 ± 0·2
Ni^{2+}	1000	4·0	99·6 ± 0·5
Ni^{2+}	100	4 0	99·6 ± 0·5
Fe^{2+}	1000	2·0	0·9 ± 0·1
Fe^{2+}	100	2·0	0·7 ± 0·1
Fe^{2+}*	100	5·0	98·3 ± 0·5
Cu^{2+}	1000	4·0	100·0 ± 0·0
Cu^{2+}	100	4·0	99·1 ± 1·2
Cr^{3+}	1000	4·0	92·3 ± 2 2
Cr^{3+}	100	4·0	99·2 ± 0 0
Pb^{2+}	1000	4·0	91·8 ± 1·3
Pb^{2+}	100	4·0	99·0 ± 0·4
Ag^{+}†	1000	2·0	93·3 ± 0·7
Ag^{+}	100	2·0	97·2 ± 0·6
Pt^{4+}	100	4·0	97·6 ± 0·8
Pt^{4+}	10	4·0	99·7 ± 0·2
Rh^{3+}	10	4·0	99·0 ± 0·1
Ir^{4+}	10	4·0	99·0 ± 0·1

* Contained 2·5 g of sodium potassium tartrate per 50·0 ml of solution.

† Silver nitrate used; nitric acid substituted for hydrochloric acid.

From the amount of palladium remaining in each solution after a single pass through the foam, the fraction of palladium adsorbed onto the foam was calculated and the effect of each metal on that process was evaluated. The results are listed in Table 3.

At the 1000-ppm level, iron, chromium, lead and silver substantially reduced the adsorption of palladium by the treated foam. Under the experimental conditions used here, none of these ions forms a complex with dimethylglyoxime, thus the lower adsorption of palladium metal could be attributed to a "blocking effect" caused by the high concentration of foreign metal ion in solution. Iron, however, forms a complex with palladium and almost completely hinders the complexation of palladium with dimethylglyoxime, even at a concentration of 100 ppm. A releasing agent was used (sodium potassium tartrate) and at 100 ppm of iron, a good palladium extraction was achieved. No other ions interfered extensively with palladium extraction at the 100-ppm level. This indicates that solutions containing iron, chromium, lead and silver in appreciable concentrations (*i.e.*, greater than 100 ppm) must first be freed from these metal ions. In addition, the nitrate form of palladium lent itself well to adsorption by the treated foam. This is illustrated in the case where silver was the foreign ion under study.

DISCUSSION

This work shows that silicone-rubber foam can be used as a solid support for chromatographic separations. An attractive feature of these foams is their chemical stability in mineral acids. Foams soaked in *aqua regia* for 24 hr showed no signs of disintegration or deformation. Concentrated sulphuric acid, however, completely dissolve the foam on contact.

The foams were re-used as many as ten times without showing any noticeable changes in the flexibility or in the dimensions of the foam. Foams were recycled by subjecting them to the normal wash procedure.

Dimethylglyoxime-treated silicone-rubber foams provide an easy means of separating platinum and palladium. Quantitative results are obtained for samples containing a moderate concentration of palladium (*i.e.*, greater than 0·1 ppm). Prior separation of other noble metals accompanying platinum and palladium is unnecessary. The complexed palladium metal can be quantitatively recovered with little effort.

For quantitative separation on 50·0 ml solution, a minimum time of about 4 hr is needed. However, since few operations are required, many samples could be run simultaneously. If base metals are present, removal of these is essential to the efficiency of the separation.

Because of the moderate solubility of dimethylglyoxime, only small volumes of samples can be handled, necessitating preconcentration if the volume of solution exceeds 100 ml.

The capacity of the dimethylglyoxime-treated silicone-rubber foam for adsorption of palladium chloride was determined under the normal experimental conditions to be 0·53 mg of palladium per g of treated foam.

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SIMULTANEOUS DETERMINATION OF TOTAL, NON-CARBONATE AND CARBONATE WATER HARDNESSES BY DIRECT POTENTIOMETRY

I. SEKERKA and J. F. LECHNER

Department of the Environment, Canada Centre for Inland Waters, Burlington, Ontario, Canada

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Summary—Total, non-carbonate and carbonate water hardness have been determined simultaneously by manual and automated direct potentiometry, using the bivalent ion-selective electrode, and known addition–known dilution technique. The automated and programmable system produces direct print-out of total, non-carbonate and carbonate water hardnesses. The optimum sampling rate is 20 samples per hour. This time-saving method compares well with the standard method.

The determination of various types of water hardness is of great technical importance and is a frequent constituent of the routine analysis of water samples. The development of automated direct potentiometry and known addition–known dilution technique combined with the capability of the bivalent cation electrode to sense activities of calcium and magnesium ions and the complexation of calcium and magnesium ions by carbonate and bicarbonate led to the development of the method described in this paper.

Total hardness is defined here, in accordance with ASTM,[1] as a characteristic of water generally accepted to represent the total concentration of calcium and magnesium ions and is commonly expressed in terms of ppm $CaCO_3$. Carbonate hardness is that part of the total hardness which disappears on boiling: it is represented by bicarbonates of calcium and magnesium which are precipitated as carbonates on heating. The difference between the carbonate and total hardness is called non-carbonate hardness. These terms replace the formerly used terms "temporary" and "permanent" hardness.[2]

The methods for determining total water hardness are based, generally, on the complex-forming ability of EDTA, *e.g.*, the titration in the presence of Eriochrome Black T indicator,[3,4] potentiometric titration monitored by a water-hardness electrode,[5] and the automated colorimetric method.[6,7]

Orion Research-Inc., also recommends direct determination of water hardness by combining the measurements of water-hardness activity and specific conductance, with a nomogramic estimation of a correction factor to calculate the water hardness concentration.[5] Martin and Poudou found a good agreement between the complexometric and ion-selective electrode methods.[8]

The procedure for determining non-carbonate hardness requires boiling (20–30 min), cooling and filtering of the sample, followed by a complexometric titration.[9]

EXPERIMENTAL

Reagents

All chemicals were of reagent grade. Demineralized doubly distilled water was used.

Apparatus

The equipment used in this study included a bivalent cation liquid ion-exchanger electrode (Orion Model 92-32) and a double-junction reference electrode (Orion 90-02-00). The results reported were obtained with a modified version of the automated apparatus for direct potentiometry described previously.[10–12] The apparatus consisted of a Fisher 9-319-50 thermostated electrode-elevator and turntable assembly, a Desaga peristaltic pump, a multichannel peristaltic cassette pump (Manostat), PAX millivoltmeter with BCD output (Sargent-Welch S-29998) interfaced to a Wang 600 minicomputer and a printer. All the signals necessary for timing and controlling the components originated in a control module of our own design.[11] A block diagram of the equipment assembly is shown in Fig. 1.

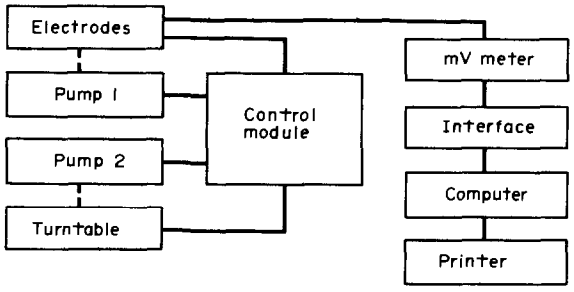

Fig. 1. Block diagram of equipment assembly.

The on-line computer treatment of potentiometric measurements provides a direct print-out in ppm of water hardness and eliminates additional graphical and mathematical operations. The computer program used has the following functions:

(1) memorization of the standard data (mV of water-hardness electrode in standard solution);
(2) memorization of the sample data (mV reading in the sample);
(3) memorization of the data after known addition;
(4) memorization of the data after 1:1 dilution; and
(5) computation, print-out, and indexing of total, carbonate and non-carbonate water hardness (ppm).

Figure 2 is a flow chart for the computer program. The complete listing of the program can be obtained from the authors on request.

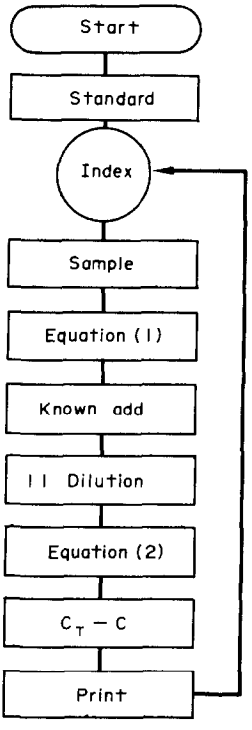

Fig. 2. Flow chart for the computer program.

Procedures

Manual. All consecutive mV readings were taken after waiting for electrode equilibrium. A sample aliquot (50·0 ml) was pipetted into a 150-ml beaker and stirred magnetically. The electrodes were immersed and an initial reading (*A*) was taken, followed by an addition of 0·5 ml of standard solution, containing 2·0 mg of calcium carbonate at pH 7·0. The second reading (*B*) was taken. After dilution of the sample with 50·0 ml of distilled water and taking of the third reading (*C*), the non-carbonate hardness was obtained from reading *A* by using the calibration curve.[5] The total hardness was calculated from the readings *A*, *B* and *C* by a nomogramic procedure.[13] The difference between these two values gave the carbonate hardness.

Automated. A standard solution (50·0 ml in a 200-ml beaker) containing the equivalent of 100 ppm $CaCO_3$ was placed in the first position of the turntable, followed by water samples (50·0 ml). The apparatus carried out automatically the immersion of the electrodes, stirring, reading and memorizing the standard data, rinsing of the electrodes and changing of the samples, reading and memorizing the sample data, known addition (0·5 ml of the solution containing 2·0 mg of calcium carbonate at pH 7·0), memorizing the reading, 1:1 dilution and

memorizing the reading, computation, indexing and printing the ppm of total, non-carbonate and carbonate water hardnesses after the preselected time period (2, 3, 6 or 12 min).

Non-carbonate water hardness was calculated according to equation (1) for direct potentiometry

$$C = C_S\left[\text{antilog}\left(\frac{E_0 - E_1}{29{\cdot}5}\right)\right] \tag{1}$$

where C is the non-carbonate hardness of the sample, C_S is the ppm of $CaCO_3$ in the standard, E_0 is the potential of the standard, E_1 is the potential of the sample.

Total water hardness was obtained by solving equation (2) for known addition–known dilution technique, involving a 1:1 sample dilution with water.[13]

$$C_T = C_A\left[\left\{\text{antilog}\left(\frac{\Delta E \log 2}{E_2 - E_3}\right)\right\} - 1\right]^{-1} \tag{2}$$

where C_T is the total water hardness of the sample, C_A is the ppm of $CaCO_3$ of the addition before it is added to the sample, ΔE is the potential difference between initial and final millivolt values when the addition is made, E_2 is the potential after the known addition, and E_3 is the potential after the 1:1 dilution.

RESULTS AND DISCUSSION

The determination of total water hardness connot be achieved by direct potentiometry because of the complexation of calcium and magnesium ions by carbonate and bicarbonate. The potential of the water hardness electrode, immersed in a water sample, corresponds to the free calcium and magnesium concentration, and therefore possibly to the non-carbonate (permanent) hardness.

On the other hand, the known-addition technique eliminates the difficulties encountered in solutions with high background concentration of other ions or complexing agents and facilitates the determination of the total concentration of an analyte in a complex system. This technique has been successfully applied for the determination of total hardness.[11]

The carbonate (temporary) hardness is represented by the amount of calcium and magnesium that can stoichiometrically be considered bound to carbonic acid, and can be obtained by subtraction of non-carbonate hardness from total water hardness.[9] In more practical terms, it is the amount of cations precipitated on boiling. It can, however, be assumed that this amount may also be equivalent to the complexed or bound amount of cations that is not sensed by direct potentiometry.

These three facts lead us to the assumption of possible determination of the non-carbonate hardness by direct potentiometry, the total hardness by known-addition technique and of the calculation of the carbonate hardness by subtraction. Theoretical treatment of this assumption based on the comparison of the solubility products and stability constants of participant ions is difficult to discuss, because of the uncertainties involved in the operational definitions, lack of information and because of the varying concentration ratio of calcium and magnesium in water. The large difference of the solubility products of $CaCO_3$ (5×10^{-9}) and $MgCO_3$ (1×10^{-5}) illustrates the complication.

In order to verify this assumption, a series of synthetic water samples of different water hardnesses was analysed by the standard EDTA titration method for total[1] and carbonate[14] hardness and the results were compared with those obtained by the proposed manual method. As can be seen from Table 1, the correlation of both methods is very good.

Table 1. Comparative analysis of synthetic samples

Calculated total hardness of the sample, *ppm*	Found,* *ppm*			
	Total hardness		Carbonate hardness	
	EDTA titn.	Electrode	EDTA titn.	Electrode
5	4	4	1	1
10	8	7	2	3
50	38	39	12	11
100	80	83	20	17
500	410	415	90	85

* 10 determinations at each concentration

The results showed that the amount of calcium and magnesium ions precipitated by boiling (carbonate hardness), is practically equivalent to the amount of calcium and magnesium ions bound to carbonate and bicarbonate ions in the primary sample.

Among major impurities of water samples, sulphate and phosphate ions are potentially interfering substances, owing to their known complexation of calcium and magnesium ions.[15] The interference of sulphate and phosphate ions was determined by the measurements of calcium ion activity in $1 \times 10^{-3}M$ calcium solutions in the presence of various concentrations of sulphate and/or phosphate ions. The results, summarized in Fig. 3, show that the interference by carbonate ions is much more significant than the interference caused by the sulphate and phosphate ions. Concentrations of sulphate and phosphate ions, equimolar with the calcium concentration, do not affect the potential of the electrode, whereas the interference by carbonate ions is well pronounced at a molar ratio lower than $[CO_3^{2-}]:[Ca^{2+}] = 0{\cdot}1$. It is obvious that the sulphate and phosphate ions at the levels usually found in the majority of natural waters ($10^{-7}M$ PO_4^{3-}, $10^{-4}M$ SO_4^{2-}) do not interfere. Chelating compounds such as EDTA, NTA, tartrate, *etc.*, interfere, of course. However, the concentration of such substances in natural waters is well below a hundredth of that of total bivalent cations and as a result they do not affect the hardness analysis in any significant manner.

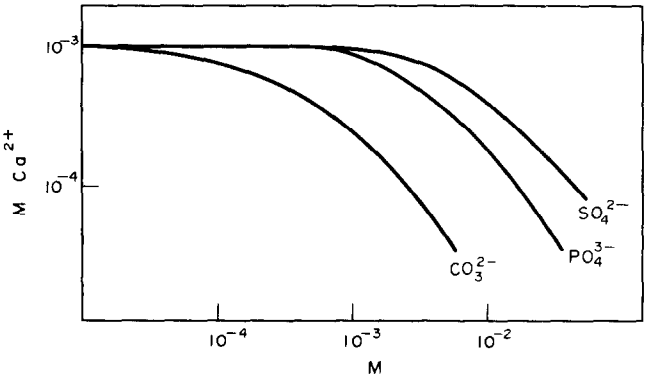

Fig. 3. Interference of CO_3^{2-}, SO_4^{2-} and PO_4^{3-} in the measurement of $1 \times 10^{-3}M$ Ca^{+2}.

The practical application of the proposed method has been verified by the determination of total carbonate and non-carbonate hardness for a variety of natural and industrial water samples and by the comparison of the results with those obtained by the standard method. The results given in Table 2 again show very good agreement of both methods. A sampling rate of 20 samples per hour was found to be optimal.

On a single sample basis, the manual procedure is at least 30 min shorter than the conventional method (20 and 50 min). The conventional serial analysis of 20 samples using simultaneous boiling, cooling and filtration of 20 samples plus successive measurements

Table 2. Determination of water hardness in actual water samples

Sample no.	Total hardness, *ppm*		Carbonate hardness, *ppm*		Non-carbonate hardness, *ppm*	
	EDTA titn.	Electrode	EDTA titn.	Electrode	EDTA titn.	Electrode
1	10	10	—	—	10	10
2	15	15	5	4	10	11
3	17	16	—	1	17	15
4	25	24	5	4	20	20
5	41	42	11	10	30	32
6	68	69	16	16	52	53
7	83	81	21	18	62	63
8	97	98	27	25	70	73
9	135	133	42	39	93	94
10	252	255	131	130	121	125

by titration takes about 100 min, against 20 automated measurements at 3 min each for a total of 60 min. From these facts, it follows that the present method allows a sufficiently accurate automated and simultaneous determination of total, non-carbonate and carbonate water hardnesses to be performed with a considerable saving of time. The manual procedure with its inherent simplicity, inexpensiveness and speed is most convenient for the analysis of small numbers of samples, and *in situ* measurements, whereas the automated system improves the overall economy of serial analysis of large numbers of water samples.

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TRACE METAL ANALYSIS OF ROCKS BY FLAMELESS ATOMIC-ABSORPTION SPECTROMETRY WITH A METAL MICRO-TUBE ATOMIZER

KIYOHISA OHTA and MASAMI SUZUKI®

Department of Chemistry, Faculty of Engineering, Mie University, Kamihama-cho, Tsu-shi, Mie-ken, Japan

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Summary—Flameless atomic-absorption spectrometry with a metal micro-tube atomizer has been studied. The element to be determined was atomized by electrical heating of the micro-tube in an inert atmosphere within a glass chamber. A detailed study of the atomic-absorption characteristics of the micro-tube atomizer is presented. The absolute sensitivities were $2{\cdot}6 \times 10^{-12}$, $2{\cdot}9 \times 10^{-11}$, $2{\cdot}5 \times 10^{-10}$, $1{\cdot}1 \times 10^{-10}$ and $1{\cdot}4 \times 10^{-10}$ g for copper, cobalt, aluminium, palladium and selenium, respectively. The interferences of cations were studied for determination of cobalt and copper. Cobalt and copper in rock samples were determined in order to evaluate the metal micro-tube atomizer.

Flameless atomic-absorption spectrometry has become increasingly useful for trace analysis. The graphite-tube furnace and the carbon-rod atomizers are commercially available. Both require a high-voltage power supply. Use of a metal strip or filament as atomizer simplifies the power supply because only a low current and voltage are needed for the electrical heating.[1–5] However, the filament position relative to the light-beam from the hollow-cathode lamp is critical for sensitivity because of the variation in atom populations with height above the filament.

In this paper, a metal micro-tube atomizer is described and characterized. With it, only short heating is needed to provide an environment with uniform temperature throughout the atomizer. It requires only low power and in an enclosed system shows higher sensitivity, better reproducibility and lower tendency to matrix effects than does the unenclosed filament atomizer. This paper also describes the analysis of rocks for cobalt and copper to illustrate the application of the micro-tube atomizer.

EXPERIMENTAL

Apparatus

Atomizer. The atomizer is shown in Fig. 1. It is fabricated from molybdenum sheet for long life. The bore is 0·5 mm and the overall length 17 mm. A 0·3-mm hole is drilled at the midpoint to enable sample solution to be placed in the tube. The ends of the tube are clamped firmly in the copper supports by means of two bolts. A stainless-steel slit (0·5 mm) is positioned in front of the tube to provide a narrow beam of light about 0·5 mm in diameter. The atomizer is enclosed in a glass chamber,[1] on which silica end-windows are sealed. The glass

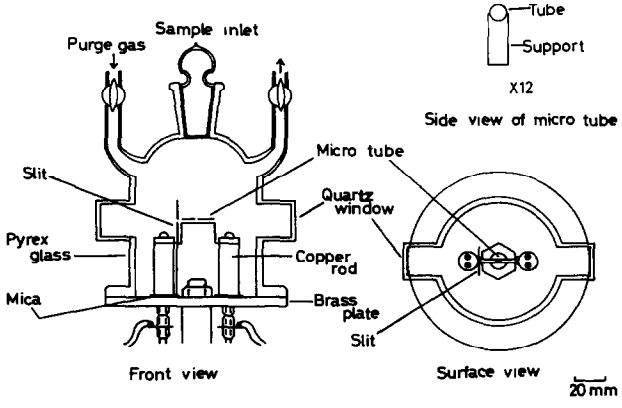

Fig. 1. Metal micro-tube atomization apparatus.

chamber is flushed with inert gas to protect the atomizer from oxidation by entrained air. The radiation from the hollow-cathode lamp enters the atomizer after passing through the slit, followed by further focusing onto the entrance slit of the monochromator. The atomizer serves as collimator. The atomizer is heated electrically by connecting the copper supports to a stepdown transformer, giving 0–4 V across the micro-tube with a maximum-load current of 50 A. The atomizer is heated uniformly with this unit without condensation of atomic vapour in the ends of the tube. Switching is done with a manual double-pole double-throw switch, and timing is done with a stopwatch. The temperature of the atomizer can be measured with an optical pyrometer.

Spectrometer. A Nippon Jarrell–Ash Ebert-type monochromator fitted with an HTV R-106 photomultiplier was used. The entrance slit-width of the monochromator was 0·1 mm, corresponding to a spectral bandpass of 0·02 nm. The output from the photomultiplier was recorded on a Hitachi 056–1001 recorder (0·4-sec full-scale deflection) and peak-height was measured for analysis. The amplifier of the detection system was of the usual type for flame spectrometry. The hollow-cathode lamps were modulated electronically at 90 Hz. A deuterium lamp was used for background correction. Atomic-absorption measurements were performed at 324·8, 240·7, 309·3, 196·1 and 244·8 nm for copper, cobalt, aluminium, selenium and palladium, respectively. All sample injections were done with a laboratory-made glass micropipette to prevent contamination from metals. Rock samples were decomposed in Uni-seal decomposition vessels.

Reagents

Standard stock solutions. Prepared from high-purity metals. Dilute standard solutions were freshly prepared just before use.

DDTC (sodium diethyldithiocarbamate) solution, 2% *w/v.*

"Coniferron" (o-nitrosoresorcinol monomethyl ether) solution, 0·04% *w/v in carbon tetrachloride.*

Reagents were of analytical grade. All water was first distilled and then passed through a mixed cation-anion exchange resin.

Measurement technique

The sample solution (5 μl) was placed in the micro-tube atomizer by means of glass micro-pipette. The tube was switched on at low power (0·5–0·8 V, 14–20 A) to evaporate the solvent from the sample slowly. The current was switched off and the voltage increased to that determined to be optimum for the interested element. The tube current was then turned on to atomize the sample. All atomic-absorption signals were recorded. The height of the absorption peak was measured.

RESULTS AND DISCUSSION

Atomizer characteristics

Effect of inert-gas flow-rate on signal. The absorption signals are shown in Fig. 2 as a function of flow-rate of argon. Hydrogen (20 ml/min for 0·46 l./min of argon) was added because it gave more effective atomization of the elements. Hydrogen was effective in preventing oxidation of the atomizer by traces of oxygen in the argon. The absorption signals were not much influenced by increasing flow-rate of argon except for copper and palladium, the copper absorption being lowered with increase in the argon flow-rate, and that for palladium having a maximum.

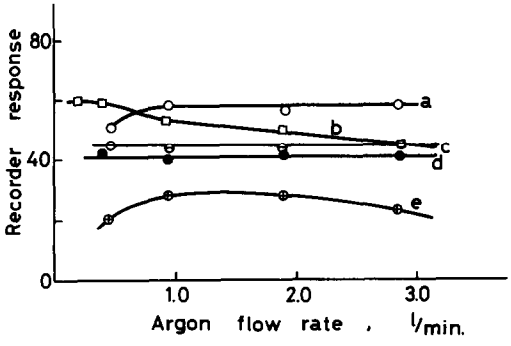

Fig. 2. Effect of argon flow-rate on atomic-absorption signal (chloride salts used): *a*, Al 12 ng (2500°); *b*, Cu 0·1 ng (1800°); *c*, Se 5 ng (2500°); *d*, Co 1·0 ng (2500°); *e*, Pd 3·5 ng (2200°).

Effect of tube temperature. The atomic absorption of five elements at different temperatures is shown in Fig. 3. Copper, cobalt, palladium and selenium all had an optimum temperature, the profiles resembling those obtained with a filament atomizer. For aluminium, a temperature above the melting point of molybdenum may be needed for effective atomization. The response time of the electronic circuitry used was not short enough to permit accurate recording of rapid atomization of elements at higher temperature. This is one of the reasons for the apparently lower absorption at higher temperature. Thermal expansion of the inert gas in the micro-tube will also be partly responsible for the temperature effect,

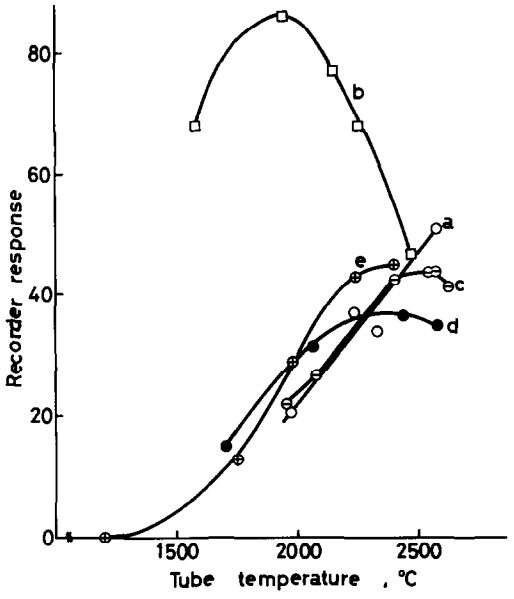

Fig. 3. Effect of micro-tube temperature on atomic-absorption signal (chloride salts used; argon flow-rate 0·46 l/min) *a*, Al 12 ng; *b*, Cu 0·1 ng; *c*, Se 5 ng; *d*, Co 1·0 ng; *e*, Pd 3·5 ng.

resulting in rapid diffusion of atoms from the open ends of the atomizer. Similar temperature effects were found with the filament atomizer.[1,6,7] Hwang *et al.*,[6] described the contribution of various factors to decrease in sensitivity with the filament atomizer at higher temperature: slow response of detection system to rapid generation of free atoms (discussed also by Cantle *et al.*[5]), thermal expansion of the sheathing gas and consequently lower concentration of gaseous analyte atoms, increased turbulence, and possible line-broadening.

Table 1. Sensitivities (1% absorption) for metal micro-tube atomizer

Element	Line, *nm*	Sensitivity, *g*
Cu	324·8	$2{\cdot}6 \times 10^{-12}$
Co	240·7	$2{\cdot}9 \times 10^{-11}$
Al	309·3	$2{\cdot}5 \times 10^{-10}$
Se	196·1	$1{\cdot}4 \times 10^{-10}$
Pd	244·8	$1{\cdot}1 \times 10^{-10}$

Sensitivity. The sensitivity for five elements was tested under optimized conditions and found to be about one order of magnitude better than with the filament atomizer (Table 1).

Accuracy and reproducibility. The accuracy was determined by analysis of vitamin B12 solutions for cobalt. The recovery was 100 ± 10% at a cobalt level of 1·8 μg/ml. The reproducibility was determined by measuring repetitively a standard solution of copper. The coefficient of variation was 2% for 5×10^{-10} g of copper. Reproducibilities were similar for other elements.

No memory effect was observed provided the tube was heated at 2500° in an atmosphere of hydrogen before the sample was added. Zero absorption at non-absorbing lines close to the absorbing lines showed that the signals at the absorbing lines originated purely from atomic absorption.

Interferences. Interferences by various metals were tested for cobalt and copper (Table 2). All samples were checked for background effects, which are probably due to molecular absorption or light-scattering. No background was observed for copper but a correction

Table 2. Interferences in determination of cobalt (2·5 ng) and copper (0·1 ng) with the metal micro-tube atomizer

Interfering element†	% Change of cobalt signal*		% Change of copper signal*	
	200-fold‡	1000-fold‡	200-fold‡	1000-fold‡
Al	+14	−12	−24	−76
Ca	−8	−58	−5	−8
Co	—	—	+6	−17
Cr	+13	−58	+24	+14
Cu	0	−31	—	—
Fe	−6	−8	−15	+21
Mg	+42	−16	−16	+14
Mo	−19	−57	−68	−66
Na	−15	−51	0	−23
Ni	−18	+11	0	−21
Pb	−6	0	−30	−25
Sn	+9	−27	−25	−15
V	−15	−51	0	−15
Zn	+24	−24	0	−22

* Background corrections made for interfering elements
† Chlorides used, except for Mo (MoO_4^{2-}) and V (VO_4^{3-}).
‡ Ratio (w/w) of interferent to determined.

was necessary for cobalt. Almost all the elements tested showed depression or enhancement effects on cobalt and copper. Similar interferences were observed with the filament atomizer. The mechanism of the interferences appears to be complex and is difficult to elucidate at the present stage.

Determination of cobalt and copper in rocks

Attempts to determine cobalt and copper in rock samples directly were unsuccessful; the large salt concentration prevented an accurate determination of the trace metals. Therefore, the cobalt and copper were separated from the matrix salts by solvent extraction.

Procedure. Samples of 0·5–1 g were treated with nitric and hydrofluoric acids in Uni-seal decomposition vessels and heated for 2·5 hr in an oven at 120°. After the decomposition, the solution was evaporated in a Teflon beaker by heating on a water-bath, and the evaporation repeated twice more with addition of hydrochloric acid in between. Finally, the residue was dissolved in water and cobalt and copper were extracted from separate samples by the following procedures. For cobalt, the coniferron complex was extracted with 5 ml of carbon tetrachloride solution of coniferron from 5 ml of solutions (adjusted to pH 8 with citrate buffer solution) by shaking for 10 min, followed by extraction with 5 ml of carbon tetrachloride. The organic phases were combined for analysis. For copper, the DDTC complex was extracted into 5 ml of carbon tetrachloride from 5 ml of solution (adjusted to pH 9 with citrate buffer solution) by shaking for 10 min. Only one extraction was needed for copper.

Aliquots (5 μl) of organic phase were introduced into the micro-tube atomizer; cobalt and copper were atomized by heating at *ca.* 4 V (35 A) for 10 sec and *ca.* 3 V (40 A) for 10 sec, respectively. These correspond to micro-tube temperatures of 2500° and 1800° respectively. Analytical working curves were constructed with standard solutions subjected to the same preparation procedure as the rock samples.

Some results for standard rock samples are listed in Table 3. The small sample size taken is not recommended, because of inhomogeneity of the samples. Lower results were obtained by extraction of the DDTC complex for cobalt, presumably because of interference by co-extracted elements. Coniferron[8] gives better results.

Table 3. Cobalt and copper analyses on standard rock samples

Sample	Cobalt, *ppm*		Copper, *ppm*	
	Found	Reported*	Found	Reported*
JG-1 (Granodiorite)	3·9 ± 0·3 (3)	3·87–<20	3·2 ± 0·2 (5)	3–16
USGS-G-2 (Granite)	4·7 ± 0·1 (3)	2–21	8·3 ± 0·5 (5)	<2–17
USGS-GSP-1 (Granodiorite)	4·5 ± 0·5 (4)	<3–22	29·8 ± 1·0 (4)	15–54

Values given in parentheses are number of determinations.
* Figures from U.S. Geological Survey and Geological Survey of Japan.

The metal micro-tube atomizer is simple to fabricate and requires only low power for heating. The good sensitivities and precision suggest that this atomizer should have widespread application in atomic-absorption spectrometry. However, a preliminary selective extraction is preferable for improving the accuracy in analysis of complex samples such as rocks. Further investigation is being made of application of this device to analysis of various types of samples.

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SHORT COMMUNICATIONS

DIRECT COMPLEXOMETRIC DETERMINATION OF ALUMINIUM IN "ALZINOY"

(*Received* 30 *July* 1974. *Accepted* 12 *October* 1974)

"Alzinoy" (a binary alloy of aluminium and zinc) is extensively employed in the galvanizing of steel. The concentration of aluminium in the zinc bath is critical, owing to the role of aluminium in controlling the formation of iron–zinc alloy and the surface quality of the finished zinc coating.

The ASTM method[1] for determining aluminium in zinc-base alloys employs a time-consuming mercury cathode separation before the gravimetric determination either as oxide or the hydroxyquinolinate. Some methods have been based on the determination of zinc by EDTA and subtraction from 100% to obtain the aluminium content. This approach is subject to error owing to the presence of lead and iron in "Alzinoy". The use of lead and Xylenol Orange for back-titration of EDTA, and the masking of aluminium with fluoride, have long been known, and have been described by, amongst others, Přibil and co-workers,[2] and are now utilized for determination of aluminium in the zinc alloy.

EXPERIMENTAL

Reagents

Hexamine.

Xylenol Orange indicator solution, 0·1% aqueous.

Standard EDTA solution, 0·01M. Standardize with high-purity bismuth metal (99·999%), Pyrocatechol Violet being used as indicator, according to Schwazenbach's method.[3]

Standard lead nitrate solution, 0·01M. Dissolve 3·3123 g of $Pb(NO_3)_2$ in water; add a drop of nitric acid and dilute to about 800 ml with water. The pH should be 4; if not, adjust with a drop or so of 2*M* sodium hydroxide. Make up to volume with water in a 1-litre volumetric flask. Alternatively dissolve 2·0721 g of high-purity lead (99·99%) in nitric acid (1 + 1) and adjust the pH to 4 with 2*M* sodium hydroxide before diluting to 1 litre. Standardize by direct titration with EDTA or reverse titration as follows. Pipette 10 ml of EDTA solution into a 250-ml beaker, add 1 ml of 2*M* hydrochloric acid, dilute to 70 ml with water, adjust to pH 4 (close-range pH paper) with 2*M* sodium hydroxide, add 1 g of hexamine and 2 or 3 drops of Xylenol Orange indicator, and titrate with the lead solution.

Ammonium fluoride 10% w/v aqueous solution. Prepare fresh and store in a polyethylene container.

Procedure

Weigh a 0·2-g sample (filings or turnings) into a 150-ml beaker. Add 5 ml of hydrochloric acid (1 + 1) and warm to dissolve. Clear the solution by adding 2 or 3 drops of nitric acid and boil for 1–2 min. Cool and dilute to 100 ml in a volumetric flask. Pipette a 10-ml aliquot into a 250-ml beaker. Add from a burette 40·00 ml of 0·01*M* EDTA. Adjust the pH to 4 with 2*M* sodium hydroxide. Boil gently for 5 min and cool to room temperature, Wash down the inside of the beaker with water. Add 1 g of hexamine and stir to dissolve. Add 7 drops of Xylenol Orange indicator and titrate with 0·01*M* lead solution. The colour change is from yellow to pink.

Then add 10 ml of 10% ammonium fluoride solution and boil gently for 2–3 min. Cool to room temperature and rinse down the inside of the beaker. Titrate the liberated EDTA with 0·01*M* lead solution. The colour changes from a faded pink to a sharp and distinct pink. Record the titration value, *T* ml. Then % Al = $T \times 27{\cdot}98 \times M/S$ where *M* is the lead solution molarity and *S* is the sample weight (g).

RESULTS AND DISCUSSION

Two methods for determining aluminium in "Alzinoy", by difference after electrogravimetric or complexometric determination of zinc, were investigated. Both of these methods provided acceptable accuracy for determining zinc, but when aluminium was computed by difference, considerable errors were found. The presence of both lead and iron (about 0·5% each) also contributed to the inaccuracy.

EDTA forms complexes with zinc, iron, lead and aluminium at a pH of 4–5, but aluminium forms with fluoride a complex of far greater stability than that with EDTA. In the approach reported here, all the elements above are complexed stoichiometrically with EDTA. On addition of fluoride the EDTA combined with the aluminium is released and titrated with standard lead solution.

Synthetic solutions containing zinc, lead, iron and aluminium were prepared. A known excess of EDTA was added. After adjustment of the pH to 4 the solution was heated (90°) for 20 min to complete the complex formation between EDTA and zinc, lead, iron and aluminium. After buffering with hexamine the excess of EDTA was titrated with standard lead solution, using Xylenol Orange as indicator. Ammonium fluoride was then added and the solution heated (90°) for 20 min. The EDTA liberated from the aluminium complex was titrated with lead solution. Table 1 records the recovery of aluminium in the zinc matrix alone. Table 2 shows the effect of lead and iron on determination of aluminium in the zinc matrix.

Table 1. Recovery of aluminium in zinc

Zn present, *mg*	Al added, *mg*	Al taken, %	Al found, %	$\bar{X}$, %	Rel. error, %
20	1	4·76	4·64, 4·70	4·67	0·6
20	2	9·09	9·05, 9·05, 8·96, 8·92	9·00	1·2
20	3	13·04	12·91, 13·00, 12·80	12·90	1·1

Table 2. Effect of Pb, Fe on determination of Al in zinc

Zn present, *mg*	Pb added, *mg*	Fe added, *mg*	Al added, *mg*	Al taken, %	Al found, %	$\bar{X}$, %	Rel. error, %
20	0·1	0·05	2	9·04	8·90, 9·03	8·96	0·9
20	0·1	0·1	2	9·01	8·94, 8·94, 8·94, 8·89	8·93	0·9
20	0·1	0·2	2	8·98	8·84, 8·84	8·84	1·6

The precision and the relative error are acceptable. There is no appreciable interference from any lead or iron encountered in "Alzinoy".

Zinc, lead and iron form complexes with EDTA instantaneously under the conditions of the procedure. However, the rate of complex formation of aluminium with EDTA is slow and hence it has been a general practice to heat the solution (at ~90°) for about 20 min. It was thought desirable to investigate whether this could be accelerated by boiling the solution. Test solutions were boiled for various times; the results are shown in Table 3.

Table 3. Effect of boiling time on Al–EDTA complex formation

Zn present, *mg**	Al present, *mg*	Al taken, %	Boiling time, *min*	Al found, %
20	2	9·09	5	8·97, 8·95, 8·95, 9·01
20	2	9·09	10	9·06
20	2	9·09	20	9·01

* Plus 0·1 mg each of lead and iron.

It is evident that 5 min boiling is adequate for the complete formation of the Al–EDTA complex. The precision is satisfactory. Analysis of Morris P. Kirk Standard Alzinoy samples gave 10·20% Al for sample 762 (certificate value 10·45%) and 9·70% for sample ZB2 (9·70%).

The method described has been in routine control use for the last 8 years. A suite of 4 samples can be analysed in about 45 min. The method has also been applied satisfactorily for the determinum of aluminium in ferroaluminium.

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Chemical and Metallurgical Laboratories
The Steel Company of Canada Limited
Wilcox Street
Hamilton, Ontario, Canada

OM P. BHARGAVA

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Summary—A simple and precise method for the complexometric determination of aluminium in "Alzinoy" (a binary alloy of aluminium and zinc) is described. After dissolution of the sample in hydrochloric acid, aluminium, zinc and any lead and iron are complexed with excess of EDTA. The excess of EDTA is titrated with lead solution, with Xylenol Orange as indicator. Ammonium fluoride is then added to decompose the Al–EDTA complex, and the EDTA liberated is titrated with lead solution. Four samples can be analysed in about 45 min.

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MULTIPLE NUCLEATION IN THE PRECIPITATION OF NICKEL DIMETHYLGLYOXIMATE FROM HOMOGENEOUS SOLUTION

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Dimethylglyoxime has been widely used for many years as a reagent for nickel. The processes of nucleation and crystal growth in this reaction have been studied by a number of experimental techniques, including electron microscopy[1] and a Coulter counting technique.[2]

Nickel dimethylgloximate has also been precipitated from homogeneous solution.[3] The kinetics of the reaction of biacetyl with hydroxylamine to form dimethylglyoxime, in both the absence and presence of nickel, were studied by Salesin, Abrahamson and Gordon,[4] who proposed the occurrence of multiple nucleation steps. Walton has pointed out that heterogeneous nucleation occurs in this precipitation from homogeneous solution.[5]

The present study was undertaken to examine quantitatively the multiple nucleation and the persistent periods of supersaturated conditions, in the precipitation of nickel dimethylglyoximate from homogeneous solution.

EXPERIMENTAL

Reagents

Hydroxylamine hydrochloride was recrystallized from ethanol containing a small amount of water, dried, and stored over calcium chloride in a vacuum desiccator. Reagent grade nickel sulphate hexahydrate, biacetyl solution, and ammonia were used without purification. Aqueous solutions were prepared in the following concentrations: hydroxylamine hydrochloride, 0·702*M*; nickel sulphate, $2{\cdot}99 \times 10^{-2}M$; biacetyl, $2{\cdot}16 \times 10^{-3}$M.

Apparatus

Measurements of pH were made with a Beckman model 72 pH meter. A Cary model 14 spectrophotometer was used for all spectrophotometric measurements. Electron-microscope observations were made with a Hitachi instrument.

Procedure

The nickel sulphate solution was pipetted into a 100-ml beaker and the desired volume of hydroxylamine solution added. The pH was adjusted to 6·0 ± 0·1 with ammonia solution and the solution transferred quantitatively to a 100-ml volumetric flask. The desired volume of biacetyl solution was added and the final volume brought up to 100 ml. The solution was mixed quickly and the time noted. All reactions were carried out at room temperature.

An aliquot of the reaction mixture was transferred into a 1-cm cell for spectrophotometric measurements. The spectra were recorded from 540 to 580 nm and from 320 to 380 nm every 5 or 10 min for a total of 240 min, and the time of appearance of the red precipitate was recorded. A few drops of the reaction mixture were periodically withdrawn for mounting and electron-microscope observation by conventional techniques.

RESULTS AND DISCUSSION

Spectrophotometry

Dissolved nickel dimethylglyoximate has absorption maxima at 260, 300 and 360 nm ($\epsilon = 1{\cdot}52 \times 10^4$, $3{\cdot}80 \times 10^3$ and $3{\cdot}04 \times 10^3$ $l.mol^{-1}.cm^{-1}$ respectively). No starting material or intermediate reaction product interferes with the absorption at 360 nm, which can be taken as a measure of the concentration of nickel dimethylglyoximate in solution, but it is necesary to correct the apparent absorbance at 360 nm for light-scattering as soon as the first precipitate forms. In separate measurements, it was found that only the scattering is observed at 560 nm and that the ratio of the scatter at 360 nm to that at 560 nm is 0·77. Hence, the corrected absorbance of the dissolved nickel dimethylglyoximate at 360 nm (A) may be calculated from the observed absorbances at 360 and 560 nm (A_{360} and A_{560}):

$$A = A_{360} - 0{\cdot}77A_{560}$$

Typical absorbance *vs.* time curves are shown in Fig. 1. The times of appearance of the red precipitate are given in Table 1, and indicate that the rate of nucleation is dependent on the initial concentrations of nickel and biacetyl. In each series the time for appearance of the red precipitate corresponded to the first maximum on the absorbance *vs.* time curve, which indicates the first burst of nucleation.

The first maxima in Fig. 1 are at supersaturation concentrations several hundred times the equilibrium solubility of nickel dimethylglyoximate as determined by Christopherson and Sandell.[6] To confirm this factor, each reaction mixture was allowed to stand for 48 hr, which was assumed to be sufficient for equilibrium solubility to be reached, and the absorbance of the filtrate was measured at 360 nm for comparison with the maximum on the absorbance *vs.* time curve.

The persistence of supersaturated solutions, along with the occurrence of multiple bursts of nucleation, could explain the low results obtained in determining small amounts of nickel.[7]

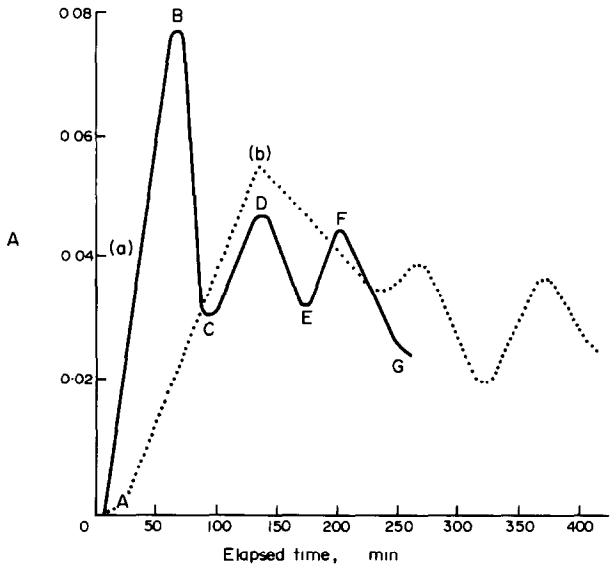

Fig. 1. Concentration of nickel dimethylglyoximate in solution (in terms of absorbance) *vs.* time of reaction. Biacetyl $2{\cdot}16 \times 10^{-4}M$; hydroxylamine $7{\cdot}02 \times 10^{-2}M$; nickel (*a*) $2{\cdot}99 \times 10^{-3}M$, (*b*), $9{\cdot}94 \times 10^{-5}M$.

Table 1. Time of appearance of red precipitate as a function of starting material concentrations

Series	Initial concentrations			Appearance time, *min*
	Ni^{2+}, *M*	Biacetyl, *M*	Hydroxylamine, *M*	
1	$2{\cdot}99 \times 10^{-3}$	$2{\cdot}16 \times 10^{-4}$	$7{\cdot}02 \times 10^{-2}$	55
2	$9{\cdot}94 \times 10^{-5}$	$2{\cdot}16 \times 10^{-4}$	$7{\cdot}02 \times 10^{-2}$	110
3	$2{\cdot}99 \times 10^{-3}$	$2{\cdot}16 \times 10^{-2}$	$7{\cdot}02 \times 10^{-2}$	15

The multiple rises in the curves on Fig. 1 could be due to the rate of crystal growth being slower than the rate of generation of nickel dimethylglyoximate molecules in the solution. In this case, the supersaturation would increase after each burst of nucleation until the next burst of precipitate particles appeared.

Electron microscopy

The precipitated particles were examined at frequent intervals during the precipitation process. Crystals of nickel dimethylglyoximate are needle- or stick-like in appearance and are easily recognizable.[1] With reference to curve *a* in Fig. 1, the following observations were made.

In the first 40 min of reaction, only some amorphous particles were observed. These were also found in the absence of nickel, so cannot be nickel dimethylglyoximate, though they may be involved in its nucleation and may account for the earlier report that nucleation in this process is heterogeneous.[5]

Some needle- or stick-shaped particles appeared shortly before the absorbance reached its first maximum. point B. Thick particles which were present before the maximum, plus many new thin particles, were observed in the region B–C. No new thin particles were observed in the region C–D, in which only thick particles were seen. This alternation continued, new thin particles being observed in the regions D–E and F–G, and only thick ones in the region E–F. There is almost no change in the cross-section of the thick particles from region B onwards, the main change being in the periodic appearance of thin particles and their growth to become thicker ones. This confirms that the growth rate is less than the rate of generation of nickel dimethylglyoximate in solution.

Additional experiments were conducted to determine whether occurrence of multiple nucleation steps in precipitation from homogeneous solution is limited to this particular reaction. By means of particle-counting techniques and electron-microscope observations, it was found that multiple bursts of nucleation do occur, at least under some experimental conditions, in the precipitation of cadmium sulphide by the hydrolysis of thioacetamide, and of barium sulphate by liberation of barium from its EDTA complex by oxidation with hydrogen peroxide.

College of Sciences
Meshed University, Meshed, Iran
ABDOLREZA SALAJEGHEH*

California State College
Dominguez Hills, California 90747, *U.S.A.*
ROBERT B. FISCHER*

* Experimental work done in Department of Chemistry, Indiana University, Bloomington, Indiana.

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Summary—Spectrophotometric measurements of undissociated nickel dimethylglyoximate molecules in solution and electron-microscope observations of the precipitated particles have confirmed and extended previous information on the nucleation of nickel dimethylglyoximate precipitated from homogeneous solution. Supersaturated concentrations several hundred times the equilibrium solubility may persist for as long as 2 hr. Nucleation occurs not all at one initial time but rather in multiple "bursts" spread out over several hours.

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POLAROGRAPHIC REDUCTION OF METHYLENE BLUE IN PRESENCE OF CLAY MINERALS

(*Received* 5 *September* 1974. *Accepted* 17 *October* 1974)

Adsorption of the cationic dye Methylene Blue on clays has been studied by various workers.[1–6] As the dye is known to give a well-defined polarographic wave in buffered media, the effect of clays on its polarographic reduction behaviour was investigated. This paper reports the possibility of estimating the clay fraction by a polarographic method and the results obtained on the binding of the dye on clay particles. The method proposed here is simple, rapid, and needs only small samples.

EXPERIMENTAL

Reagents

Standard clays, bentonite, kaolinite and illite were obtained from Ward's Natural Clay Corporation, New York. The Methylene Blue used was a B.D.H. product. Stock clay suspensions were prepared and converted into the hydrogen form by ion-exchange treatment (Amberlite IR-120) and the particle size was controlled by centrifugation.

Apparatus

A Heyrovský polarograph (Model LP 55 A) was operated manually in conjunction with a Pye Scalamp galvanometer (Model 7903/5). The capillary constant $m^{2/3}t^{1/6}$ was 2·985; the drop time was 3·4 sec (open circuit) and nitrogen was used for deaeration of solutions. All measurements were made at 30 ± 0·01°.

So far no suitable vessel has been developed[7] which could be used for heterogeneous systems, and the vessel used by Beckmann[8] in gas analysis was therefore employed in these studies. In this cell the stream of gas and the circulating solution ensure uniform mixing of the suspension, pumping the solution at constant speed past the electrode, and maintaining of an inert atmosphere. It is worth mentioning that the vessels used for homogeneous kinetic investigations are useless for such systems as they permit investigations of only static solutions.

Preparation of solutions

The requisite amount of dye (effective concentration 1×10^{-3} and $8 \times 10^{-5}M$ in the case of bentonite and $8 \times 10^{-5}M$ in the case of kaolinite and illite) was taken in tubes along with different amounts of the clays and the total volume made up to 20 ml. The pH was adjusted to 2·9, 4·9 and 9·2 (checked by pH-meter) in the case of bentonite–dye suspensions and 2·9 in the case of kaolinite–dye and illite–dye suspensions.

RESULTS AND DISCUSSION

Polarograms of Methylene Blue ($1 \times 10^{-3}M$) in the presence of different amounts of bentonite at pH 2·9, 4·9 and 9·2 are shown in Fig. 1. Similar curves are obtained at a concentration of $8 \times 10^{-5}M$ and also for the polarograms of the dye in presence of varying amounts of kaolinite and illite at pH 2·9. The $E_{1/2}$ values of the dye were found to be −0·02, −0·28 and −0·32 V at pH 2·9, 4·9 and 9·2 respectively, in good agreement with the half-wave potentials reported by Clark,[9] who also found that the $E_{1/2}$ of the normal wave corresponds closely to the oxidation potential of the thermodynamically reversible Methylene Blue system.

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EXPERIMENTAL

Reagents

Standard clays, bentonite, kaolinite and illite were obtained from Ward's Natural Clay Corporation, New York. The Methylene Blue used was a B.D.H. product. Stock clay suspensions were prepared and converted into the hydrogen form by ion-exchange treatment (Amberlite IR-120) and the particle size was controlled by centrifugation.

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Preparation of solutions

The requisite amount of dye (effective concentration 1×10^{-3} and $8 \times 10^{-5}M$ in the case of bentonite and $8 \times 10^{-5}M$ in the case of kaolinite and illite) was taken in tubes along with different amounts of the clays and the total volume made up to 20 ml. The pH was adjusted to 2·9, 4·9 and 9·2 (checked by pH-meter) in the case of bentonite–dye suspensions and 2·9 in the case of kaolinite–dye and illite–dye suspensions.

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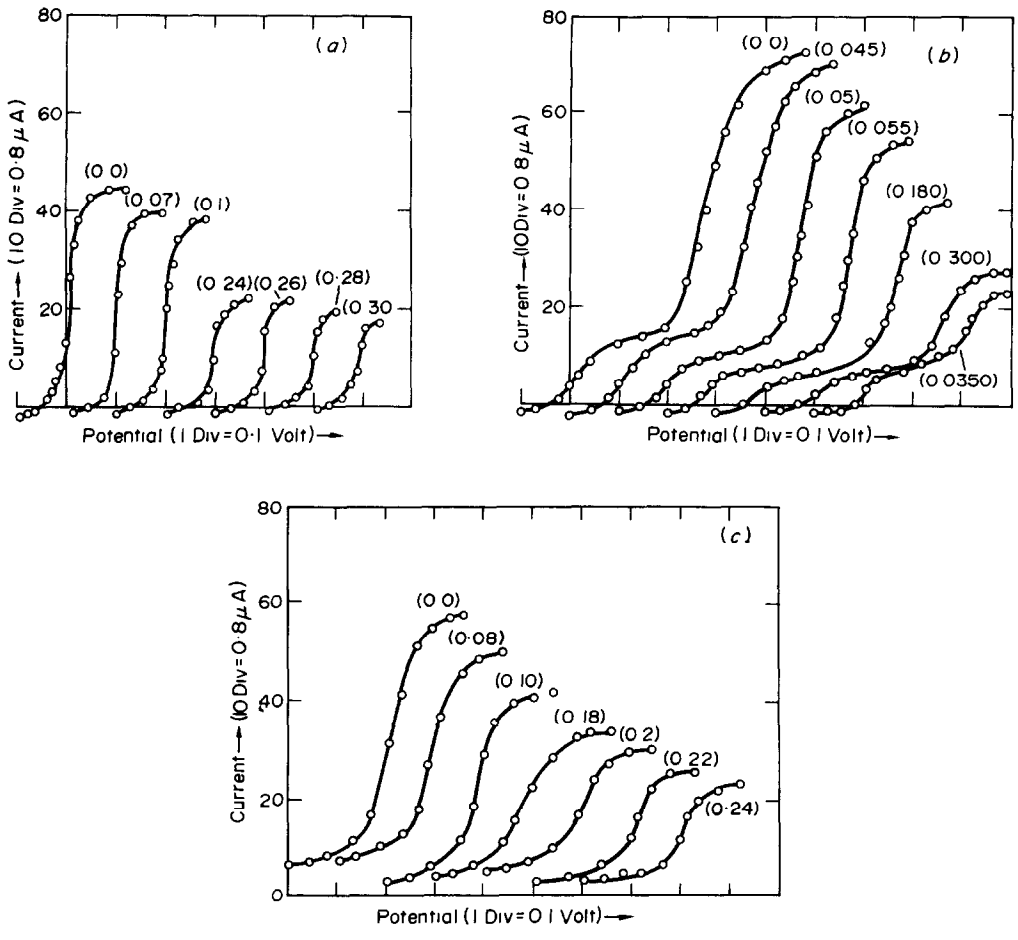

Fig. 1. Polarograms of Methylene Blue ($1 \times 10^{-3}M$) in presence of various amounts of bentonite (g). (*a*) pH 2·9, (*b*) pH 4·9, (*c*) pH 9·2. All curves start at +0·1 V applied potential.

A prewave with $E_{1/2} = -0{\cdot}01$ V is realized at pH 4·9 (Fig. 1*b*). The normal reduction wave disappears below the concentration $6 \times 10^{-5}M$ and therefore a concentration higher than this was chosen for subsequent studies.

The striking features of the reduction of the various clay-dye suspensions are as follows.

(*i*) The diffusion current of the pure dye is considerably reduced in presence of clays. The effect is, however, most pronounced in the case of bentonite, as compared to the other two minerals.
(*ii*) The decrease in the diffusion current increases with gradual increase in the amount of mineral added.
(*iii*) The $E_{1/2}$ of the dye does not change.

A decrease of 1·36 μA, in the diffusion current is observed on adding 40 mg of bentonite whereas reductions of 0·45 and 0·22 μA are obtained by adding the same amount of illite and kaolinite under identical conditions for the dye solution.

Polarograms at pH 4·9 (Fig. 1*b*) show that low amounts of bentonite added decrease the height of the normal reduction wave without causing any effect on the prewave. Higher amounts of this material, however, shift the half-wave potential of the prewave towards the more positive side, along with the decrease in the height of the normal reduction wave.

A linear relationship is found between the decrease in wave height ($i_{d_o} - i_d$) and the amount of mineral present. It is thus possible to calculate the amount of free dye (from the values of i_d/i_{d_o}) as well as the amount of dye bound to the clay particles. The amount of dye bound to bentonite at different concentrations and pH are given in Tables 1 and 2.

It is observed that the amount of dye bound to bentonite is abnormally high if the solution is as concentrated as $1 \times 10^{-3}M$. Factors such as aggregation of dye molecules at such high concentrations, and multiple adsorption, account for this behaviour. As suggested by Bergmann and O'Konski[10] there is a greater probability of the binding of aggregated species than monomers on the crystal surface. At lower concentration of the dye ($8 \times 10^{-5}M$) and the dye–clay ratio mentioned in Table 2, the binding is small, being of the same order as required for exchange adsorption. Thus when the dye concentration is initially low there is no physical adsorption and even a single polarographic measurement can give an estimate of exchange capacity.

The amount of bound dye is also found to increase with increase in pH. This can be explained by assuming that the edges acquire a negative charge[11] at higher pH (through broken Si–O and Al–O bonds) with the result that more of the cationic dye is adsorbed.

Table 1. Distribution of Methylene Blue (initial concentration $1 \times 10^{-3}M$)

pH	Amount of bentonite added, g	Concentration of free dye, $10^{-3}M$	Concentration of bound dye, $10^{-3}M$
2·9	0·07	0·83	0·17
	0·10	0·78	0·22
	0·24	0·47	0·53
	0·26	0·40	0·60
	0·28	0·30	0·70
	0·30	0·28	0·72
9·2	0·08	0·71	0·29
	0·10	0·66	0·34
	0·18	0·47	0·53
	0·20	0·45	0·55
	0·22	0·38	0·62
	0·24	0·32	0·58

Table 2. Distribution of Methylene Blue at pH 2·9 (initial concentration $8 \times 10^{-5}M$)

Amount of bentonite added, g	Concentration of free dye, $10^{-5}M$	Concentration of bound dye, $10^{-5}M$
0·12	6·80	1·20
0·16	6·24	1·76
0·40	3·84	4·16
0·45	3·36	4·64
0·50	2·88	5·12
0·55	2·40	5·60

Various mixtures of bentonite, illite or kaolinite with a non-clay material were prepared. These samples had different cation-exchange capacities depending on the amount of non-clay material present in them. Polarograms of Methylene Blue ($8 \times 10^{-5}M$, pH 2·9) in the presence of these samples were taken and a linear relationship was found between the mineral content of these samples and the decrease in the diffusion current ($i_{d_o}-i_d$). This goes to show that the reduction of Methylene Blue in the presence of various clays or soil samples can possibly be used in estimating the clay content and its exchange capacity, and in the identification of various minerals. Further work in this direction is in progress.

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Chemistry Department
University of Roorkee
Roorkee, U. P., India

S. K. Srivastava
Pushpati Razdan

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Summary—Clay–Methylene Blue suspensions have been examined polarographically. The degree of binding of the dye on the clay particles has been calculated. The possibility of using the data in estimating the clay content of a sample and identifying the mineral is suggested.

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ZERO-CURRENT BIPOTENTIOMETRIC END-POINT INDICATION WITH PRETREATED ELECTRODES—III

MATHEMATICAL SIMULATION OF THE TITRATION CURVES

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A zero-current bipotentiometric indication technique based on pretreatment effects on noble metal electrodes has been reported from this laboratory,[1] by which redox titrations have been followed by using a pair of platinum[2] or gold[3] electrodes, Fe(II) being titrated. The bipotentiometric titration curves obtained for different conditions of pretreatment and titrants could be divided according to their shape into four categories.[3] A qualitative explanation for the shape of these curves has been advanced.[1–3] This paper presents an approach to the quantitative analysis of these curves.

As the electrodes are connected directly to the measuring instrument, the bipotentiometric titration curves appear as the difference of the sigmoidal potentiometric curves exhibited by each of the indicator electrodes used. Therefore the corresponding function $\phi(x)$ of the bipotentiometric titration curves can be obtained as the difference of functions $f(x)$ and $g(x)$:

$$\phi(x) = f(x) - g(x) \tag{1}$$

these latter representing the usual titration functions of the electrodes, *i.e.*, their transference functions. Pretreatment of an electrode generally changes the slope, the potential break near the equivalence point and the relative position with respect to the x and/or y axes. Thus $g(x)$ can be considered as being obtained by the elementary transformation of $f(x)$:

$$g(x) = \alpha f(\beta x + \gamma) + \delta \tag{2}$$

The function $g(x)$ is evaluated in two steps. First, starting from function $f(x)$ (see Fig. 1) a new function $f(\beta t + \epsilon)$ is obtained by using the transformation $x = \beta t + \epsilon$ so that the interval $[a'b']$ is transformed into an interval $[c,d]$:

$$[c,d] = \frac{(1-\beta)b' + (1+\beta)a'}{2}, \frac{(1+\beta)b' + (1-\beta)a'}{2} \tag{3}$$

ϵ being a function of β. It is easy to see that $[a'b']$ and $[c,d]$ have the same mid-point. As the second step we transform these functions by using the parameter θ. Thus for each set of α and β values a set of $g(x)$ functions is obtained:

$$g(x) = \alpha f(\beta x + \epsilon + \theta) \tag{4}$$

with θ varied. Hence γ in equation (2) is equal to $\epsilon + \theta$, when δ is zero. Values of θ are given in terms of Δ (Fig. 1):

$$\Delta = \frac{m + m'}{2} \tag{5}$$

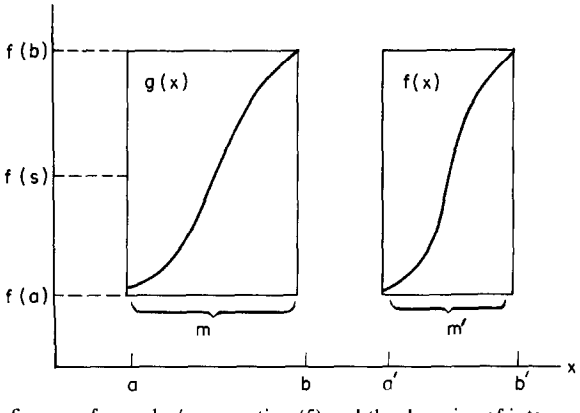

Fig. 1. Significance of m and m' in equation (5) and the domains of interpretation.

For experimental reasons α and β may take the values

$$0 < \alpha < 1; \alpha = 1; 1 < \alpha$$
$$0 < \beta < 1; \beta = 1; 1 < \beta$$

For a given β we considered $\theta < -\Delta$, $\theta = -\Delta$, $-\Delta < \theta < 0$, $\theta = 0$, $0 < \theta < \Delta$, $\theta = \Delta$, $\Delta < \theta$. For numerical calculations the exact functions of the potentiometric titration curves with real parameters could not be used because of their complexity. Therefore in order to obtain different possible curve-forms for $\phi(x)$ [equation (1)] a simulation procedure was adopted, taking for $f(x)$ a function that was simpler but still possessing the properties of a real potentiometric titration curve: inflexion point, break near this point, slope, *etc.* Function $g(x)$ differs from $f(x)$ by one or more of the parameters represented by α, β, γ and δ in equation (2). The functions used were

$$f(x) = \sqrt{x^2 + x - 1} - \sqrt{x^2 - x + 1} \tag{6}$$

and

$$g(x) = \alpha\sqrt{(\beta x + \gamma)^2 + \beta x + \gamma - 1} - \sqrt{(\beta x + \gamma)^2 - \beta x + \gamma + 1} \tag{7}$$

respectively. Displacement of $g(x)$ relative to $f(x)$ along the y axis was not considered [$\delta = 0$ in equation (2)], having no physical meaning. The domains of interpretation of the functions were also restricted, it being considered that $f(a') = \text{constant} = 0$ for $x = a'$, and $f(b') = \text{constant}$ for $x = b'$ respectively. In our case we considered $a' = 0$; $b' = 2$; $\alpha \epsilon \{1; 1.5\}$; $\beta \epsilon \{0.75; 1; 1.5\}$ and $\theta \epsilon \{-\Delta - \frac{2}{3}; -\Delta; -\frac{\Delta}{2}; 0; \frac{\Delta}{2}; \Delta; \Delta + \frac{2}{3}\}$. The curves plotted for such conditions were considered to represent the characteristic part of a titration curve, and were used for the construction of the differential curves. Following this procedure 42 $g(x)$ functions were computed (Olivetti Programma 101) and by graphical subtraction the corresponding overall titration curves were generated. The main results are as follows.

A. (*i*) $\alpha = \beta = 1$. The $f(x)$ and $g(x)$ curves are identical but not superimposed along the x-axis, the displacement being given by γ. If $\gamma = 0$, $f(x) = g(x)$ and $\phi(x) = 0$ (Fig. 2, curve 1).

This case could not be realized in practice (see, *e.g.*, Fig. 1 in reference 1). Even with apparently identical electrodes there always exist small differences in the potential-determining parameters α, β, and γ, resulting in a bipotentiometric signal at the end-point.

(*ii*) $\gamma > 0$. For small γ values $\phi(x)$ has the form of the first derivative of $f(x)$ (Fig. 2, curve 2.). In several cases very sharp peaks have been obtained experimentally. With increasing γ the $\phi(x)$ curves become less sharp. These forms have not been obtained, denoting that pretreatment effects cause only small potential lags between the electrodes during the titration.

(*iii*) $\gamma < 0$. The same situation as before, with the difference that the peaks of the resulting differential curves are oriented downwards. In all these cases the $\phi(x)$ curves are symmetrical.

B, $\alpha = 1$ but $\beta \neq 1$, that is $g(x)$ is extended or compressed along the x-axis relative to $f(x)$. In this case the $\phi(x)$ curves have much the same shape as before but they are no longer symmetrical. Similar forms have been obtained for $\beta < 1$ (0·75) or for $\beta > 1$ (1·5), respectively. From these forms curves corresponding to $\gamma \leqslant \Delta/2$ have also been obtained in practice. An increase in the lag between the basic curves results in less sharply differential curves which are not encountered in practical zero-current bipotentiometric titrations. For negative values of γ the same curves appear but oriented downwards. Generally when $\alpha = 1$ there appear $\phi(x)$ curves which are similar to the first derivative of a sigmoidal potentiometric curve, but only when the lag between the basic curves is small. Under our simulation conditions this is the case when $0 < \gamma < \Delta$. In cases *A* and *B* second-derivative forms do not appear.

C. $\alpha > 1$. β is equal to, greater or less than 1. This means that $g(x)$ is modified relative to $f(x)$ with respect to the y-axis also (except for parallel displacement). For small values of γ the $\phi(x)$ curves obtained had some intermediate forms between those of the first and second derivatives of a normal potentiometric curve (Fig. 3, curve 1). In the titrations performed so far, types similar to that corresponding to $\Delta/2$ (Fig. 3) have most frequently been encountered. For γ values less than $\Delta/2$, $\phi(x)$ approaches the form of the second derivative. Meanwhile many intermediate forms appear, *e.g.*, those of types II and IV (see reference 3). Nevertheless the practical curves have sharp peaks suggesting only a small lag between the basic curves. When $\alpha < 1$, $f(x)$ and $g(x)$ change their role, resulting in the same $\phi(x)$ forms as before.

In conclusion, using the model functions indicated, we have been able to simulate the zero-current bipotentiometric titration curves encountered in practice so far, but reality is more complex. The exact form of a potentio-

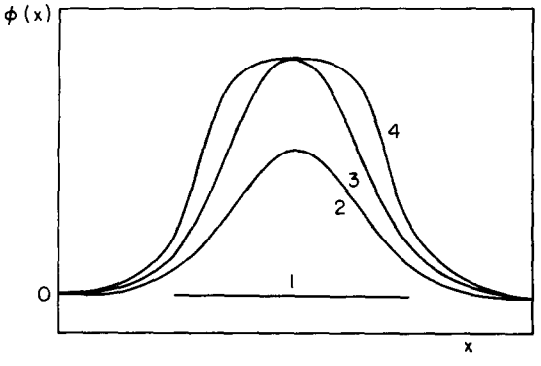

Fig. 2. Representation of $\phi(x)$ for $\alpha = \beta = 1$ and different values of γ:
1 − 0; *2* − $\Delta/2$; *3* − Δ; *4* − $\Delta + 4$

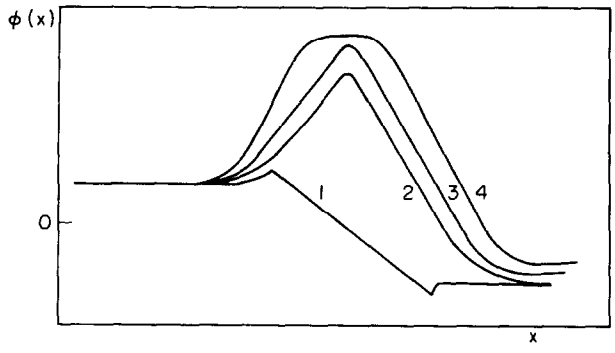

Fig. 3. Representation of $\phi(x)$ for $\alpha > 1$ and $\beta \leqq 1$ and different values of γ as in Fig. 2.

metric curve is influenced in a more complex way by pretreatment and real titration parameters than in the treatment by relatively simple functions used here. This is illustrated by the great number of intermediate curve forms actually obtained. But this does not affect the essence of the problem, the reasons for the appearance of zero-current bipotentiometric titration curves obtained with differently pretreated electrodes. The present results reveal the contribution of each individual transfer function of the electrodes to the appearance of a particular bipotentiometric titration curve.

Department of Analytical Chemistry L. KÉKEDY
Babeş-Bolyai University
Str. Arany J. nr. 11
Cluj, Romania
Mathematical Institute P. NEY
Romanian Academy of Sciences
Str. Republicii nr. 35
Cluj, Romania

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Summary—A mathematical model is described which simulates the appearance of the bipotentiometric titration curves obtained experimentally with two differently pretreated indicator electrodes. Simplified equations are used to calculate the individual potentiometric curves, and the bipotentiometric curve is obtained by difference, as corresponds to the experimental technique.

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RAPID POLAROGRAPHIC METHOD FOR DETERMINATION OF ARSENIC IN FERROTUNGSTEN

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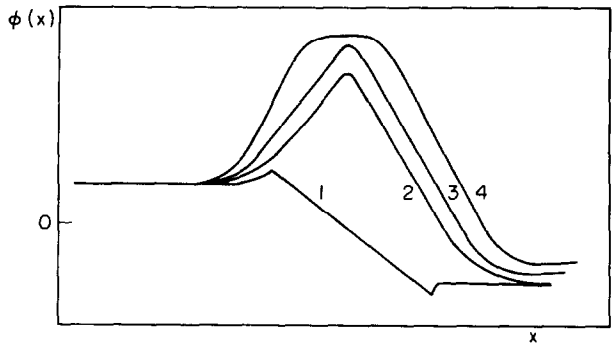
Methods for the determination of micro- or macroamounts of arsenic in ferrous alloys are usually based on three steps: oxidative attack of the sample, quantitative separation of the arsenic to eliminate interfering elements by extraction,[1] distillation[2] or co-precipitation,[3] and subsequent determination of the arsenic by a gravimetric, volumetric, spectrophotometric or polarographic method.[4] The Russian Standard method[5] for arsenic in ferrotungsten involves decomposition of the sample with sodium peroxide, treatment with thioacetamide to separate the arsenic as sulphide, and a spectrophotometric determination as molybdenum blue. For content of 0·1 and 0·002% the precision of the method is 20 and 50% respectively



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Department of Analytical Chemistry L. KÉKEDY
Babeş-Bolyai University
Str. Arany J. nr. 11
Cluj, Romania
Mathematical Institute P. NEY
Romanian Academy of Sciences
Str. Republicii nr. 35
Cluj, Romania

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The British Standard method[6] involves evolution of arsenic and its absorption in a pyridine solution of silver diethyldithiocarbamate. The precision is 50 and 3% for contents of 0·003 and 0·15% arsenic respectively.

Although many other methods have been reported,[7] none is sufficiently rapid, accurate and sensitive for routine determination. This paper describes a sensitive and accurate determination of arsenic in ferrotungsten, suitable for routine control analysis.

EXPERIMENTAL

Apparatus

Polarograms were recorded with Heyrovský Polarograph model LP-60, using a mercury electrode with a drop time of 2·97 sec in 0·1*M* potassium chloride and $m = 4{\cdot}65$ mg/sec. A saturated calomel reference electrode was used for all measurements, in conjuction with a 0·033*M* sodium sulphate bridge.

Reagents

Concentrated hydrochloric, nitric and sulphuric acids; saturated potassium metabisulphite solution; 8% ascorbic acid solution; 0·1% Methyl Orange solution; citrate buffer (2·5*M*) prepared by dissolving 105 g of citric acid monohydrate in hot distilled water, cooling and diluting to 200 ml and neutralizing carefully with solid sodium hydroxide to pH = 3·0; 1% gelatine solution, freshly made at frequent intervals; 0·1*M* mangenese sulphate; arsenic-free iron (less than 0·001% arsenic). Standard arsenic solution (0·01*M*) was prepared by dissolving about 0·25 g of arsenic trioxide (~95% pure) by boiling it with 100–150 ml of redistilled water and then diluting to the mark in a 250-ml volumetric flask. It was standardized by the bromate method.[15] Ten ml of the stock solution were diluted to 100 ml with redistilled water to give (in our case) $9{\cdot}28 \pm 0{\cdot}03 \times 10^{-4}M$ standard solution. The standard arsenic solution may be prepared by dissolving higher purity As_2O_3 (0·2473 g) in 5 ml of 5% sodium hydroxide solution, neutralizing with sulphuric acid (1 + 1) and diluting the solution to 250 ml.

Procedure

Weigh 0·5–1 g of ferrotungsten into a porcelain crucible and ignite it in a muffle furnace at 800° for 2 hr. Transfer the sample to a 100-ml beaker, add 15–30 ml of *aqua regia* ($HCl:HNO_3$, 3:1), cover with a watch-glass and heat on a sand-bath for 30 min. Raise the watch-glass and add more *aqua regia* if necessary. Cool to room temperature, wash the watch-glass with water and remove it. Add 10 ml of sulphuric acid (1 + 1), heat to fuming, cool, dilute with 10–14 ml of distilled water and again heat gently until fumes of sulphuric acid appear. Add 5–7 ml of potassium metabisulphite solution and 5 ml of redistilled water and evaporate almost to dryness. Repeat the treatment with metabisulphite, then add 5–10 ml of water and heat on a sand-bath to remove SO_2 and to diminish the acidity of the sample. Filter through a dense filter paper into a 100-ml volumetric flask, wash well with water and dilute to the mark. Mix well and transfer three 25-ml aliquots into three 50-ml volumetric flasks. Add to each flask 2 ml of 0·1*M* manganese sulphate, 5 ml of 8% ascorbic acid solution, 1–2 drops of Methyl Orange solution and neutralize with 20% sodium hydroxide solution. Add 5 ml of citrate buffer, 2·5 ml of 1% gelatine solution and dilute to the mark. Record the polarogram from −0·6 to −1·6 V *vs* SCE, without removal of oxygen.

Preparation of calibration graph

The calibration graphs are prepared by using the same quantity of pure iron as in the samples of the ferrotungsten and treated exactly as the sample, with 3·0, 2·0, 1·5, 1·0, 0·5 and 0·25 ml of the standard arsenic solution added to 25-ml aliquots in 50-ml volumetric flasks.

RESULTS AND DISCUSSION

The method is based on oxidative decomposition of the sample to prevent loss of arsenic as arsine and to separate the tungsten as $WO_3.H_2O$, followed by reduction of As (V) with potassium metabisulphite ($K_2S_2O_5$) and subsequent polarographic determination of the arsenic(III). The method is sensitive and less tedious than the other methods, and there is no interference from Fe, W, Bi, Si, P, Sn, Sb, Pb and Cu.

Table 1. The effect of sample pretreatment on the arsenic determination

Arsenic added, as μg/ml in final solution	Measured wave-height (mean) As added before (I) i_I, μA	n	As added after (II) i_{II}, μA	n	Statistical tests F, exp.	$F(95)$	t, exp.	$t(95)$
4·17	3·41	5	3·41	10	1·32	3·63	0·03	2·16
2·78	2·05	7	2·50	10				
2·08	1·64	6	1·84	9	3·23	3·69	1·36	2·16
1·74	1·37	8	1·36	9				
1·39	0·88	9	0·94	9				
0·70	0·50	6	0·50	8	3·06	3·97	0·39	2·18

n = Number of individual measurements on several separately prepared solutions.

Dissolution of the sample and reduction of the As(V) and Fe(III)

As ferrotungsten dissolves very slowly in *aqua regia*, the samples were first calcined by heating at 750–800° in a porcelain crucible for 2 hr.[8] After dissolution, the solution was treated with sulphuric acid, evaporated to

dryness and heated to expel oxides of nitrogen, since the latter interfere with the polarographic determination. The reduction step is necessary since Fe(III) interferes. Of the reducing agents investigated, hydrazine sulphate, oxalic and ascorbic acids and metabisulphite, the last was found to be the most suitable for the As(V), and ascorbic acid for the Fe(III). The tungsten(VI) was not attacked, either in solution or in the precipitate of $WO_3.H_2O$ under the conditions of the method.

Various factors which could affect the completeness of the reduction of As(V) and Fe(III), the preliminary calcination at 800° and the possible adsorption of the arsenic by the precipitate of $WO_3 . H_2O$ were investigated. Standard samples were prepared from high-purity iron (0·1 g) and tungsten (0·4 g). Then different amounts of arsenic(III) were added before and after the dissolution of the samples, and determined by the procedure described below. Included in Table 1 are the wave-heights obtained on addition of arsenic before (I) and after (II) the decomposition of the samples, for n determinations. The equations of both linear calibration curves, calculated by the method of least squares,[9] were $i_I = 0{\cdot}78\ C_{As}$ and $i_{II} = 0{\cdot}83\ C_{As}$ where i is the current in μA and C_{As} the arsenic concentration in μg/ml. The slopes of the lines were compared by the Student-t criterion[10] [$t = 1{\cdot}90 < t_{(95,\ f=24)} = 2{\cdot}06$]. The difference between them was found to be determined only by random errors. In addition the mean currents of the two lines at a given arsenic concentration were compared by the F- and t-tests.[9] The values of t and F indicate that there is no significant difference between the two currents and consequently the dissolution process has no influence on the arsenic determination.

Effect of some other elements and pH on the polarographic determination of arsenic

The elements in ferrotungsten which would interfere with the arsenic determination are Mn, Cu, Sb, Sn, Bi, Pb, Fe and W. Some of them (W, Sb, Pb) are separated in part by the preliminary treatment of the sample with acid mixture. Sb(III), Sn(II), Bi(III), Mn(II), Pb(II), W(VI) form weak complexes both with ascorbic and with citric acid,[11–13] giving polarographic waves at other potentials than that for As(III) and therefore might not affect the polarographic reduction of arsenic.[14] Nevertheless, the influence of Cu, Mn, Sn, Sb, Bi and Pb was investigated for concentrations from 2 to 20 times that of the arsenic ($5 \times 10^{-5} M$). All experiments were carried out with samples prepared from 0·1 g of high-purity iron since we found that the shape and height of the wave depended on the presence of Fe(II) in the supporting electrolyte. The presence of Fe(II), Mn(II) and the ions of some other heavy metals has a considerable influence on the limiting current of arsenic. Further investigations would have to be made to determine the cause of this interesting effect. On the basis of these results we recorded all polarograms of arsenic at constant Fe(II) and Mn(II) concentrations. The maximum wave-height was found to depend on the arsenic concentration, at a given pH, under the following conditions: 0·25M citric acid, 0·045M ascorbic acid, $C_{Fe} = 0{\cdot}01M$, $C_{Mn} = 4 \times 10^{-3} M$, and 0·5% gelatine. Figure 1 gives some data showing that pH has a considerable effect: as the pH increases, the wave-height decreases. The solutions were therefore adjusted to be 0·25M in citric acid with pH = 3·00. Figure 2 illustrates typical waves for arsenic in the range 0·35–4·17 μg/ml (0·25M citric acid, 0·045M ascorbic acid, $C_{Mn} = 4 \times 10^{-3} M$, $C_{Fe} = 0{\cdot}01M$, 0·05% gelatine and at pH = 3·0).

Accuracy and presion

From the average wave-heights of four individual determinations, the equation found for the calibration curve was

$$i = -0{\cdot}32 + (127 \pm 4).C_{As}$$

where i is the current in μA and C_{As} the concentration of the arsenic in μg/ml, over the range 0·3–4·2 μg/ml.

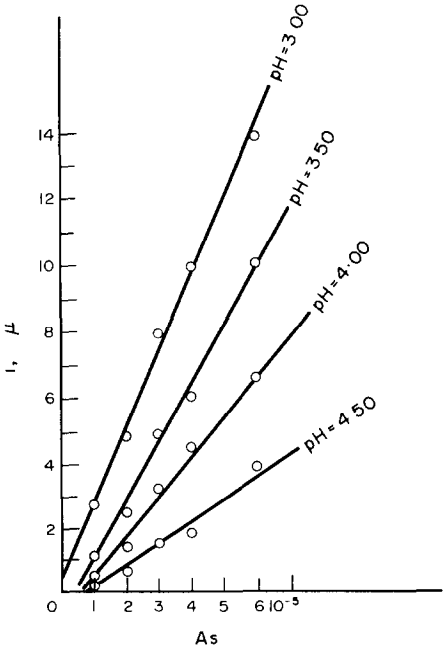

Fig. 1. The effect of pH on the calibration graph for arsenic.

Table 2. Statistical analysis of the accuracy and the precision of the method

No.	As taken, % (μ_0)	n	As found, % x	S	Confid. limit	$t = \frac{(x-\mu_0)\sqrt{n}}{S}$	$t_{(95,\,f)}$	Relative error, %
1	0·167	5	0·175	0·01095	0·014	1·55	2·78	+8·1
2	0·111	2	0·129	0·01908	0·017	1·33	12·70	+15·5
3	0·083	6	0·065	0·01619	0·017	0·45	2·57	−20·4
4	0·070	11	0·064	0·01269	0·008	1·49	2·23	−12·2

* n = Number of individual measurements on several separately prepared solutions.

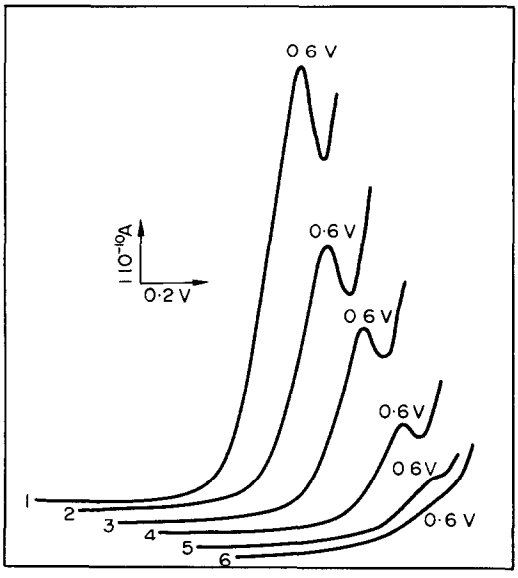

Fig. 2. Polarograms for the calibration in the determination of arsenic in ferrotungsten. C_{As}, μg/ml: 1—4·17; 2—2·78; 3—2·08; 4—1·39; 5—0·695; 6—0·378.

Table 3. Data for the arsenic analysis of ferrotungsten by the polarographic and the spectrophotometric Russian Standard method

	Polarographic method $\%As = \frac{(i+0{\cdot}32)5}{12{\cdot}3\,V.W}$				Photometric method $\%As = \frac{E.25}{4{\cdot}3\,V.W}$			
No.	W,* g	V *ml* (aliquot from 100 ml)	i, μA	% As	W,* g	V *ml* (aliquot from 100 ml)	E, absorbance	% As
1	0·5000	direct	1·65	0·0161	0·4763	direct	1·065	0·0136
2	0·4986	direct	2·40	0·0222	0·5084	direct	1·540	0·0188
3	0·5000	direct	2·90	0·0262	0·4991	10	0·137	0·0166
4	0·5000	direct	2·90	0·0262	0·5005	10	0·248	0·0300
5	0·4994	40	0·90	0·0249	0·4969	10	0·204	0·0249
6	0·4993	40	1·00	0·0269	0·4975	10	0·189	0·0230
7	0·5006	40	0·60	0·0187	0·5223	10	0·190	0·0220
8	0·4998	40	0·55	0·0177	0·5019	10	0·140	0·0169
9	0·5000	25	0·42	0·0215			mean	0·0207%
10	0·4969	25	0·70	0·0334				
11	0·5223	25	0·75	0·0334				
12	0·5019	25	0·42	0·0240				
			mean	0·0247%				

* W = sample weight.

Table 4. The test for systematic errors

No.	W, g	i, μA	%As taken, x_i	%As found = $\frac{(i + 0{\cdot}43)0{\cdot}2}{12{\cdot}7\ W}$ y_i
1	0·5070	7·00	0·164	0·235
2	0·5070	6·50	0·164	0·219
3	0·4945	5·85	0·169	0·203
4	0·4945	5·60	0·169	0·195
5	0·4934	2·90	0·084	0·106
6	0·4934	3·20	0·084	0·116
7	0·4983	3·45	0·084	0·123
8	0·4983	3·10	0·084	0·112
9	0·5062	1·80	0·034	0·068
10	0·4932	1 40	0 028	0·057
11	0·5062	1·50	0·034	0·059
12	0·4932	1 26	0·028	0 052

The coefficients of the regression line were tested by the F-criterion.[9] The test [$F = 12{\cdot}5 > F_{(95,\, f_1=1,\, f_2=5)} = 6{\cdot}61$] shows that the intercept is not zero.

The accuracy and the precision of the method were studied with samples prepared from 0·4 g of tungsten and 0·1 of iron and different amounts of arsenic added before the treatment of the samples with *aqua regia*. The statistical analysis of the results is given in Table 2. The values in the t-table used for calculating the confidence limits were also used in the comparison of the mean with the standard value (μ_0). It can be seen that the values for t are smaller than those in the tables and so there is no significant difference between the values taken and found.

Then samples of ferrotungsten (W = 72·1%, Si = 1·25%, C = 0·18%, S = 0 08%, P = 0·003%) were analysed by the proposed method. The results were compared with those obtained by the Russian Standard method[5] (see Table 3). The F-test [$F = 1{\cdot}11 < F_{(95, f_1=7, f_2=11)} = 3{\cdot}00$] discloses no significant difference in the precision of the two methods. Then the two means were compared by the t-test [$t = 1{\cdot}68 < t_{(95,\, f=18)} = 2{\cdot}10$], which showed that the results obtained by the two different methods were in acceptable agreement.

The accuracy of the method was studied by fitting the line $y = a + bx$ to the data, where x stands for the arsenic content, y for amount found (see Table 4) and a for the initial content of arsenic in the ferrotungsten sample. It was found that the line $y_i = 0{\cdot}022 + 1{\cdot}14\,x_i$ fitted the data and the t-test [$t = 2{\cdot}03 < t_{(95,\, f=11)} = 2{\cdot}20$] showed that the intercept corresponded to the arsenic content in the ferrotungsten sample (see Table 3), 0·0247 ± 0·0029% As. The slope of the line was unity and therefore, except for random errors, the amounts found were equal to the amounts taken.

The lower limit of determination was 0·0032%, corresponding to an As concentration of 0·32 μg/ml, calculated from the linear calibration curve.[9] This lower limit corresponds to the lowest measurable signal ($i_{min} = 0{\cdot}24\ \mu A$).

Higher Institute of Chemical Technology
Department of Analytical Chemistry
Sofia-56, Bulgaria

N. G. ELENKOVA
R. A. TSONEVA

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Summary—A simple and sensitive method for determining arsenic in ferrotungsten is presented. The alloy is dissolved in *aqua regia* and the arsenic reduced with $K_2S_2O_5$. The polarographic wave is recorded for an electrolyte at pH 3·0 and containing Fe(II), Mn(II), citric acid and ascorbic acid Levels of 0·2% and 0·003% As can be determined with errors of ±8 and ±20% respectively. The limit of detection is 0·003%.

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SPECTROGRAPHIC DETERMINATION OF IMPURITIES IN ULTRAPURE TUNGSTEN AND TUNGSTEN OXIDE

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During the last few years the interest in tungsten and tungsten compounds of high purity has been continuously rising, and new methods for the determination of the impurity elements in tungsten have been developed. These methods have to take account of the multiplicity of spectroscopic lines obtained with the tungsten matrix and the high melting and boiling points of tungsten.

When the excitation occurs in the crater of a graphite electrode (and especially in the presence of graphite powder) involatile tungsten carbides are formed. In this way the interfering effect of the matrix element is removed to a considerable extent. All available methods for the direct determination of the impurity elements in tungsten and tungsten oxide are based on this finding.[1–14] The carburization usually occurs on the electrode, but it could be carried out in advance in a furnace.[10] The preliminary carburization could be used to identify the optimal conditions for the vaporization of the impurities and for their separate excitation. The carburization on the working electrode offers the advantages of ease and rapidity of performance.

In many cases, in order to enhance the sensitivity of the analysis, additives such as zinc oxide, sodium chloride, gallium and indium sesquioxides, barium chloride and potassium iodide, are introduced into the sample; they have been found to interfere with the formation of carbides of the impurity elements, but have no influence on the carburization of the matrix element.[1,5]

A preliminary separation of the impurities from the matrix is also possible.[2,5,14] The advantages of these methods are the high sensitivity and simplified preparation of the standards. The possibilities offered by physical or chemical separation are limited by the selectivity and the permissible amounts of impurities introduced by the reagents.

Another possibility of enhancing the sensitivity of direct spectrographic methods consists of using an external magnetic field. The magnetic field has been found[15,16] to increase the spectroscopic line intensity of the impurity elements provided that substances of low ionization potential are not present in large amounts in the arc plasma. This condition is met when a carbon arc is used[17] and when impurities are determined in bases which are not easily vaporized.[18]

In the present paper we report the effects of an external magnetic field and of the diameter of the anode on the spectroscopic line intensity of the impurity elements in ultrapure tungsten and tungsten oxide, and how they could be used to develop a new more sensitive method for the determination of these impurities.

EXPERIMENTAL

Preparation of standards and samples

The basic standard was prepared by mixing in a "Teflon" grinder a weighed amount of spectroscopically pure tungsten oxide (Johnson Matthey) with salts or oxides of the impurity elements. The subsequent standards were obtained by dilution of the basic standard with pure tungsten oxide. To each standard, 20% of graphite powder was added, and this powder caused the reduction of the tungsten oxide to metallic tungsten and the formation of the involatile carbides, WC and W_2C.[19] Thus the intensity of the tungsten spectrum and the background was reduced and the detection limits of the impurities were lowered. The samples of tungsten oxide were prepared in a similar manner. The oxidation of the samples of metallic tungsten and the powdered tungsten has been described elsewhere.[7,11] Consequently the method proposed in our paper is also applicable to the analysis of tungsten.

The impurity elements and their concentrations in the standards are shown in Table 1.

Choice of conditions for excitation and exposure

In order to obtain lower detection limits we have used a d.c. generator and a grating spectrograph. The solenoid, which is described elsewhere,[20] was placed coaxially under the graphite electrodes. The samples and

Table 1. Concentration of impurities (*ppm*) in the standards prepared with tungsten oxide as a base

Standard no.	Cu, Mg	Mn, Fe, Ni, Cr, Si, Pb, Al, V	Mo
1	10	100	1000
2	3	30	300
3	1	10	100
4	0·3	3	30
5	0·1	1	10
6	0·01	0·1	1
7	0·001	0·01	0·1
8	0·0001	0·001	0·01

the standards were always placed on the lower electrode (anode). The optimal arc current,[21] for anodes of 6 mm in diameter, is 9 A, and for anodes of 14 mm in diameter it is 18 A.

We have chosen the method of fractional evaporation: owing to the carburization of tungsten an increase in the amount of the sample introduced into the crater of the electrode is followed by an increase in the spectroscopic line intensity of the impurity elements and hence by an increase in the sensitivity of the analysis. If the anodic craters are deep the part of the sample which is at the bottom of the crater cannot react with the carbon and the impurities cannot be vaporized at the lower temperatures prevailing there. Consequently there is an optimal depth of the anodic crater and an optimal weight of sample. Using graphite electrodes (external diameter 6 mm, diameter of crater 3·5 mm) of 6, 8, 10 and 12 mm depth of crater with 60, 70, 80 and 90 mg weights of sample we have found that the time of total vaporization of the impurity elements is 40, 50, 60 and 60 sec respectively. The finding that the impurities are evaporated for identical times from electrodes having crater depths of 10 and 12 mm shows that if the depth of the crater is more than 10 mm the sample in the crater cannot be sufficiently heated and for this reason it cannot contribute to the evaporation curves. This is confirmed by the values of the quantity $\Delta Y = \log I_1/I_b$ shown in Table 2. As seen from this Table the optimal depth of the anodic crater is 8 mm and all subsequent experiments were carried out with electrodes of that crater depth.

Table 2. $\Delta Y = \log I_1/I_b$ as a function of the depth of the anodic crater

Depth of the crater, *mm*	Si 251·6 *nm*	Mn 279·5 *nm*	Pb 283·3 *nm*	Fe 259·9 *nm*	Ni 305·1 *nm*	Al 308·2 *nm*	Mo 313·2 *nm*
6	1·32	1·62	0·78	1·21	0·92	1·22	1·57
8	1·49	1·78	0·83	1·47	0·99	1·48	1·65
10	1·40	1·74	0·86	1·37	0·85	1·30	1·59
12	1·31	1·54	0·83	1·21	0·77	1·12	1·55

The analytical sensitivity is considerably affected by the manner of illuminating the slit. As reported by Mannkopf[8] the intensity of the lines is increased in the area of the d.c. arc near the cathode. We have shown in an earlier paper[17] that the effect of intensification of the line intensity in a magnetic field is greatest for this area.

For tungsten oxide we found little difference in ΔY for the intensity of the lines originating in the near-cathode and central areas of the arc. The accuracy of the analysis will be higher (but the sensitivity lower) if we use the central area of the arc.

To achieve optimal line densities we had to use photoplates for which the density due to the background spectrum is at the start of the linear part of the characteristic curve.[22] In the present work, when using photoplates ORWO-WU-3, a background density of 0·2–0·3 could be obtained.

Table 3. Conditions for excitation and photography

	Anodes 6 *mm*	Anodes 14 *mm*
Excitation source	d.c. arc 280 V, 9 A	d.c. arc 280 V, 18 A
Electrodes	Anode as sample carrier Diameter of the crater 3·5 mm, depth 8 mm Cathode 6 mm shaped as intersected cone	Anode as sample carrier Diameter of the crater 10 mm, depth 8 mm Cathode 6 mm shaped as intersected cone
Weight of the sample	70 mg	200 mg
Electrode gap	3 mm	3 mm
Grating spectrograph type PGS-2 (VEB Karl Zeiss), grating 625 lines/mm, blaze angle at 280 nm (second order)		
Exposure time	60 sec	
Slit width	20 μm	
Illumination of the slit	One lens with a quartz condenser (f = 30 mm) and projection of the centre of the interelectrode space	
Photoplates	ORWO-WU-3 9 × 24 cm	
Distance between the solenoid and the electrodes	130 mm	
Vertical component of the magnetic field	60 gauss	

The density of the significant lines of the recorded spectra was compared with that of the background close to the chosen analytical lines. As shown elsewhere[11] this value correlates better with the analytical line intensity than the line intensities of internal standards. The calibration curves were plotted as ΔY *vs.* log C. The conditions of excitation and photography are summarized in Table 3.

Detection limits

Using the excitation and photography conditions specified above we have determined, by the 6-sigma criterion,[23] the detection limits for 9 elements excited in graphite electrodes 6 mm in diameter and for 7 elements excited in graphite anodes of 14 mm diameter. The reproducibility of the method is characterized by a relative standard deviation between 7 and 12% and the reproducibility for the larger anodes was found to be better.

Table 4. Comparison of detection limits (*ppm*)

Element line, *nm*	Dyck[4]	Kucharzewski[6]	Scholze[11]	Lounamaa[7]	Our data	
					6-*mm* anode	14-*mm* anode
Si 256·1	1	—	3	1	—	—
Mn 279·5	—	—	0·08	0·03	0·07	0·01
Pb 283·3	2	2	0·5	0·1	0·1	0·02
Fe 259·9	0·4	3	0·2	0·3	0·1	0·02
Ni 305·1	0·4	2	0·5	3	4·5	0·2
Al 308·2	0·09	1	—	—	0·04	—
Mo 313·2	8	—	7	1000	15	4
V 318·5	0·8	7	—	—	9	0·6
Cu 327·4	0·1	1	0·07	0·3	0·006	—
Cr 284·3	0·2	1	7	3	3	0·1
Mg 279·5	0·1	1	0·03	0·1	—	—

RESULTS

We have summarized our results in Table 4 together with the results obtained by other authors. The impossibility of finding the detection limits for silicon and magnesium is due to contamination, and that for aluminium and copper to the high concentration of these elements in the graphite electrodes. As seen from Table 4 in both cases our results are superior to those thus far obtained. The substantial increase in sensitivity found for anodes of the larger diameter we attribute to (*a*) the greater weight of sample, (*b*) greater intensification of the line intensity in a magnetic field because of the larger diameter of the anode and (*c*) the ease of vaporization of the impurity elements owing to the larger free surface in the anodic crater. The detection limits obtained for anodes of 14 mm in diameter may not be the best—we have not determined the optimal depth of the anodic crater and the corresponding weight of sample. Nevertheless the data clearly show the benefit of using anodes of larger diameter for an arc with an applied external magnetic field.

Institute of General and Inorganic Chemistry
Bulgarian Academy of Sciences
Sofia 13, *Bulgaria*

YU. HARIZANOV
N. JORDANOV

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Summary—The effects of an external magnetic field and of the diameter of the anode on the spectroscopic line intensity of the impurity elements in ultrapure tungsten and tungsten oxide have been studied. The results obtained are used for the development of a more sensitivie method for the determination of these impurities (Mn, Pb, Fe, Ni, Al, Mo, V, Cu, Cr).

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REACTION OF MERCURY(II) AND XYLENOL ORANGE—III

DETERMINATION OF MICROAMOUNTS OF MERCURY

A. CABRERA-MARTÍN, J. L. PERAL-FERNÁNDEZ and F. BURRIEL-MARTÍ
Departamento de Química Analítica del C.S.I.C., Facultad de Ciencias,
Universidad Complutense de Madrid, Spain

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Summary—Xylenol Orange and mercury(II) react in the presence of various bases, such as hexamine, pyridine and ammonia, to form ternary complexes, which conform to Beer's law. The 1:1:1 Hg(II)/XO/base complex at pH 6·1 has an absorption maximum at 590 nm and a molar absorptivity of $2{\cdot}2 \times 10^5$ $l.mole^{-1}.cm^{-1}$. In the absence of the base the $Hg(II)(XO)_2$ complex at pH 7·5 and 580 nm has a molar absorptivity of $1{\cdot}7 \times 10^5$ $l.mole^{-1}.cm^{-1}$. Interferences are discussed.

The characteristics of the reaction of the Hg(II) ion with Xylenol Orange (XO) in various media have been reported.[1,2] Of the systems studied, two have been chosen as being most suitable for the spectrophotometric determination of traces of Hg(II), and are reported on here. These are Hg(II)/XO/citric acid/Na_2HPO_4 and Hg(II)/XO/hexamine, at wavelengths of 580 and 590 nm respectively, and at pH 7·5.

EXPERIMENTAL

Reagents

Xylenol Orange solution, $10^{-3}M$.

Mercury(II) nitrate solution, $10^{-3}M$ in $5 \times 10^{-4}M$ nitric acid.

Citric acid solution, 0·2*M*.

Disodium hydrogen phosphate solution, 0·4*M*.

Hexamethylenetetramine (*HMTA*), saturated aqueous solution.

Sulphuric acid, 3·5*M*.

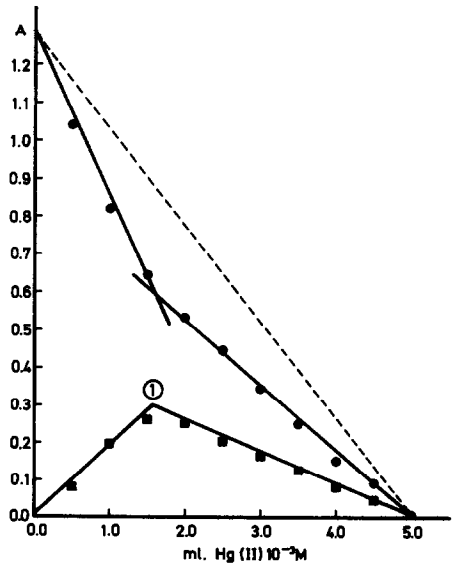

Fig. 1. Graph of continuous variations in amine-free media. pH 7·5 (citrate–phosphate); $\lambda = 580$ nm; ① Hg(II)/XO = 1·55:3·45 = 1:2.

Composition of the complexes

The composition of the possible complexes formed by Hg(II) and XO in the buffered media was studied by the continuous variations and mole-ratio methods (Figs. 1 and 2). Both methods showed that when citrate was the buffer a 1:2 ratio of Hg:XO was observed. However, when HMTA was used two phenomena were observed by the method of continuous variations. (1) A sharp maximum corresponding to a 1:1 Hg(II)/XO composition; (2) a series of maxima and minima not clearly differentiated, corresponding to complexes with a higher mercuric ion content, but with compositions which were difficult to determine (Fig. 2). By contrast the mole-ratio method indicated three different complexes with Hg(II)/XO ratios of 1:1, 1:2 and 1:3. The last two showed less absorbance than the XO reagent blank, but the 1:1 complex was strongly coloured. This 1:1 complex was the only one that followed Beer's law over the range 5–12 ppm Hg(II), thus providing a sensitive method of determination.

Since it had been assumed that this 1:1 complex was ternary,[1] solutions of constant concentration of Hg(II) and XO were titrated spectrophotometrically with HMTA in order to find the ratio at which the latter participates in the formation of the complex at pH 7·5. Two spectrophotometric blanks were used, one of them saturated with

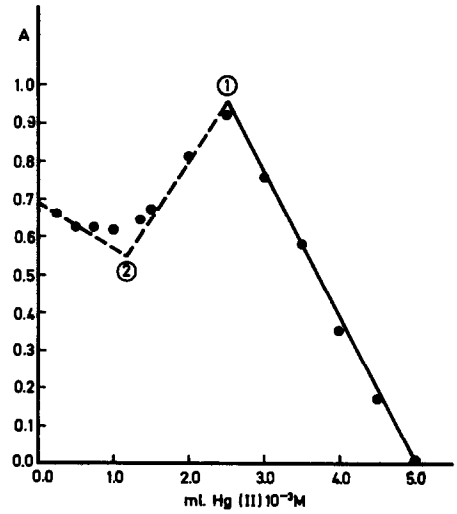

Fig. 2. Graph of continuous variations in media containing amines. pH 7·5 (H_2SO_4–HMTA); $\lambda = 590$ nm; ① Hg(II)/XO = 2·5:2·5 = 1:1; ② complex or complexes formed in XO excess.

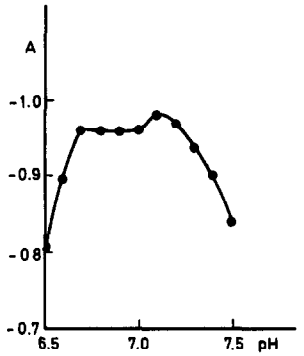

Fig. 3. Influence of pH (citrate–phosphate buffer); λ = 580 nm.

HMTA. By this method the composition of the complex was found to be 1:1:1 Hg(II)/XO/HMTA.

Identical results were obtained when pyridine was present in the buffer.

Influence of pH on the complexes formed

Citric acid–phosphate medium, pH 6·7–7·2. Within this pH range the absorbance of the reagent is higher than that of the complex, with a practically constant minimum at pH 7·1 (Fig. 3). The pK_{a3} of XO, H_6R, is 6·4, hence in this medium it exists mainly as H_3R^{3-} and H_2R^{4-} with the latter predominating.[1]

Sulphuric acid—HMTA medium, pH 5·9–7·0. When working with the 1:1:1 Hg(II)/XO/HMTA complex, a maximum of absorbance was obtained at pH 6·1 (Fig. 4). At this pH H_3R^{3-} is the major species of XO, but the 590-nm band indicates the reacting species to be H_2R^{4-}, which is responsible for the strong hyperchromic effect observed.

The other two complexes of composition 1:2 and 1:3 Hg(II)/XO are not considered suitable for the determination of Hg(II). These are less coloured than the reagent, exist over a very limited pH range, and offer very little analytical sensitivity.

Stability of the complexes

Stability *vs.* time studies were performed with the two types of complexes, 1:2 and 1:1:1. At room temperature and in the dark the absorbance of both complexes remained constant for more than 48 hr. When the complexes were placed in a thermally insulated chamber and subjected for 30 min to radiation of wavelengths between 340 and 800 nm no change was observed in the absorbance. The effect of different temperatures (25°, 30°, 50° and 100°) on the complexes was studied. Only at 100° was total destruction of the complexes observed.

Calibration surves

Citric acid–phosphate medium. At pH 7·1 and 580 nm, Beer's law was obeyed over the Hg(II) concentration range

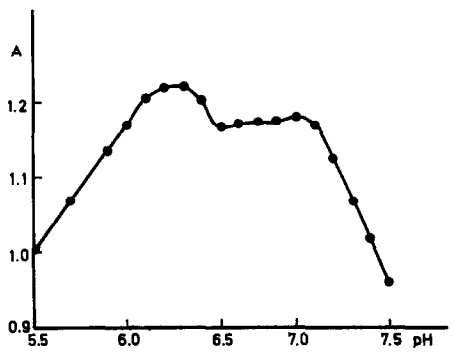

Fig. 4. Influence of pH (H_2SO_4–HMTA); λ = 590 nm.

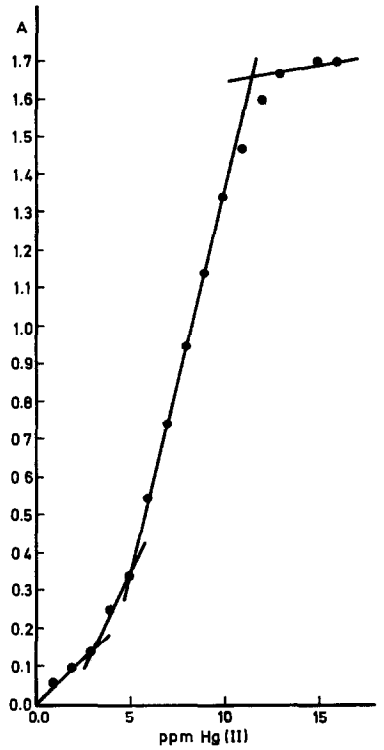

Fig. 5. Hg(II) determination; pH 6·1; λ = 590 nm; 1-cm glass cells.

0·5–9 ppm (1-cm glass cells). For the range 0·2–2 ppm 4-cm cuvettes were used. In both cases the molar absorptivity was found to be $1{\cdot}7 \times 10^5$ l. mole^{-1}.cm^{-1}.

Sulphuric acid—HMTA medium. Two pH values were used in the determination, 6·1 (Fig. 5) and 7·5.[1] For 5–12 ppm Hg(II), 1-cm cuvettes, and a wavelength of 590 nm, the molar absorptivity was $2{\cdot}2 \times 10^5$ l. mole^{-1}.cm^{-1} at pH 6·1 and $2{\cdot}05 \times 10^5$ l. mole^{-1}.cm^{-1} at pH 7·5, indicating that the same 1:1:1 complex is formed at both pH's.

Accuracy and precision

Accuracy may be affected by systematic and/or random errors. Statistical treatment of random errors by the method of Ringbom[3] gives the relative concentration error. The values thus obtained for 1% error in transmittance (or scale reading) for the 1:2 Hg(II)/XO complex are presented in Table 1.

This method is not valid for the 1:1:1 Hg(II)/XO/HMTA complex, which does not obey Beer's law over the whole concentration interval.

Individual measurements of the accuracy obtainable with both complexes are shown in Table 2.

Table 1. Errors in measurement of absorbance of $Hg(XO)_2$

Concentration interval, *ppm*	Errors in the analytical measurements of absorbance,%
0·2–2·0	3·0
0·4–4·0	2·1
0·5–5·0	1·9
0·6–6·0	1·7
0·8–8·0	1·7
1·0–10·0	1·7
1·2–12·0	1·8
1·4–14·0	1·9
1·6–16·0	2·0

Table 2. Errors in determination of Hg as $Hg(XO)_2$ and Hg(XO)HMTA

$Hg(XO)_2$			Hg(XO)HMTA		
Hg(II), *ppm* present	found	Relative error, %	Hg(II), *ppm* present	found	Relative error, %
2·5	$2·5_5$	+ 2	5·5	5·5	0
2·3	2·3	0	6·0	6·0	0
5·0	5·0	0	6·8	6·7	−1·5
6·5	$6·4_5$	−1	7·5	7·5	0
8·0	7·9	−1	8·0	8·1	+1
9·0	9·0	0	8·3	8·3	0
0·5	$0·5_5$	+10	9·1	9·1	0
4·2	$4·2_5$	+ 1	9·3	9·4	+1
4·8	4·8	0	10·0	9·9	−1
3·1	$3·1_5$	+ 2	10·5	10·6	+1

The precision was determined by analysing 20 solutions containing 6·0 ppm Hg(II) for the 1:2 complex and 7·0 ppm for the 1:1:1 complex. The standard deviations were found to be 0·02 and $0·01_6$ ppm Hg(II) respectively.

DISCUSSION

Structure of the complexes

1:2 Hg(II)XO complex (citric acid–phosphate medium). The XO species in solution at pH 7·1 are mainly H_3R^{3-} and H_2R^{4-} in equilibrium. When the reaction with Hg(II) takes place, a shift in the equilibrium causes the total conversion of the system into the more ionized species of the two. It is this species which is responsible for the formation of the chelate ring. The Hg(II) ion in solution exists as a solvated ion, either simply hydrated or in a polynuclear form.[4–7] Presumably, the Hg(II) takes the form of the polynuclear cation $[Hg(HgO)_2]^{2+}$, even though it is not very stable, for if a higher quantity of the solvated ion were present at the pH used, it would precipitate as HgO. It may be assumed then that the complex cation is destroyed when it reacts with XO, thus liberating the Hg(II) to form the complex.

From the stoichiometry 1:2 Hg(II)/XO, a mechanism for the reaction is proposed. This can be visualized with the aid of atomic models (Fig. 6).

The XO active group capable of forming the chelate is a zwitterion. The Hg(II) ion replaces the proton, which may then migrate towards the central carbon atom of the reagent's phthalein skeleton, a possibility that exists for all the triphenylmethane derivates. The quinonoid ring becomes phenolic and forms the chelate ring with the mercury atom through a co-ordinate bond with the nitrogen atom, and an ionic bond with the oxygen atom.

As can be seen from molecular models, the two Xylenol Orange molecules must be oriented in such a way as to make coplanar the $-CH_3$ groups located *ortho* to the oxygen atoms participating in the bond. This forms a hole between the two molecules, capable of accommodating the mercury atom in a tetrahedral co-ordination by its d^{10} electronic structure.

1:1:1 Hg(II)/XO/HMTA complex (sulphuric acid–HMTA medium). At pH 6·1 the main reagent species

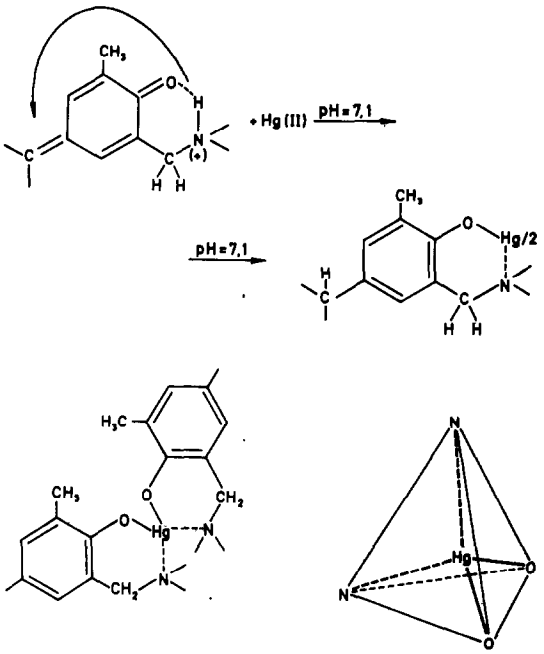

Fig. 6. Mechanism of formation of 1:2 complex, pH 7·1.

are H_3R^{3-} and H_2R^{4-}, with the latter predominating. The XO active group capable of forming the chelate with Hg(II) must be the one that has not yet formed the zwitterion at pH 6·1. Hg(II) may bond with the nitrogen atom of the complexing group located in an *ortho* position with respect to the —OH group of the phenolic ring, displacing the proton from the nitrogen atom and forming an ionic bond. The imino nitrogen atom will thus be converted into a positively charged quaternary nitrogen atom. At the same time, the mercury atom forms a co-ordination link with the oxygen atom from the —OH group, since this group does not lose its proton in the formation of the chelate.

The other ionic charge on the Hg(II) can be neutralized by bonding nitrogen atoms through a similar mechanism. The nitrogen atom adopts the quaternary ammonium configuration and the hexamine becomes positively charged.

The Hg(II) ion can form only linear, tetrahedral, or octahedral complexes. The linear configuration is not possible in this case. Neither is the octahedral because the tetrahedral is favoured when the crystal field stabilization energy of the ion is zero and, in this case, the ion possesses a d^{10} electronic structure with a $10D_q$ value of zero. Since HMTA forms complexes with mercury compounds, similar to those obtained with ammonia, it is possible to substitute one of the HMTA molecules by one of XO (Fig. 7) in such a way as to form a tetrahedral complex. In order to achieve co-ordination saturation, a water molecule is needed to form a co-ordinate bond with the mercury atom through its oxygen atom.

It is concluded that the Hg(II) atom occupies the middle of an irregular tetrahedron. The resulting dis-

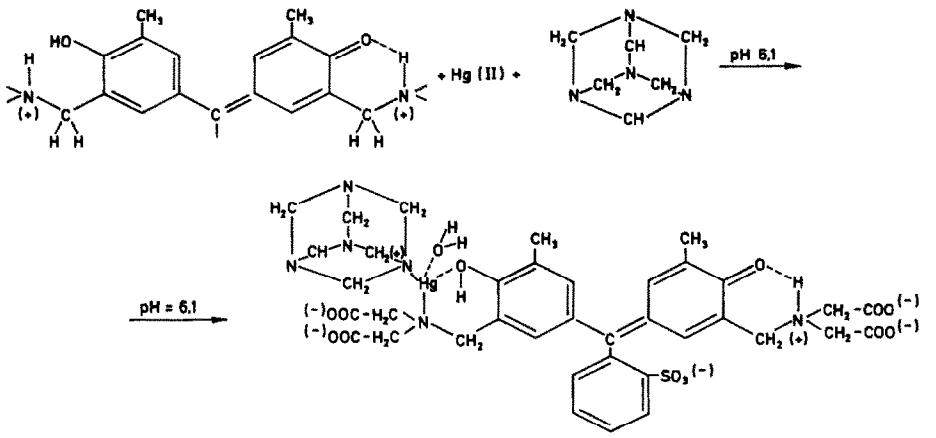

Fig. 7. Mechanism of formation of 1:1:1 complex, pH 6·1.

tortion may make it very sensitive to the action of competitive complexing agents.

Determination of the apparent dissociation constants

The continuous variations and molar-ratio methods were used for the determination of the apparent dissociation constants. For the 1:2 complex, at pH 7·1, the average value of K_i obtained is $3{\cdot}65 \times 10^{-12}$. Since the 1:1:1 complex does not follow Beer's law, only the continuous variations methods was used. A K_i value of $9{\cdot}9 \times 10^{-13}$ was obtained at both pH 6·1 and 7·5.

Interferences

A study was conducted of atoms, ions, ionic groups, or molecules that may influence the reaction, either by inhibiting it or by altering it through salt effects (ionic strength), or through competition in the formation of the complexes.

The effect of ionic strength on the analysis was studied with sodium perchlorate, sodium nitrate and potasium nitrate as added electrolyte. Neither nitrate had any effect on the reagent or the 1:2 complex at 580 nm, for ionic strength between 0·001 and 0·1*M*. However, in the presence of the perchlorate, the absorbance values for the complex increased, although for the reagent they remained constant. Perchlorate must therefore be absent.

The 1:1:1 complex was found to be much more sensitive to variations in ionic strength. For a solution of ionic strength 0·1*M* and pH 6·1, there was an increase in the absorbance of the reagent and a considerable decrease in that of the complex, regardless of the nature of the added electroylte. The effect decreased with decreasing electrolyte concentration, and disappeared at $\mu < 0{\cdot}001M$.

The interference due to the presence of foreign substances was studied by mixing Hg(II) solution, foreign substances, reagent and buffer, in that order, and then diluting. The readings were made 30 min after the preparation of the samples and an XO solution was used as spectrophotometric blank. The foreign substances were added in concentration 10^3, 10^2 and 10 times that of the Hg(II).

1:2 complex. The following anions showed no interference at all concentrations: Cl^-, NO_3^-, F^-, $C_2O_4^{2-}$, tartrate, AsO_2^-, $HAsO_4^{2-}$, IO_3^-, SO_4^{2-}, CH_3COO^-, ClO_3^-, BrO_3^-, NO_3^-, MoO_4^{2-}, HMTA, BO_2^- and $S_2O_8^{2-}$; NH_4^+ did not interfere in 100-fold amounts and WO_4^{2-} in tenfold amounts.

Tenfold concentrations (relative to Hg) of the following cations did not interfere: Pb, Tl(I), Cu(II), Cr(III), Ce(III), Ce(IV), La, Th, U(VI), Be, Ca, Sr, Ba, Mg, K and Na. The results for the other ions studied are presented in Table 3.

It can be seen that several anions show strong interference, possibly by a competitive mechanism in the formation of the complex. The interference due to S^{2-} is important whether the anion comes from a fresh solution of Na_2S or from saturating the solution of the complex with H_2S.

The interference due to some species arises because they cannot coexist with free Hg(II) [*e.g.*, Sn(II), S^{2-}].

Table 3. Interferences with 1:2 complex

Foreign ion (X)	Absorbance [X]/[Hg] = 10^3	Absorbance [X]/[Hg] = 10^2	[X]/[Hg] = 10
—	−0·550	−0·550	−0·550
$S_2O_3^{2-}$	+0·010	−0·015	−0·040
SO_3^{2-}	−0·030	−0·025	−0·030
SeO_3^{2-}	−0·430	−0·420	−0·490
S^{2-}(Na_2S)	+0·840		
S^{2-}(H_2S)	−0·665		
CN^-	+0·170	+0·040	−0·010
SCN^-	+0·005	+0·087	−0·160
Br^-	+0·040	−0·045	−0·425
I^-	−0·012	−0·060	
EDTA	+0·005	−0·065	
CO_3^{2-}	+0·150	−0·450	−0·500
$Fe(CN)_6^{4-}$	−0·010	−0·020	−0·150
$Fe(CN)_6^{3-}$	+0·150	+0·017	−0·275
MnO_4^-	> +2·0	−1·8	−0·800
VO_3^-	−1·45	−1·45	−1·45
Ag			−0·430
Hg(I)			−0·730
Bi			−1·4
Cd			−0·225
Sb(III)			−1·3
Sn(II)			−1·4
Fe(III)			−1·26
Al			−0·830
Zr			−1·3
Ni			+0·227
Co(II)			+0·350
Mn(II)			−0·027
Zn			+0·100

Table 4. Effect of interferences with Hg(XO)HMTA

Foreign ion (X)	Absorbance [X]/[Hg] = 10^3	[X]/[Hg] = 10^2	[X]/[Hg] = 10
—	+0·960	+0·960	+0·960
S^{2-} (Na_2S)	+1·02		
S^{2-} (H_2S)	−0·025		
SCN^-	−0·030	−0·025	+0·325
Br^-	0·000	−0·010	+0·060
I^-	+0·017	+0·030	+0·070
EDTA	−0·162	−0·042	−0·032
AsO_2^-	+0·175	+0·300	+0·500
$Fe(CN)_6^{4-}$	−0·115	−0·090	−0·050
$Fe(CN)_6^{3-}$	−0·097	−0·021	−0·010
MnO_4^-	>2·0	+0·182	+0·020
VO_3^-	+0·860	+0·460	+0·160
Hg(I)			+1·7
Pb			+1·35
Bi			+0·050
Cu			+1·04
Cd			+1·5
Sb(III)			+0·650
Sn(II)			+0·470
Al			+0·540
Ce(III)			+1·45
Ce(IV)			+1·22
La			+1·12
Th			+0·950
U(VI)			+0·960
Zr			+0·960
Ni			+1·7
Co(II)			+1·5
Mn(II)			+0·970
Be			+0·550

The interferences due to certain cations may be eliminated by addition of convenient quantities of fluoride, oxalate and tartrate as masking agents. The use of a complexing buffer solution also facilitates their elimination.

1:1:1 complex. There was no interference at any concentration from BO_2^-, F^-, $C_2O_4^{2-}$, BrO_3^-, ClO_4^- and NO_3^- or from tenfold concentrations of NH_4^+, $S_2O_8^{2-}$, CH_3COO^-, SeO_3^{2-}, Cl^-, citrate, $HAsO_4^{2-}$, CrO_4^{2-}, WO_4^{2-}, MoO_4^{2-}, Ag, Tl(I), Fe(III), Cr(III), Zr, Zn, Ca, Sr, Ba, Mg, K and Na. The effect of other ions is shown in Table 4.

CONCLUSIONS

The complex formed by the reaction between Hg(II) and XO depends on the nature of the substances used as buffers. If the buffer does not contain amine-type nitrogen compounds, one only complex of stoichiometry Hg(II)/XO = 1:2, is formed. This complex is less strongly coloured than the reagent and makes possible the determination of Hg(II) traces in the range 1·0–9·0 ppm (1-cm cells). The mercury atom is totally locked within a tetrahedron formed by active complexing groups of the XO, but with no effect on the geometry of the molecule.

On the other hand, in the presence of amine-type nitrogen atoms, and more so when they belong to a cyclic molecule like hexamine, three complexes are formed with Hg(II)/XO molar ratios of 1:1, 1:2 and 1:3. Only the 1:1 is suitable for the determination of Hg(II) traces and in fact is a ternary complex with HMTA/Hg(II)/XO = 1:1:1. Although this complex does not obey Beer's law, it permits the determination of Hg(II) traces with great sensitivity in the range 5·0–12·0 ppm Hg(II).

It is possible that a water molecule from the solvent takes part in the formation of this complex. The mercury atom is locked within a distorted tetrahedron, the vertices of which are formed by two nitrogen atoms, from the reagent and the hexamine, and two oxygen atoms, from the reagent and the water molecule.

Both complexes seem to be suitable for the determination of mercury and are superior, in regards to sensitivity and ease of handling (no extraction is necessary), to those accepted by IUPAC, and in general to the dithizone method. The media used are slightly basic, or of very low acidity, which prevents the interference of high concentrations of a great number of cations.

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THE PROGRESS OF ANALYTICAL CHEMISTRY 1910–1970

*R. R. BROOKS and L. E. SMYTHE

School of Chemistry, University of New South Wales, Sydney, Australia

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Summary—The progress of analytical chemistry during the period 1910–1970 is reviewed. Topics considered are: the volume of the relevant literature, the countries in which the work was done, the language in which the papers were written, the literature of analytical chemistry, broad trends in the subject, methods used, and the analytical chemistry of individual elements. Some tentative conclusions are made about future short-term trends.

The progress of analytical chemistry during the 20th century has been much greater than in all of its previous history. This progress has closely followed the general field of chemistry and during the past decade has become so great that there obviously needs to be an evaluation of what has been achieved during the past sixty or so years in order to use hindsight to look a little into the future and try to predict the probable course of this branch of chemistry in the 1970's.

Histories of analytical chemistry are fairly numerous,[1–16] but are in the main confined to three types: pre-1900 accounts,[1–3] single-country histories,[10–12,14] or modern trends confined to a limited period of five or ten years.[4–8] Perhaps the best known attempt at a general coverage of the history of analytical chemistry is a book by Svabadváry[9] which gives an excellent account of the pre-1900 period, but unfortunately ends at 1960, before many of the exciting newer developments in analytical chemistry.

Analytical chemists, both in the educational and applied fields, are vitally interested in the progress of their discipline. The educationalist needs to know what new developments are taking place in order to tailor his courses accordingly. He also needs to know the most important languages of scientific communication. The applied analytical chemist needs to know past and future trends in order to make the best choice of scientific equipment, and he also needs to know about the most important journals which will publish his manscripts or which will give him the necessary scientific information.

Perhaps the best publications to serve the requirements of analytical chemists have been reviews for 1946,[6] 1955,[7] and 1965.[8] These papers have sought to answer some of the questions above, but there is clearly a need for a much wider survey, paying particular attention to the 1960's when so much new progress was made in analytical chemistry. Such a survey would also need to extend back in time at least to the early 1900's in order to evaluate some of the long-term trends of this century. We have attempted to undertake such a history and our data are presented in this paper. We have tried to broaden the scope of the 1946–1965 reviews,[6–8] but acknowledge with gratitude their contribution towards our own efforts. A large number of journals was used to obtain information for this history. These included *Chemical Abstracts*, *Analytical Abstracts*, *Current Contents*, and the major journals of analytical chemistry. The period of study chosen was from 1910 to 1970, i.e., from just after the start of *Chemical Abstracts* to the latest date for which data were fully and easily available.

THE VOLUME OF LITERATURE ON ANALYTICAL CHEMISTRY

Procedure

The volume of literature on analytical chemistry was derived largely from study of *Chemical Abstracts* and *Analytical Abstracts*. These studies were made for five-year intervals for the period 1910–1970. It was a comparatively simple matter to obtain the total number of abstracts for each year by multiplying the average number of entries per column by the number of columns.

The determination of the total number of papers for analytical chemistry was a considerably more difficult problem. For a study of this magnitude it was hardly practicable to count all the analytical entries in all sections of *Chemical Abstracts*. Fischer[8] estimated that 48% of all analytical abstracts would be found in the "Analytical Chemistry" section of *Chemical Abstracts* for the year 1965. One solution to the problem would therefore be to assume that this ratio has remained constant for the 60 yr period, and to multiply the "Analytical Chemistry" section figures by 2.1. We were, however, able to form a more accurate estimate in the following way. All entries for 25 common elements were counted for the entire years 1955, 1960, 1965 and 1970 in both *Chemical* and *Analytical Abstracts*. On this basis, *Analytical Abstracts* contained only 54% of the total for these elements in *Chemical Abstracts*. Entries for *Analytical Abstracts* (which were easily counted) were therefore

multiplied by 1.86 to give values which in turn were found to be 2·49 times the total number of entries in the "Analytical Chemistry" section of *Chemical Abstracts*. To obtain an estimate therefore, for the total number of analytical papers in any one year, the total number of entries for the "Analytical Chemistry" section of *Chemical Abstracts* was counted and multiplied by 2·5. The values for the years 1955 and 1965 were found to be 6610 and 12,750, respectively, compared with 5460 and 10,100 given in the surveys of 1955[7] and 1965,[8] or about 25% higher.

Results and discussion

Figure 1 shows "analytical" and "total" chemical abstracts as a function of year. The analytical plot also shows the data as a percentage of the total. There is obviously a close similarity between the two plots, particularly after 1935. Total abstracts show a slight decline in 1915, as might be expected because of World War I; thereafter there is a rise in 1920 and an exponential increase for 1920–1930. The exponential increase is not maintained for 1930–1935, probably because of the influence of the Great Depression. An expected decrease for the war years is followed by an exponential increase from 1950 onwards.

The pattern for analytical abstracts differs slightly for the period 1910–1950. In 1915 there was an overall increase in numbers, perhaps because wartime conditions tended to encourage the more applied sciences, and in 1920 there was a very high increase in analytical papers. This big increase was probably a result of the accumulation of a backlog of German papers during the war and these papers tended to have a higher analytical content then those from other countries because of the pre-eminence of Germany in this field at that time (see Fig. 2).

During the Great Depression, the analytical papers increased from 5·6% to a total of 6·5%. Once again this is probably due to the effect of periods of adversity which tend to encourage the more applied disciplines to the detriment of the purer "luxury" studies.

In 1950 there was no evidence for a surge of analytical papers similar to that of 1920. This is because of the combination of several factors. German publications were more available during World War II than World War I so that the relative backlog was less. Moreover, as will be seen later, Germany was not as pre-eminent in analytical chemistry in 1945 as she was in 1918. In any case any backlog had probably been accounted for in the issues for 1946–1949.

The percentage of analytical papers was reasonably constant and apart from 1920, never fell outside the limits of 5·6–7·5%. The post-1945 years were even more consistent, with values ranging only between 6·5 and 7·3%. There is also very good agreement between our data and those of other workers. For example, our value of 6·5% for 1965 compares with 6·0%,[8] whereas our values of 7·3% for 1955 agrees well with a figure of 7·2%.[7] Overall it appears that analytical chemistry is at least maintaining itself in relation to chemistry as a whole.

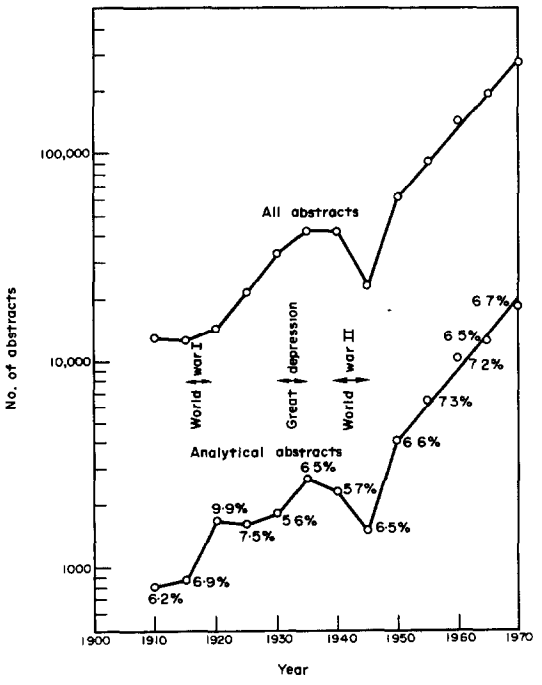

Fig. 1. Totals for analytical and all chemical papers for the period 1910–1970.

COUNTRIES IN WHICH ANALYTICAL CHEMISTRY WAS CARRIED OUT

Procedure

In order to determine the countries in which analytical chemistry was carried out, the last five issues of *Chemical Abstracts* were examined for each year. This amounted to about 25% of all issues. Only the section entitled "Analytical Chemistry" was studied. This survey therefore involved a visual inspection of 10% of all analytical abstracts for the year concerned, because the analytical section contains only about 40% of all analytical entries. The total number of entries studied was about 100 for 1910 and 1500 for 1970. Each abstract was assigned to a particular country on the basis of the author's address. The address is given for the early and late issues but not for those published in the 1920's and 1930's. In such cases, the assignment was done according to the country of origin of the journal. This procedure was fairly unambiguous for all languages except English. In such cases, assignment was done according to the author's method of writing his name, *i.e.*, Joseph S. Smith (USA) or J. S. Smith (UK). In cases of doubt, authors were assigned to country of publication, *i.e.*, doubtful cases in *The Analyst* were assumed to be British, whereas in *Analytical Chemistry* they were assumed to be American.

Table 1. Percentage of analytical work carried out in various countries

Country	Year 1910	1915	1920	1925	1930	1935	1940	1945	1950	1955	1960	1965	1970
U.S.S.R.	1·0	—	—	0·8	5·7	29·4	30·8	18·2	17·8	13·0	22·9	25·4	28·4
U.S.A.	28·9	30·4	25·3	13·4	18·8	14·6	25·0	48·3	19·9	18·0	20·7	15·8	17·7
Japan	1·0	1·0	—	3·2	2·6	3·1	2·9	—	5·0	12·3	7·7	11·0	7·7
Germany*	31·9	30·4	19·9	39·7	26·3	16·4	10·5	2·5	6·7	12·1	4·8	6·4	6·1
U.K.	17·6	20·2	12·3	11·9	10·5	6·4	7·1	12·4	12·0	8·2	6·0	4·3	5·9
Czechoslovakia	—	—	—	4·8	3·5	2·8	1·7	—	6·0	8·1	3·8	5·3	5·6
France	10·3	4·5	21·0	7·1	14·5	7·6	3·8	2·5	9·2	4·7	3·1	3·5	2·6
India	—	—	—	—	1·3	1·8	0·8	2·1	0·6	4·3	5·0	3·5	2·6
Scandinavia	—	1·1	1·8	3·9	1·8	0·8	2·1	2·6	3·3	2·4	1·0	0·7	2·1
Romania	—	2·3	3·5	4·8	—	0·8	0·4	—	—	0·8	2·0	3·5	2·0
Poland	—	—	—	—	2·2	2·0	—	—	—	1·6	1·5	4·1	1·8
Spain	2·1	1·1	1·8	0·8	2·2	2·1	2·5	1·6	4·2	1·8	1·7	1·8	1·5
Netherlands	—	3·4	8·8	3·2	1·3	1·5	2·9	0·5	0·8	0·8	0·8	0·8	1·3
Italy	—	1·1	—	4·0	1·8	4·1	2·5	—	2·3	4·2	2·5	1·7	1·0
China	—	—	—	—	—	2·6	—	—	0·8	—	5·6	3·1	—
Rest of the world	7·2	4·4	5·1	2·4	7·7	4·0	7·0	9·3	11·4	7·7	10·9	9·1	11·1

* Includes both East and West Germany.

Results and discussion

The data are shown in Table 1, which expresses numbers of analytical papers for various contries as a percentage of the whole. The data for six leading countries are also given in Fig. 2. The pattern for the United States vis-à-vis the Soviet Union is somewhat illuminating. There is a general impression in the West that the Soviet Union lagged a long way behind the United States in analytical papers before 1945, and finally overtook that country about 1960. This impression is supported by the data of the reviews of 1946,[6] 1955,[7] and 1965.[8] These reviews do not, however, tell the full story. As will be seen from Fig. 2 the Soviet Union took the lead in analytical papers as early as 1935 and lost it again only in 1945, no doubt owing to the effects of the war, when many well-known publications such as *Zavodskaya Laboratoriya* temporarily ceased publication. Part of the apparent drop in publications for 1945 may also be due to non-availability of journals for abstracting. The pre-eminence of the Soviet Union in numbers of publications is, however, partly due to Russian papers being in general shorter than in the West.

Data for the United States and the United Kingdom show similar trends. Both show a fairly steady decrease in analytical publications relative to the rest of the world, and with an accelerated decrease during the Great Depression of 1930–1935. In both cases the immediate prewar years and the years of the war itself stimulated the publication of analytical papers. In the former period, rearmament and the easing of the effects of the Great Depression may have been responsible. The war years produced an enormous relative increase, particularly in the United States. This is probably partly because more English and American journals may have been abstracted relative to others because of easier availability during wartime conditions, and partly because of the stimulus to analytical research by joint US–UK undertakings such as the Manhattan Project. Another factor may have been the fact that American was the only country during the war able to afford the "luxury" of extensive research into analytical chemistry.

Britain and France show a fairly similar pattern of a steadily decreasing percentage of world publications. Unlike the case of Britain, the French publication rate was severely reduced by World War II.

The early pre-eminence of Germany in analytical chemistry is reflected in Fig. 2. Apart from 1920, when the war years had affected publication rate (or possibly abstraction rate which is an entirely different

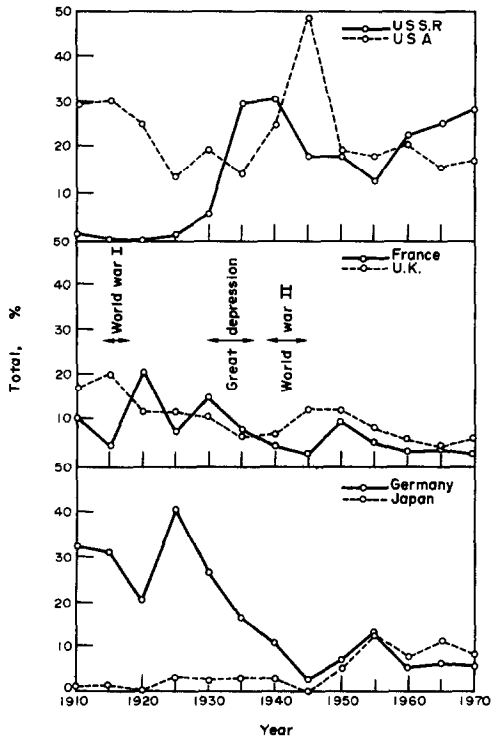

Fig. 2. Numbers of analytical papers published in six leading countries for the period 1910–1970.

Table 2. Languages in which analytical papers are published, %

Language	Year 1910	1915	1920	1925	1930	1935	1940	1945	1950	1955	1960	1965	1970
English	50·6	51·7	40·4	26·1	32·8	23·8	34·1	64·9	35·4	32·3	34·2	24·8	30·3
Russian	1·0	—	—	0·8	5·7	29·4	30·8	18·2	17·8	13·0	22·9	25·4	28·4
German	32·9	31·5	21·7	39·7	27·6	16·7	12·6	3·0	9·2	14·0	6·7	9·8	8·1
Japanese	1·0	1·1	—	3·2	2·6	3·1	2·9	—	5·0	12·3	7·7	11·0	7·7
Czech	—	—	—	4·8	3·5	2·8	1·7	—	6·0	8·1	3·8	5·3	5·6
French	12·4	5·6	21·0	7·9	16·7	8·4	4·2	2·5	11·7	5·2	3·5	4·2	3·6
Spanish	2·1	2·2	2·3	1·6	4·0	2·9	5·4	7·8	5·9	3·1	3·7	1·8	2·6
Scandinavian	—	1·1	1·8	3·9	1·8	0·8	2·1	2·6	3·3	2·4	1·0	0·7	2·1
Romanian	—	2·3	3·5	4·8	—	0·8	0·4	—	—	0·8	2·0	3·5	2·0
Polish	—	—	—	—	2·2	2·0	—	—	—	1·6	1·5	4·1	1·8
Hungarian	—	—	—	—	—	0·8	—	—	0·8	0·2	1·9	1·0	1·8
Dutch	—	3·4	8·8	3·2	1·3	1·5	2·9	0·5	0·8	0·8	0·8	0·8	1·3
Italian	—	1·1	0·5	4·0	1·8	4·1	2·5	—	2·3	4·2	2·5	1·7	1·0
Chinese	—	—	—	—	—	2·6	—	—	0·8	—	5·6	3·1	—
Other	—	—	—	—	—	0·3	0·4	0·5	1·0	2·0	2·2	2·8	3·7

matter), the German percentage of the world total of analytical papers was the highest of all countries until it was overtaken by the Soviet Union in 1935. After a low point in 1945 (again possibly because of the low abstraction rate rather than low publication rate), there was an appreciable increase until 1955 and thereafter a gradual relative decrease. The course of Japanese publications followed that of Germany. Before the Second World War Japan's percentage of the world total was fairly constant at about 3%. After zero abstracts in 1945, the percentage climbed rapidly, overtook Germany in 1955, and has now stabilized at around 9% of the world total.

From Table 1 it can be seen that one of the world's major publishers of papers in analytical chemistry is Czechoslovakia, which was eminent in this field even as far back as 1925. The Czech percentage (apart from the war years) has been fairly constant at around 5% of the world total. Other important countries are India, Scandinavia, Romania, Poland, Spain, the Netherlands and Italy. The Netherlands had a flourishing school of analytical chemistry at Leyden University in the early years of this century and this is reflected in a high publication rate for the period 1915–1925. China has an erratic record. In the immediate period before the "China Incident" of 1936, this country was publishing analytical papers. The long war with Japan resulted in a very low abstraction rate. By 1960, under a new government, analytical papers were starting to appear in greater numbers but apparently none appeared in 1970. It may be that this was a result of the "Cultural Revolution" or it may be because of lack of availability of journals for abstracting.

The total for the "Rest of the World" shows a steady increase. This is not unexpected, owing to rapid industrialization since World War II. In previous reviews,[6–8] percentage values have been assigned to individual countries on the basis of a single publication. Such a procedure is not meaningful since only about 25% of all abstracts were examined, and if a certain country had only a single publication for the year, there would only be a 1 in 4 chance of its being reported in the Survey. For this reason, no individual data are given for the approximately thirty countries classified under "Rest of the World".

LANGUAGE OF PUBLICATION

Procedure

The data obtained above for countries in which the work was done were rearranged to provide information concerning the language of publication. The "English" category included the United States, United Kingdom, Canada, Australia, India, and countries of Southern Africa. The "French" category included France and Belgium, and the "German" group included East and West Germany, Switzerland and Austria. As before, the data were expressed as a percentage of all analytical publications. A large part of the Japanese total is published in an English edition, but this unknown quantity remains in the "Japanese" section and has not been added to the "English" category. The "Spanish" entry included South America, except Brazil.

Results and discussion

The data are shown in Table 2. It is evident that English has remained the most important language for scientific communication. It was surpassed only by German in 1925, and possibly by Russian in 1965, although if half of the Japanese category is added on, English was still pre-eminent even in 1965. The high percentage for English in 1945 (64·9%) was probably partly due to the easier availability of English journals for abstracting during the war years. With one or two exceptions, English has yearly contributed about 30–35% of the literature of analytical chemistry. The Russian share has been steadily increasing since 1955, and if this trend is maintained, it is likely to become the most important language in the future for the field of analytical chemistry. In 1970, the order of importance for the various major languages was: English, Russian, German, Japanese, Czech, French

and Spanish. About half of the "Spanish" share is due to countries of South America.

If foreign language courses are tailored to the needs of the analytical chemist, it is clear that the traditional English, German, and French of "reading-knowledge" courses would be far better replaced by English, German, and Russian, since even Czech is a more widely used language than French among the languages of analytical chemistry.

THE LITERATURE OF ANALYTICAL CHEMISTRY

Procedure

The most important journals catering exclusively or almost exclusively for analytical chemistry were selected by making a short list of journals abstracted by *Analytical Abstracts*, and the number of papers for 1970 was counted for each. In the case of *Chemist-Analyst*, which ceased publication in 1967, entries for what year were recorded.

The number of books on analytical chemistry published each year was obtained from *Chemical Abstracts*, but was only complete up to 1966 because books were not listed together after that date.

A number of leading journals were also studied to obtain an indication of the volume of papers in each over a period of time.

Results and discussion

In Fig. 3, the number of analytical books published is plotted as a function of year in which abstracted. Predictably enough, there is a sharp drop during the years of the two World Wars. The general trend is towards an arithmetic increase rather than the geometric increase of analytical publications in general (see Fig. 1). The inference of this observation is that textbooks on analytical chemistry are perhaps increasing in size to allow for the geometric increase

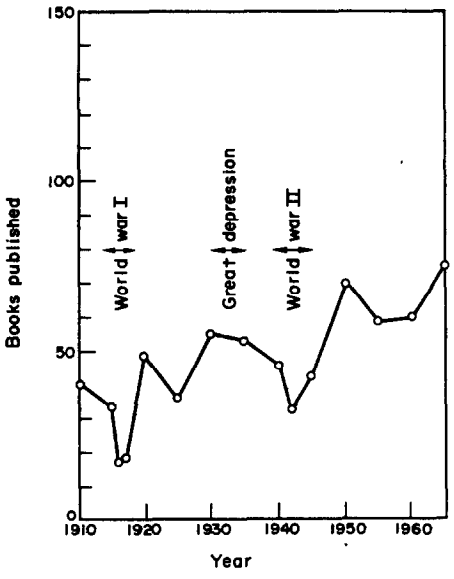

Fig. 3. Numbers of books on analytical chemistry published in the period 1910–1966.

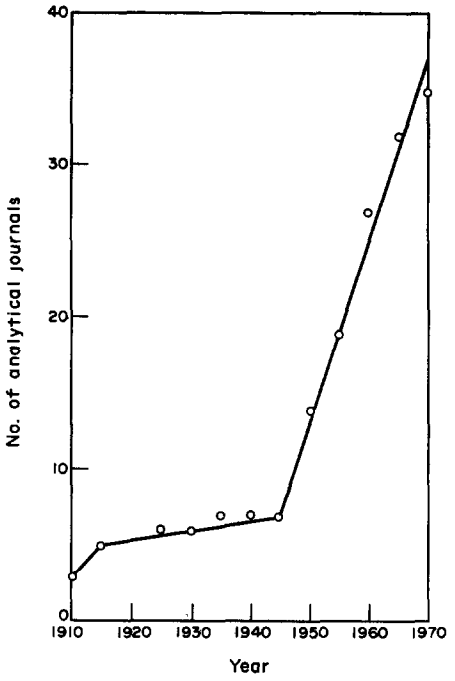

Fig. 4. Cumulative total of journals catering exclusively (or almost exclusively) for analytical chemistry.

of analytical knowledge. Although we have not investigated this subject in detail, it is well known that a standard textbook such as Vogel's *A Textbook of Quantitative Inorganic Analysis* increases progressively in size with each new edition.

The cumulative total of major journals catering exclusively (or almost exclusively) for analytical chemistry is shown in Fig. 4, expressed as a function of year. The pattern is quite clear. There is a slight arithmetic progression until the end of World War II in 1945, and thereafter there is a much sharper increase which nevertheless is still arithmetic rather than geometric. There can be only three explanations for the arithmetic increase in journals as coupled with a geometric increase in analytical papers: (*a*) specialist journals are increasing in size to allow for the geometric increase, or (*b*) the size of the papers is being reduced, or (*c*) papers in analytical chemistry are appearing in greater numbers in journals not specifically analytical in scope.

In order to investigate this problem more closely, four analytical journals of the United States, Britain, Germany and the Soviet Union (*Analytical Chemistry, The Analyst, Zeitschrift für Analytische Chemie, Zavodskaya Laboratoriya*), were examined for the 1955–1970 period by counting the number of articles and pages. The results are shown in Table 3.

The overall pattern is that all four journals have stabilized their numbers of pages and the number of articles which they contain. Presumably this has been achieved either by a more selective editorial policy or by the diversion of articles into more specialized analytical journals or into journals not catering exclusively for analytical chemistry.

Table 3. Numbers of articles and pages for leading analytical journals in the period 1950–1970

	Anal. Chem.		*The Analyst*		*Z. Anal. Chem.**		*Zavodsk. Lab.*	
Year	Articles	Pages	Articles	Pages	Articles	Pages	Articles	Pages
1950	499	1593	142	693	58	1000	—	—
1955	690	2026	151	912	200	3200	—	—
1960	782	1930	184	928	220	3250	620	1400
1965	624	1812	128	760	252	3000	710	1450
1970	539	1880	163	1048	244	4800†	705	1500

* The major part of this journal is devoted to abstracts.
† Allowance made for larger page size in 1970.

A question of great concern to all analytical chemists is the identity of the world's major analytical journals, the percentage of the total world's articles which they carry, and the language in which they are published.

It is found that some 26 journals accounted for 35% of the world total of papers in analytical chemistry in 1970 (assessed at 18,475). Of these journals, the oldest were *Zeitschrift für Analytische Chemie* and *The Analyst*. It is interesting to observe that the Czech journal *Chemicke Listy* first appeared in 1906 (thirteen years before the foundation of Czechoslovakia).

The major journals (each containing more than 1·0% of the world total), arranged alphabetically, are as follows:

Analytica Chimica Acta, Analytical Biochemistry, Analytical Chemistry, Japan Analyst, Journal of Electroanalytical Chemistry, Journal of the Association of Official Analytical Chemists, Mikrochimica Acta, Nukleonika, Talanta, The Analyst, Zavodskaya Laboratoriya, Zeitschrift für Analytische Chemie and *Zhurnal po Analiticheskoi Khimii.*

These 13 journals together accounted for about 30% of the world total.

The language in which the 26 journals were written was predominantly English (25%), followed by Russian (9%), German (3·5%), French (2%), Japanese (1·4%), Polish (1·3%) and Czech (0·6%).

It is interesting to observe that the major journals of analytical chemistry carry nearly half the world's total analytical papers, and about half of all analytical abstracts appear in the "Analytical Chemistry" section of *Chemical Abstracts*. The more applied papers found elsewhere in *Chemical Abstracts* are probably found mainly in applied journals.

Although the Russian language accounted for only 8·7% of the papers in the major analytical journals in 1970, it accounted for 28·4% of all analytical papers in that year. The conclusion that can be reached from this is that Soviet analytical papers are much more dispersed outside the leading journals. This is to be expected since all of the 16 republics of the Soviet Union support a fairly comprehensive range of scientific publications, many of which are in the local language.

BROAD TRENDS IN ANALYTICAL CHEMISTRY

Procedure

The June and December issues of *Analytical Abstracts* for each year of the period 1955–1970 were examined to evaluate trends in seven broad categories of analytical chemistry. The data were expressed as a percentage of all entries in the issues studied. It was assumed that the results were indicative of trends for the entire year.

Results and discussion

The data are shown in Fig. 5. They show a surprisingly constant level for "agricultural analysis", "food analysis" and "pharmaceutical analysis".

There is an appreciable increase in the relative proportion of "biochemical analysis" and "technical apparatus", and a smaller increase in analysis of "water, air and effluent". These trends appear to be at the expense of "inorganic" and "organic analysis" which both show significant downward trends except for the last three years of "inorganic analysis". These trends were not unexpected, because of the phenomenal rise of biochemistry during the past 15 yr. Because of the increasing use of instrumental methods of analysis, it is not surprising that there has been a significant increase in the proportion of papers in analytical chemistry dealing with this subject.

It is somewhat surprising that the proportion of papers dealing with "environmental" analytical chemistry by 1970 had only increased slightly. It may be that a different pattern will emerge in a few years time. However, the slight rise in "inorganic analysis" during the past 3 yr may also be due to an increase in environmental analysis.

METHODS USED IN ANALYTICAL CHEMISTRY

Procedure

The main source for the evaluation of methods used in analytical chemistry was the biennial reviews in *Analytical Chemistry*. There were certain pitfalls in the use of these reviews. The main problem was that, although the reviewer often started out with the admirable intention of giving a comprehensive review, after a few years his task often became so enormous that his reviews became selective in their

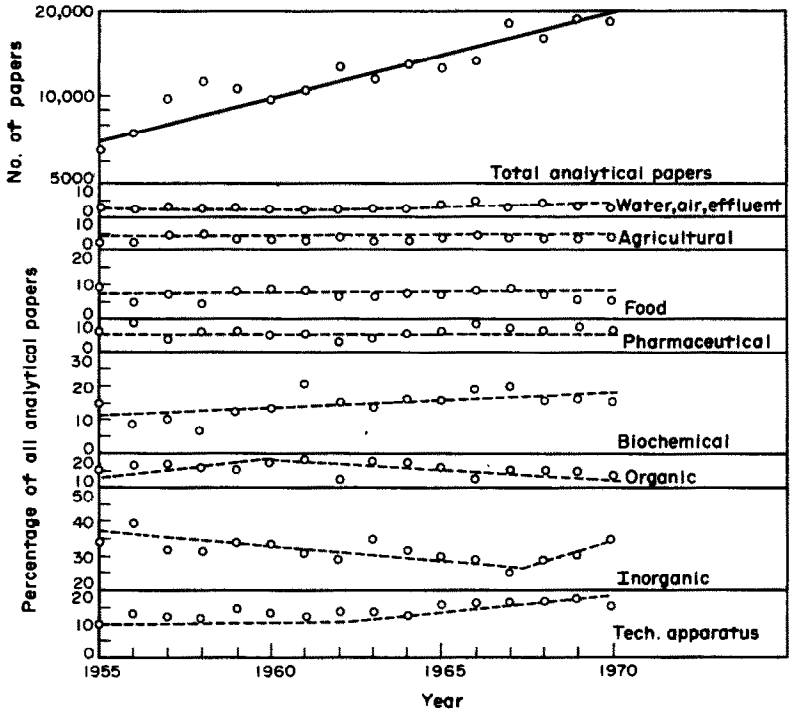

Fig. 5. Broad trends for eight categories of analytical chemistry for the period 1955–1970. Data expressed as percentage of total number of analytical papers.

coverage, and were no longer useful for estimating the total number of papers for any one method. The journal *Atomic Absorption Newsletter* was used to determine the number of entries for atomic-absorption and atomic-fluorescence spectrophotometry.

Results and discussion

The results are shown in Fig. 6, and have been collected under six groupings.

Among electrometric methods, organic polarography shows the greatest number of entries and the technique is maintaining its percentage of all analytical papers, as can be seen by comparison with the graph for all analytical papers. Other methods such as general polarography are decreasing in favour relative to all analytical papers.

The group of absorption and emission methods shows that atomic-absorption and atomic-fluorescence spectrophotometry papers have the sharpest rate of increase, and are increasing exponentially at a rate which is greater than for the total of all analytical papers. X-Ray fluorescence continues to be very popular, but shows a rather characteristic pattern for most newer methods. At first, in the enthusiasm of the early days, there is a scramble to publish, but after a decade or so, the increase slows down to a rate similar to that for all analytical papers. This "surge" is characteristic for many new techniques and can be seen in several cases in Fig. 6.

Among the spectrometric methods reported, NMR appears to be in the lead, and has not yet reached the top of the "surge". Mass spectrometry has been in existence too long to show the "surge effect" and is now well established with a rate equal to those for the total of all analytical papers. Raman spectroscopy is an interesting case. Although it is a long-established technique its popularity dropped to a low point in 1956 but has now recovered strongly.

The "classical" titrimetric and gravimetric techniques have, as might be expected, failed to maintain their popularity in the face of so many new instrumental methods. The same fate is obvious for inorganic and organic microchemistry, which have somewhat arbitrarily been assigned to the same analytical group of methods, although titrimetry and gravimetry are a somewhat small component of the methods used in microchemistry. Although the number of papers appearing each year is fairly constant, this represents a decline relative to the total of all analytical papers.

Among the group classified as "other methods", nucleonics exhibits the typical "surge" pattern, and is now increasing at the same rate as "all papers". The early popularity of thermal analysis appears also to be waning slightly.

Separation methods in general continue to be popular except for distillation techniques which show a classical case of a "death". The predominance of distillation as a separation method dates back well into the 19th century. It is no accident that the great decline of the technique occurred when gas chromatography began its development. Most other separation methods seem to have been able to maintain themselves in spite of the competition from the new instrumental methods.

To summarize, there appear to be three main categories of techniques of analytical chemistry: classical methods such as titrimetry and gravimetry which are in relative decline; newer techniques such as atomic absorption and NMR which are in the critical stages of the typical "surge" pattern; well-established techniques such as nucleonics and X-ray fluorescence which have passed the "surge stage" and are now increasing at a rate about equal to those of the total of all analytical papers.

THE RELATIONSHIP BETWEEN NUMBERS OF INSTRUMENTS AND PUBLICATION OUTPUT

Procedure

For any one instrumental method, it is very difficult to establish the relationship between publication output and the number of available instruments, because of the lack of precise information on instruments sold. It was, however, possible to obtain reliable information on numbers of atomic-absorption spectrophotometers, because all these instruments are produced under licence to C.S.I.R.O. in Australia, and the relevant data were readily available.[13] Precise figures were also available for the number of atomic-absorption publications from annual reviews in *Atomic Absorption Newsletter* by W. and S. Slavin.

Results and discussion

Figure 7 shows a logarithmic plot of numbers of existing atomic-absorption spectrophotometers for any one year, expressed as a function of total atomic-absorption papers published in the same year. The sigmoid shape of curve can be explained quite easily. At first there is a rush for scientists to publish in the new field. This may be referred to as the "band-waggon effect". Later in time when the method becomes well established, the ever-increasing number

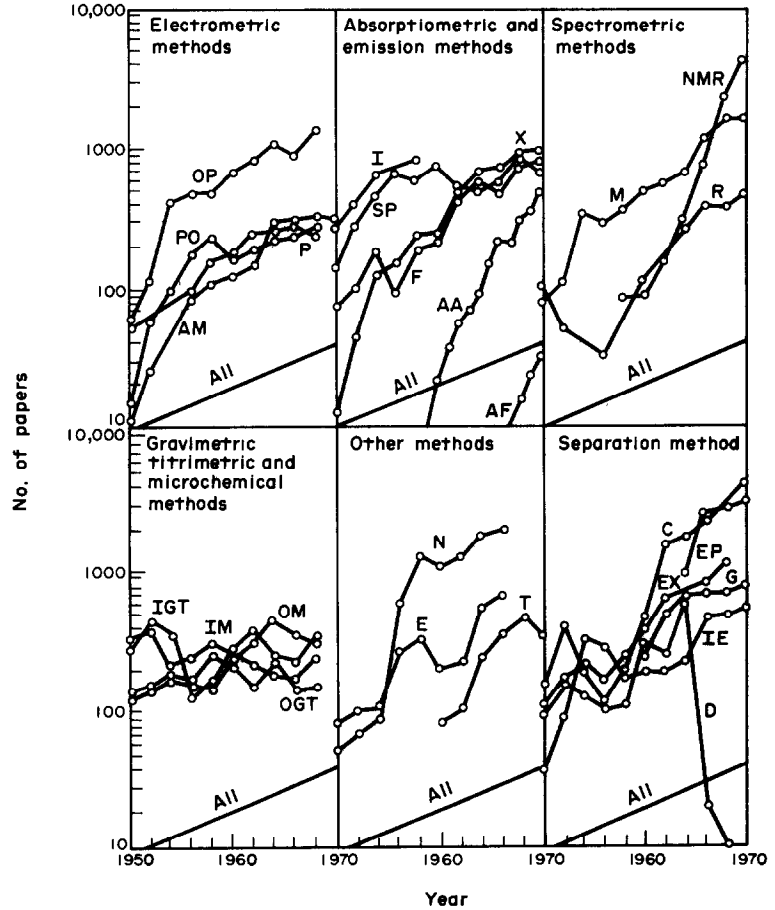

Fig. 6. Methods used in analytical chemistry during the period 1950–1970. Data expressed as percentage of total numbers of papers. *Electrometric methods*—AM, amperometry; OP, organic polarography; P, polarography; PO, potentiometry. *Absorptiometric and emission methods*—AA, atomic absorption; AF, atomic fluorescence; F, fluorimetry; I, infrared spectroscopy; SP, spectrophotometry; X, X-ray fluorescence. *Spectrometric methods*—R, Raman spectrometry; M, mass spectrometry; NMR, nuclear magnetic resonance. *Gravimetric, titrimetric and microchemical methods*—IGT, inorganic gravimetry and titrimetry; IM, inorganic microchemistry; OGT, organic gravimetry and titrimetry; OM, organic microchemistry. *Other methods*—E, electron microscopy; N, nucleonics; T, thermal analysis, *Separation methods*—C, chromatography; D, distillation; EP, electrophoresis; EX, extraction; G, gas chromatography; IE, ion-exchange.

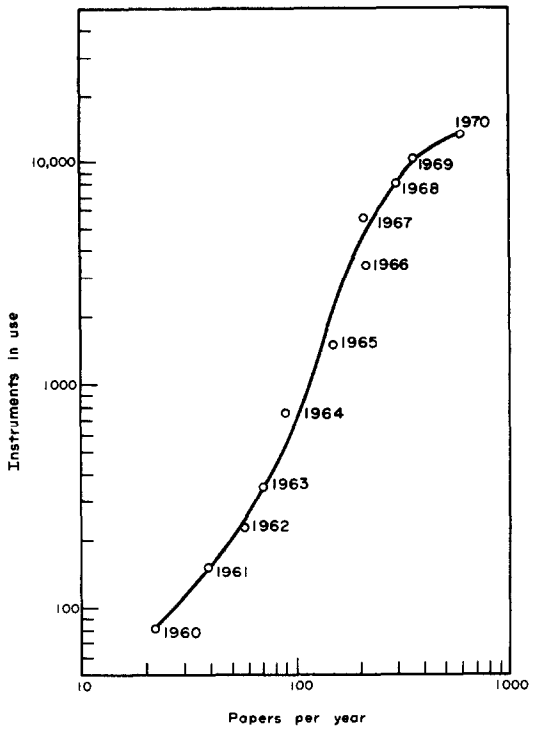

Fig. 7. The relationship between the total number of atomic-absorption spectrophotometers in existence in any one year and the total number of atomic-absorption papers published in the same year.

of instruments are used more and more for routine analysis rather than for "publishable" research topics. There is no reason why this pattern should not apply equally well to other new instrumental techniques, and it is only lack of reliable data which has discouraged us from investigating this topic further.

THE ANALYTICAL CHEMISTRY OF INDIVIDUAL ELEMENTS

Procedure

The total number of entries listed under "Analysis" were compiled for 25 elements in *Chemical Abstracts* for 5-yr intervals from 1910 to 1970. The results were expressed as a percentage of all analytical abstracts for the year concerned.

Results and discussion

The data are summarized in Table 4. The most important elements used in heavy industry, such as aluminium, chromium, cobalt, copper, iron, lead, manganese, nickel, silver, tin and zinc, show a surprisingly constant percentage of all analytical abstracts. For example, copper varies only between 1·95 and 3·97% during the entire 60-yr period. Other elements, however, show a sudden increase or decrease of attention at certain specified periods of time. For example, interest in arsenic determinations dropped sharply in 1945, owing perhaps to an unusual interest in the forensic chemistry of this element before World War II.

There is a sharp increase in determinations involving germanium (from 0·12 to 0·32%) in the period 1950–1955, due no doubt to the emergence of the transistor industry and its associated electronics. A similar increase in lithium determinations is apparent during the same period. This may reflect the increased use of lithium in medicine and (along with germanium) in the electronics industry as, for example, in lithium-drifted germanium detectors.

An enhanced interest in environmental problems is reflected in an increase of the level of mercury

Table 4. Distribution of analytical papers among different elements (percentage of all analytical papers)

Element	1910	1915	1920	1925	1930	1935	1940	1945	1950	1955	1960	1965	1970
Aluminium	0·36	0·68	0·77	1·35	1·87	2·29	1·90	1·95	1·86	1·52	2·30	1·22	1·97
Arsenic	1·16	2·23	1·41	1·35	1·67	2·02	1·64	0·65	1·04	0·98	0·68	0·70	0·79
Beryllium	0	0	0·06	0	0·34	0·29	0·34	0·45	0·72	0·40	0·92	0·50	0·40
Cadmium	0·36	0·26	0·35	0·98	0·59	0·83	0·91	0·95	1·19	1·30	0·91	0·96	1·42
Chromium	1·08	0·34	1·12	0·55	0·98	0·56	1·10	1·41	1·58	1·19	0·74	0·80	1·37
Cobalt	1·16	0·60	0·47	0·80	1·57	1·19	1·33	1·10	1·46	1·75	1·40	1·09	1·79
Copper	2·32	1·97	1·95	3·68	3·54	3·42	3·97	3·86	3·47	3·35	3·47	2·30	3·61
Germanium	0	0	0·06	0·18	0	0·20	0·19	0·25	0·12	0·42	0·49	0·35	0·33
Gold	0	0·60	0·24	0·43	0·69	0·86	0·68	0·50	0·50	0·45	0·41	0·55	1·01
Iron	1·79	1·89	2·54	3·12	3·69	3·48	3·43	4·36	4·71	3·58	3·51	2·58	3·46
Lanthanum	0	0	0·06	0	0·09	0·03	0·08	0·05	0·05	0·18	0·27	0·28	0·66
Lead	1·43	1·20	1·36	1·78	2·31	2·79	2·94	2·40	1·86	2·32	2·16	1·30	2·05
Lithium	0·09	0·08	1·20	0·12	0·25	0·36	0·30	0·25	0·14	0·55	0·43	1·12	0·20
Manganese	1·16	1·37	1·29	1·41	1·57	2·02	2·49	2·45	2·38	1·70	0·95	1·39	1·89
Mercury	1·34	0·34	1·18	0·98	1·33	0·99	1·08	0·80	0·91	1·07	1·05	0·80	1·48
Molybdenum	0·63	0·17	0·71	0·61	0·64	0·73	0·84	1·15	1·21	0·81	1·21	0·82	1·21
Nickel	1·52	0·51	0·83	1·28	1·48	1·36	1·75	2·61	2·35	2·01	1·42	1·27	2·03
Platinum	0	0·68	0·11	0·12	0·20	0·46	0·11	0·15	0·39	0·18	0·82	0·33	0·53
Selenium	0·18	0·51	0·11	0·18	0·15	0·39	0·42	0·40	0·17	0·27	0·58	0·58	0·49
Silver	0·89	0·60	0·59	0·67	1·33	0·76	0·91	0·80	0·89	1·01	0·94	0·73	1·15
Tin	0·71	0·60	1·06	1·28	0·98	1·09	1·14	1·30	1·16	1·01	1·07	0·65	0·89
Titanium	0·53	0·08	0·41	0·55	0·59	1·03	0·57	1·05	1·11	0·84	1·19	0·94	1·22
Tungsten	0·71	0·43	0·36	0·31	0·64	0·36	0·49	0·60	0·37	0·48	0·39	0·56	0·74
Uranium	0	0·08	0·24	0·31	0·19	0·13	0·53	0·35	0·69	0·68	2·65	1·17	1·21
Zinc	1·07	1·11	1·12	1·84	1·38	1·89	1·90	2·20	2·23	2·36	1·79	1·70	2·01

determinations in the period 1965–1970, probably as a result of development of flameless atomic absorption during this period.

Selenium is another element which shows an increase in analytical papers (during the 1955–1960 period). This is probably because of the increasing use of this element in industry (*e.g.*, photocells and rectifiers) and because of the discovery of the important role played by selenium in animal and plant nutrition.

Apart from general interest in the transuranic elements, interest in uranium has increased sharply in recent years. An increase in the years 1935–1955 can be attributed to the great importance of this element in the production of nuclear energy and in military applications. A further substantial increase is evident for the period 1955–1970, due no doubt to the ever-increasing number of analytical methods which are being developed for this element (*e.g.*, gamma spectrometry).

Surprisingly enough, only a few elements show a strong trend in Table 4, and there appears to be a general tendency for interest in most elements to proceed at a steady level unaffected by external trends and events. Some care must be taken in assuming too literally that interest in a particular element is due to the influence of external factors. Very often this interest is due to the "bandwaggon effect". When a new technique, *e.g.*, atomic fluorescence, is developed, there is a tendency for many workers to enter the field in order to achieve prominence and dominance before the end of the surge of interest. For this reason there will be a tendency to work only on those elements which are easily determined by the new method but not by other techniques. Hence an additional reason for interest in mercury (flameless atomic absorption) and selenium (atomic fluorescence).

FUTURE PROSPECTS

It is notoriously difficult to predict the future. For example, who would have imagined in 1945, or even in 1950, that we were on the threshold of tremendous new advances? Who could have predicted in 1955 that in ten years time the technique of atomic-absorption spectrophotometry would replace so many of the classical "wet" methods of analysis? If the trends of the past twenty years are to be maintained, however, we can expect a continuation of the present exponential growth of analytical papers, which should exceed 40,000 per year by 1980. This growth will probably be achieved by increasing the number of specialist journals, and by the diversion of analytical papers into other non-specific journals.

The present lead of the Soviet Union may or may not be maintained. The growth rate of the Soviet economy has slackened in recent years, and this may have an effect on output of analytical papers. It is probable that English will continue to be the most important language of analytical chemistry until the end of the 1970's.

We may expect a further relative decline in the classical techniques of titrimetry and gravimetry, as well as a relative decline in some separation methods such as extraction or ion-exchange due to the continual development of an ever-increasing number of new instrumental methods.

Whatever the future holds, it seems certain that analytical chemistry will maintain its importance in the coming years and will remain a repository of many new and exciting ideas, particularly in the field of instrumental methods of analysis.

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THE COMPLEXOMETRY OF TIN(IV)

J. KRAGTEN

Natuurkundig Laboratorium Universiteit van Amsterdam, Valckenierstraat 65, Amsterdam-C, The Netherlands

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Summary—Tin(IV) very readily hydrolyses in solution, and forms hydrous tin oxide $SnO_2.nH_2O$ even in rather strongly acidic solution. In spite of a lack of reliable data on the hydrolysis of tin(IV) a consistent picture of the behaviour of tin(IV) in solution has been constructed. Some values for the formation of hydroxide and chloride complexes were deduced from electrochemical data. In agreement with more or less qualitative remarks by other investigators a value of log $K_{so} = -3$ has been found for the solubility constant. For the stability constant of tin(IV)–EDTA, log $K_{SnY} = 34{\cdot}5$ was found experimentally. A survey is given of the pitfalls which exist in handling tin solutions. A back-titration procedure is presented that provides for the complexometric determination of tin(IV) at concentrations down to 3 ppm, with an error of 1% or better. Thorium is used as back-titrant with Semi-Xylenol Orange as indicator. The method has successfully been applied to the analysis of organotin compounds.

The behaviour of tin(IV) in solution renders special precautions necessary in the complexometric determination of this element. The more important factors to be taken into account can be summarized as follows. Tin(IV) readily forms an insoluble hydrous oxide ($SnO_2.nH_2O$), even in $10^{-2}M$ solution at pH 0. Its solubility decreases sharply with increasing pH and is minimal between pH 3 and 7. The precipitate is rather unreactive at pH above 1·5. It is not constant in its properties.[1] The oxide can occur in two varieties. The α-form is amphoteric and can rapidly be dissolved in strongly acidic or alkaline solutions; the β-form (metastannic acid), which is formed by the action of nitric acid on metallic tin or by the hydrolysis of stannic salts in hot solutions, can scarcely be dissolved in strongly acidic media. The X-ray diffraction patterns, however, are identical. Therefore it is assumed that although the reactivity differs, the solubility product is the same for both compounds.

It will be shown that a consistent picture of the behaviour of tin(IV) in solution can be constructed in spite of a lack of reliable data. In turn this has resulted in a procedure for an accurate determination of tin by back-titration. The procedure has been applied to the microanalysis of organotin compounds, with favourable results. An estimation of the stability constant of the tin(IV)–EDTA complex has also been made.

An attempt has also been made to estimate the equilibrium constants of the hydroxo- and chloro-complexes in order to determine the partial side-reaction coefficients.

Hydroxide formation

The following normal potentials are known from the literature[2–4]

$$Sn^{2+} + 2e \rightleftharpoons Sn \quad E_1^0 = -0{\cdot}136\,V \qquad (1)$$

$$Sn^{4+} + 2e \rightleftharpoons Sn^{2+} \quad E_2^0 = +0{\cdot}154\,V \qquad (2)$$

At pH < 0 and concentrations of tin $< 10^{-3}M$ the interaction between tin(IV) and hydroxide ions can be neglected;[2–4] this means[5]

$$\log \alpha_{Sn(IV)(OH)} = 0 \qquad (3)$$

For the calculation of $\alpha_{Sn(IV)(OH)}$ the constants of the hydroxo-complexes should be known. In the case of tin(IV) only the constant of the highest complex can be deduced from electrochemical data. Both hydrous tin(IV) oxide and tin(II) hydroxide dissolve in strongly alkaline medium. The stannate(IV) and stannate(II) ions formed can be written as $Sn(OH)_6^{2-}$ and $HSnO_2^-$ [$\equiv Sn(OH)_3^-$]. The normal potentials for the two half-reactions involving these compounds are:[1,2,4]

$$HSnO_2^- + H_2O + 2e \rightleftharpoons Sn + 3OH^- \quad E_3^0 = -0{\cdot}91\,V \qquad (4)$$

$$Sn(OH)_6^{2-} + 2e \rightleftharpoons HSnO_2^- + H_2O + 3OH^- \quad E_4^0 = -0{\cdot}90\,V \qquad (5)$$

The following equilibrium constants are defined in agreement with IUPAC notation:[6]

$$*\beta_{6OH}^{4+} = \frac{[Sn(OH)_6^{2-}].[H^+]^6}{[Sn^{4+}]}$$

and

$$*\beta_{3OH}^{2+} = \frac{[HSnO_2^-].[H^+]^3}{[Sn^{2+}]} \qquad (6)$$

By combining the normal potentials of reactions (1), (2), (4) and (5) with equation (6) and the Nernst equation for the electrode reactions (1), (2), (4) and (5), the following values have been found:

$$\log *\beta_{3OH}^{2+} = -15{\cdot}8 \qquad (7)$$

$$\log *\beta_{6OH}^{4+} = -22 \qquad (8)$$

The value in equation (7) agrees with the value $-16{\cdot}6$ calculated from the stepwise constants[7] which are found from solubility measurements. The stepwise constants for Sn(IV) are unknown. The constants should follow from measurements in the pH range 2–7, but in this range the solubility is too small for reliable measurements. However, as the analytical procedures for tin in solution are applied in either highly acidic or highly alkaline solution, knowledge of the intermediate constants is not of analytical importance.

Chloride formation

Tin(II) and tin(IV) have such a strong tendency to form chloride complexes that in 1*M* chloride only the highest complexes $SnCl_6^{2-}$ and $SnCl_4^{2-}$ are formed.[2,8] The formal potentials for pH = 0, which excludes the formation of hydroxo-complexes, and a chloride concentration of 1*M* are:[2]

$$SnCl_4^{2-} + 2e \rightleftharpoons Sn + 4Cl^- \quad E_5^0 = -0{\cdot}19\,V \quad (9)$$

$$SnCl_6^{2-} + 2e \rightleftharpoons SnCl_4^{2-} + 2Cl^- \quad E_6^0 = +0{\cdot}14\,V \quad (10)$$

It is not certain that the bivalent tin compound actually is $SnCl_4^{2-}$, but it does not matter here, as it has no influence on the calculation of the equilibrium constant

$$\beta_{6Cl}^{4+} = \frac{[SnCl_6^{2-}]}{[Sn^{4+}].[Cl^-]^6} \quad (11)$$

for the reaction $Sn^{4+} + 6Cl^- \rightleftharpoons SnCl_6^{2-}$ in which we are interested.

Similarly to the procedure for the hydroxo-complexes this constant can be calculated by combining the normal potentials in (1) and (2) and the formal potentials in (9) and (10) with equation (11) and the Nernst equation:

$$\log \beta_{6Cl}^{4+} = 2{\cdot}0 \quad (12)$$

Huey and Tartar[9] found that the formal potential given in (10) decreases with decreasing chloride concentration; it approaches the value E_2^0 for $[Cl^-] \simeq 0{\cdot}2M$ and remains constant at lower chloride concentrations. This suggests that $SnCl_6^{2-}$ also predominates at chloride concentrations lower than 1*M*, which means that the partial side-reaction coefficient $\alpha_{Sn(Cl)}$ can be approximated by

$$\alpha_{Sn(Cl)} = 1 + \beta_{6Cl}^{4+}.[Cl^-]^6 = 1 + 100.[Cl^-]^6 \quad (13)$$

The solubility constant of tin(IV) oxide

Generally the formation of a precipitate depends on the solubility constant, which for tin(IV) can be written as[6]

$$^*K_{So} = [Sn^{4+}]/[H^+]^4 \quad (14)$$

From this equation and the definition of the side-reaction coefficient it follows that the maximum concentration of tin(IV), $[Sn']_{max}$, is determined by

$$\log [Sn']_{max} = \log {}^*K_{So} - 4pH + \log \alpha_{Sn} \quad (15)$$

Only a few data for $^*K_{So}$ are in the literature. Latimer[4] reports $\log {}^*K_{So} \sim -1$ and Ringbom[10] $\log K_{So} = 0$, without information about the way the data were found.

From procedures for the preparation of stock solutions[11,12] we know that a $10^{-3}M$ tin(IV) solution can be kept for a long time if its sulphuric acid concentration is greater than 1·5*M*. From a series of experiments with decreasing sulphuric acid concentrations we found that mg amounts of tin precipitate at the glass wall when the sulphuric acid concentration of the $10^{-3}M$ Sn(IV) stock solution is below 0·75*M*. This acidity corresponds to pH = 0·0.[13] Substitution in equation (15) together with $\log \alpha_{Sn} = 0$ [equation (3)] leads to

$$\log {}^*K_{So} = -3{\cdot}0 \quad (16a)$$

Although from potential measurements under these conditions no measurable interaction between Sn(IV) and OH^- in solution can be found, precipitation of tin(IV) oxide still occurs because of the extremely small solubility constant. J. D. Smith[14] reports that tin(IV) is precipitated from a $10^{-2}M$ solution when the hydrochloric acid concentration is less than 0·7*M*. According to Michaelis and Granick,[13] and Bates,[15] this acidity corresponds to pH 0·14; the chloride concentration leads to $\log \alpha_{Sn} = \log \alpha_{Sn(Cl)} = 1{\cdot}2$. Substitution in equation (15) gives

$$\log {}^*K_{So} = -2{\cdot}8 \quad (16b)$$

From a paper by A. E. Smith[16] it can be deduced that tin is precipitated when the pH of a solution $10^{-5}M$ in Sn(IV) and 1·5–2*M* in chloride exceeds 1·5. According to equation (8) the chloride concentration leads to a $\log \alpha_{Sn(Cl)}$ value between 3 and 4. Substitution in equation (15) leads to a value for $\log {}^*K_{So}$ between -2 and -3.

There is some uncertainty about the reliability of the values deduced, but

$$\log {}^*K_{So} = -3 \quad (17)$$

can be regarded as a useful estimation.

The solubility region

In this section a consistent system of equations will be derived which describes the solubility of tin(IV) in aqueous solution and with which the behaviour of tin(IV) can be explained. Later it will be used for the development of a titration procedure in the same way as was done for aluminium.[17]

As we are dealing with dilute solutions the existence of polynuclear hydroxo-complexes has been neglected.[17,18] The remaining reactions are

$$Sn^{4+} \rightleftharpoons Sn(OH)^{3+} \rightleftharpoons Sn(OH)_2^{2+} \rightleftharpoons Sn(OH)_3^{+} \rightleftharpoons Sn(OH)_4 \rightleftharpoons Sn(OH)_5^{-} \rightleftharpoons Sn(OH)_6^{2-}$$
$$\downarrow\uparrow$$
$$(\text{solid } SnO_2.nH_2O) \quad (18)$$

The corresponding side-reaction coefficient is

$$\alpha_{Sn(H)} = 1 + 10^{(pH - p^*\beta_1)} + 10^{(2pH - p^*\beta_2)} + \ldots\ldots + 10^{(6pH - p^*\beta_6)} \quad (19)$$

in which $p^*\beta_i$ represents $-\log {}^*\beta_{iOH}^{4+}$.

There are distinct pH regions in which one of the complexes predominates, and then $\alpha_{Sn(OH)}$ can be approximated by the corresponding term

$$\log \alpha_{Sn(OH)} = (i\text{pH} - \text{p}^*\beta_i) \quad (i = 0,1,2,\ldots\ldots 6;\ \text{p}^*\beta_0 = 0) \qquad (20)$$

Substitution of equation (20) together with $\log {}^*K_{S_0} = -3$ in equation (15) leads to the following equation for a chloride-free medium:

$$\text{p}[\text{Sn}']_{max} = (3 + \text{p}^*\beta_i) + (4 - i)\text{pH} \qquad (21)$$

In the graphical representation of $\text{p}[\text{Sn}']_{max}$ *vs.* pH equation (21) leads to six straight lines. The overall curve is the rounded-off line connecting the line segments corresponding to the smallest values. Just as in a previous paper on aluminium,[17] this boundary curve surrounds the region of precipitation.

From the literature little is known about the different $\text{p}^*\beta_i$ values for tin(IV). It happens, as will be shown hereafter, that the boundary curve is only known for strongly acidic and strongly basic medium. However, this does not cause complications, as the missing intermediate part is not of practical importance for the purpose of this paper.

From equation (3) we know that $\alpha_{Sn(OH)} = 1$ at pH 0. If equation (19) is compared with this result it follows that the pH-dependent terms must be negligibly small at pH 0. This can only occur if the constants $\text{p}^*\beta_i$ in equation (19) are >1. It may be supposed that tin resembles other metals in that the constants $\text{p}^*\beta_1$, $\text{p}^*\beta_2$ and $\text{p}^*\beta_3$ should increase consecutively. More information is not available, but this is sufficient. It can be concluded that up to pH 1 $\log \alpha_{Sn(OH)}$ remains small enough to be neglected (in comparison with the uncertainty of $\log {}^*K_{S_0}$ for instance). Hence up to pH 1 the precipitation region will be bounded by the first line ($i = 0$) of the series given by equation (21):

$$\text{p}[\text{Sn}']_{max} = 3 + 4\text{pH} \qquad (22)$$

For the second line $\text{p}^*\beta_1 > 1$; substitution in equation (21) with $i = 1$ shows that this line will not contribute to the actual curve below pH 1. Analogous considerations hold for the other lines. This also means that below pH 1 the hydroxide formation is negligible.

As this paper deals with photometric titrations, we are only interested in concentrations of tin(IV) larger than about $10^{-7}M$. From the solubility product (17) this means that we can restrict ourselves to pH values smaller than 1, provided that $\log \alpha_{Sn}$ is negligibly small in this pH region. The last condition is satisfied, as we know from the foregoing. Hence in the region of practical interest, featured by $[\text{Sn}] > 10^{-7}M$ and pH < 1, only equation (22) needs to be considered; it corresponds to line *a* in Fig. 1.

When chloride is also present in the solutions, equations (21) and (22) have to be extended with

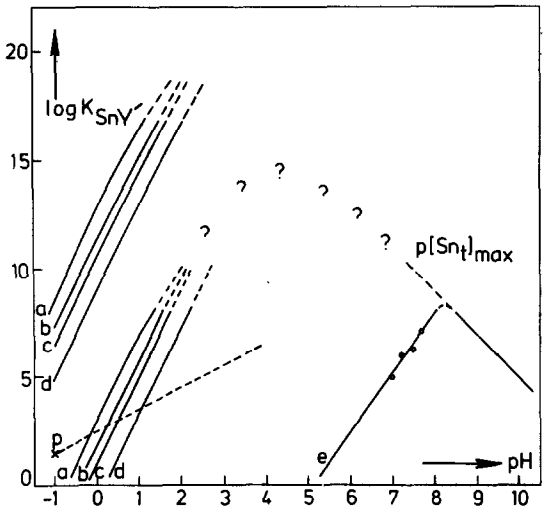

Fig. 1. The conditional constant $K_{SnY'}$ and the concentration limit $\text{p}[\text{Sn}']_{max}$ for tin oxide precipitation *vs.* pH at different chloride concentrations. [Cl^-]: *a*, <0·2*M*; *b*, 0·7*M*; *c*, 1*M*; *d*, 2*M*. The region of precipitation lies under the curve. Boundary curve *e* corresponds to a 50% excess of EDTA. The dotted line through *P* indicates the penetration of the precipitation region on dilution.

$\alpha_{Sn(Cl)}$. For acid medium the equation for the boundary line then becomes

$$\text{p}[\text{Sn}']_{max} = 3 + 4\text{pH} - \log \alpha_{Sn(Cl)} \qquad (23)$$

The lines *b*, *c* and *d* were calculated by using this formula in combination with equation (13) and correspond to chloride concentrations of 0·7, 1·0 and 2·0*M* respectively. Below a chloride concentration of 0·2*M* the line coincides with line *a*. Only at chloride concentrations above 0·2*M* does the solubility increase.

At high pH values only the line corresponding to $Sn(OH)_6$ needs to be considered in the concentration range of practical importance (pSn' < 7). As $\text{p}^*\beta_6 = 22$ [equation (8)], the boundary line can be estimated for this area by

$$\text{p}[\text{Sn}']_{max} = 25 - 2\text{pH} \qquad (24)$$

The last part of the curve in Fig. 1 corresponds to this equation.

The curves represented in Fig. 1 are much less accurately known than in the case of aluminium.[17] Nevertheless sufficient information has been obtained for consideration of the complexometry of tin(IV).

The properties of tin(IV)–EDTA

In acid medium tin(IV) and EDTA react quickly, forming a 1:1 complex. Numerous back-titration procedures have been worked out.[19,20] All the papers warn that the results will be inaccurate if the neutralization, necessary for the titration of the excess of EDTA, is not performed carefully. The main origin of the errors is that Sn(IV)–EDTA dissociates in the vicinity of the added base, forming a colloidal tin oxide, which is partly unreactive with respect to EDTA. In the presence of EDTA, tin

oxide precipitates quantitatively between pH 8 and 9; below pH 7 and above pH 10 no precipitation occurs,[21,22] so the original precipitation region is appreciably diminished on the low-pH side. In this range α_{Sn} is made several orders of magnitude larger by the presence of EDTA [equation (15)]; α_{Sn} can be approximated by $\alpha_{Sn(Y)}$

$$\alpha_{Sn} = \alpha_{Sn(Y)} = [Y'] . K_{SnY}/\alpha_{Y(H)} \qquad (25)$$

where [Y'] is the total concentration of EDTA not bound to tin.

Substitution of equation (25) in equation (15) gives

$$\log [Sn']_{max} = \log {}^*K_{So} - 4pH + \log K_{SnY} + \log[Y'] - \log \alpha_{Y(H)} \qquad (26)$$

which leads to curve *e* in Fig. 1.

This equation can be used to estimate K_{SnY}. The idea is that if the precipitation region is entered, a subsequent titration will show a negative error as unreactive tin oxide is formed. The experiments are performed analogously to the procedure in the next section. EDTA is added in excess to the acidic tin solution, after which the pH is increased homogeneously by adding hexamine and boiling.[17] The increase in pH can be stopped by cooling. The solution is acidified and the back-titrations performed at pH 2. In our experiments the concentration of EDTA was $2 \times 10^{-5}M$; the concentration of tin was $10^{-5}M$. No negative error was encountered until the pH was increased to 7·0. Increase to pH 7·2 led to an error of 10%. At pH 7·5 and 7·7 respectively 6 and 0% of the tin was left in solution. Substitution of these data in equation (23) leads to an estimate of

$$\log K_{SnY} = 34{\cdot}5 \qquad (27)$$

(see corresponding points in Fig. 1). The reliability of this value is mainly dependent on the uncertainty in $\log {}^*K_{So}$, for which ± 1 is suggested. In calculating the value in equation (27) no allowance has been made for the possible existence of mixed complexes with hydrogen and hydroxyl ions.

The conditional constant for the tin(IV)–EDTA complex has been calculated by means of the value in equation (27). Log $K_{Sn'Y'}$ *vs.* pH is represented in Fig. 1. The lines *a'*, *b'*, *c'* and *d'* correspond to the same chloride concentrations as the lines *a*, *b*, *c* and *d*.

The complexometric titration of tin(IV)

A direct titration of metal ions is only possible under conditions where $\log (C_M K_{MY})$ exceed a certain minimum value. In the case of a photometric end-point determination by means of an indicator the value is 3·8.[23–25]

The solubility of tin oxide sets a stringent maximum value to log (*CK*). From the vertical distance between the corresponding lines (*a–d*) in Fig. 1 it follows that this maximum is about 9·5. The difference between maximum and minimum is sufficiently large to make a direct titration theoretically possible. In practice a hydrogen-ion concentration of at least $1M$ is required to prevent the formation of unreactive oxide. At this acidity, however, a suitable indicator could not be found. Other suitable end-point detection methods could not be found either, so our attention has been directed to the development of a back-titration procedure.

From the equilibrium condition it can be derived[17] that the concentration of free metal remaining in solution is determined by

$$\log[Sn'] = -\log K_{Sn'Y'} - \log \frac{[Y']}{[SnY]} \qquad (28)$$

Usually the excess of EDTA is about 50%, making the last term in equation (25) zero. Anyhow, this term is commonly negligible with respect to the other terms, which makes the curve for the equilibrium concentration *vs.* pH approximately coincident with the curve for the conditional constant. From the curves in Fig. 1 it can be concluded that tin is quantitatively bound at pH < 0 even at a concentration of $10^{-5}M$.

After the addition of EDTA, the pH generally has to be changed as dictated by the back-titrant used. The pH adjustment was carried out homogeneously for the reasons mentioned in the previous section. When the starting solution is strongly acidic, considerable amounts of hexamine are necessary. Although commercially available hexamine contains only trace amounts of metals, systematic deviations were found in these cases. When chloride is added to the solution in order to prevent precipitations of tin oxide, the starting pH can be higher and consequently smaller amounts of hexamine can be used for the pH adjustment. The systematic deviations can be kept negligibly small in this way, even in the titration of micro-amounts of tin(IV).

A comment should be made concerning the dilution of tin(IV) solutions. If, for instance, 100 mg of tin are dissolved in 1 ml of sulphuric acid (1+1), the solution roughly corresponds to point *P* in Fig. 1. When this solution is diluted with water this "conditional" point will shift along the dotted line. Even a tenfold dilution causes a penetration of the precipitation region. This shows that if EDTA is not present in the solution, care should be taken with the addition of water during the preparation of stock solutions and titration media. Even the EDTA solution should be acidified. It is generally recommended to dilute tin (IV) solutions with a solution at least $1M$ in hydrochloric acid.

The conditional constant for tin(IV)–EDTA is so extremely large compared with the conditional constants for other metals, that there are no restrictions on the choice of the back-titrant.[26] For larger concentrations of tin, thorium (with Xylenol Orange as indicator) was found very suitable both for visual and for photometric end-point detection. Other techniques were not tried. For smaller concentrations this couple cannot be applied because of the 2:2 complex-formation between thorium and Xylenol

Orange (XO), which causes systematic errors.[24,25] Bismuth cannot be used because of the chloride present. The combination cerium (III)–XO has been tried and gives acceptable results; a disadvantage of this couple is that appreciable amounts of hexamine have to be added in order to reach the required pH of 5·5. Very accurate results were obtained with a photometric procedure at pH 1·8–2·0 with thorium and Semi-Xylenol Orange (SXO). The procedure for this titration will be outlined in the next section.

EXPERIMENTAL

Apparatus

The photometric titrations were carried out in a Zeiss PMQII spectrophotometer with a titration assembly for 10- and 20-ml cells (2-cm path-length). The titrant solutions were added with Metrohm microburettes, Type E 457. The tips of the 0·5-ml assemblies were bent upwards in order to prevent gravitational losses when immersed in the fluid.

The water was purified by sub-boiling demineralized water in quartz distillation apparatus[27] (Quartz and Silice, Paris).

Reagents

All solutions were prepared from analytical-reagent grade chemicals and sub-boiled water.

Ethylenediaminetetra-acetic acid disodium salt solution ($5 \times 10^{-3}M$ brought to pH 0 with conc. hydrochloric acid). The EDTA solution was standardized against copper with purified 1-(2-thiazolylazo)-2-resorcinol (TAR) as indicator. (PAR and PAN cannot be used because their K_{MI} values are too large.)[23]

Thorium(IV) standard solution ($5 \times 10^{-3}M$ thorium nitrate brought to pH 2 with conc. hydrochloric acid). This solution was standardized by photometric titration against EDTA with SXO as indicator.

Table 1. Photometric back-titration of tin

Series I		Series II	
Taken, *μmole*	Found, *μmole*	Taken, *μmole*	Found, *μmole*
1·190	1·189	0·968	0·965
(141·3 μg)	1·190	(114·9 μg)	0·962
	1·193		0·960
	1·191		0·969
	1·193		0·965
	1·191		0·963
	1·197		0·970
	1·193		0·962
	$\bar{x}_1$ = 1·192		$\bar{x}_2$ = 0·965
	Sx = 0·002		Sx = 0·004

Hexamine solution. Hexamine (2·4 g) dissolved in about 20 ml of water and brought to pH 1–3 with hydrochloric acid, and prepared fresh daily.

Indicator. A solid mixture (1:100) of SXO and potassium nitrate. The indicator is prepared by Mannich condensation of Cresol Red, formaldehyde and iminodiacetic acid and purified by extraction. The preparation and purification procedures will be published in detail by Dr. C. J. C. Pijpers.

Tin solution. Pure tin (50–100 mg) dissolved in 15 ml of hydrochloric acid (1 + 1), and the solution diluted to 100 ml with 1*M* hydrochloric acid. Portions were taken from this solution either directly by means of a microburette (250 μl), or with a pipette after 20-fold dilution.

Procedure

Introduce the sample, containing 1 μmole of dissolved tin(IV) into a 20-ml titration cell containing about 10 ml of 1*M* hydrochloric acid. Add 250–300 μl of $5 \times 10^{-3}M$ EDTA, which corresponds to a 25–50% excess, and 3 ml of the acidified hexamine solution. Heat for 10 min at almost 100° and then cool. The pH should lie between 1·8 and 2·1. Finally add 10–20 mg of the indicator mixture and titrate the excess of EDTA with thorium(IV) solution. The optimum wavelength is 530 nm.

It must be emphasized that as long as EDTA is not present in the solution all liquids which have to be added for rinsing (*e.g.*, of the glass electrode) or for diluting, should be 1*M* hydrochloric acid. Once EDTA is present the liquid added may be less acid (pH < 6).

RESULTS AND DISCUSSION

Some results for different amounts of tin are given in Tables 1 and 2. From the series I–IV it follows that the titrations can be performed with high precision. The standard deviation is about 0·004 μmole (0·4 μg) for a single titration (Table 1) and about the same as the approximate value 0·005 μmole that follows from the correlation coefficient (r) of series III (Table 2) (r is an indication of the accuracy of fit).

In series III-V the slopes deviate by only 0·3% from the theoretical values. The maximum amounts of impurities stated in the specifications of the reagents used correspond to 0·002 μmole, which correlates with the values found for the procedural error b and σ_x in series III and IV.

The less accurate values in series V are due to the fact that in this case tin metal was dissolved

Table 2. Linear increase procedure in the photometric back-titration of tin

Series III		Series IV		Series V	
Taken, *μmole*	Found, *μmole*	Taken, *μmole*	Found, *μmole*	Taken, *μmole*	Found, *μmole*
0·387	0·394	0·534	0·535	0·464	0·480
(45·9 μg)	0·398		0·534		0·479
0·774	0·778	1·068	1·069	0·928	0·900
	0·780		1·069		0·906
1·161	1·169	1·603	1·604	1·392	1·383
	1·168		1·602		1·384
1·548	1·559	2·137	2·139	1·856	1·870
	1·557		2·136		1·868
Correlation coefficient					
r = 0·99999		r = 0·99999		r = 0·99943	
Procedural error					
b = +0·006 μmole		b = 0·000 μmole		b = −0·005 μmole	
Slope = 0·388 μmole per step		Slope = $0{\cdot}534_7$ μmole per step		Slope = $0{\cdot}465_5$ μmole per step	

Table 3. Tetracyclohexyltin analysis

Taken, *μmole*	Found, *μmole*
0·363	0·360
	0·361
0·727	0·725
	0·724
1·091	1·092
	1·085
1·454	1·444
	1·445

Correlation coefficient (r) = 0·99996
Procedural error (b) = 0·0009 μmole
Slope = $0{\cdot}361_5$ μmole/step.

in a mixture of sulphuric and nitric acid, the solution evaporated to dryness and the SnO_2 residue dissolved in 5 ml of conc. hydrochloric acid after heating. This procedure was introduced in order to investigate the possibility of using this titration technique for the determination of tin in organotin compounds which are commonly decomposed with these acids. Nitric acid (and perchloric acid) do not interfere; sulphate ions interfere in concentrations above 0·005*M*. The increased uncertainty in series V is not caused by the acids, but by the evaporation to dryness. During the drying stage SnO_2 precipitates, and in the dry state is transformed into the unreactive β-form. As small amounts of sulphate are permissible it is advised to evaporate till nearly dry; the wet residue can easily be dissolved in concentrated hydrochloric acid.

Tetracyclohexyltin was used as a standard in order to check the destruction and titration. Its theoretical tin content is 26·30%. Some results are given in Table 3. An 82·05-mg sample was decomposed with 0·5 ml of conc. sulphuric acid and 0·5 ml of nitric acid. The solution was made up to 50·0 ml with 1*M* hydrochloric acid. Multiples of 100 μl were taken from this solution. According to the manufacturer's specification, the tin content is 99·0% of the theoretical value, which agreed with our gravimetric results (99·1%). The result in Table 3 (99·4%) agrees with the actual content within the standard deviation of 0·7% (calculated from r).

As the procedure seemed rather promising for the microanalysis of organotin compounds, some technical samples were analysed. In all cases 65–80 mg amounts were destroyed, leading to about 0·4 μmole of tin in the 100-μl portions used. The results are presented in Table 4.

Table 4.

Compound	Procedural error (b), %	Standard deviation,%	Systematic deviation,%
Tributyltin chloride	+6	1·5	−3·5
(tin content· 36·5%)	+3	1	−2·8
	+4	0·5	−2·8
Tributyltin acetate	0·2	0·5	−4·5
(tin content: 36·6%	0·2	0·8	−4·0
Tributyltin fluoride	0·2	1	−5·0
(tin content· 38·5%)	0·8	1	−3·0
Triphenyltin acetate	1·0	0·8	−1·3
(tin content. 29·0%)	0·6	1·0	−1·5

* All percentages given are relative to the tin content found.

As far as is known the procedure presented here is the only method in which tin can be determined with a precision of better than 1% in concentrations down to 60 μg in 20 ml (3 ppm). A drawback is that a separation usually has to precede the tin determination. Another drawback for the microdetermination is that the indicator SXO is not commercially available.

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ACID–BASE EQUILIBRIA IN ETHYLENE GLYCOL—II

AUTOPROTOLYSIS CONSTANTS AND ACID–BASE PROPERTIES OF ETHYLENE GLYCOL AND ITS MIXTURES

P. ZIKOLOV, A. ASTRUG and O. BUDEVSKY
Faculty of Pharmacy, Academy of Medicine, Ekz. Josif No. 15, Sofia, Bulgaria

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Summary—The acid–base behaviour of ethylene glycol and its mixtures with water (1, 5 and 10%), methanol, ethanol, isopropanol, nitromethane (each 10%) and ethyl methyl ketone–chloroform (5 + 5%) have been investigated by potentiometric titration, in a cell without liquid junction, equipped with a glass and a silver–silver chloride electrode. The autoprotolysis as well the protolysis constants of phthalic acid were determined for each mixture. The added solvents improve the properties of ethylene glycol, decreasing the viscosity without changing the acid–base behaviour of the ethylene glycol itself, which is favourable for the titration of weak bases. Water increases the basic, and nitromethane the acidic, properties of the mixture. Small quantities of water (*ca.* 1%) do not impair the titration conditions.

Ethylene glycol (EG) and its mixtures with other solvents have been used as solvent medium mainly for acid–base titrations of basic substances.[1] The mixtures are preferred because of the high viscosity of pure ethylene glycol. In most cases, the titration conditions in EG medium have been selected empirically, because of the scarcity of data which characterize the acid–base behaviour of the solvent,[2] as well as the behaviour of protolytes dissolved in this medium.[2,3]

The aim of the present work was to investigate EG and some mixtures containing it, by means of a potentiometric titration technique and to establish their applicability as media for non-aqueous titrations. The autoprotolysis constant of a solvent has a great significance for every titration in that solvent, because it defines the length of the pH-scale. That is why, in the present investigations the autoprotolysis constants for EG with additions of other solvents with various acid–base properties and different dielectric constants have been determined. The second aim was to investigate the influence of the added solvents on the acid–base behaviour of the EG, for which purpose phthalic acid was chosen as a reference standard. The protolysis constants of the latter were determined potentiometrically in each EG mixture. From the change in the pK-values of phthalic acid and its conjugate base conclusions are drawn about the change in the acid–base behaviour of EG caused by the added cosolvent.

The EG mixtures are treated as separate solvents with their own acid–base properties and dielectric constant, not excluding the possibility of a protolysis reaction between the two solvents. According to this concept, the thermodynamic (K_s) and concentration (K_s^c) autoprotolysis constants of the solvent SH are given by the following equations:

$$2SH = SH_2^+ + S^-$$
$$K^s = \{SH_2^+\}\{S^-\}\ ;\ K_s^c = [SH_2^+][S^-] \qquad (1)$$

The protolysis, and the protolysis constant for phthalic acid (H_2Ph) are given by the equations:

$$H_2Ph + SH = HPh^- + SH_2^+$$
$$K_{H_2Ph} = \{SH_2^+\}(\{HPh^-\}/\{H_2Ph\});$$
$$K^c_{H_2Ph} = [SH_2^+]([HPh^-]/[H_2Ph]) \qquad (2)$$

The protolysis, and the protolysis constant for the conjugate base, the biphthalate ion (HPh^-), are represented by the equations

$$HPh^- + SH = H_2Ph + S^-$$
$$K_{HPh^-} = \{S^-\}(\{H_2Ph\}/\{HPh^-\}) = K_s/K_{H_2Ph} \qquad (3)$$

EXPERIMENTAL

Reagents

Ethylene glycol (reagent-grade solvent) was purified as described before.[3] Reagent-grade potassium chloride and potassium biphthalate were dried before use. The solvents methanol, ethanol, isopropanol, nitromethane, ethyl methyl ketone and chloroform were also purified.[4] Water was freshly redistilled. The EG mixtures were prepared by mixing measured volumes of EG and solvent. The titrants were prepared by dilution of a concentrated (*ca.* 0·2M) solution of hydrogen chloride in EG[3] and standardized by potentiometric titration of potassium biphthalate in the same solvent. The sodium glycoxide solution was prepared in the titration vessel *in situ* by dissolving sodium metal (*pro analysi*) in the solvent and standardized by potentiometric titration with hydrochloric acid in the same solvent.

Apparatus

The autoprotolysis constants were determined with a cell of type (I):

$$\begin{matrix}\text{glass}\\ \text{electrode}\end{matrix} \;\|\; 0{\cdot}1M(\text{Na glycoxide} + \text{HCl} + \text{KCl}),\ SH\,|\,AgCl\text{–}Ag \qquad (1)$$

For determination of the protolysis constants of phthalic acid a cell of type (II) was used:

$$\begin{matrix}\text{glass}\\ \text{electrode}\end{matrix} \;\|\; 0{\cdot}1M\ (KHPh + HCl + KCl,\ SH\,|\,AgCl\text{–}Ag \qquad (II)$$

The cells (I) and (II) do not contain a liquid junction, which provides advantages discussed earlier.[3]

The experimental arrangement consisted of a thermostated titration vessel, a Radiometer glass electrode type 202 B, a silver–silver chloride reference electrode prepared according to Brown,[5] an automatic burette, Radiometer type ABU 12, a digital pH-meter, Radiometer PHM 52, accurate to ± 0·1 mV, and a magnetic stirrer.

Titrations

Both the room and the titration vessel were kept at 25° ± 0·2° and the ionic strength of all the solutions was maintained at 0·1 by addition of potassium chloride (see footnote on p. 488 of ref. 3). The standardized 0·1*M* hydrochloric acid was used to titrate sodium glycoxide solutions (*ca.* 0·01*M*) for the determination of the autoprotolysis constants, and potassium biphthalate solutions (*ca.* 0·025*M*) for the determination of the protolysis constants of phthalic acid. In both cases the titrations were continued past the equivalence point to yield data which were used to calibrate the electrochemical cell in terms of the $E^{0'}$ value for the particular experiment.

RESULTS

Autoprotolysis constant of EG and its mixtures

The e.m.f. of cell (I) at 25° is given by the following equations:

$$E = E_a^{0'} - 0{\cdot}05916 \log[SH_2^+] \quad (4)$$

$$E = E_b^{0'} + 0{\cdot}05916 \log[S^-] \quad (5)$$

where $[SH_2^+]$ and $[S^-]$ are the molar concentrations of the lyonium and lyate ions of the solvent, and $E_a^{0'}$ and $E_b^{0'}$ are specific constants of the cell for the acidic and alkaline ranges, and include the standard electrode potential of the glass electrode, the potential of the reference electrode and activity factors. From (1), (4) and (5) the concentration autoprotolysis constant is obtained:

$$pK_s^c = \frac{E_b^{0'} - E_a^{0'}}{0{\cdot}05916}$$

The determination of E_a^0 and E_b^0 by means of equations (4) and (5) is not difficult because both the hydrochloric acid and the sodium glycoxide are completely dissociated in both EG and the mixtures as indicated by the constancy of $E_a^{0'}$ and $E_b^{0'}$ throughout the whole experiment.

The thermodynamic autoprotolysis constant was calculated from the concentration constant:

$$pK_s = pK_s^c - 2 \log f_\pm$$

where the activity coefficient was calculated by the extended Debye–Hückel equation

$$-\log f_\pm = \frac{Az^2\sqrt{\mu}}{1 + Ba\sqrt{\mu}} \quad (6)$$

In the calculations of the constants $A = 1{\cdot}825 \times 10^6 (\epsilon T)^{-3/2}$ and $B = 50{\cdot}29(\epsilon T)^{-1/2}$ the dielectric constant (see Table 2) was estimated by assuming the values to be additive. The ionic strength μ was taken as 0·1 and the ion size parameter a as 5.

The experimental data from a potentiometric titration and their treatment for the calculation of the concentration autoprotolysis constant of EG are shown in Table 1. The calculation of $E_b^{0'}$ by means

Table 1. Experimental data and their treatment for the calculation of pK_s^c of ethylene glycol

1*a*. Calculation of $E_b^{0'}$

V_{HCl}, *ml*	E, *mV*	ϕ × 10^{-6}	$[S^-]$ × 10^3	$-\log [S^-]$	$-\log [S^-] \times 59{\cdot}16$, *mV*	$E_b^{0'}$, *mV*
0·200	280·9	1·12	6·79	2·19	129·84	410·74
0·400	276·3	0·93	5·34	2·27	134·43	410·73
0·600	271·0	0·78	4·32	2·36	139·88	410·88
0·800	264·3	0·60	3·32	2·48	146·66	410·98
1·000	255·2	0·43	2·33	2·62	155·71	410·91
1·200	241·1	0·25	1·37	2·86	169·43	410·53
					Mean $E_b^{0'}$ = 410·8 mV	

1*b*. Calculation of $E_a^{0'}$

V_{HCl}, *ml*	E, *mV*	ϕ' × 10^{-7}	$[SH_2^+]$ × 10^3	$-\log [SH_2^+]$	$-\log [SH_2^+] \times 59{\cdot}16$, *mV*	$E_a^{0'}$, *mV*
2·000	−312·0	0·40	1·11	2·95	174·71	−486·71
2·200	−326·8	0·71	2·00	2·70	159·61	−486·41
2·400	−336·1	1·07	2·88	2·54	150·31	−486·41
2·700	−345·4	1·52	4·16	2·38	140·84	−486·24
3·000	−352·5	2·08	5·14	2·27	134·09	−486·59
3·500	−360·7	2·83	7·42	2·13	125·97	−486·67
4·000	−366·8	3·80	9·35	2·03	120·04	−486·84
					Mean $E_a^{0'}$ = −486·5 mV	

$$pK_s^c = \frac{410{\cdot}8 + 486{\cdot}5}{59{\cdot}16} = 15{\cdot}168 \qquad pK_s = 15{\cdot}168 + 0{\cdot}554 = 15{\cdot}72$$

Conditions: 20 ml of 7·46 × $10^{-3}M$ sodium glycoxide titrated with 0·1001*M* hydrochloric acid in ethylene glycol 0·1*M* in potassium chloride. The sodium glycoxide was neutralized with 1·490 ml hydrochloric acid, and the sodium glycoxide and basic impurities with 1·755 ml (the volumes are determined by extrapolation of the ϕ and ϕ' functions.)

Table 2. Autoprotolysis constants of ethylene glycol and its mixtures

Solvent*	$E_b^{0'}$, mV	$E_a^{0'}$, mV	pK_s^c	ϵ	$-2\log f_\pm$	pK_s
W	497·7 ± 0·3	−319·0 ± 0·1	13·805 ± 0·005	78·3	0·213	14·02
EG–W (10%)	419·5 ± 0·2	−408·3 ± 0·2	13·992 ± 0·004	41·8	0·485	14·49
EG–W (5%)	415·3 ± 0·3	−432·7 ± 0·3	14·334 ± 0·005	39·7	0·518	14·85
EG–W (1%)	412·0 ± 0·3	−468·9 ± 0·3	14·891 ± 0·005	38·1	0·546	15·44
EG	410·8 ± 0·2	−486·5 ± 0·1	15·168 ± 0·003	37·7	0·554	15·72
EG–EMK–Ch	414·5 ± 0·1	−484·7 ± 0·3	15·200 ± 0·005	35·1	0·607	15·81
EG–iPrOH	415·9 ± 0·2	−488·8 ± 0·4	15·292 ± 0·006	35·8	0·593	15·88
EG–EtOH	418·8 ± 0·2	−488·2 ± 0·1	15·331 ± 0·003	36·4	0·580	15·91
EG–MeOH	415·2 ± 0·2	−488·6 ± 0·4	15·276 ± 0·006	37·2	0·563	15·84
EG–NM	316·9 ± 0·1	−487·3 ± 0·2	13·594 ± 0·003	37·5	0·558	14·15

* Symbols: EG—ethylene glycol, W—water, EMK–Ch—ethyl methyl ketone–chloroform (5 + 5%), iPrOH—isopropanol (10%), EtOH—ethanol (10%), MeOH—methanol (10%), NM—nitromethane (10%).

of equation (5) is shown in Table 1*a*. The molar concentration of the lyate ions $[S^-]$ at every titration point was calculated by the difference between their total concentration and the molar concentration of the added hydrochloric acid in the course of the titration. The total concentration of the lyate ions in the solution was determined from a Gran plot[6] of the potentiometric titration data before the equivalence point. In Table 1*b* the determination of $E_a^{0'}$ by equation (4) is shown. The molar concentration of the lyonium ions in the solution $[SH_2^+]$ is calculated from the volume and the molarity of the hydrochloric acid added after the neutralization of the sodium glycoxide and the impurities of basic character. The equivalence point was again found from a Gran plot of the titration data.

The values of the autoprotolysis constants for EG and its mixtures are summarized in Table 2.

Protolysis constants of phthalic acid in EG and its mixtures

The e.m.f. (E) of cell (II) at 25° is given by equation (4). After $E_a^{0'}$ of the cell has been determined, the value of $pc_H = -\log[SH_2^+]$ for each titration point can be determined according to the equation:

$$pc_H = \frac{E - E_a^{0'}}{0{\cdot}05916} \qquad (7)$$

From (2) and (7), the following equation is obtained for the concentration protolysis constant of phthalic acid:

$$pK^c_{H_2Ph} = pc_H + \log \frac{[H_2Ph]}{[HPh^-]}$$

In practice, $pK^c_{H_2Ph}$ for each titration point is calculated from the relationship

$$pK^c_{H_2Ph} = pc_H + \log \frac{[HCl]}{[HPh^-]_{tot} - [HCl]}$$

where [HCl] is the molar concentration of the added acid and $[HPh^-]_{tot}$ is the total concentration of the biphthalate ions as determined by a Gran plot; pc_H is calculated from equation (7), after determination of $E_a^{0'}$ from measurements made after the equivalence point (see Table 1*b*).

The thermodynamic protolysis constants are calculated by correcting for the activity coefficients:

$$pK_{H_2Ph} = pK^c_{H_2Ph} - 2\log f_\pm$$

where $f_\pm$ is calculated from equation (6).

The experimental data from the potentiometric titration and their treatment for the determination of the concentration protolysis constant of phthalic acid in EG are given in Table 3. The values for pure EG and the mixtures are summarized in Table 4, which also includes the protolysis constants of the

Table 3. Experimental data and their treatment for the calculation of $pK^c_{H_2Ph}$ in ethylene glycol

V_{HCl}, ml	E, mV	τ × 10^2	$[H_2Ph]$ × 10^3	$[HPh^-]$ × 10^3	$\log([H_2Ph]/[HPh^-])$	pc_H	$pK^c_{H_2Ph}$
1·500	125·7	1·13	6·98	16·29	−0·368	6·095	5·727
2·000	137·0	0·97	9·10	13·65	−0·176	5·904	5·728
2·500	147·0	0·81	11·12	11·12	±0·000	5·725	5·725
3·000	157·7	0·65	13·06	8·70	0·176	5·554	5·730
3·500	169·1	0·48	14·91	6·39	0·368	5·361	5·729
4·000	183·0	0·32	16·68	4·17	0·602	5·126	5·728
4·500	203·8	0·16	18·39	2·04	0·954	4·775	5·729
						Mean $pK^c_{H_2Ph}$ = 5·728	
				$pK_{H_2Ph} = 5{\cdot}728 + 0{\cdot}554 = 6{\cdot}28$			

Conditions: 20 ml of $2{\cdot}50 \times 10^{-2}M$ potassium biphthalate were titrated with $0{\cdot}1001M$ hydrochloric acid in ethylene glycol $0{\cdot}1M$ in potassium chloride. The biphthalate ions were neutralized with 5·00 ml of hydrochloric acid (volume determined by extrapolation of the τ function). The value of $E_a^{0'}$ is −486·3 ± 0·3 mV, calculated from the data of the same titration after the equivalence point, as shown in Table 1*b*.

Table 4. Protolysis constants of phthalic acid in ethylene glycol and its mixtures

Solvent*	$E_a^{0'}$, mV	$pK^c_{H_2Ph}$	pK_{H_2Ph}	pK_{HPh^-}
W			2·95†	11·05
EG–W (10%)	−408·8 ± 0·5	4·472 ± 0·009	4·96	9·53
EG–W (5%)	−433·4 ± 0·3	4·864 ± 0·005	5·38	9·47
EG–W (1%)	−468·5 ± 0·2	5·436 ± 0·003	5·98	9·46
EG	−486·3 ± 0·3	5·728 ± 0·007	6·28	9·44
EG–EMK–Ch	−486·3 ± 0·4	5·661 ± 0·006	6·27	9·54
EG–iPrOH	−489·8 ± 0·2	5·778 ± 0·008	6·37	9·51
EG–EtOH	−488·5 ± 0·2	5·818 ± 0·003	6·40	9·51
EG–MeOH	−488·5 ± 0·1	5·834 ± 0·002	6·40	9·44
EG–NM	−486·3 ± 0·2	5·827 ± 0·011	6·38	7·77

* Symbols are the same as in Table 2.
† See ref. 7.

conjugated base of phthalic acid calculated from the relationship.

$$pK_{HPh^-} = pK_S - pK_{H_2Ph}$$

The agreement between the constants determined in the present work and those reported by Kundu and Das[2] is good: those determined in the present investigation at 25° being $pK_S = 15{\cdot}72$ and $pK_{H_2Ph} = 6{\cdot}28$, while the reported values for 30° are $pK_S = 15{\cdot}60$ and $pK_{H_2Ph} = 6{\cdot}42$. Good agreement is also observed between the autoprotolysis constant for water at 25° determined in the present work (14·02—the thermodynamic value and 13·80—in 0·1*M* potassium chloride) and the corresponding values (14·00 and 13·78) determined by using a hydrogen electrode.[7]

DISCUSSION

From the data in Table 2 it can be seen that most of the added solvents investigated alter the pK_S-values of pure EG, *i.e.*, the length of the pH-scale, negligibly. Only water and nitromethane cause a significant shortening of the pH-scale of EG, and this can be attributed to the more basic properties of water and the more acidic properties of nitromethane in comparison with EG.

Conclusions concerning the acid–base behaviour of EG and its mixtures can be drawn from the protolysis constants of phthalic acid and its conjugate base (Table 4). The protolysis of the base (the biphthalate ion) $HPh^- + SH = H_2Ph + S^-$ involves no charge separation. The equilibrium constant for this reaction represents the basic strength of the anion HPh^-; therefore it may be expected that this constant reflects the intrinsic acidic strength of EG and its mixtures. The comparison of these values with those of water shows that the biphthalate ion is a stronger base in EG. Hence, EG is a more acidic solvent than water, and its acidic properties do not change when other solvents (with the exception of nitromethane) are added. Nitromethane renders the mixture more acidic. Phthalic acid is weaker in EG than in water, but becomes stronger as water is added to the mixture, partly owing to the greater acidity and partly to the lower dielectric constant of EG.

The final effect of the added solvents on the acid–base properties of EG is illustrated in Fig. 1 where the pH-scales of the investigated solvents (and the pK_S-values) are plotted on a relative scale, with their mutual disposition determined by the relevant protolysis constant of phthalic acid. Thus the added solvents methanol (10%), ethanol (10%), isopropanol (10%) and ethyl methyl ketone–chloroform (5 + 5%) do not significantly affect the acidity or the length of the pH-scale of EG, which is undoubtedly advantageous for titrations in EG medium, because the

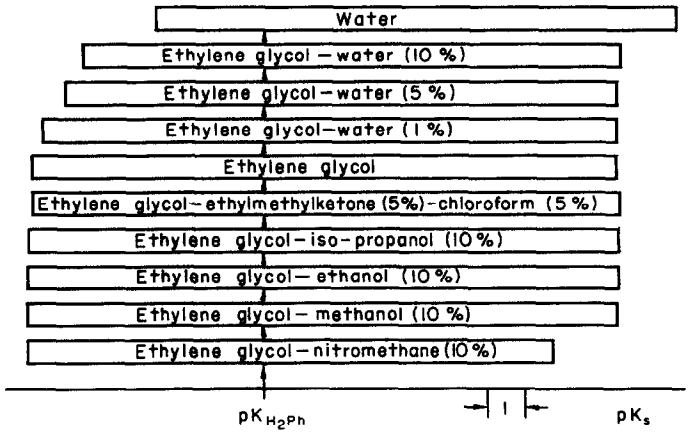

Fig. 1. Disposition of pH-scales of ethylene glycol and its mixtures *vs.* protolysis constants of phthalic acid.

viscosity of the solvent may be lowered without changing the other favourable properties. It is interesting to note that this effect concerns added solvents of different nature (alcohols, ketones, chlorinated hydrocarbons). From this point of view, the presence of various added solvents extends the applicability of a particular medium while preserving the positive attributes of the EG itself. Water, owing to its more basic properties, shortens the pH-scale of EG at its acid end and for this reason has an unfavourable influence on the titration of bases. As this effect is negligible at low water concentrations (*ca* 1%) the removal of traces of water from EG is not as critical as it is for other solvents commonly used in non-aqueous titrations. Nitromethane is more acidic than EG, and therefore shortens the pH-scale of EG at its basic end. This is of little consequence however, because EG and its mixtures are used mainly for titrations of weak bases.

The present investigation has shown that the added solvents methanol, ethanol, isopropanol, nitromethane and ethyl methyl ketone–chloroform improve the properties of EG as a medium for the non-aqueous titration of weak bases.

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EIN SCHNELLER KONTINUIERLICHER FLÜSSIGKEITSEINLASS ZUR MASSENSPEKTROMETRIE*

WALTER WALISCH®, GÜNTHER BECKER und DIETER HEISE

Organische und Instrumentelle Analytik, Universität des Saarlandes, 66 Saarbrücken, B.R.D.

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Zusammenfassung—Es wird ein zweistufiges Einlaßsystem beschrieben, welches einen schnellen, kontinuierlichen und quantitativen Transfer von Flüssigkeitsgemischen in ein Massenspektrometer ermöglicht. Hierzu wird der mit konstanter Geschwindigkeit in eine Mischkammer einströmenden Probe etwa die zehnfache Menge eines inerten Trägergases zugesetzt, welches die Flüssigkeit mit hoher Geschwindigkeit als Film durch eine gekühlte Kapillare in eine geheizte Verdampferkammer (473 K, 50 mb) treibt, wo eine schnelle und vollständige Verdampfung auf einer Glasfritte erfolgt. Vom Verdampfer führt eine Kapillare viskos unmittelbar ins Massenspektrometer. Totzeit und Einstellzeit des gesamten Systems (einschließlich des langsamen Elektrometerverstärkers) betragen z. Zt. 0,8 bzw. 0,9 s; die Nachweisgrenze liegt mit einem kleinen Massenspektrometer ohne SEV bei 0,1% und die relative Genauigkeit bei der Gemischanalyse beträgt ±2%. An Anwendungsbeispielen wird gezeigt, in welcher Weise das System zur Prozeßkontrolle oder zur LC–MS-Kopplung eingesetzt werden kann.

Zur massenspektrometrischen Untersuchung von Flüssigkeiten verwendet man üblicherweise die indirekte Probeneinführung,[1] bei der die flüssige Probe in einen aufgeheizten und evakuierten Vorratsbehälter gebracht und verdampft wird. Die eingebrachte Probenmenge ist so zu bemessen, daß sich im Vorratsbehälter ein Totaldruck der Größenordnung 0,1 mb einstellt. Durch das molekulare Leck, das den Vorratsbehälter mit dem Massenspektrometer verbindet, strömt dann die Probe als Gas gemäß den Gesetzen der molekularen Strömung in das Massenspektrometer. Dort erfolgt bei abnehmendem Druck die Aufnahme des Spektrums. Die je nach Molgewicht verschiedene Einströmgeschwindigkeit der einzelnen Komponenten führt zu einer Anreicherung der "schwereren" Komponenten im Vorratsbehälter.

Neben dem hier kurz skizzierten indirekten Flüssigkeitseinlaß mit diskontinuierlicher Probenzugabe und Massendiskriminierung setzt man insbesondere bei höher siedenden Flüssigkeiten den direkten Schubstangeneinlaß[1] ein, bei dem die Flüssigkeit mittels einer Einschubstange unmittelbar vor die Eintrittsöffnung der Ionenquelle geschoben und dort kontrolliert in die Ionenquelle hinein verdampft wird. Auch hier ist bei Gemischen die Dampfzusammensetzung in der Regel *nicht* mit der Zusammensetzung der Flüssigkeit identisch. Dies gilt gleichermaßen für den Direkteinlaß mittels einer Felddesorptions- oder einer Feldionisationssonde.[2,3]

Beide gebräuchlichen Einlaßsysteme sind also diskontinuierlich und lassen eine stetige, repräsentative Probenzufuhr zur Quelle aus einer zeitlich veränderlichen flüssigen Probe *nicht* zu†. Damit sind dem Einsatz der Massenspektrometrie in der Flüssigkeitschromatographie enge Grenzen gesetzt, und eine direkte LC–MS-Kopplung erscheint unmöglich.[4] Vielmehr wird üblicherweise von Zeit zu Zeit eine Probe entnommen und mittels eines der beschriebenen Verfahren dem Massenspektrometer zugeführt.[4] Dieser Vorgang wurde von Lovins und Mitarbb.[5] weitgehend automatisiert. Damit während der Probeneinführung und Spektrenaufnahme keine Information verloren geht, wird der Fluß im Chromatographen während dieser Zeit unterbrochen.

Einen völlig anderen Weg sind Tal'roze und Mitarbb.[6–12] gegangen. Sie versuchen erstmals die kontinuierliche Verdampfung der Flüssigkeit in das Massenspektrometer hinein. Hierzu taucht man einen extrem engen Spalt, der durch Zusammenpressen des Endes eines Rohres, das unmittelbar zum Massenspektrometer führt, in das Rohr, durch das die zeitlich veränderliche flüssige Probe strömt. Durch Unterdruck und Oberflächenspannung steigt die Flüssigkeit im kapillaren Spalt hoch und verdampft beim Übergang zum größeren Querschnitt. Die Herstellung reproduzierbarer Spalte ist offenbar extrem schwierig, die in der Einlaßsonde "gespeicherte" Flüssigkeitsmenge produziert große Tot- und Einstellzeiten, die Kapillarkräfte bestimmen wesentlich den Fluß und eine Massendiskriminierung ist nicht auszuschließen. Damit scheidet dieses sehr langsame System u.E. für viele Problemstellungen aus. Trotzdem wurde der Einsatz als Detektor in der Flüssigkeitschromatographie versucht.[9]

Auch der Einsatz[12] einer extrem engen, langen Kapillare führt zu Tot- und Einstellzeiten der Größenordnung 10 s, und ein Gleichgewichtszustand

* Diese Arbeit wurde als Projekt des Sonderforschungsbereichs Analytik durchgeführt. Wir danken der Deutschen Forschungsgemeinschaft für die Bereitstellung der Mittel.

† Beide Systeme sind Notlösungen; der indirekte Einlaß ist eigentlich ein Gaseinlaß und die Schubstange ist für feste Stoffe konzipiert. Der flüssige Zustand der Probe wirkt sich in beiden Fällen eher störend aus und wird nicht ausgenutzt.

wird oft erst nach 200 s erreicht. Lediglich bei der $^2H/^1H$-Analyse von Wasser[13] hat sich dieser einstufige, direkte Transfer offenbar bewährt. Für die quantitative Analyse von Flüssigkeiten mit schnell veränderlicher Zusammensetzung ist er jedoch keinesfalls geeignet, und es fehlt immer noch ein Einlaßsystem für Flüssigkeiten, das: die Probe kontinuierlich in das Massenspektrometer gelangen läßt; mit geringen Tot- und Einstellzeiten behaftet ist; einen repräsentativen Teil der Probe in der Quelle garantiert und damit quantitative Messungen ermöglicht; unanfällig gegenüber Verstopfungen und wenig abhängig von Oberflächenspannung, Polarität und Viskosität der untersuchten Flüssigkeit ist.

Ziel dieser Arbeit ist es, den ersten Schritt in Richtung auf einen derartigen schnellen, kontinuierlichen und quantitativen Flüssigkeitseinlaß zu tun.

PRINZIP DES EINLASS-SYSTEMS

Wie die Arbeiten der Gruppe Tal'roze gezeigt haben, ist ein kontinuierlicher, einstufiger Flüssigkeitseinlaß nur dann zu realisieren, wenn man hinsichtlich des Zeitverhaltens (Tot- und Einstellzeiten), der Betriebssicherheit (Verstopfungsgefahr bei extrem dünnen Kapillaren) und der Abhängigkeit von Flüssigkeitseigenschaften (Oberflächenspannung, "Polarität", Viskosität) sehr große Zugeständnisse macht. Den eingangs erhobenen Forderungen kann ein solches System offenbar grundsätzlich nicht entsprechen, da ein *schneller* und *quantitativer* Transfer eines repräsentativen Teils der zu untersuchenden Flüssigkeit einstufig nicht möglich ist. Dagegen ist das in Abb. 1 dargestellte *zweistufige* System durchaus in der Lage, den wichtigsten Erfordernissen zu entsprechen.

Dieser Flüssigkeitseinlaß besteht aus der Mischkammer MK, dem Verdampfer VD und der Einlaßsonde EK. In die Mischkammer wird aus der Druckflasche DF über das Feinreduzierventil FRV, das auf den Gasdruck p_G eingestellt ist, durch den Gaskapillarschlauch GK ein konstanter Trägergasstrom (Stickstoff oder Helium) eingeblasen. Dieser Trägergasstrom ist so dimensioniert, daß ein Teil bei GA ins Freie tritt, wodurch einerseits gewährleistet wird, daß in der Mischkammer der konstante Außendruck p_0 herrscht und andererseits sichergestellt ist, daß keine atmosphärischen Verunreinigungen in die Mischkammer gelangen können. Nach unten strömt das Trägergas durch die Vorvakuumkapillare VK in den Verdampfer VD. Die Stahlkanüle VK (l = 50 mm, ϕ_i = 0,4 mm) ist so dimensioniert, daß bei einem Trägergasstrom von 8 Nml/s (Nml = Normal-ml bezogen auf p_0) in der Verdampferkammer VDK ein Druck p_0 = 50 bis 60 mb entsteht, wenn die Membranpumpe MP (Type NV 725.3 der Firma Neuberger KG., Freiburg) eingeschaltet ist.

In das untere Ende der Verdampferkammer VDK ragt die zylindrische Einlaßkapillare EK hinein, die aus Pyrexglas gezogen ist. Sie ist in den Teflondoppelkonus TDK eingebettet, der durch Anziehen der Überwurfmutter ÜM eine ausgezeichnete Abdichtung des Hochvakuumanschlusses HVA gegenüber EK und der Atmosphäre gewährleistet. Bei geschlossenem Hochvakuumventil HVV kann die Einlaßkapillare EK sehr leicht ausgewechselt werden. Die Einlaßkapillare EK führt über das Ventil HVV direkt in die Ionenquelle des Massenspektrometers MS, die

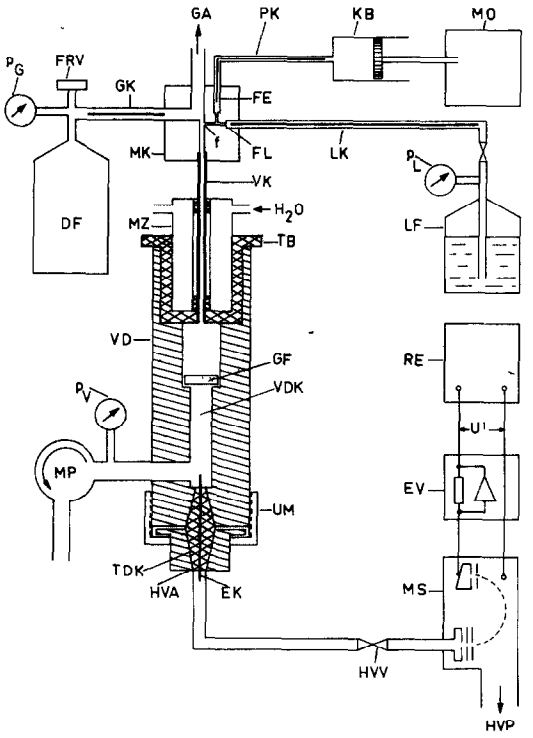

Abb. 1. Aufbau des Einlaßsystems.

durch das Hochvakuumpumpensystem HVP auf einem Druck von etwa 10 nb gehalten wird. In dieser Betriebsweise zeigt die Ausgangsspannung U' des Elektrometerverstärkers EV ausschließlich das Spektrum des Trägergases an, das vom Registriergerät RE registriert wird.

Die zu untersuchenden Flüssigkeiten werden durch FE oder FL bei f in die Mischkammer eingespritzt. Ein konstanter Flüssigkeitsstrom wird entweder durch den konstanten Überdruck p_L über der Lösungsmittelflasche LF oder mit der Kolbenbürette KB, die vom Motor MO angetrieben wird, erzeugt. Die Kapillarschläuche PK und LK gewährleisten kurze Laufzeiten zwischen den Flüssigkeitsreservoirs LF oder KB und der Mischkammer. Bei f wird der Flüssigkeitsstrom vom Trägergasstrom mitgerissen, in Form eines "gewellten" Flüssigkeitsfilms schnell durch die Vorvakuumkapillare VK getrieben, auf die Glasfritte GF gesprüht und dort nahezu momentan verdampft, so daß ein Trägergas/Probendampf-Gemisch an EK vorbei zur Membranpumpe strömt. Verdampferkammer VDK und Hochvakuumanschluß HVA sind so hoch geheizt (wegen des Teflondoppelkegels dürfen vorerst 493 K nicht überschritten werden), daß die eintretende Flüssigkeit mit Sicherheit vollständig verdampft wird und keine Kondensation in der Einlaßkapillare erfolgt.

Wie in einer früheren Arbeit[14] gezeigt ist, wird, wenn Druck p_V und Temperatur T_V der Verdampferkammer konstant sind, der in das Massenspektrometer gelangende Gasstrom nur noch von der Viskosität des Gasgemisches bestimmt. Da einerseits die meisten organischen Dämpfe im fraglichen Temperaturbereich Viskositäten haben, die denen der verwendeten Trägergase vergleichbar sind und da andererseits Probendampfkonzentrationen von 10% nicht überschritten werden, sind die früher[14,15] für quantitative Messungen genannten Bedingungen weitgehend erfüllt. Die in der Ionenquelle entstehenden Partialdrucke p_i der in der Flüssigkeit enthaltenen Komponenten i entsprechen den jeweiligen Partialdrucken im Verdampfer, und diese sind wiederum der molaren Zusammensetzung proportional.

Der beschriebene Flüssigkeitseinlaß hat als neuralgische Punkte die Mischstelle Gas/Flüssigkeit bei f und die Aus-

trittsöffnung der Vorvakuumkapillare VK. Die Mischstelle besteht aus einer glatten Bohrung ($\phi = 0{,}5$ mm), in die die Flüssigkeitszufuhr durch eine seitliche Bohrung ($\phi =$ 0,2 mm) erfolgt. Ein Grat darf nicht vorhanden sein, da sonst der stetige Abfluß der Flüssigkeit, der allein ein stabiles Signal garantiert, in ein pulsierendes Strömen mit entsprechenden Folgen übergeht.

Zur Vermeidung einer zu weitgehenden Verdampfung in der Vorvakuumkapillare ist diese in einen wassergekühlten Messingzylinder MZ eingesetzt, der gleichzeitig den Verdampfer nach oben abschließt. Zwischen MZ und VD ist eine Teflonbüchse TB geschraubt, die sowohl den hohen Temperaturgradienten zwischen MZ und VD aufnimmt als auch einwandfrei abdichtet. Die bis dahin gekühlte Kapillare VK schließt genau mit dem unteren Boden von TB ab. An dieser Stelle erfolgt der Temperatursprung von Kühlwassertemperatur (283 K) auf Verdampfertemperatur. Auch der Druck nimmt besonders steil am Ende der Kapillare ab; dort herrscht dementsprechend eine sehr hohe lineare Trägergasgeschwindigkeit (80 m/s) und eine extrem kurze Verweilzeit. Eine störende Verdampfung innerhalb der Kapillare wurde von uns nicht beobachtet.

KONTROLLUNTERSUCHUNGEN

Das zeitliche Verhalten des Flüssigkeitseinlasses wurde mit der in Abb. 1 wiedergegebenen Anordnung gemessen. Hierzu fließt aus der Lösungsmittelvorratsflasche LF ein konstanter Methanolstrom (330 nl/s). Diesem Lösungsmittelstrom wird aus der Kolbenbürette KB durch Ein- und Ausschalten des Motors (Anlaufzeit 30 ms) ein Probenstrom mit der einstellbaren Geschwindigkeit v als Konzentrationsimpuls zugemischt.

In allen von uns untersuchten Fällen erhielten wir in etwa das gleiche Ergebnis wie es in Abb. 2 für Propanol wiedergegeben ist. Die Totzeit t_0 zwischen Auslösen des Konzentrationsimpulses und Beginn des Anstiegs der entsprechenden Ausgangsspannung U^i (im Falle von Propanol wurde U^{59} registriert) beträgt 0,8 s, die Anstiegszeit t_a (10–90%) liegt bei 1,1 s, während die Abfallzeit t_b (90–10%) mit 0,7 s deutlich kürzer ist. Dieser leicht unsymmetrische Kurvenverlauf ist reproduzierbar. Eine Erklärung haben wir vorerst nicht.

Die Totzeit resultiert aus den Laufzeiten in der Mischkammer, der Vorvakuumkapillare, der Verdampferkammer, der Einlaßkapillare und der Hochvakuumleitung zwischen EK und MS. Die beiden letzteren tragen mit etwa 100 ms dazu bei; die Laufzeit in der Mischkammer beträgt höchstens 120 ms. Damit bleiben für die schwer faßbaren Laufzeiten in VK und VDK noch etwa 500 ms. Da das Volumen von VK 7 μl und der gesamte Flüssigkeitsstrom nur 0,4 μl/s beträgt, muß der Flüssigkeitsfilm in VK sehr dünn sein. Dies wird durch zeitgedehnte Filmaufnahmen bestätigt, die zeigen, daß sich an der Innenwand der Kapillare ein Flüssigkeitsfilm mit spitzen Maxima und flachen Minima ausbildet, der vom Trägergas mit so großer Geschwindigkeit vorangetrieben wird, daß wir davon ausgehen können, daß die gemessene Totzeit zum Teil ihren Ursprung in der Verdampferkammer selbst hat.

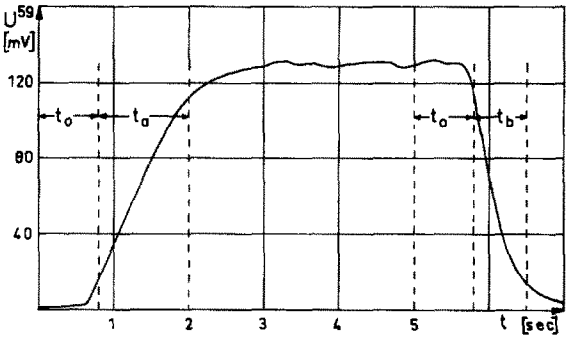

Abb. 2. Einstellverhalten bei Zugabe eines Propanolimpulses von 5 s.

Die gemessene mittlere Einstellzeit ($t_e = 0{,}9$ s) ist sicher zu einem Teil durch Vorgänge in der Verdampferkammer begründet, denn die ersten Modelle unseres Einlaßsystems, die ein größeres Volumen hatten, zeigten Einstellzeiten von einigen Sekunden. Eine weitere Verkleinerung der Verdampferkammer (jetzt 2,5 ml) ist vorerst nicht angebracht, da der Elektrometerverstärker EV des für die Versuche benutzten Massenspektrometers (VARIAN-MAT, GD 150 mit Permanentmagnet von 6700 Gauss) selbst eine Einstellzeit von 0,5 s besitzt und damit erheblich zum Kurvenverlauf in Abb. 2 beiträgt.

Die quantitativen Eigenschaften können ebenfalls mit der in Abb. 1 dargestellten Anordnung untersucht werden. Hierzu wird die in der Kolbenbürette befindliche Probenflüssigkeit mit verschiedenen Geschwindigkeiten in die Mischkammer gespritzt und die Intensität U^i des ausgewählten Peaks in Abhängigkeit von der Zugabegeschwindigkeit v gemessen. Wie aus Abb. 3 hervorgeht, ergibt U^i (v) bei den untersuchten Proben Äthanol und Propanol jeweils eine Gerade, die durch den Nullpunkt geht. Ein entsprechendes Verhalten zeigten alle untersuchten Proben; die Intensität des für die Probe repräsentativen Massenpeaks war der jeweiligen Zugabegeschwindigkeit proportional und damit auch der Konzentration im konstant strömenden "Lösungsmittel" Methanol.

Die Untersuchung der Brauchbarkeit des Systems zur Prozeßkontrolle erfolgt mit der in Abb. 4 dargestellten Anordnung am Beispiel der Veresterung von Essigsäureanhydrid mit Methanol. Diese Reaktion läuft in einem Überschuß von Methanol ohne Katalysator nach erster Ordnung ab und kann über die Zunahme der Essigsäuremethylesterkonzentration, die über die Molekülpeakintensität U^{74} zugängig ist, beobachtet werden.

Die Reaktionslösung RL (etwa 10 Mol% Anhydrid in trockenem Methanol) befindet sich im thermostatisierten (313 K) Reaktionsgefäß RG. Eine nahezu stoßfreie, chemisch resistente Umlaufpumpe UP (ISMATEC pmp-10) pumpt die Reaktionslösung mit etwa 0,2 ml/s durch eine dünne, kurze Schlauchleitung (Teflon) zum Dreiwegstück DW und von dort zurück zum Reaktionsgefäß. Der an DW angebrachte Drosselhahn DH wird so gestellt, daß ein

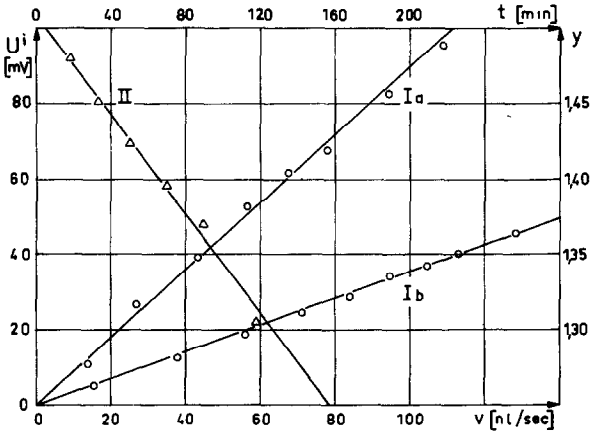

Abb. 3. Kontrollergebnisse; Ia = Äthanol: $U^{45} = f(v)$; Ib = Propanol: $U^{59} = f(v)$; II: $y = \log(U^{74}_{t+118} - U^{74}_t) = f(t)$.

konstanter Überdruck von 100 mb entsteht. Dieser Überdruck reicht aus, um etwa 0,2 µl/s durch die feine Kanüle KA in die Mischkammer MK zu fördern, von wo die Flüssigkeit mit dem Trägergasstrom N_2 in die Verdampferkammer VD gelangt, die über die Einlaßkapillare EK mit dem Massenspektrometer MS in Verbindung steht. Auf diese Weise erhält man fortlaufend einen repräsentativen Anteil der Reaktionslösung als Gasgemisch in der Ionenquelle und kann durch periodische Aufnahme von Massenspektren die Vorgänge im Reaktionsgefäß qualitativ beobachten (bspw. zur Feststellung kurzlebiger Zwischenprodukte).

In unserem Falle bleibt das Massenspektrometer auf dem Peak der Masse 74 eingestellt, und $U^{74} = f(t)$ wird registriert. Die Auswertung dieser Messungen nach Guggenheim ergibt für $\log(U^{74}_{t+118} - U^{74}_t) = f(t)$ die in Abb. 3 gezeichnete Gerade II, aus deren Anstieg sich die Geschwindigkeitskonstante $k_1 = 4 \cdot 10^{-3}$ min^{-1} ergibt. Caudri[16] hat unter sonst analogen Reaktionsbedingungen bei 298 K für k_1 den Wert $1{,}8 \cdot 10^{-3}$ min^{-1} gefunden. Die Übereinstimmung ist ausreichend.

SCHLUSSBETRACHTUNG

Der beschriebene kontinuierliche Flüssigkeitseinlaß stellt keinesfalls das Ende, sondern eher den Anfang einer Entwicklung dar, und wir sind uns der noch vorhandenen Schwächen sehr wohl bewußt. Diese Schwächen beginnen bei den für die Prototypen verwendeten Materialien (Plexiglas für die Mischkammer, Messing für den Verdampfer und Teflon zur Dichtung).

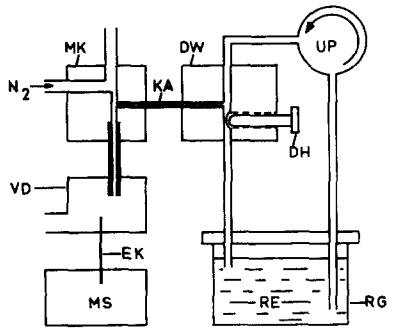

Abb. 4. Meßanordnung für kinetische Untersuchungen.

Für die Mischkammerversuche wurde das durchsichtige Plexiglas gewählt, weil nur unter dauernder visueller Beobachtung die Präzision in den Bohrungen erreicht werden konnte, die für eine pulsfreie "Filmströmung" der Flüssigkeit erforderlich ist. Das durchscheinende "Voltaleff", das chemisch sehr resistent ist, bietet sich als Alternative an.

Für die Kapillaren VK (Abb. 1) und KA (Abb. 4) haben sich rostfreie Stahlkanülen, wie sie beispielsweise von Hamilton in reicher Auswahl angeboten werden, gut bewährt. Das gilt auch für die Einlaßkapillare EK, die aus Pyrex- oder Quarzglas in langen Stücken gezogen (ϕ_i *ca.* 0,05 mm) und dann auf die benötigte Länge von 20 bis 30 mm geschnitten wird. Selbstverständlich wäre auch eine entsprechend enge Metallkapillare als Einlaßkapillare einsetzbar.

Die Verdampferkammer mit den Dichtungen TB und TDK bereitet die größten technologischen Sorgen. Durch die Verwendung von Teflondichtungen ist die Verdampfertemperatur nach oben bei 493 K begrenzt. Bei dieser Temperatur erreichen aber noch nicht alle interessierenden Flüssigkeiten den für eine vollständige Verdampfung erforderlichen Dampfdruck von 5 mb. Andererseits sind viele feste Verbindungen so flüchtig, daß sie ohne weiteres in gelöster Form zugegeben und in die Anwendung mit einbezogen werden können. Da Messing gegen agressive Dämpfe anfällig ist, haben wir die letzte Verdampferkammer aus rostfreiem Stahl angefertigt. Erfahrungen liegen mit dieser Kammer noch nicht vor, doch ist zu befürchten, daß auch die üblichen rostfreien Stähle nicht völlig resistent gegen manche Säure- und Halogendämpfe sind. Die Herstellung des Verdampfers aus Glas bereitet aber so große technische Schwierigkeiten, daß wir vorerst davon abgesehen haben. Insbesondere ist das schnelle Auswechseln der Einlaßkapillare dann nicht mehr gewährleistet. Inwieweit die bei einem metallischen Verdampfer zu befürchtende katalytische Zersetzung stören wird, bleibt abzuwarten.

Das zeitliche Einstellverhalten ist mit einer Totzeit von 0,8 s und einer Einstellzeit von 0,9 s bereits zufriedenstellend. Eine Verbesserung erscheint möglich; sie sollte aber nur in Verbindung mit einem schnelleren Verstärker oder einem SEV betrieben werden. Da die mit Sekundärelektronenvervielfachern ausgestatteten großen Massenspektrometer in der Zuleitung und im Hochvakuum selbst Einstellzeiten von etwa 100 ms aufweisen, ist die untere Grenze absehbar. Für die meisten Fälle (auch für die LC–MS-Kopplung) sind Tot- und Einstellzeiten von einigen 100 ms noch tragbar.

Die quantitative Genauigkeit ist bei der beobachteten Unruhe des Peakmaximums von $\pm 1\%$ die sowohl durch eine ungleichmäßige Strömung durch

die Vorvakuumkapillare als auch durch unregelmäßiges Verdampfen verursacht sein kann, noch verbesserungsfähig, wenngleich betont werden muß, daß die Ausgangsspannung schon jetzt wesentlich ruhiger ist, als beim Schubstangendirekteinlaß. Dagegen reicht die Empfindlichkeit für einige Zwecke noch nicht aus.

Wenn das Massenspektrum der zu bestimmenden Komponente einen ungestörten, intensiven Peak aufweist, können mit der beschriebenen Einrichtung Probenkonzentrationen von 0,1% nachgewiesen werden. Mit Helium als Trägergas und einem SEV zur Ionenstrommessung dürfte die Ansprechempfindlichkeit jeweils um eine Zehnerpotenz gesteigert werden können. Eine Nachweisgrenze von 10 ppm (bezogen auf die flüssige Probe) scheint demnach ohne besondere Schwierigkeiten erreichbar, und 1 ppm ist im Rahmen des Möglichen. Damit kann in geeigneten Fällen der "on line-Betrieb" eines Massenspektrometers zur Detektion in der Flüssigkeitschromatographie in Erwägung gezogen werden. Hierzu wird der Auslauf der Säule an das Dreiwegstück DW (Abb. 4) angeschlossen. Mittels des Drosselhahns DH wird der benötigte Überdruck eingestellt, der in Verbindung mit der Kapillare KA den benötigten konstanten Fluß zur Mischkammer bewirkt. Selbstverständlich sind vorerst nur Flüssigkeitsgemische analysierbar, die rückstandsfrei verdampfen.

Die Bedienung des Einlaßsystems ist außerordentlich einfach. Zur Aufnahme des Spektrums einer flüssigen Probe wird diese in eine Mikrokolbenbürette gesaugt und mittels eines Motorantriebes mit konstanter Geschwindigkeit in die Mischkammer geleitet. Bei sehr viskosen Proben empfiehlt sich der Zusatz eines geeigneten Lösungsmittels (wie in Abb. 1 gezeigt). Die Probenflüssigkeit kann aber auch dadurch in die Mischkammer getrieben werden, daß eine mit Probe gefüllte Kanüle als "Anschlußnippel" auf die Mischkammer gesteckt word. Der konstante Lösungsmittelstrom treibt dann als "Kolben" die Probe in die Mischkammer. Dieses Verfahren ist wenig aufwendig, ermöglicht einen schnellen Probenwechsel und spült—nach Durchlaufen der Probe—das ganze System.

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A REINVESTIGATION OF THE REACTION BETWEEN TITANIUM(IV) AND SALICYLIC ACID IN CONCENTRATED SULPHURIC ACID

R. S. RAMAKRISHNA, V. PARAMASIGAMANI and M. MAHENDRAN

Department of Chemistry, University of Ceylon, Colombo 3, Ceylon

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Summary—It is shown that the coloured species formed between TiO^{2+} and salicylic acid in concentrated sulphuric acid may be a π-complex rather than a chelate. Similar species are formed by other hydroxybenzoic acids where chelating sites for TiO^{2+} are not available. The ultraviolet and NMR spectral characteristics of hydroxybenzoic acids in water, concentrated sulphuric acid and deuterochloroform are presented as evidence for the π-complex formation. The reaction of VO^{2+} with salicylic acid in concentrated sulphuric acid is shown to be due to increasing electron-donation in the π-component of the V–O bond of $VO(H_2O)_5^{2+}$ as the concentration of sulphuric acid is increased, and not to the presence of salicylic acid.

Titania, TiO_2, a principal constituent of ilmenite and rutile, is usually brought into solution as the titanyl ion, TiO^{2+}, by fusion with potassium hydrogen sulphate and extraction with sulphuric acid. Ilmenite sands containing titania combined or associated with ferrous and ferric oxides have been beneficiated by leaching with sulphuric acid. This "sulphate process" is controlled by the formation of soluble $TiOSO_4$ and crystallizable sulphates of iron from the resulting leach liquor.

Hulquist[1] has reported the formation of a 1:1 complex of TiO^{2+} with salicylic acid in a concentrated sulphuric acid medium, the complex being characterized by λ_{max} at 410 nm. The use of thymol to characterize Ti(IV) in concentrated sulphuric acid medium was reported by Lenher and Crawford[2] as early as 1913. The use of phenolic compounds such as chromotropic acid (1,8-dihydroxy-3,6-disulphonic acid),[3] and gallic acid,[4] for the colorimetric determination of Ti(IV) has also been reported. As in many colorimetric procedures, little attention has been given to the nature of the coloured species formed. The reaction of salicylic acid in concentrated sulphuric acid medium has also been utilized for the estimation of VO^{2+} and more recently by de Salles *et al.*[5] for the estimation of niobium. Hulquist[1] observes that the coloured species formed with TiO^{2+} or VO^{2+} is obtainable only in the presence of a large excess of salicylic acid and concludes that the species is appreciably dissociated. In view of the behaviour of TiO^{2+} in sulphuric acid media, the reported reaction with salicylic acid has been re-examined, to elucidate the nature of the coloured species formed.

EXPERIMENTAL

Reagents

Analytical-grade chemicals were used throughout. Solvents and pyridine were redistilled.

Titanium(IV) solutions. Prepared from 99·6% pure TiO_2 by fusion with potassium bisulphate and leaching with 5% sulphuric acid, and standardized by the Jones's reductor and tannin methods, then diluted accordingly, or prepared from air-dried potassium titanyl oxalate by heating with concentrated sulphuric acid until all the reaction products had been removed and then diluted with water and sufficient sulphuric acid to give the required concentration. Aliquots of the stock solution were then standardized by the Jones's reductor method.

Vanadium(IV) solutions. Prepared from vanadyl sulphate and standardized by photometric titration with potassium bromate.[6]

RESULTS AND DISCUSSION

The absorption spectra of solutions of Ti(IV) in concentrated sulphuric acid in the presence of salicylic or sulphosalicylic acid (where the ligands are close enough for chelation) as well as in the presence of *m*- or *p*-hydroxybenzoic acid (where the ligands are remote from each other) were similar (Fig. 1). The observation of such similar spectral characteristics with phenols but not with benzoic acids indicates that this behaviour is characteristic of phenolic compounds.

Effect of reagents

The variation of absorbance at 420 nm for a series of solutions containing TiO^{2+} and differing amounts of salicylic acid in a concentrated sulphuric acid medium (Fig. 2) showed that a minimum mole-ratio of reagent to TiO^{2+} of 25:1 is required for maximum absorbance, thus confirming the findings of Hulquist. The effect of added water on the absorbance at 420 nm (Fig. 3) indicated that water could be present up to about 20% without causing appreciable change, but more than this decreased the absorbance.

The effect of increasing sulphuric acid concentration on absorbance at λ_{max} of aqueous solutions containing titanyl sulphate and sulphosalicylic acid

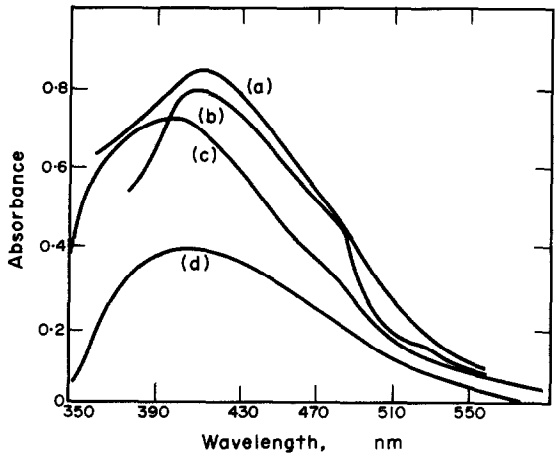


Fig. 1. Absorption spectra of solutions in concentrated H_2SO_4.
(*a*) TiO^{2+} ($4{\cdot}00 \times 10^{-4}M$) + *o*-hydroxybenzoic acid ($5{\cdot}70 \times 10^{-2}M$), $\lambda_{max} = 420$ nm.
(*b*) TiO^{2+}($4{\cdot}00 \times 10^{-4}M$) + *m*-hydroxybenzoic acid ($5{\cdot}70 + 10^{-2}M$), $\lambda_{max} = 412$ nm.
(*c*) TiO^{2+} ($4{\cdot}00 \times 10^{-4}M$) + sulphosalicylic acid ($5{\cdot}70 \times 10^{-2}M$), $\lambda_{max} = 400$ nm.
(*d*) TiO^{2+} ($4{\cdot}00 \times 10^{-4}M$) + *p*-hydroxybenzoic acid ($5{\cdot}70 \times 10^{-2}M$), $\lambda_{max} = 410$ nm.

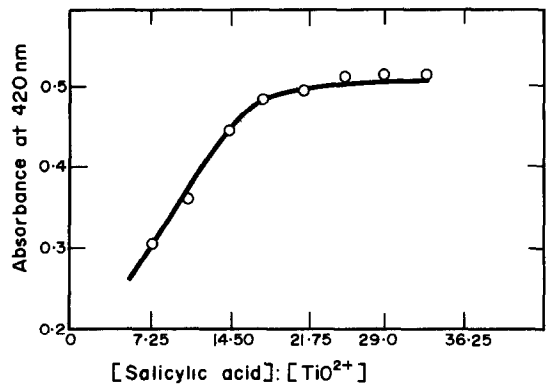


Fig. 2. Effect of reagent on absorbance at 420 nm of solutions containing TiO^{2+} ($2{\cdot}50 \times 10^{-4}M$) and varying amounts of salicylic acid in concentrated H_2SO_4.

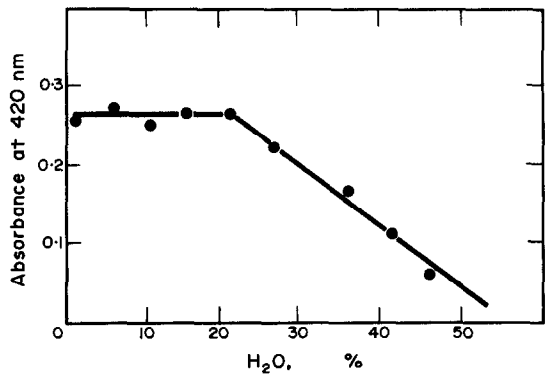


Fig. 3. Effect of H_2O content on absorbance at 420 nm of solutions containing TiO^{2+} ($1{\cdot}30 \times 10^{-4}M$) and salicyclic acid ($5{\cdot}70 \times 10^{-2}M$) in concentrated H_2SO_4.

showed a progressive increase in absorbance at 400 nm. The stoichiometry of the coloured species formed by TiO^{2+} with salicylic acid or with *p*-hydroxybenzoic acid in solutions of concentrated sulphuric acid was found, by Job's method,[7] to be 1:1 (Fig. 4). The complexes obeyed Beer's law from 1·28 to 12·8 ppm (absorbance 0·1–1·0).

Similar experiments with VO^{2+} showed that an aqueous solution of VO^{2+} [characterized by λ_{max} 775 nm ($\epsilon_{max} = 20{\cdot}91.mole^{-1}.cm^{-1}$)] gave a greenish blue solution with salicylic acid in concentrated sulphuric acid medium, accompanied by a hypsochromic shift of λ_{max} to 695 nm ($\epsilon_{max} = 33{\cdot}5$). However, the addition of >20% of water restored λ_{max} to 775 nm. A 1:1 species was found to be formed in the concentrated acid medium; it obeyed Beer's law at 695 nm.

Arris and Duffy[8] showed that the λ_{max} of VO^{2+} at 770 nm in aqueous solution shifts to shorter wavelengths as the concentration of sulphuric acid in the medium is increased, a phenomenon which occurs even in the absence of reagents such as salicylic acid. The spectral characteristics of a solution of vanadyl sulphate in sulphuric acid of various concentrations in the presence and absence of salicylic acid are shown in Table 1.

This observation has been interpreted in terms of the molecular orbital scheme for VO^{2+} by Ballhausen.[9] All the spectral bands given by the 6-coordinated VO^{2+} ion are assigned to transitions which involve bonding or antibonding π-orbitals of the V–O bond. Any factor which increases the extent of electron donation from O to V in the π-component of the V–O bond would have the effect of lowering the energy of the e_π bonding m.o. and raising that of the e_π^* m.o. and thus increase the energy of transition

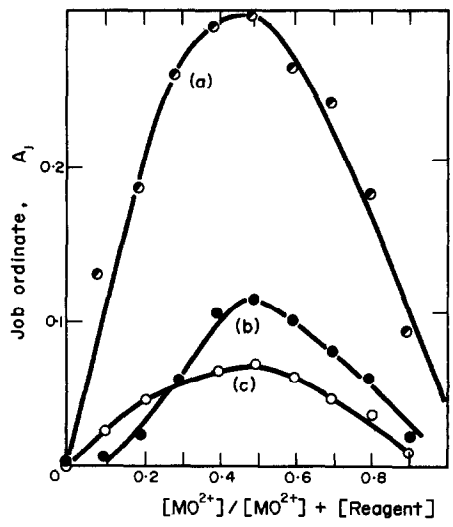


Fig. 4. Composition by Job's method
(*a*) $[TiO^{2+}]$ = [salicylic acid] = $2{\cdot}0 \times 10^{-3}M$; $\lambda = 420$ nm.
(*b*) $[VO^{2+}]$ = [salicylic acid] = $5{\cdot}0 \times 10^{-2}M$; $\lambda = 695$ nm.
(*c*) $[TiO^{2+}]$ = [*p*-hydroxybenzoic acid] = $2{\cdot}0 \times 10^{-3}M$; $\lambda = 410$ nm.

Table 1. Spectral characteristics of aqueous solutions of VO^{2+} and aqueous solutions of VO^{2+} containing salicylic acid in varying concentrations of H_2SO_4

	VO^{2+} ($4 \times 10^{-2}M$)			VO^{2+} ($1 \times 10^{-2}M$) + salicylic acid ($1{\cdot}25 \times 10^{-1}M$)	
Medium, $\%H_2SO_4$	λ_{max}, nm	ϵ_{max}, $l.\ mole^{-1}.\ cm^{-1}$	Medium, $\%H_2SO_4$	λ_{max}, nm	ϵ_{max}, $l.\ mole^{-1}.\ cm^{-1}$
0	770	20·9	0	—	—
20	760	21·6	25	750	24·5
30	755	22·8	40	750	24·0
50	750	24·0	60	735	26·0
70	710	26·5	75	695	29·2
90	695	32·5	95	685	40·5

and cause the shift of the λ_{max} of these bands to shorter wavelengths. Hence it would appear that the change of solvent from water to sulphuric acid alters the co-ordination sphere and increases the electron donation in the π-component of the V–O bond.

Shnaiderman and Pleskonos[10] studied the vanadium (IV)–pyrogallol system in concentrated sulphuric acid and reported that the absorption maximum at 500 nm shifted progressively to longer wavelengths on addition of water, finally giving a blue solution characteristic of VO^{2+} in water. They also found that this shift was accompanied by a decrease in absorptivity, a phenomenon similar to that observed in this study for the salicylic acid system. However, the possibility of reduction of V(IV) to V(III) and V(II) in the pyrogallol system cannot be overlooked and this aspect is currently being studied by us.

Similar measurements with TiO^{2+} in water with progressive increase in sulphuric acid concentration showed a line spectrum (expected for a d^0 system) that moved to longer wavelengths as the acid content increased (Fig. 5), a phenomenon which was very unlike that for VO^{2+} and could be attributed to the replacement of the water ligands around TiO^{2+} by SO_4^{2-} and HSO_4^- which give weaker crystal fields, thus causing the shift to longer wavelengths as observed. Adeer and Hisky[11] observed a similar trend in the ultraviolet line-spectra of solutions of Nb_2O_5 in sulphuric acid.

Nature of the TiO^{2+} species formed

That the species formed between TiO^{2+} and salicylic acid in concentrated sulphuric acid medium is not a chelate is demonstrated by the formation of similar species with *m*- and *p*-hydroxybenzoic acid, where chelation is improbable or impossible. The absorption band in the visible region for the titanyl/salicylic acid/conc. H_2SO_4 system has higher absorptivity, λ_{max} at a wavelength longer by about 65 nm, and a broader absorption band than the titanyl salicylate chelate in aqueous solution. These are features characteristic of weak binding in the complex in the ground-state.

In an attempt to identify the nature of the complex species, ultraviolet absorption spectra of the reagent in water and in sulphuric acid were compared with those of sulphuric acid solutions containing the metal ion and reagent.

Figure 6 indicates that the reagent shows bands at around 238 and 300 nm in water, which shift with increasing sulphuric acid concentration to 260 and

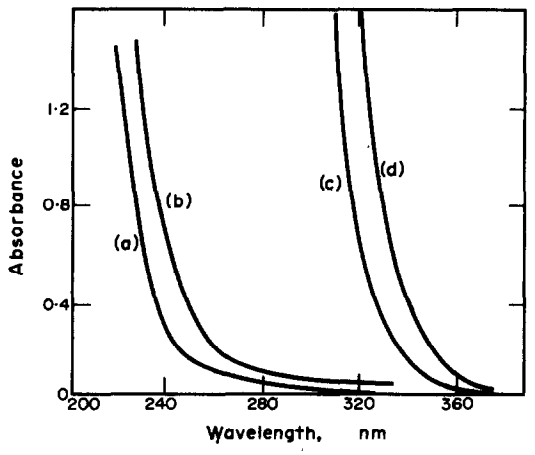


Fig. 5. Absorption spectra of solutions containing TiO^{2+} ($2{\cdot}50 \times 10^{-4}M$) in H_2SO_4. [H_2SO_4]: (*a*) 3*N*; (*b*) 10*N*; (*c*) 20*N*; (*d*) 30*N*.

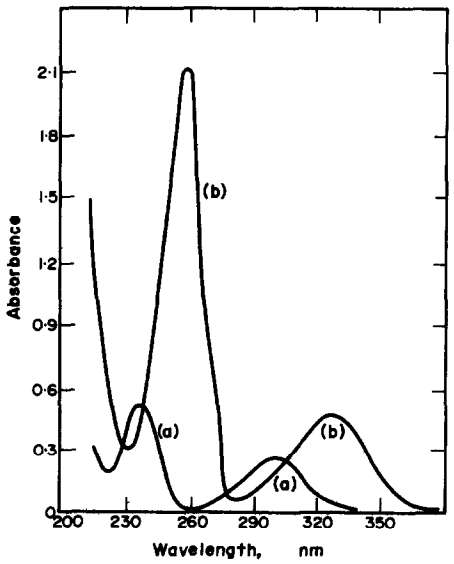


Fig. 6. Absorption spectra.
(*a*) Aqueous solution of salicylic acid, $1{\cdot}45 \times 10^{-4}M$.
(*b*) Conc. H_2SO_4 solution of salicylic acid, $1{\cdot}45 \times 10^{-4}M$.

Table 2. Variation of λ_{max} of aqueous solutions of salicylic acid in varying concentrations of H_2SO_4

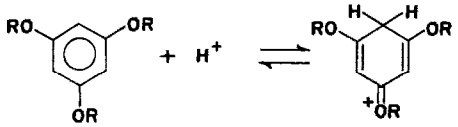
Conc. H_2SO_4, %	0	20	40	60	80	85	90	95	98
λ_{max}, nm	297	302	303	303	305	315	320	323	328

330 nm respectively in the concentrated acid (Table 2); the 330 nm band for the acid medium (300 nm for aqueous medium) could be attributed to intramolecular hydrogen-bonding in salicylic acid.

The absorption bands observed in the ultraviolet region for solutions of salicylic acid in both water and sulphuric acid are found to be retained when TiO^{2+} is also present.

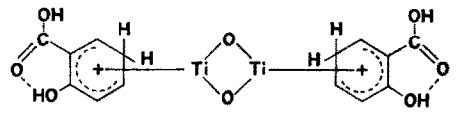
These observations would suggest the formation of the coloured species only at sulphuric acid concentrations greater than 80% and are compatible with the effect of water on the stability of the coloured species as shown in Fig. 3.

Schubert and Quacchia[12] have studied the equilibrium carbon protonation of phloroglucinol and its methyl ethers in 40–65% perchloric acid by ultraviolet spectrophotometric methods and report that the spectrum of 1,3,5-trimethoxybenzene in 95% ethanol is characterized by a strong band at <230 nm and a weakly absorbing peak at 266 nm, and that as the perchloric acid concentration increases, these are replaced by strong peaks at 247 and 347 nm, corresponding to the conjugate acid:



It therefore appears probable that salicylic acid might exist in a protonated form stabilized by intramolecular hydrogen-bonding in a medium such as concentrated sulphuric acid:

In that case it is also probable that the protonated form of the reagent is retained in the presence of TiO^{2+}. The protonated reagent could thus bind with the TiO^{2+} to form a π-complex:



NMR studies

In an attempt to obtain additional evidence for the formation of a protonated species in concentrated sulphuric acid, the NMR spectra of a solution of salicylic acid in concentrated sulphuric acid with and without TiO^{2+} present and of a solution of salicylic acid in deuterochloroform were obtained, with a 60-MHz NMR spectrometer (Figs. 7 and 8). The spectra obtained showed the following characteristics.

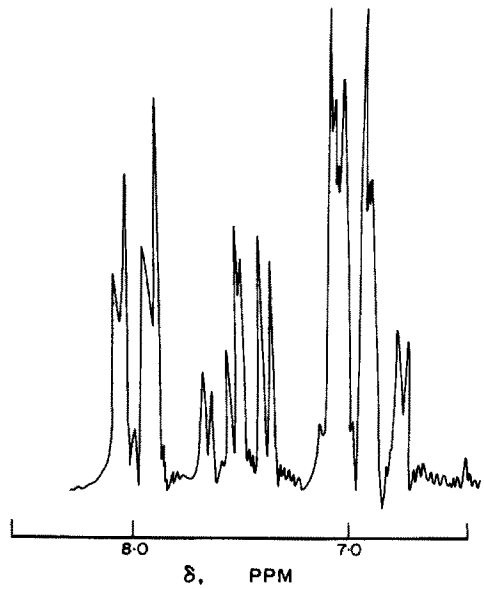


Fig. 7. NMR spectrum of a solution of salicylic acid in $CDCl_3$.

(*i*) The NMR spectrum of salicylic acid in $CDCl_3$ was grossly different from that obtainable in concentrated sulphuric acid. The former was characterized by four aromatic protons in the region 7·0–8·0 ppm with multiplets in the ratio 1:1:2, but the latter suggested the presence of three protons in the region 7·95–9·2 ppm with a singlet and two doublets in the ratio 1:1:1. This would suggest the loss of an aromatic proton and hence the possible presence of a

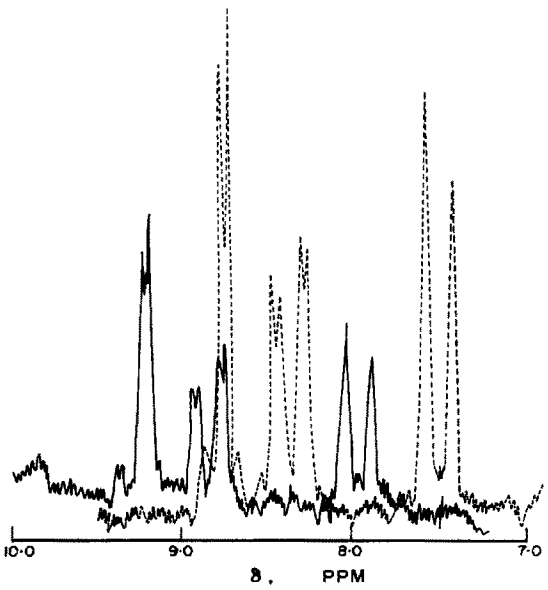


Fig. 8. NMR spectrum of a solution containing salicylic acid and TiO_2 in concentrated H_2SO_4 (.....), superposed on the NMR spectrum of a solution of salicylic acid in concentrated H_2SO_4(——).

protonated species of salicylic acid in concentrated sulphuric acid as suggested.

(*ii*) The NMR spectra of the sulphuric acid solutions of salicylic acid with and without TiO^{2+} were similar, suggesting that this protonated species is retained in the presence of TiO^{2+}, but in the presence of TiO^{2+} there was a high-field shift from 7·95–9·2 ppm to 7·5–8·75 ppm.

These characteristics lend further support for the suggested nature of the coloured species as a π-complex. Similar proton chemical shifts for protonated aromatic compounds (arenonium ions) have been reported.[13]

Dilution of a sulphuric acid solution of TiO^{2+} and salicylic acid resulted in recovery of salicylic acid, which was shown not to be sulphonated, thus excluding the possibility of sulphonation of the salicylic acid under the conditions employed.

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COLOUR CHANGES OF CHEMICAL INDICATORS—VI METALLOCHROMIC INDICATORS FOR DIRECT CHELOMETRIC TITRATIONS OF ZINC*

KAREL VYTŘAS, JARMILA VYTŘASOVÁ and STANISLAV KOTRLÝ

Department of Analytical Chemistry, College of Chemical Technology, 53210 Pardubice, Czechoslovakia

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Summary—Eriochrome Blue SE, Eriochrome Red B, Naphthylazoxine 6S, SNAZOXS, and Zincon have been studied in order to find optimum conditions for their use as metallochromic indicators in direct visual chelometric titrations of zinc. The sharpness of the indicator transitions has been investigated by means of photometric titrations and the colour quality has been specified with the aid of the C.I.E. chromaticity systems. Zincon and Eriochrome Blue SE have been found to be the most convenient for visual titrations of zinc.

Objective approaches to the specification of colour changes of chemical indicators have received only limited attention (for a literature survey see ref. 1) despite the wide analytical applicability of such quantitative data. The significance of a suitable quantitative scale for describing the quality of indicator colour changes has been discussed by Reilley and Schmid.[2] Two criteria must be distinguished: the colour quality of the indicator transition, and the sharpness of the transition attained under specified conditions for a given titration. Although various theoretical attempts have been made to characterize the colour changes of metallochromic indicators,[2,3] and have already been treated elsewhere,[4] only a little experimental work has been done to provide a basis for critical comparisons and classifications of the vast number of metallochromic indicators at present available.

The experimental techniques and approaches to evaluation used in a previous investigation of metallochromic indicators for lead,[5] have been further developed; in the present study they have been applied to various metallochromic indicators for direct chelatometric titration of zinc. The colours observed during the indicator transition are described in terms of the C.I.E. chromaticity systems,[1] and the optimum medium for titration is chosen by considering the photometric titration curves obtained under various titration conditions.[6]

Of the metallochromic indicators recommended for zinc only those were chosen which were found to be sufficiently pure and to form predominantly a single zinc complex. These were Zincon, SNAZOXS, Naphthylazoxine 6S, Eriochrome Blue SE, and Eriochrome Red B.

Zincon, the monosodium salt of 2-[2-[α-(2-hydroxy-5-sulphophenylazo)benzylidene]hydrazino]benzoic acid, was recommended originally for spectrophotometric determination of zinc[7,8] but soon found applications as a metallochromic indicator for zinc, in ammoniacal[9] or triethanolamine[2] buffer media.

The indicator SNAZOXS, the disodium salt of 8-hydroxy-7-[(4-sulphonaphthyl)azo]-5-quinolinesulphonic acid has been advocated for chelometric titrations of bivalent and tervalent metal ions;[10,11] zinc is titrated in acetate or pyridine buffer.

Naphthylazoxine 6S, the disodium salt of 8-hydroxy-7-[(6-sulpho-2-naphthyl)azo]-5-quinolinesulphonic acid, is an analogue of SNAZOXS and is used for the chelometric titration of copper(II), cadmium, and zinc in a pyridine buffer of pH 6 and for magnesium and calcium at pH 10.[12]

Eriochrome Blue SE, the disodium salt of 4,5-dihydroxy-3-[(5-chloro-2-hydroxyphenyl)azo]-2,7-naphthalenedisulphonic acid, was introduced as a metallochromic indicator for calcium and magnesium[13] but soon also found application for other metals.[14] As with Eriochrome Black T, zinc is titrated in an ammoniacal buffer at pH ~10.

Eriochrome Red B, the sodium salt of 1-(3-methyl-5-oxo-1-phenyl-2-pyrazolin-4-ylazo)-2-naphthol-4-sulphonic acid, has been introduced as another indicator from the family of *o,o'*-dihydroxyazo dyestuffs.[15] With this indicator zinc is titrated either in an acetate or hexamine buffer at pH 6·5 or in ammoniacal buffer at pH 10.

This choice of indicators and the aims of the present study are necessarily rather restrictive. It is to be hoped that further quantitative information on characterization of colour changes of chemical indicators will be accumulated in future.

EXPERIMENTAL

Apparatus

Absorption spectra in the visible region (380–770 nm) were obtained with a Zeiss VSU-1 spectrophotometer.

* Part V—*Sb. Ved, Praci, Vys. Sk. Chem. Technol., Pardubice*, 1971, **26**, 3.

Cells of optimum path-length were used in the measurements and the results were recalculated to a 50-mm standard path-length.

Photometric titrations were performed on a Zeiss Spekol spectrophotometer equipped with a microtitration attachment of special design,[16] a photocell housing, and an amplifier (type ZV, Zeiss). Glass cells (type C, Zeiss) with a 50-mm path-length and 20 ml capacity were used for titrations. The two spectrophotometers were tested with standard spectrophotometric solutions.[17]

A Radelkis Model OP-201/2 pH-meter with a glass–saturated calomel electrode pair was calibrated on the operational pH-scale with standard reference buffer solutions.[18]

A home-made 400-μl micrometer syringe burette was used for the photometric titrations, the tip of a fine polyethylene capillary jet being immersed in the titrand. The microburette was calibrated by weighing water delivered under a layer of paraffin oil.

Reagents

Reagents of analytical grade and redistilled water were used in all experiments.

EDTA solution (0·01*M*) was standardized by visual titration of recrystallized lead chloride,[19] Xylenol Orange being used as indicator.[6]

Acetate buffers[20] for the pH range 3·6–5·9 were obtained by mixing 0·2*M* acetic acid and 0·2*M* sodium acetate. Hexamine buffers were prepared from a stock 0·5*M* solution by adjustment of the pH with 1*M* nitric acid. Ammoniacal buffers of pH 7·9–10·2 were prepared by appropriate additions of dilute ammonia solution (1 + 4) to 50 ml of 0·5*M* ammonium chloride and dilution to 100 ml.

Indicator solutions

Stock 0·0015*M* solutions of the indicators were prepared by dissolving the following amounts of reagents in 100 ml of water: 0·0060 g of Zincon, 0·0778 g of Eriochrome Blue SE, 0·0683 g of Eriochrome Red B, 0·0755 g of SNAZOXS and Naphthylazoxine 6S. For easier dissolution three drops of saturated ammonia solution were used if necessary. A few crystals of hydroxylamine hydrochloride were added to stabilize the stock solutions, which were diluted to 0·00015–0·0003*M* just before the titrations.

The purity of the indicators was checked by descending paper chromatography on Whatman No. 1 paper with butanol–acetic acid–water (2:1:1) for Zincon, ethyl acetate–methanol–water (1:1:1) for SNAZOXS, Naphthylazoxine 6S, and Eriochrome Blue SE, and butanol–acetone–concentrated ammonia solution (4:3:3) for Eriochrome Red B. All the indicators were found to be free from other dyestuffs.

Procedure for photometric microtitrations

A 3-ml portion of 0·001*M* zinc is transferred to the titration cuvette (length 50 mm), 2 ml of buffer solution and 2–4 ml of approx. $1{\cdot}5 \times 10^{-4}M$ indicator are added, and solution diluted to 20 ml and titrated with 0·01*M* EDTA.

RESULTS AND DISCUSSION

Zincon

The indicator species H_3In present in acidic media is red–violet, changing at lower acidity to yellow [$pK_{a1}(H_3In) = 4$].[21,22] The next deprotonation ($pK_{a2} = 7{\cdot}85$) gives a colour change to orange–yellow. In 10*M* potassium hydroxide medium the violet colour of the fully deprotonated indicator appears ($pK_{a3} \sim 15$).

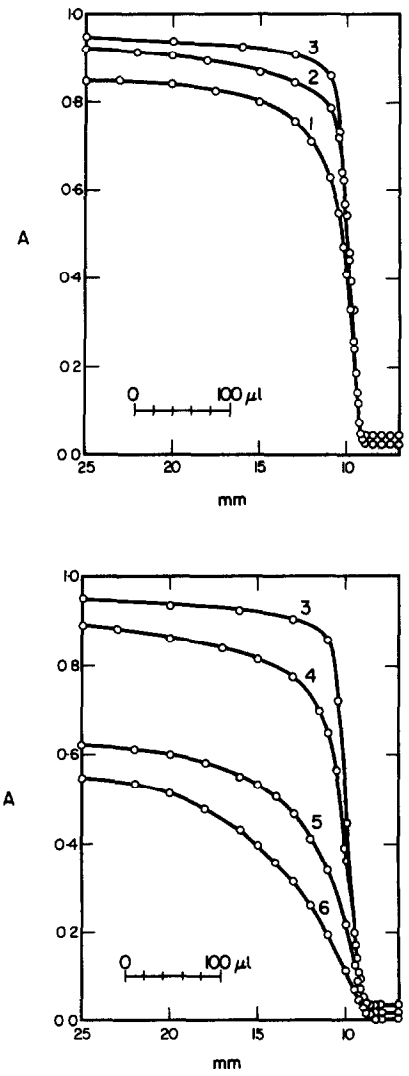

Fig. 1*a,b*. Photometric titration curves of zinc with Zincon as indicator ($c_{Zn} = 1{\cdot}5 \times 10^{-4}M$, $c_{In} = 3 \times 10^{-5}M$, λ = 625 nm) at the following pH values: 1—7·68; 2—8·25; 3—8·65; 4—9·68; 5—9·80; 6—10·27.

The effect of pH on the titration in dilute ammoniacal buffer media is illustrated by the curves in Fig. 1 (obtained at 625 nm). The steepest break is obtained at pH 8·6, but slightly lower pH values have no practical effect on the sharpness of the indicator transition. The optimum pH is thus 8·6, in agreement with the results obtained for spectrophotometric determination of zinc.[7]

The absorption spectra in Fig. 2 illustrate the indicator colour change. The blue metal–indicator complex has an absorption maximum at 620 nm (*cf.* Tables 1 and 2). The indicator transition proceeds *via* purplish-grey to the yellowish–orange of the free form of the indicator ($\lambda_{max} = 480$ nm; curve 3 in Fig. 2). There is an isosbestic point at 525 nm. The colour change of Zincon under the given conditions is characterized by the chromaticity co-ordinates in Tables 1 and 2 and the position of the transition chromaticity curves in Figs. 7 and 8, respectively.

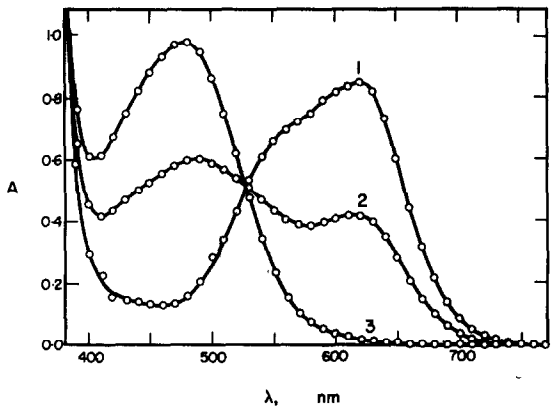

Fig. 2. Absorption spectra for a solution of zinc titrated with 0·01*M* EDTA, using Zincon as indicator ($c_{Zn} = 1{\cdot}5 \times 10^{-4}M$, $c_{In} = 3 \times 10^{-5}M$, pH = 8·65, $d = 50$ mm) at the following consumptions of titrant: 1—0·0; 2—285·4 μl; 3—373·0 μl.

SNAZOXS

This indicator has the following acid–base colour changes in the absence of bivalent metal ions: the purple colour of an acidic solution is first changed to pink [$pK_{a1}(H_2In) = 3{\cdot}0$;[23]] and then in neutral medium to orange–yellow [$pK_{a2}(HIn) = 7{\cdot}0$]. The metal–indicator complexes formed in mildly acidic medium are yellow.

The pH effect on chelometric titration of zinc(II) with SNAZOXS in acetate buffer medium is shown in Fig. 3. The slope of the section before equivalence is pH-dependent in the pH range 3·7–5·5. The sharpest transition is obtained at pH 5·5. Further increase in pH has no effect up to about pH 6, where the second acid–base transition of the indicator begins to interfere.

SNAZOXS forms a yellow complex with zinc ($\lambda_{max} = 455$ nm; curve 1 in Fig. 4), and the colour

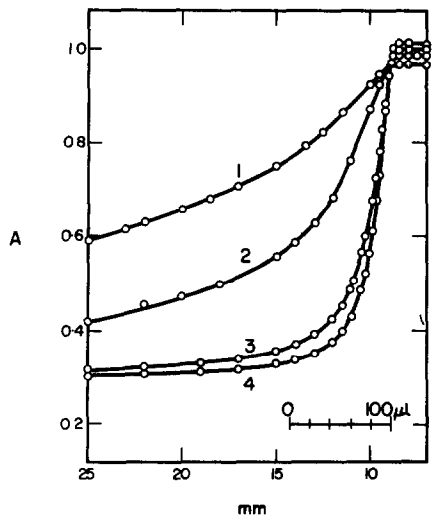

Fig. 3. Photometric titration curves of zinc with SNAZOXS as indicator ($c_{Zn} = 1{\cdot}5 \times 10^{-4}M$, $c_{In} = 1{\cdot}5 \times 10^{-5}M$, $\lambda = 540$ nm, $d = 50$ nm) at various pH values: 1—3·72; 2—4·30; 3—5·08; 4—5·45.

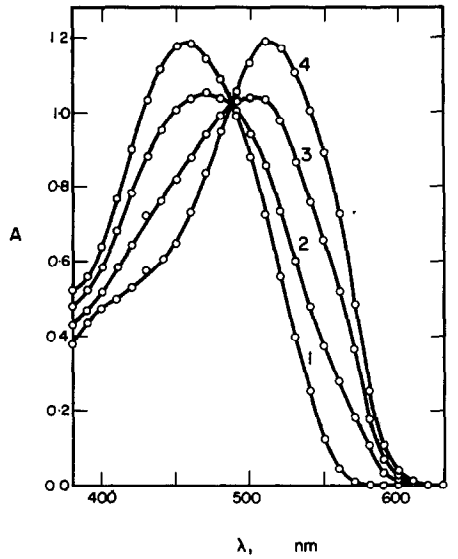

Fig. 4. Absorption spectra of SNAZOXS during titration of zinc with 0·01*M* EDTA ($c_{Zn} = 1{\cdot}5 \times 10^{-4}M$, $c_{In} = 1{\cdot}5 \times 10^{-5}M$, pH = 5·45, $d = 50$ mm). Added titrant: 1—0·0; 2—268·6 μl; 3—289·3 μl; 4—373·0 μl.

change proceeds through orange to the pink of the free indicator ($\lambda_{max} = 510$, curve 4). There is one isosbestic point at 489 nm and a second at 348 nm. The chromaticity co-ordinates for the colour change of SNAZOXS are given in Tables 1 and 2 along with the concentration fraction of all free indicator species, $\alpha = [In']/c_{In}$. The transition chromaticity curves are shown in Figs. 7 and 8.

Naphthylazoxine 6S

The free form of Naphthylazoxine 6S is pink between the two dissociation steps with pK_a 3·1 and 7·4 at $I = 0{\cdot}1$ and 25°,[23] where the indicator species HIn prevails. The indicator forms a complex ZnIn with $\log \beta = 7{\cdot}2$.

Naphthylazoxine 6S is similar in its properties to SNAZOXS, which is reflected in the effect of pH on the photometric titration curves at 540 nm (acetate buffer). The sharpest indicator colour change is obtained at pH ~5·9. A further increase in pH has no effect, up to pH 6·4, where the acid–base colour change at pK_a 7·4 begins to interfere (Fig. 5).

The colour change during chelometric titration of zinc is similar to that with SNAZOXS (Fig. 6). The chromaticity co-ordinates are given in Tables 1 and 2. The sequence of hues is characterized by the transition chromaticity curves in Figs. 7 and 8.

Eriochrome Blue SE

The acid–base transition of this indicator begins with a red colour at pH <7·5, followed by blue over the pH range 8·5–10·0, and violet at pH >10·5. The final deprotonation occurs in strongly basic medium but there is no conspicuous colour change. A potentiometric study[24] gave the pK_a values as 8·0, 10·5, and 11·9.

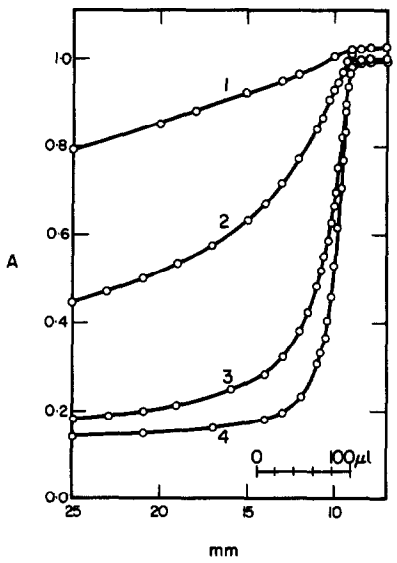

Fig. 5. Photometric titration curves for Naphthylazoxine 6S as indicator ($c_{Zn} = 1{\cdot}5 \times 10^{-4}M$, $c_{In} = 1{\cdot}5 \times 10^{-5}M$, $\lambda = 540$ nm, $d = 50$ mm) at various pH values: 1—3·74; 2—4·31; 3—5·35; 4—5·85.

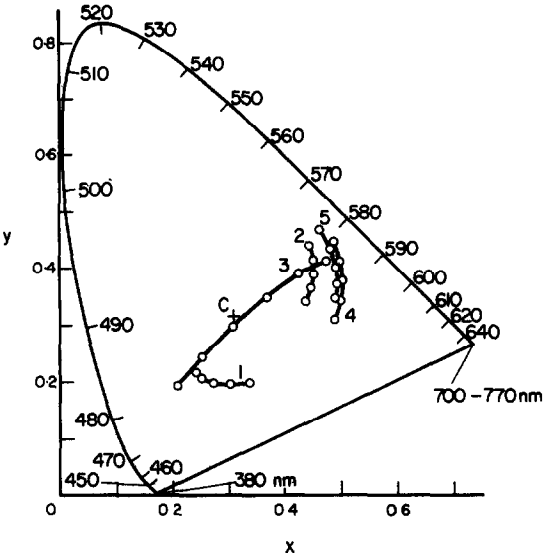

Fig. 7. Chromaticity diagram C.I.E.—*xy* (1931) showing the chromaticity transition curves of the following indicators: 1—Eriochrome Blue SE; 2—Eriochrome Red B; 3—Zincon; 4—SNAZOXS; 5—Naphthylazoxine 6S. The point of achromatic colour corresponds to the C.I.E. standard source C. For computations see ref. 26.

The effect of pH on the titration of this indicator during chelometric titration of zinc was investigated at 625 nm, *i.e.*, the absorption maximum of the free indicator, in ammoniacal buffers. No marked difference in the shape of the titration curves was observed from pH 7·75 up to pH about 10, where the acid–base equilibrium begins to affect the colour transition. Thus a pH of about 9 is best for visual titration and investigation of the indicator colour change.

At the beginning of the titration the zinc–indicator complex has a purple colour ($\lambda_{max} = 555$ nm; cf. Tables 1 and 2), and at the end the free form of the indicator is blue (λ_{max} 600 nm; *cf.* Figs. 7 and 8). The absorbance curves intersect at an isosbestic point at 582 nm.

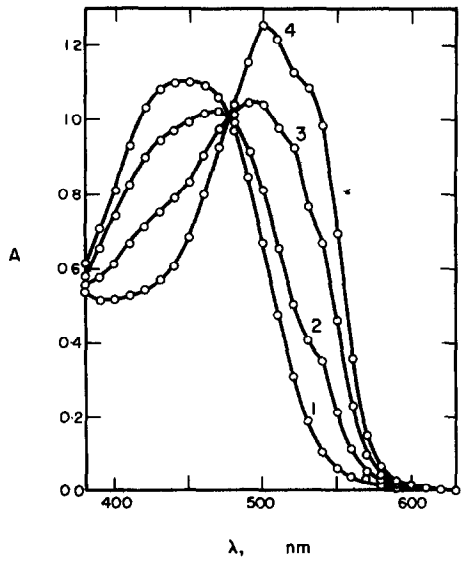

Fig. 6. Absorption spectra of Naphthylazoxine 6S during titration of zinc ($c_{Zn} = 1{\cdot}5 \times 10^{-4}M$, $c_{In} = 1{\cdot}5 \times 10^{-5}M$, pH = 5·85, $d = 50$ mm). Volume of 0·01*M* EDTA added: 1—0·0; 2—268·6 µl; 3—286·3 µl; 4—373·0 µl.

Eriochrome Red B

The free form of the indicator is yellow, and the colour is not significantly influenced by the acid–base equilibrium with pK_a 6·28 ($I = 0{\cdot}01$),[25] but the absorbance at 470 nm decreases with increasing acidity.

The steepness of the photometric titration curves at 520 nm is practically unaffected in the medium of dilute ammoniacal buffers over the pH range 6·95–9·7. A pH of about 8 was chosen for further study.

The absorption spectra during the colour change of Eriochrome Red B show isosbestic points at 484

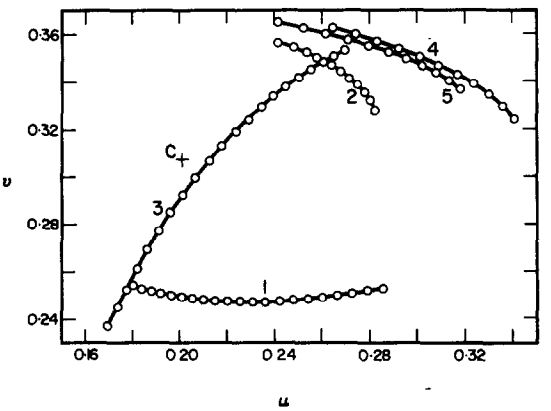

Fig. 8. Section from the uniform chromaticity spacing diagram C.I.E.—*uv* (1960) introducing the chromaticity transition curves of the following indicators: 1—Eriochrome Blue SE; 2—Eriochrome Red B; 3—Zincon; 4—SNAZOXS; 5—Naphthylazoxine 6S. The point corresponding to the C.I.E. standard source C is marked with a cross.

Table 1. Chromaticity co-ordinates for the colour changes of some metallochromic indicators for zinc

Indicator	pH	α*	C.I.E.-xy			C.I.E.-uv		Dominant wavelength and excitation purity	
			Y	x	y	u	v	λ_d, nm	p_e
Zincon	8·65	0·0	27·2	0·209	0·195	0·170	0·237	474·0	0·515
		0·5	35·5	0·338	0·324	0·218	0·313	594·8	0·097
		1·0	60·4	0·473	0·413	0·270	0·353	584·9	0·694
SNAZOXS	5·45	0·0	66·7	0·487	0·444	0·265	0·362	582·1	0·818
		0·5	47·0	0·503	0·376	0·309	0·347	593·5	0·678
		1·0	36·7	0·489	0·310	0·341	0·324	622·5	0·464
Naphthylazoxine 6S	5·85	0·0	76·6	0·462	0·466	0·241	0·365	577·9	0·809
		0·5	56·7	0·492	0·401	0·288	0·352	588·2	0·716
		1·0	47·1	0·491	0·347	0·318	0·337	600·5	0·567
Eriochrome Blue SE	9·05	0·0	27·2	0·336	0·199	0·286	0·253	−537·0	0·523
		0·5	25·2	0·273	0·200	0·225	0·247	−563·7	0·399
		1·0	27·7	0·232	0·219	0·180	0·255	473·1	0·401
Eriochrome Red B	8·05	0·0	60·0	0·437	0·339	0·282	0·328	599·8	0·402
		0·5	62·4	0·452	0·387	0·268	0·345	587·3	0·570
		1·0	69·4	0·445	0·439	0·241	0·357	578·9	0·691

* α = fraction of all free indicator species.

Table 2. Complementary chromaticity co-ordinates

Indicator	α	Q_x	Q_y	J	K_λ (at λ, nm)
Zincon	0·0	0·433	0·437	1·020	1·198 (620)
	1·0	0·151	0·191	1·126	1·154 (480)
SNAZOXS	0·0	0·142	0·145	1·310	1·109 (460)
	1·0	0·184	0·350	1·342	1·126 (510)
Napthylazoxine 6S	0·0	0·142	0·105	1·184	1·075 (450)
	1·0	0·154	0·315	1·252	0·998 (500)
Eriochrome Blue SE	0·0	0·299	0·473	1·065	1·076 (560)
	1·0	0·397	0·410	1·041	1·410 (600)
Eriochrome Red B	0·0	0·131	0·317	0·837	0·778 (510)
	1·0	0·156	0·141	1·031	1·043 (470)

The quantities Q_x, Q_y, and J are defined in refs. 1 and 28. The calculation and application of the constant K_λ is presented in ref. 29.

and 558 nm. At the beginning of the titration the zinc complex has an absorption maximum at about 510 nm (see Tables 1 and 2). The displacement of zinc from the red indicator complex results in a sequence of orange hues, ending with the orange–yellow of the free indicator (λ_{max} 470 nm). This colour change, which resembles that of Methyl Orange, is characterized by the transition chromaticity curves in Figs. 7 and 8.

Conclusion

The sharpness of colour change of all five indicators at the optimum pH is sufficient for accurate visual titration of zinc with 0·01*M* EDTA, but Zincon gives the best colour quality of transition. As shown by Figs. 7 and 8, the colour change from blue to orange–yellow passes close to the point of achromatic colour. Such a colour change between complementary colours is considered to be the best for visual end-point detection. A large colour difference is also achieved with Eriochrome Blue SE, the colour change of which resembles that of Eriochrome Black T. The colour changes of SNAZOXS and Naphthylazoxine 6S are not so conspicuous and a long experience may be required to achieve precise results. The colour quality of Eriochrome Red B is somewhat lower, but the transition sharpness is high enough; the colour change may be considerably improved by screening with a suitable background colour (*e.g.*, ref. 27). The best combination of screening dyes can be computed from the complementary chromaticity co-ordinates given in Table 2. This objective approach[28,29] will be further studied.

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SIMPLE SEMIQUANTITATIVE DETERMINATION OF TRACE METAL IONS BY USE OF REAGENT GEL COLUMNS—I

DETERMINATION OF MERCURY WITH DITHIZONE GEL

YONG KEUN LEE

Department of Chemistry and Natural Science Research Institute, Yonsei University, Seoul 120, Korea

KYU JA WHANG

Department of Manufacturing Pharmacy, College of Pharmacy, Sookmyung Women's University, Seoul 140, Korea

and

KEIHEI UENO

Department of Organic Synthesis, Faculty of Engineering, Kyushu University, Fukuoka 812, Japan

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Summary—Mercury(II) at the sub-ppm level was determined by using a column packed with gel beads containing dithizone stabilized as the zinc complex. The beads turned from pink to green when the acidified sample solution was passed through the column. If the solution contained mercury (II), the colour of the gel beads turned to orange owing to the formation of mercury dithizonate. The length of the coloured zone was proportional to the amount of mercury in the sample. With 0·01% dithizone gel, as little as 0·1 ppm of mercury(II) could be determined in a 20-ml sample at a flow-rate of 1 ml/min.

In a previous paper, we reported the use of a column containing dithizone gel beads for the extraction of trace amounts of metal ions from aqueous solution.[1] When an aqueous solution containing mercury(II) at less than the ppm level was passed through the column, a sharp colour change of the dithizone gel from the green of free dithizone to the orange of the mercury dithizonate was observed. The fact that the length of the orange zone was proportional to the total amount of mercury(II) in the solution passed through the column, suggested the use of a dithizone gel column for the semiquantitative determination of mercury(II) at very low concentrations.

Various devices such as test papers or detector tubes containing ion-exchange resins or other particles impregnated with chromogenic reagents have been proposed for the semiquantitative determination of metal ions,[2] but few could be used for mercury(II) at less than the ppm level.

This paper reports the use of the dithizone gel bead column for the semiquantitative determination of mercury(II) at the sub-ppm level. The method could be used in the field for samples of environmental origin.

EXPERIMENTAL

Reagents

All reagents were of analytical grade. Dithizone was used without further purification. Zinc dithizonate [$Zn(HDz)_2$] was prepared by the conventional method[3] and was recrystallized from chloroform.

Preparation of dithizone gel beads

The procedure was substantially that reported previously,[1] but the gel beads were prepared from 1 g of styrene–divinylbenzene copolymer (2% divinylbenzene, particle size 70–100 mesh) by soaking in 10 ml of 0·01% dithizone solution in chlorobenzene for 3 hr in a refrigerator. After removal of excess of solvent by centrifugation, the gel beads were suspended in about 100 ml of 1% zinc sulphate solution to obtain the pink zinc dithizonate gel beads. Finally, the gel beads were washed several times with water saturated with chlorobenzene.

Alternatively, dry polymer beads could be soaked with 10 ml of 0·01% zinc dithizonate solution which was prepared by dissolving crystalline zinc dithizonate [$Zn(HDz)_2$] in chlorobenzene, to obtain the zinc dithizonate gel beads directly.

The latter procedure has the advantage that the decomposition of dithizone during preparation of the gel beads is avoided. This becomes more important when gel beads of lower dithizone concentration are to be prepared.

Preparation of analytical gel bead column

The column consisted of a Pyrex glass tube (2·5 mm bore and 120 mm long) with a glass-wool plug at the lower end. Two procedures were employed to prepare uniformly packed gel bead columns.

In the first, 200 mg of gel beads were suspended in 200 ml of distilled water saturated with chlorobenzene, and were sucked into the column by reduced pressure. The suspension had to be stirred continuously by a magnetic stirrer to obtain a uniformly packed column. The procedure was continued until the length of gel bead layer was 100 mm. The column top was then plugged with a

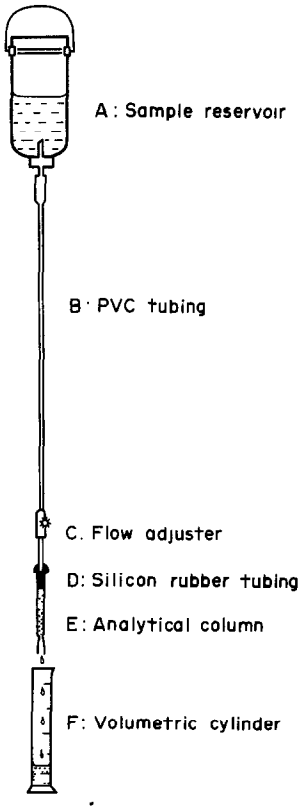

Fig. 1. Diagram of apparatus.

disc of porous PVC. Both ends of the column were sealed with polyethylene stoppers, and the column was wrapped in aluminium foil. About five columns could be filled with 1 g of gel beads.

In order to prevent the decomposition of the dithizone or the dithizone complex, the whole procedure had to be carried out at <20°, and the columns stored in a refrigerator. Columns stored for a month still give satisfactory results.

In the second procedure, the stem of a cylindrical funnel of 100 ml capacity was connected to the upper end of the column with silicone rubber tubing, and the column attached to a Büchner flask through a rubber stopper. About 200 mg of gel beads suspended in 200 ml of water were poured into the funnel, while slight suction was applied. The suspension was stirred continuously with a mechanical stirrer. When the length of the gel bead column was 100 mm, the column was removed and treated as in the first procedure.

Analytical procedure

An analytical column was connected to a sample reservoir with PVC tubing as shown in Fig. 1. The sample solution, which had been acidified with nitric acid to pH 1, was placed in the reservoir, and the flow-rate was adjusted to 1 ml/min.

As the sample solution flowed through the column, the pink gel turned to green as zinc dithizonate was decomposed by the acid sample to liberate free dithizone. Then the complexation of mercury(II) with dithizone took place from the top of the column to give an orange band. After passage of a measured volume of sample solution, the length of the orange zone was measured and the amount of mercury was calculated from a calibration curve, which was either linear or slightly convex.

RESULTS AND DISCUSSION

Gel beads and analytical column

Dithizone decomposes so readily that the gel beads of 0·01% or lower free dithizone concentration could not be stored for more than a few days even in a cool dark place. On the other hand, metal dithizonates are stable, so zinc dithizonate was employed in this experiment, because the gel beads were stable for many weeks. The free dithizone gel could be released by treatment with dilute acid.

As the concentration of dithizone in the gel beads is directly related to the zone length of the mercury complex, stability of the dithizone is essential for an accurate result. When 0·01% dithizone solution was used, a 10-mm length of complexed mercury corresponded to 1·6–1·8 μg of mercury. At a dithizone concentration of 0·005%, a 10-mm length corresponded to 0·5–0·7 μg of mercury. However, the decomposition of dithizone became more critical in the latter case.

The sharpness of the zone boundary partly depended on the particle size of the beads. Gel beads of larger size than 70–100 mesh gave more indefinite zone boundaries, while those of finer particle size gave difficulties in packing the columns and obtaining suitable flow-rates.

Uniformity of column packing is essential for reproducible results. Both packing procedures described were satisfactory, but the first gave a denser column and so the length of the mercury complex zone was 50% greater for the second packing procedure.

Conditions for the analytical procedure

The length of coloured zone and the sharpness of the boundary were also affected by the flow-rate. When sample solution containing 0·2 ppm of mercury(II) was passed through the column at a flow-rate of 2·0–0·4 ml/min, the zine length increased almost linearly with the total amount of mercury(II). However, the zone boundary became diffuse when the flow-rate was increased beyond this range. In the standard procedure, the flow-rate was fixed at 1·0 ml/min.

Under these conditions, the relation between the zone length and the volume of sample solution containing a given amount of mercury(II) was linear (Fig. 2). Accordingly, the mercury concentration can be determined either by observing the zone length after passage of a known amount of sample solution, or by measuring the volume of sample solution needed for the coloured zone to reach a given point.

With 0·01% dithizone gel beads, as little as 0·1 ppm of mercury(II) could be determined with a 20-ml sample at a flow-rate of 1 ml/min. The error is about ±10% at the 2–4 μg level and ±4% at the 10–15 μg level.

With the use of 0·005% dithizone gel beads, as little as 50 ppM (parts per milliard) of mercury(II) was determined. However, in the latter case, it is recommended to use fresh analytical columns to

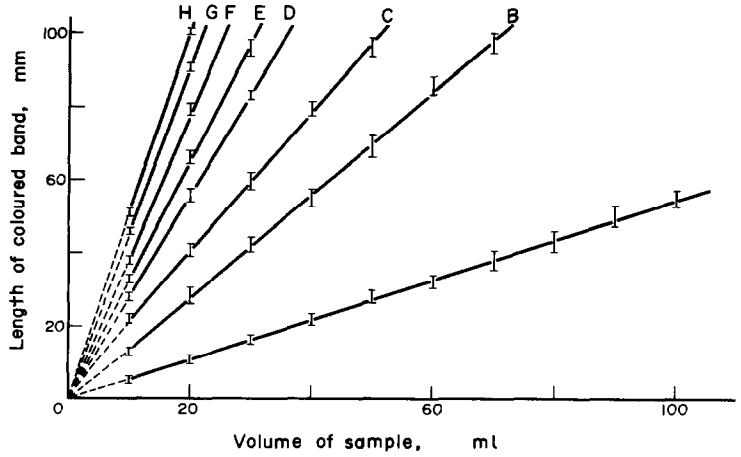

Fig. 2. Relationship between the length of coloured band and the sample volume at various mercury ion concentrations. Analytical columns were prepared with gel beads containing 0·01% dithizone. Flow-rate 1 ml/min. [Hg]: *A*, 0·1; *B*, 0·2; *C*, 0·3; *D*, 0·4; *E*, 0·5; *F*, 0·6; *G*, 0·7; *H*, 0·8 μg/ml.

avoid an error due to partial decomposition of the dithizone.

When a large volume of sample solution was passed through the column, the gel beads tended to shrink, owing to the loss of chlorobenzene into the aqueous phase, causing channels in the column. Accordingly, the sample solution had to be saturated with chlorobenzene before it was placed in the sample reservoir. However, in the standard procedure where only 20 ml of sample solution was passed through the column, presaturation was not necessary.

Conditions for the colour reaction

The mode of complexation with dithizone depends upon the pH of the solution. In the acidic range, an orange primary complex [$Hg(HDz)_2$] is formed, whereas in the higher pH range, a pink secondary complex [$Hg_2(Dz)_2$] is formed.[4] Since the complexation is more specific for mercury(II) in the lower pH region, the sample solution was acidified to pH 1 with nitric or sulphuric acid. Under these conditions, the reaction sequence can be written as:

$$\underset{\text{pink}}{Zn(HDz)_2} + 2\,H^+ \rightarrow 2\,\underset{\text{green}}{H_2Dz} + Zn^{2+}$$

$$2\,\underset{\text{green}}{H_2Dz} + Hg^{2+} \rightarrow \underset{\text{orange}}{Hg(HDz)_2} + 2\,H^+$$

Similar reactions occurred at pH 3. However, the reactions were slow and the boundary of the coloured zone was so diffuse that the zone length could not be determined with accuracy.

In the neutral pH region, the following exchange reaction must proceed:

$$\underset{\text{pink}}{Zn(HDz)_2} + 2\,Hg^{2+} \rightarrow Hg_2(Dz)_2 + \underset{\text{pink}}{Zn^{2+}} + 2\,H^+$$

However, a definite colour change cannot be expected and the complexation reaction is not specific for mercury(II), so the reaction is not useful for the present purposes.

Dithizone is known to be highly selective for mercury(II) at pH 1, and the only interfering ions are copper(II) and silver(I). Although silver gives the same colour reaction as mercury on the dithizone gel column, it seldom occurs in environmental samples and the interference can be masked by adding a small amount of chloride ion (<100 ppm, see below). The colour reaction with copper(II) was not so significant, and less than 2·5 ppm of copper did not give any serious interference. In the presence of a larger amount of copper (5–10 ppm), the colour of the mercury complex zone became brown, indicating interference by copper.

Anions, with the exception of halides, did not interfere. The only interfering anion in environmental samples may be the chloride ion, but this does not give any significant error if its concentration is lower than 100 ppm. In the presence of higher concentrations, as in sea-water, the complexation reaction proceeds as follows:[5]

$$HgCl^+ + H_2Dz \rightarrow \underset{\text{orange}}{HgCl(HDz)} + H^+$$
$$\text{green}$$

Thus, the reaction ratio of dithizone to mercury is 1:1, whereas the ratio in the absence of chloride is 2:1. Accordingly, for sea-water the zone length is about twice the normal and a separate calibration curve has to be prepared.

Table 1. Determination of mercury(II) in practical samples

Sample	Hg found, *ppm*	Recovery of Mercury: Hg added, *ppm*	Recovery of Mercury: Hg found, *ppm*
River-water (Han R.)	none	0·1	~ 0·1
		0·4	0·3 ~ 0·4
		0·8	0·7 ~ 0·8
Industrial effluent (fermentation plant)	none	0·1	~ 0·1
		0·4	0·3 ~ 0·4
		0·8	0·7 ~ 0·8
Sea-water (Inchon, Songdo, Korea)	none	0·1	~ 0·1
		0·4	0·3 ~ 0·4
		0·8	0·8 ~ 0·9

Table 1 summarizes some results obtained by applying this method to the analysis of samples with and without a known added amount of mercury.

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SHORT COMMUNICATIONS

FLOTATION OF TRACES OF SILVER AND COPPER(II) IONS WITH A METHYL CELLOSOLVE SOLUTION OF DITHIZONE

(*Received* 23 *July* 1974. *Revised* 15 *October* 1974. *Accepted* 13 *November* 1974)

Although collection of traces of various metal ions on inorganic or organic precipitates offers a useful separation technique in trace analysis and radiochemistry, difficulties sometimes arise in separating the precipitate from the mother liquor. The dithizone precipitate formed by adding an acetone solution of dithizone to an aqueous sample solution is a good collector for gold, silver, mercury, palladium, and copper,[1] but cannot be filtered off easily; it clogs the pores of a porosity-4 sintered-glass filter (5–10 μm) and passes through a porosity-3 filter (20–30 μm). Centrifugation is not applicable because of incomplete sedimentation. We have tried replacing acetone by methyl cellosolve as a solvent for dithizone, but still experienced the same difficulties. Therefore, the flotation technique has been applied. The precipitate is readily separated from the mother liquor and then dissolved in nitric acid, followed by addition of acetone, for radioactivity measurements or atomic-absorption spectrophotometry. This separation technique has been successfully applied to the determination of quantities from a tenth to a few ppm of silver and copper in high-purity lead and zinc metals.

EXPERIMENTAL

Apparatus

A Fujitsu well-type NaI(Tl) scintillation counter, and a Nippon Jarrell–Ash model AA-1 Mark II atomic-absorption spectrophotometer with an SA-61 slit burner and a Yanaco model YR-101 recorder were employed. Figure 1 shows the flotation cell.

Reagents

Standard solutions were prepared from silver nitrate, and copper, lead and zinc metals. Dithizone solutions were prepared by dissolving dithizone in methyl cellosolve immediately before use. All reagents used were of reagent grade and employed without further purification, unless otherwise stated. Water was purified by distillation and ion-exchange. ^{110m}Ag and ^{64}Cu were used as tracers.

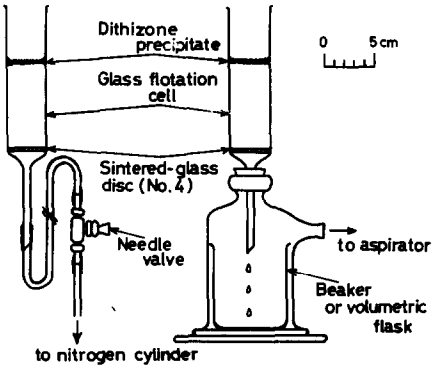

Fig. 1. Flotation and separation apparatus.

Procedure

Place 100 ml of 0·1*M* nitric acid containing microgram quantities of silver or copper(II) in a 200-ml beaker, and add 5 ml of 0·4% w/v dithizone solution in small portions while stirring with a magnetic stirrer. Cover the beaker and stir the solution vigorously for 30 min to coagulate the precipitate. Transfer the contents of the beaker (excluding the stirring bar) to a flotation cell, and wash the beaker with 5 ml of water. Pass nitrogen at a flow-rate of 9 ml/min from the lower end of the cell for 10–15 sec to effect complete agitation followed by flotation of the precipitate. Suck off the mother liquor through the sintered-glass disc, and wash the precipitate with 10 ml of 0·1*M* nitric acid. Add 1 ml of 13·8*M* nitric acid and 3 ml of acetone to the cell to dissolve the precipitate, and collect the filtrate in a 5-ml volumetric flask, by suction. Wash the sintered-glass disc with water and dilute to the mark. Measure the metal-ion concentration by a suitable technique.

RESULTS AND DISCUSSION

Flotation of dithizone precipitate

The dithizone precipitate is coagulated during the magnetic stirring, and is easily floated with the aid of small nitrogen bubbles (30–100 μm dia.). The flotation is also possible with an acetone solution of dithizone, but methyl cellosolve is preferred because of its much lower vapour pressure. The flotation has always been successful, with use of several different lots of commercial reagent-grade methyl cellosolve with and without further purification by distillation. Neither solvent is essential to the flotation itself, because the dithizone precipitate formed by acidifying (to pH 1) an ammoniacal solution of dithizone is also easily floated.

Reaction conditions

Table 1 shows that a solution of 20–30 mg of dithizone in 4–10 ml of methyl cellosolve is required for quantitative

Table 1. Silver recovery as a function of quantities of dithizone and methyl cellosolve

Dithizone solution containing		
dithizone, *mg*	methyl cellosolve, *ml*	^{110m}Ag recovered, %
1	4	86, 95*
10	4	94, 99*
15	4	95, 100*
20	4	98, 97*
20	5	99, 100, 99*
20	10	98, 98*
30	10	99, 98*

3 μg of labelled Ag in 100 ml of 0·1*M* HNO_3.
* Purified methyl cellosolve used.

Table 2. Recovery of silver at various concentration levels

Labelled Ag in 100 ml of 0·1*M* nitric acid, *μg*	^{110m}Ag recovered, %
0·05	88, 92, 61*
0·1	88, 80*
0·3	88, 99*
0·5	100, 95*
3·0	100, 99*
20	101, 100*
50	97, 101*

5 ml of 0·4% w/v dithizone solution.
* Purified methyl cellosolve used.

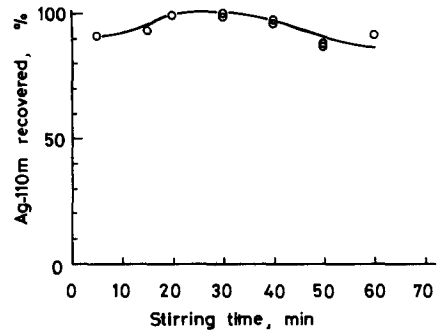

Fig. 2. Effect of length of stirring.

separation of 3 *μg* of silver from 100 ml of 0·1*M* nitric acid, with 30 min of stirring followed by flotation. With 5 ml of 0·4% w/v dithizone solution, 0·5–50 *μg* of silver could be recovered nearly completely, but less than 0·3 *μg* of silver could not, as shown in Table 2.

Figure 2 shows that the optimal stirring time is 30 min. The recovery of 3 *μg* of silver was >96% at original acidities of 0·001–0·3*M*, decreasing at higher acidities.

Separation of traces of silver from matrix elements

The pH of 90 ml of a nitrate solution containing a matrix element (lead or zinc) and 3 *μg* of labelled silver was adjusted to 1 with aqueous ammonia or nitric acid, 5 ml of 0·4% w/v dithizone solution were added, and the silver was separated as described under *Procedure*. The silver recoveries were 96–100% (in presence of 5 g of lead), 99–100% (1 g of lead) and 95–98% (5 g of zinc). The lead or zinc accompanying silver was determined by atomic-absorption spectrophotometry at 283·3 or 213·9 nm, respectively, in order to obtain the concentration factors* of silver with respect to lead or zinc. The concentration factors were 450–1200 for 2–5 g of lead and 1000–2400 for 2–5 g of zinc.

Separation of traces of copper(II) by flotation

This method is also applicable to the separation of traces of copper(II). From 100 ml of 0·001–0·3*M* nitric acid, 0·4–50 *μg* of copper(II) was separated in >98% yields by 30 min of stirring with 5 ml of 0·4% w/v dithizone solution, followed by flotation; 5 g of lead or zinc did not interfere.

Determination of traces of silver and copper in high-purity metals

The proposed method has been employed as a preconcentration technique for the analysis of high-purity lead and zinc metals.

Recommended procedure. Place a 2- or 5-g metal sample in a covered 200- or 300-ml beaker. Add 5 or 10 ml of 5*M* nitric acid per g of lead or zinc, respectively, in small portions, and heat gently till dissolution is complete. Dilute the solution (or an aliquot) to about 90 ml with water, and adjust the pH to 1–1·5 with aqueous ammonia. Add 5 ml of 0·4% w/v dithizone solution, and proceed as described under *Procedure*. Determine the silver and copper by atomic-absorption spectrophotometry at 328·1 and 324·7 nm, respectively, under suitable operating conditions [for our instrument, slit-widths 0·10 mm (entrance) and 0·15 mm (exit), hollow-cathode tube current 10 mA, acetylene 2·0 l./min, air 8·5 l./min, height of the light beam above the burner top 22 mm].

Construct calibration curves as follows. Place 250 mg of dithizone in a 50-ml volumetric flask, and add 35 ml of acetone. Add cautiously 12·5 ml of 13·8*M* nitric acid in small portions, and allow to stand for 10 min without a stopper. Stopper and shake the volumetric flask, then dilute to the mark with acetone. Place 4 ml of this solution and portions of standard solution containing 0–20·0 *μg* of silver or copper(II) in a 5-ml volumetric flask, and dilute to the mark with water.

Table 3. Determination of silver and copper in high-purity metals

Sample taken, *g*		Aliquot taken	Found, *μg* Ag	Found, *μg* Cu	*ppm* in sample Ag	*ppm* in sample Cu
Lead	5·11	2/5	6·5	3·0	3·2	1·5
	5·11	2/5*	7·5	8·0	3·2	1·5
	5·04		15·5	6·0	3·1	1·2
	2·06		6·5	2·5	3·2	1·2
					Av. 3·2†	1·4
Zinc	4·97		0·5	2·5	0·1	0·5
	2·09		not detected	1·0	—	0·5
					Av. 0·1	0·5

* 1·0 *μg* of Ag and 5·0 *μg* of Cu(II) added.
† 3·1 ppm by another method.[2]

The calibration curves are linear up to at least 20·0 *μg*, with maximum deviations of 0·2 *μg*, and identical with those constructed by carrying out the whole procedure, including the flotation step. The background absorption is the same as that of water. The presence of 20 mg of lead or zinc does not affect the absorbance. Table 3 shows the analytical results for samples of commercial high-purity lead (reagent grade) and zinc (99·999%) by the recommended procedure. Blanks gave zero values for silver and copper. The analytical results for silver in lead are in good agreement with those obtained by the amalgamation–atomic-absorption method.[2] The time required for a determination was about 90 min.

Faculty of Engineering
Nagoya University
Chikusa-ku
Nagoya, Japan

MASATAKA HIRAIDE
ATSUSHI MIZUIKE

* Concentration factor = $(Q_T/Q_M)/(Q_T^0/Q_M^0)$, where Q_T^0 is the quantity of the trace element in the sample, Q_M^0 the quantity of the matrix element in the sample, and Q_T and Q_M are the corresponding quantities after the separation.

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Summary—Microgram quantities of silver and copper(II) ions in aqueous solutions are collected on dithizone precipitates, which are then floated with the aid of small nitrogen bubbles. This separation technique has been successfully applied to the atomic-absorption spectrophotometric determination of down to a tenth ppm of silver and copper in high-purity lead and zinc metals.

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MASKING OF IRON WITH FLUORIDE IN THE EXTRACTIVE ATOMIC-ABSORPTION SPECTROMETRIC DETERMINATION OF CHROMIUM IN STEEL

(*Received* 22 *July* 1974. *Revised* 31 *October* 1974. *Accepted* 14 *November* 1974)

The determination of chromium by means of atomic-absorption spectrometry has been the subject of extensive study particularly aimed at overcoming interference from iron when using an air–acetylene flame. The mechanism of this interference has been discussed by Roos and co-workers,[1,2] and more recently by Ottaway and Pradhan,[3] who have suggested 8-hydroxyquinoline to be an effective releasing agent. Thomerson and Price[4] recommended a procedure using a nitrous oxide–acetylene flame. Iron causes an enhancement of the chromium absorption signal in the nitrous oxide flame and this increases slightly with increase in iron concentration; thus, iron has to be added to the calibration solutions.

The present study was made in an attempt to develop a procedure that is completely free from iron interference, that uses an air–acetylene flame and that does not require the use of releasing agents. This can only be done by completely separating the chromium from the iron matrix. Bryan and Dean[5] determined chromium by flame photometry after extracting chromium(VI) into 4-methyl-2-pentanone; persulphate catalysed by silver(I) was used to oxidize chromium(III) to chromium(VI). Feldman and Purdy[6] applied this extraction procedure to the determination of chromium by atomic-absorption spectrometry, permanganate being used as the oxidant; iron interference, however, was not studied.

Blundy,[7] in developing an extractive colorimetric procedure for the determination of chromium in 1958, made a study of the effectiveness of several oxidants for chromium(III) and concluded that of those studied only cerium(IV) gave complete oxidation and good reproducibility. The atomic-absorption method developed in this work is based on Blundy's extractive procedure, and iron(III) is masked by means of fluoride.

EXPERIMENTAL

Atomic-absorption measurements were made with a Hilger and Watts Atomspek H 1170, using a chromium hollow-cathode lamp supplied by V. A. Howe, Ltd.

Complete oxidation of chromium(III) was checked by comparing results obtained with a standard potassium dichromate solution and with a standard chromium(III) solution prepared by reducing potassium dichromate solution with sulphur dioxide and then boiling off the excess of sulphur dioxide. The absorbance values obtained after oxidation [in the case of chromium(III)], extraction into 4-methyl-2-pentanone and spraying into the flame were identical.

Iron(III) was also found to be extracted into 4-methyl-2-pentanone at the hydrochloric acid concentrations (*i.e.*, 1–3*M*) required to extract chromium(VI), and the atomic-absorption signal of chromium was greatly reduced as a result. A thousandfold ratio of iron(III) to chromium in the aqueous phase reduced the absorbance signal obtained on spraying the organic extract by about 50%. Several methods of separating iron were tried. Extraction of iron(III) with di-isopropyl ether from 7·75–8·25*M* hydrochloric acid[8] before the oxidation of chromium(III) was effective, but the high hydrochloric acid concentration adversely affected the subsequent oxidation by cerium(IV). Cupferron extraction of iron and precipitation of iron(III) hydroxide were both ineffective, in that low recoveries of chromium were obtained. The final procedure adopted was to mask the iron(III) with fluoride; this proved to be highly effective up to at least a thousandfold ratio of iron to chromium. Purushottam and co-workers[9] had shown previously that fluoride suppresses interference by iron when aqueous chromium samples are sprayed into the atomic-absorption flame.

The following procedure is recommended for the determination of chromium in steel. If the addition of fluoride is omitted from this procedure, interference by iron becomes apparent at iron to chromium ratios above 5:1. No difference in results was observed when the fluoride was added after the oxidation step, but the results given here were determined with fluoride added before oxidation of chromium.

Reagents

Sulphuric acid, 25% *v/v*.
Sulphuric acid, 12·5% *v/v*.
Hydrogen peroxide, 100-*vol*.

Summary—Microgram quantities of silver and copper(II) ions in aqueous solutions are collected on dithizone precipitates, which are then floated with the aid of small nitrogen bubbles. This separation technique has been successfully applied to the atomic-absorption spectrophotometric determination of down to a tenth ppm of silver and copper in high-purity lead and zinc metals.

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The determination of chromium by means of atomic-absorption spectrometry has been the subject of extensive study particularly aimed at overcoming interference from iron when using an air–acetylene flame. The mechanism of this interference has been discussed by Roos and co-workers,[1,2] and more recently by Ottaway and Pradhan,[3] who have suggested 8-hydroxyquinoline to be an effective releasing agent. Thomerson and Price[4] recommended a procedure using a nitrous oxide–acetylene flame. Iron causes an enhancement of the chromium absorption signal in the nitrous oxide flame and this increases slightly with increase in iron concentration; thus, iron has to be added to the calibration solutions.

The present study was made in an attempt to develop a procedure that is completely free from iron interference, that uses an air–acetylene flame and that does not require the use of releasing agents. This can only be done by completely separating the chromium from the iron matrix. Bryan and Dean[5] determined chromium by flame photometry after extracting chromium(VI) into 4-methyl-2-pentanone; persulphate catalysed by silver(I) was used to oxidize chromium(III) to chromium(VI). Feldman and Purdy[6] applied this extraction procedure to the determination of chromium by atomic-absorption spectrometry, permanganate being used as the oxidant; iron interference, however, was not studied.

Blundy,[7] in developing an extractive colorimetric procedure for the determination of chromium in 1958, made a study of the effectiveness of several oxidants for chromium(III) and concluded that of those studied only cerium(IV) gave complete oxidation and good reproducibility. The atomic-absorption method developed in this work is based on Blundy's extractive procedure, and iron(III) is masked by means of fluoride.

EXPERIMENTAL

Atomic-absorption measurements were made with a Hilger and Watts Atomspek H 1170, using a chromium hollow-cathode lamp supplied by V. A. Howe, Ltd.

Complete oxidation of chromium(III) was checked by comparing results obtained with a standard potassium dichromate solution and with a standard chromium(III) solution prepared by reducing potassium dichromate solution with sulphur dioxide and then boiling off the excess of sulphur dioxide. The absorbance values obtained after oxidation [in the case of chromium(III)], extraction into 4-methyl-2-pentanone and spraying into the flame were identical.

Iron(III) was also found to be extracted into 4-methyl-2-pentanone at the hydrochloric acid concentrations (*i.e.*, 1–3*M*) required to extract chromium(VI), and the atomic-absorption signal of chromium was greatly reduced as a result. A thousandfold ratio of iron(III) to chromium in the aqueous phase reduced the absorbance signal obtained on spraying the organic extract by about 50%. Several methods of separating iron were tried. Extraction of iron(III) with di-isopropyl ether from 7·75–8·25*M* hydrochloric acid[8] before the oxidation of chromium(III) was effective, but the high hydrochloric acid concentration adversely affected the subsequent oxidation by cerium(IV). Cupferron extraction of iron and precipitation of iron(III) hydroxide were both ineffective, in that low recoveries of chromium were obtained. The final procedure adopted was to mask the iron(III) with fluoride; this proved to be highly effective up to at least a thousandfold ratio of iron to chromium. Purushottam and co-workers[9] had shown previously that fluoride suppresses interference by iron when aqueous chromium samples are sprayed into the atomic-absorption flame.

The following procedure is recommended for the determination of chromium in steel. If the addition of fluoride is omitted from this procedure, interference by iron becomes apparent at iron to chromium ratios above 5:1. No difference in results was observed when the fluoride was added after the oxidation step, but the results given here were determined with fluoride added before oxidation of chromium.

Reagents

Sulphuric acid, 25% *v/v*.
Sulphuric acid, 12·5% *v/v*.
Hydrogen peroxide, 100-*vol*.

Sodium fluoride solution, 4·6% w/v.

Ammonium hexanitratocerate(IV), 1·1% *solution in* 1M *sulphuric acid.*

Hydrochloric acid 8*M*.

4-*Methyl-2-pentanone saturated with* 1M *hydrochloric acid.* Shake together vigorously equal volumes of 4-methyl-2-pentanone and 1*M* hydrochloric acid, and discard the (lower) aqueous layer. Droplets of the acid should be allowed to separate completely or removed by passing the solvent through a small filter paper.

Stock standard chromium(VI) solution, 1000 μg/ml. Dissolve 2·8282 g of analytical-reagent grade potassium dichromate in water and dilute to 1 litre in a volumetric flask.

Working standard chromium(VI) solution, 20 μg/ml. Dilute 10 ml of the stock chromium(VI) solution to 500 ml with water in a volumetric flask.

Dissolution of steel samples

Weigh 0·500 g of steel sample into a 250-ml conical flask and add 50 ml of 25% sulphuric acid. Heat gently on a hot-plate until hydrogen evolution ceases. Remove the flask from the hot-plate, allow it to cool slightly and add 100-vol hydrogen peroxide dropwise to oxidize any carbon or carbide residues. Boil the solution gently to destroy excess of hydrogen peroxide. Cool the solution and dilute to 100 ml with water in a volumetric flask.

Preparation of calibration curve

Pipette suitable volumes of working standard chromium(VI) solution containing up to 400 μg of chromium into 100-ml separating funnels. Dilute to 60 ml with water, add 10 ml of 8*M* hydrochloric acid (Note 1) and 20 ml (by pipette) of 4-methyl-2-pentanone saturated with 1*M* hydrochloric acid and shake the mixture for 1 min. Allow the two phases to separate, discard the (lower) aqueous phase and make atomic-absorption measurements on the organic layer. The organic extracts are stable for at least 4 hr.

The optimum burner height was found to be similar to that used for determining chromium in aqueous systems, *i.e.*, observations are made just above the primary reaction zone, but the flame should be less fuel-rich. Optimum instrument conditions for the Atomspek H 1170 were found to be as follows.

Wavelength	357·9 nm
Lamp current	10 mA
Slit-width	10 μm
Burner	13-cm air–acetylene, single slot
Observation height above burner head	7·5 mm
Air flowmeter	12·5 (nebulizer) at 30 psig feed pressure
	* 12 (auxiliary air) at 30 psig feed pressure
Acetylene flowmeter	* 3 at 5 psig feed pressure

* Values for use with aqueous chromium solutions: 3·6 (auxiliary air) and 4·3 (acetylene).

Sensitivities quoted by instrument manufacturers for the determination of chromium when aqueous solutions are sprayed are within the range 0·05–0·15 μg/ml. In the present work sensitivities of 0·12 and 0·07 μg/ml were obtained with aqueous and organic solutions respectively.

Procedure

Pipette an aliquot of the solution containing the steel sample (see Note 2) into a 100-ml conical flask and dilute the solution to 20 ml with 12·5% sulphuric acid. Add 4 ml of sodium fluoride solution and 25 ml of ammonium hexanitratocerate(IV) solution and heat in a boiling water-bath for 25 min. Cool in an ice-bath to 10° or less. Transfer the solution to a 100-ml separating funnel with 20 ml of water and continue as for the calibration curve procedure beginning at "add 10 ml of 8*M* hydrochloric acid".

In the case of certain steel samples the organic extracts are not particularly stable and the solvent should be sprayed within 5 min of extraction (Note 3).

Notes

1. The final hydrochloric acid concentration must be 1–3*M* for complete extraction of chromium.
2. For steel samples containing <0·1%, 0·1–0·3% and 0·3–0·5% of chromium take 20-ml, 10-ml and 5-ml aliquots of sample solution respectively.
3. The reason for this is not known but the relative instability of the extract appears to occur at high iron to chromium ratios.

RESULTS AND DISCUSSION

The calibration curve was nearly rectilinear and it was shown that up to a thousandfold ratio of iron to chromium could be tolerated without change in absorbance signal. Results obtained with a range of low alloy and mild steels are shown in Table 1.

Table 1. Analyses of British Chemical Standards steel samples

Type of steel	BCS No	Standardized chromium content, %	Chromium found,* %
Low alloy	251/1	0·51	0·51, 0·51, 0·51, 0·50, 0·53, 0·51
Low alloy	252/1	0·42	0·44, 0·41, 0·44, 0·43, 0·42, 0·42
Mild	273	0·07$_5$	0·070, 0·073, 0·070
Mild	325	0·22	0·23, 0·22, 0·22
Mild	321	0·106	0·106, 0·110, 0·100, 0·100
Mild	322	0·039	0·040, 0·040, 0·039

* Each value given is for an individual dissolution of steel sample.

The extractive procedure recommended is an alternative to methods in which aqueous sample solutions are sprayed into the flame. The procedure has two advantages over the other methods in that sensitivity is slightly increased and the chromium is separated from iron which interferes. Even the procedure of Ottaway and Pradhan, which possibly comes nearest to being interference-free, is only so at particular observation heights and with particular types of burners.[3] The procedure recommended herein has of course, the disadvantage that the oxidation and extraction steps are additional to the steps carried out in the usual procedure.

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Chemistry Department
University of Technology
Loughborough
Leics., U.K.

A. G. FOGG
S. SOLEYMANLOO
D. THORBURN BURNS

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Summary—Chromium in steel is determined by oxidation to dichromate, extraction into methyl isobutyl ketone from 1–3*M* hydrochloric acid, and atomic-absorption measurements on the extract. The interference of iron in the atomic absorption is eliminated by using fluoride to keep the iron(III) in the aqueous phase in the extraction step.

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DETERMINATION OF TIN AS STANNITE-KESTERITE AND CASSITERITE IN ORES

(*Received* 22 *August* 1974. *Accepted* 5 *November* 1974)

The Mines Branch has recently issued a zinc–tin–copper–lead ore, MP-1, as a certified reference material with recommended values for nine elements. Certain difficulties associated with the volumetric methods used in the certification of MP-1 for tin, however, became apparent in the interlaboratory programme.[1] In view of the future issuing of a second reference material, KC-1, to be certified for tin, an investigation was undertaken to find the source of these problems. For this purpose, it was desirable to have a knowledge of the relative proportions of the various tin minerals such as stannite-kesterite and cassiterite in MP-1 and KC-1.

Tin as stannite, Cu_2FeSnS_4, has been determined in the presence of cassiterite, SnO_2, by the selective decomposition of stannite with bromine in carbon tetrachloride[2,3] or with potassium chlorate in concentrated hydrochloric acid.[4] This present work describes the selective decomposition of stannite-kesterite with sodium nitrate in glacial acetic acid. This method is simple and rapid and avoids the use of liquid bromine. Its applicability to the analysis of two certified reference ores is described.

EXPERIMENTAL

Decomposition of stannite-kesterite

One g of sodium nitrate and 10 ml of glacial acetic acid are added to a 0·1–2 g sample of ore in a 600-ml beaker and mixed by gentle swirling. After a further addition of 60 ml of acetic acid, the uncovered beaker is heated to allow the acetic acid to evaporate. When the volume of the contents has decreased to approximately 5 ml or less the beaker wall is washed down with water and 5·0 ml of concentrated hydrochloric acid and more water, if necessary, are added to make the volume approximately 50 ml. The insoluble material, composed of unattacked minerals and elemental sulphur*, is filtered off on a Whatman No. 42 paper and thoroughly washed with hot water. The filtrate is reserved for the determination of the tin present as stannite-kesterite.

The tin present as cassiterite is given by the difference between the total tin content of the ore and the tin present as stannite-kesterite or it may be determined directly in the insoluble material. If determined directly, great care must be taken to ensure a quantitative transfer of the high-density cassiterite from the reaction vessel to the filter paper. The paper containing the insoluble material is ashed in a zirconium crucible and the tin content determined as below.

Iodometric determination of tin

For the determination of total tin or of tin in the insoluble material, *i.e.*, tin present as cassiterite, solid samples must be fused with a 1:1 mixture of sodium peroxide and sodium carbonate in a zirconium crucible, quenched in water and then acidified with concentrated hydrochloric acid.[5] The tin is separated from interfering ions such as copper and molybdenum by precipitation as the hydrous oxide with ammonia solution. After redissolution of the hydrous oxide in hydrochloric acid, the tin is reduced to the stannous state with iron metal in an air-free atmosphere[6] and is titrated with a standardized solution of potassium iodate.

The tin present as stannite-kesterite must be precipitated from the filtrate as the hydrous oxide for two reasons. First, the tin must be separated from the copper derived from stannite itself and, furthermore, boiling sodium nitrate–acetic acid mixture attacks other sulphide minerals containing elements that interfere in the iodometric determination of tin. Secondly, the presence of unreacted sodium nitrate in the filtrate would strongly interfere in the iodometric determination when the tin solution is acidified with hydrochloric acid.

Tin-bearing ores studied

The reactivity of stannite-kesterite with sodium nitrate–acetic acid mixture was tested with a stannite concentrate prepared from ore from Stannex Mines, British Columbia, Canada. The inertness of SnO_2 to treatment with sodium nitrate–acetic acid mixture was tested with a Bolivian cassiterite concentrate (NBS 137, 56·64% Sn) and reagent grade stannic oxide (Fisher Scientific). The certified reference materials, MP-1 and KC-1, were treated with sodium nitrate–acetic acid mixture to determine the tin present as stannite-kesterite and as cassiterite.

RESULTS AND DISCUSSION

The results of the chemical determination of the tin minerals in the stannite concentrate, cassiterite and stannic

* The sulphur produced during decomposition of the sulphidic components remains in solution in acetic acid but precipitates in finely divided form on addition of water.

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* The sulphur produced during decomposition of the sulphidic components remains in solution in acetic acid but precipitates in finely divided form on addition of water.

Table 1. Tin mineral phases in ores

Material	Tin, %			
	As stannite	As cassiterite	As stannite + cassiterite	Total tin*
Cassiterite (NBS 137)	0·0	56·4 (0·2)†	56·4	56·7 (0·3)
Stannic oxide	0·0			
Stannite concentrate	26·3 (0·2)	1·0 (0·2)	27·3	27·5 (0·1)
2:1 stannite concentrate –cassiterite	26·3§			
1:1 stannite concentrate –cassiterite	26·4§			
MP-1	0·325 (0·008)	2·10 (0·01)	2·43	2·44 (0·02)
KC-1	0·0	0·676 (0·007)	0·676	0·682 (0·003)

* Determined by Na_2O_2–Na_2CO_3 fusion.
† Numbers in parenthesis are the standard deviations.
§ Based on weight of stannite concentrate.

oxide are summarized in Table 1. The tin contents of the minerals are given as % w/w and each value is the average of at least three determinations. For obvious reasons, the total tin content of the stannic oxide and of its insoluble residue were not determined. For the 2:1 and 1:1 w/w stannite concentrate–cassiterite mixtures, it was considered sufficient to determine only the tin present as stannite-kesterite.

The results clearly illustrate that SnO_2, either as cassiterite or stannic oxide, is inert to attack by sodium nitrate–acetic acid mixture. Stannite-kesterite, however, is readily attacked. Indeed, visual observation of the disappearance of the deep blue colour (due to Cu^{2+}) of the stannite-kesterite suggests that the decomposition may be essentially complete even before the acetic acid begins to boil. Nevertheless, the procedure defined above should be followed to ensure complete decomposition.

The results for the stannite concentrate indicate the presence of a small amount of cassiterite and, indeed, a previous detailed mineralogical examination of the Stannex ore had revealed the presence of cassiterite.[7] A quantitative determination of cassiterite in this stannite concentrate was attempted by image analysis of a polished section[8] but unfortunately this was unsuccessful owing to difficulty in differentiating between the cassiterite and gangue constituents. The presence of cassiterite in the insoluble residue from the treatment of the stannite concentrate with sodium nitrate–acetic acid mixture was, however, verified both by microscopical study and microprobe analysis. The sodium nitrate–acetic acid method is effective for the determination of tin present as stannite-kesterite and as cassiterite in an ore. In addition, however, it must be pointed out that the difficulty observed in the image-analysis of the stannite concentrate is a good example of the need for a chemical method to complement the available physical methods for determining the tin minerals in an ore.

The results for the reference materials MP-1 and KC-1 are also shown in Table 1. An image-analysis of MP-1 showed the tin content as stannite-kesterite and as cassiterite in grains larger than 0·8 μm in diameter to be 0·18% and 2·26% of the ore respectively. The disagreement between these results and those from the sodium nitrate–acetic acid treatment led to further microscopical study of MP-1, in which it was discovered that much stannite-kesterite, as grains smaller than 0·8 μm in diameter, occurs as inclusions in sphalerite. The image analysis of KC-1 indicated the absence of stannite-kesterite, as did the sodium nitrate–acetic acid method.

Acknowledgement—The author wishes to thank the mineralogy group of the Mineral Sciences Division for its help in the microscopical study and image analysis of the ores.

Mineral Sciences Division, Mines Branch
Department of Energy, Mines and Resources
555, Booth Street, Ottawa, Canada

H. F. STEGER

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Summary—Tin as stannite-kesterite and as cassiterite in a tin-bearing ore can be determined by the selective decomposition of the stannite-kesterite phase with a mixture of sodium nitrate and acetic acid.

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SIMULTANEOUS AMPEROMETRIC DETERMINATION OF NICKEL AND COPPER

(*Received* 22 *May* 1974. *Revised* 8 *October* 1974. *Accepted* 7 *November* 1974)

Resacetophenone oxime has been used in the amperometric[1,2] and polarographic determination of various metal ions.[3,4] We have now investigated its use as an amperometric reagent for nickel, with which it gives a precipitate in alkaline medium, and in the simultaneous determination of copper and nickel.

EXPERIMENTAL

Reagents

All chemicals used were of analytical grade. Solutions of copper and nickel were standardized by the iodometric[5] and dimethylgloxime methods[6] respectively. The alloys nichrome, Raney nickel, constantan, german silver and manganin were dissolved and analysed by standard procedures.[7]

Apparatus

A Lange manual polarograph and a galvanometer were used. Titrations were done in an H-type cell with a saturated calomel electrode in the narrow limb. Pure hydrogen was used for deaeration and stirring before current measurement.

Procedures

Determination of nickel. Put the sample solution containing 1·0–16·0 mg of nickel in the H-cell and add 20 ml of 0·5*M* ammonium chloride, 1·5 ml of 0·2% gelatin solution, and 1·0–5·0 ml of 0·5*M* ammonia solution and 1·0–5·0 ml of alcohol, depending on the amount of nickel*. Dilute the solution to 65 ml with distilled water, deaerate it by passage of hydrogen for 15 min, and then titrate with a standard solution of resacetophenone oxime added from a microburette, taking readings of the current at −1·25 V *vs.* SCE or at −1·05 V if other metals present give a current at −1·25 V. Correct the readings for volume change and plot them against volume. An L-shaped curve is obtained.

Simultaneous determination of copper and nickel. Place the sample in the H-cell, add 20 ml of 0·5*M* ammonium chloride, 5 ml of alcohol, 1·5 ml of 0·2% gelatin solution and dilute to 65 ml with distilled water. Deaerate the solution by bubbling hydrogen through it for 15 min. Titrate amperometrically at an applied potential of −0·45 V *vs.* SCE, where only the copper yields a diffusion current, until there is no further decrease in current on additon of reagent. Change the voltage to −1·25 V, adjust the pH to 8·0–8·3 with ammonia and continue the titration. A typical titration curve is shown in Fig. 1.

DISCUSSION

Determination of nickel

The polarographic behaviour of the oxime and nickel sulphate was studied at the dropping mercury electrode in ammonium chloride–ammonia buffer of pH 8·0–8·3. Nickel gave a reduction wave with $E_{\frac{1}{2}}$ −0·96 V *vs.* SCE, with the diffusion current region starting from −1·1 V. The reagent did not yield a reduction wave in this medium. Titrations of 1·3–17·3 mg of nickel had a maximum error of about ±1·0%.

Interference of foreign ions

Nickel is associated with metals such as copper, cobalt, manganese, zinc, aluminium, iron and chromium in alloys, ores and electrolytic baths. Hence the interference of these ions in the determination was studied.

Iron, aluminium and chromium gave gelatinous precipitates under the experimental conditions. Determination of nickel in presence of these precipitates gave erratic results. Since fluoride is known to form stable complexes with iron and aluminium, sodium fluoride was added to the contents of the titration cell and the determination carried out. The results obtained indicated that nickel could be determined in the presence of considerable amounts of these metal ions. In the case of chromium, conversion to the sexivalent state with hydrogen peroxide and subsequent precipitation as barium chromate in the titration cell itself, facilitated the accurate determination of nickel. There was no need to remove the precipitate from the cell. A chromium to nickel ratio (w/w) of up to 8 could be tolerated. Both procedures could be successfully combined for the determination of nickel in presence of iron and chromium. This facilitated the determination of nickel in nichrome.

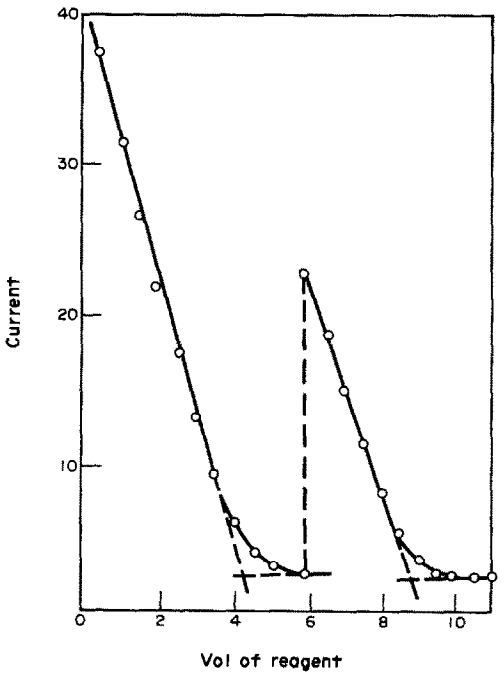

Fig. 1. Amperometric titration of a mixture of copper and nickel.

* At low nickel concentrations, high results are obtained if the ammonia and alcohol concentrations are too high, presumably because of ligand competition by the ammonia and increased solubility caused by the alcohol. The condition must be such that the first addition of titrant yields a precipitate.

Zinc and manganese did not interfere chemically as they did not yield precipitates with the reagent under the experimental conditions but they gave reduction waves at slightly more negative potentials (−1·2 and −1·55 V *vs.* SCE respectively) than the nickel. This necessitated the change of applied potential to −1·05 V for the successful determination of nickel. These metal ions could be tolerated in up to 5:1 w/w ratio to nickel.

Palladium in ammonia–ammonium chloride buffer did not yield any precipitate with the reagent, though it did in acid medium, but it exhibited a reduction wave within the same potential range as nickel with a much smaller diffusion current. Experimental results indicated that nickel could be accurately determined in presence of 2·5 times as much (w/w) palladium. Larger amounts of palladium interfered. In such cases, hydrazine sulphate was used to reduce the palladium ions to the metal.

Cobalt gave a soluble complex with the reagent under the experimental conditions and was also reduced at almost the same potential as nickel. This prevented the determination of nickel in presence of cobalt. Attempts to eliminate the interference by the conversion of cobalt(II) into cobalt(III) proved futile.

The procedures developed were applied to the determination of nickel in nichrome and Raney nickel. The results obtained are presented in Table 1 along with values obtained by standard methods. The results indicated that the present method compares well in accuracy with the standard method.

Table 1. Analysis of nichrome and Raney nickel for nickel (amperometric)

Nickel in nichrome, *mg*		Nickel in Raney nickel, *mg*	
Gravimetric	Amperometric	Gravimetric	Amperometric
4·91	4·91	4·57	4·59
7·36	7·37	6·86	6·87
8·35	8·35	8·01	7·99

Determination of copper and nickel

Reddy[1] had already reported the amperometric determination of copper with resacetophenone oxime in acidic medium (*ca.* pH 4·5), and the combination of that method with the one for nickel had obvious attractions.

From the results in Table 2 it is clear that copper and nickel can be accurately determined by successive titration with resacetophenone oxime. Chloride does not interfere as it does in the Campbell and Reilley method[8] which uses "Triene" as titrant. The accuracy is higher than that of the Levitman method[9] which uses rubeanic acid. However, amounts of nickel less than 3·0 mg cannot be estimated directly by the present procedure since that is the minimum amount required to facilitate the determination of the second end-point, but the estimation can still be carried out, by addition of a known amount of nickel, and an appropriate correction.

The direct titration procedure can be applied to the determination of copper and nickel in constantan and german silver even when the metals are present as the chlorides. Results of analyses of these alloys are given in Table 3.

Zinc, a common constituent in many alloys, does not interfere in the procedure, whereas it interferes when Triene is used[8].

Nickel in manganin was determined by the standard addition method.

Procedure. Dissolve about 100 mg of manganin, transfer the solution to a 100-ml standard flask and dilute it to the mark. Place 5 ml of the solution in the H-cell and determine the copper content as in the simultaneous determination of copper and nickel. Then add a known quantity of nickel to the solution and determine the amount of reagent required. Repeat the experiment with different added quantities of nickel. Plot amount of nickel added *vs.* amount of reagent required and extrapolate to obtain the nickel content.

Table 2. Successive amperometric estimation of copper and nickel in the same portion of solution

No.	Copper, *mg* Taken	Found	Error %	Nickel, *mg* Taken	Found	Error %
1	11·92	11·95	+0·3	3·24	3·24	0·0
2	5·42	5·42	0·0	3·34	3·33	−0·3
3	5·42	5·42	0·0	5·01	5·04	+0·6
4	5·42	5·42	0·0	10·02	10·02	0·0
5	2·71	2·71	0·0	5·01	5·04	+0·6
6	2·71	2·71	0·0	7·52	7·56	+0·6
7	2·71	2·71	0·0	10·02	10·08	+0·6
8	2·71	2·71	0·0	15·03	15·11	+0·5

Table 3. Analysis of constantan and german silver

Sample	Copper, *mg* Gravimetric	Amperometric	Error %	Nickel, *mg* Gravimetric	Amperometric	Error %
Constantan	4·79	4·80	+0·2	3·73	3·74	+0·3
	5·75	5·76	+0·2	4·57	4·56	−0·2
	7·19	7·18	−0·1	5·59	5·59	0·0
German silver	11·92	11·95	+0·3	3·23	3·23	0·0
	14·90	14·76	−0·9	4·05	4·05	0·0

The nickel content in the test sample was found to be 4·8% by the amperometric method and 4·42% by a standard method.

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Department of Chemistry Y. KRISHNA REDDY
Sri Venkateswara University S. B. RAO
Tirupati (A.P.), India N. A. RAJU

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Summary—A method is described for the amperometric titration of nickel and successive amperometric determination of copper and nickel. Nickel (1·0–16·0 mg) and copper (1·0–11·0 mg) could be determined with an average error of less than 1%. Cobalt interferes but chloride does not. Interference by aluminium, iron(III) and chromium can be eliminated. Zinc and manganese do not interfere if the correct applied voltage is chosen. The procedures can be utilized in the analysis of alloys such as nichrome, Raney nickel, constantan, german silver and manganin. It is best to use the standard addition method for less than 3 mg of nickel.

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DETERMINATION OF SUB MICROGRAM AMOUNTS OF SELENIUM IN ROCKS BY ATOMIC-ABSORPTION SPECTROSCOPY

(*Received* 23 *June* 1974. *Revised* 6 *December* 1974. *Accepted* 29 *December* 1974)

Selenium and its compounds have been used commercially for many years in the production of rectifiers, photocells, pigments, *etc.* with no long-term effects on industrial workers. However, selenium has long been regarded as a toxic substance, because of the well-known selenium-poisoning [1] of cattle ("alkali disease" and "blind-staggers") caused by the consumption of selenium-bearing plants. Elemental selenium is relatively non-toxic toward humans, but some selenium compounds, especially hydrogen selenide, are toxic. Selenium is also nutritionally important and is valuable in the treatment of a number of deficiency diseases.

Considerable attention has been devoted to trace analysis for selenium in environmental,[2] geological,[3] and biological[4] samples by various techniques. Gravimetric procedures have been employed in the determination of selenium in geological samples, but interfering ions must first be removed. Iodometry, colorimetry and polarography have also been proposed as analytical methods; however, they are dependent upon the chemical state and separation of selenium, and the reagent blanks may be significant. Neutron-activation analysis and spark-source mass spectrometry offer the required accuracy and sensitivity, but spark-source mass spectrometry is a specialized and expensive technique not commonly found in analytical laboratories, while neutron-activation analysis necessitates that an analyst have access to a nuclear reactor or a suitable neutron generator.

Therefore, it was the purpose of this investigation to determine submicrogram amounts of selenium with accuracy, reproducibility and sensitivity, by using a conventional and relatively inexpensive atomic-absorption spectrophotometer with a detection limit of 0·1 ppm Se; with the advent of the tantalum sampling-boat systems the limit may be extended down to 0·01 ppm.

In this investigation, some United States Geological Survey standard rocks, GSP-1, W-1 and BCR-1 were analysed for their selenium content and the results compared with those obtained by the slower but generally contamination-free method of neutron-activation analysis.[5]

EXPERIMENTAL

Apparatus

A Perkin-Elmer Model 403 atomic-absorption spectrophotometer equipped with a three-slot burner head and a tantalum sampling-boat system was used. An Intensitron selenium hollow-cathode lamp was operated at a current of 16 mA and the reasonance line of 196·1 nm was used with a slit setting of 12 Å, and an air–acetylene flame. The output signal was monitored on a Perkin-Elmer Model 165 10-mV strip-chart recorder with a chart speed of 66 mm/min. The absorption peaks were recorded so that peak heights could be measured after all samples had been run.

Procedure

To determine possible losses due to volatilization of selenium, three 1-g samples of each rock were dissolved in 20 ml of a 1:1 mixture of 40% hydrofluoric acid and 16 *M* nitric acid, then ^{75}Se tracer in the form of selenious acid (New England Nuclear Corp., Boston, Mass.) and of known activity was added to each sample, and the samples were digested and reduced to dryness on a steam-bath. Owing to the relatively long half-life of ^{75}Se (120·4 days) the amount lost through decay would be negligible. Then 10 ml of 16 *M* nitric acid were added to the residue and a 1-ml aliquot was counted, the observed activity being corrected to correspond to the original conditions. No loss of selenium was noted; this observation substantiates the work of Chau and Riley.[6]

For AAS analysis, 2-g samples of the three rocks were accurately weighed and digested in Teflon beakers with 40 ml of the 1:1 acid mixture. The beakers were covered and heated on a steam-bath for 12 hr. The covers were removed, the solutions evaporated to dryness, and another 40 ml of the 1:1 mixture of acids were added to each and again evaporated to dryness. Then 10 ml of 16 *M* nitric acid were added to each, and the solutions evaporated to dryness on a steam-bath. This was repeated twice more. Then 25 ml of 4 *M* hydrochloric acid were added to each residue and the resulting solutions boiled gently until the volume was reduced to 0·5 ml. Two μCi of ^{75}Se (as selenious acid) were added to each solution together with 10 ml of 9 *M* hydrobromic acid. Each beaker was placed on an NaI(Tl) crystal and the total counts were determined by the method of Covell[7] from the 401-keV peak. Afterwards each solution was poured into a 40-ml separatory funnel and 11 ml of 1% solution of phenol in benzene were added in accordance with the procedure reported by McGee *et al.*[8] Each funnel was shaken for 2·5 min, after which the whole of each solution was transferred to a 50-ml tube and allowed to separate for 2·5 min.

Summary—A method is described for the amperometric titration of nickel and successive amperometric determination of copper and nickel. Nickel (1·0–16·0 mg) and copper (1·0–11·0 mg) could be determined with an average error of less than 1%. Cobalt interferes but chloride does not. Interference by aluminium, iron(III) and chromium can be eliminated. Zinc and manganese do not interfere if the correct applied voltage is chosen. The procedures can be utilized in the analysis of alloys such as nichrome, Raney nickel, constantan, german silver and manganin. It is best to use the standard addition method for less than 3 mg of nickel.

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The aqueous and organic phases were then divided and counted. The degree of extraction of selenium into the benzene could thus be determined.

Each benzene phase was evaporated to dryness and the residues were dissolved in water (demineralized and quartz-distilled), and diluted to the mark in 10-ml volumetric flasks. These solutions were then analysed by AAS, an aliquot (5 ml) being evaporated in the tantalum boat, which was then inserted into the flame.

The primary standard solution for the AAS was prepared by dissolving 16·34 g of selenious acid in 1 litre of demineralized quartz-distilled water and standardized by the method outlined by Hillebrand *et al.*[9] The quartz-distilled water used was analysed by neutron-activation analysis and no evidence of selenium was found. A 1-ml aliquot of the stock solution was diluted to 1 litre and the resulting solution was used for the preparation of other standards for AAS.

RESULTS AND DISCUSSION

The absorption signal obtained by the sampling-boat technique represents the total mass of selenium in the sample aliquot rather than its concentration in solution. This amount was established by interpolation in a plot of peak-height *vs.* μg of selenium, a fixed volume (1 ml) of two standard selenium solutions, which closely bracketed the selenium content of the solutions obtained from the rocks, being evaporated in the tantalum boat, which was then placed in the flame. Standards were run before and after each rock solution in order to ensure accuracy and to minimize the effect of a slight decrease in the background absorbance of the boat.

The chemical yields for the solvent-extraction process appear in Table 1. The variation in degree of extraction is large and is a result of the selenium concentration being low; McGee, Lynch and Boswell[8] reported that the reproducibility of their procedure below a selenium concentration of 0·07 mg/ml (70 ppm) was very poor. As with other elements at tracer levels, selenium is also subject to losses by adsorption on the walls of the container and on colloidal particles. The AAS results were corrected by means of the chemical-yield factor.

The results for the rock samples appear in Table 2 together with trace selenium concentrations for the same geological specimens reported by Brunfelt and Steinnes[5]. The agreement may be considered excellent in view of the fact that Brunfelt and Steinnes used a different procedure (distillation) to separate selenium in the rocks, before the neutron-activation analysis. Inspection of Table 2 also indicates that the precision as measured by standard deviation and range is quite good and this provides further evidence that the chemical-yield correction is adequate. The selenium:sulphur ratio has been determined for various geological materials and found to be about 1×10^{-4} except for sea-water (1×10^{-7}) and evaporites (2×10^{-8}).[10, 11] Therefore, this ratio may be used as a check on the reliability of selenium determinations. Table 3 shows that our results approximate to the ratio of 1×10^{-4}, and this serves as further evidence that the results obtained are valid.

Table 1. Degree of extraction of selenium with use of ^{75}Se tracer

U.S.G.S. rock	Activity in aqueous phase, *cps*	Activity in organic phase, *cps*	Extraction, %
BCR-1			
Sample A	71·2	202·2	74·0
Sample B	30·1	187·5	86·2
W-1			
Sample A	150·9	105·5	41·2
Sample B	134·5	124·3	48·0
GSP-1			
Sample A	15·9	230·9	93·6
Sample B	65·6	216·9	76·8

Table 2. Trace selenium concentrations for U.S.G.S. rocks

U.S.G.S. rock	Selenium, *ppm* (this method)	Range, *ppm*	Selenium, *ppm* (neutron-activation analysis)[5]
GSP-1	0·058 ± 0·001	0·057–0·059	0·059
W-1	0·110 ± 0·005	0·103–0·116	0·110
BCR-1	0·100 ± 0·001	0·099 ± 0·100	0·103

Table 3. The selenium:sulphur ratio of some U.S.G.S. rocks

U.S.G.S. rock	Se, *ppm*	S, %[14, 15]	Se/S
GSP-1	0·058	0·05	1×10^{-4}
W-1	0·110	0·014	$8·2 \times 10^{-5}$
BCR-1	0·100	0·05	2×10^{-4}

Severne and Brooks have recently employed AAS for the determination of selenium at levels exceeding 1 ppm in geological samples,[12, 13] In our investigation, we have extended the detection of selenium down to 0·06 ppm with simplicity, accuracy and precision. We suggest that the relatively inexpensive and rapid technique of AAS and an associated boat sampling system be utilized in conjunction with activation analysis to enhance accuracy in studies of this nature.

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Department of Chemistry
Lowell Technological Institute
Lowell, Massachusetts, U.S.A.
New England Nuclear Corp. T. GOLEMBESKI
Billerica, Massachusetts

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Summary—Atomic-absorption spectroscopy was used to determine trace amounts of selenium accurately in U.S. Geological Survey standard rocks, GSP-1, W-1 and BCR-1. The results obtained were compared with those obtained by neutron-activation analysis and excellent agreement was found; in addition, the selenium:sulphur ratio was calculated and agreed with results obtained by other workers.

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ANALYTICAL DATA

PHENANTHRAQUINONE MONOTHIOSEMICARBAZONE AS INDICATOR FOR CHELATOMETRIC DETERMINATIONS

(*Received* 9 *October* 1974. *Accepted* 13 *November* 1974)

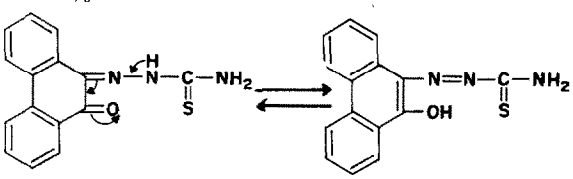
Summary—A new compound, phenanthraquinone monothiosemicarbazone, is satisfactorily used in the chelatometric determination of copper(II), zinc(II), cadmium(II), mercury(II) and nickel(II). The method is applied in the analysis of various alloys.

During an investigation on thiocarbazones, the compound phenanthraquinone monothiosemicarbazone (PTS) was found to react with bivalent copper, zinc, cadmium, mercury and nickel ions, giving intense red colours. The colour was discharged by EDTA. This observation is utilized in chelatometric determination of these metals, with PTS as indicator.

EXPERIMENTAL

Synthesis of PTS

Equimolar amounts of phenanthraquinone and thiosemicarbazide were dissolved in the minimum amount of methanol and refluxed for 3 hr. The hot solution was filtered and cooled, and red crystals of PTS were deposited. After 2 or 3 crystallizations from methanol, the m.p. was 190–192°. Calculated: C, 64·1%; H, 3·9%; found C, 64·4%; H, 4·0%.



PTS

Reagents

PTS solution (0·5% in methyl or ethyl alcohol) was either kept in the cold or prepared fresh to avoid possible decomposition. It is normally stable for 2 days. Solutions were made of analytical-reagent grade $CuSO_4.5H_2O$ in water, ZnO in perchloric acid, $Cd(CH_3COO)_2.2H_2O$ in water, metallic mercury in perchloric acid and $NiSO_4.(NH_4)_2SO_4.6H_2O$ in water and standardized if necessary. EDTA solution was standardized against a zinc solution, with Eriochrome Black T as indicator.

Acetate buffers were prepared by mixing 1*M* sodium acetate with 1*M* hydrochloric acid. For higher pH, ammonia was added.

Phthalate buffers were prepared by mixing 0·1*M* potassium biphthalate with 0·1*M* hydrochloric acid or sodium hydroxide, as required.

Analytical-reagent grade chemicals were used for all other solutions. Doubly distilled water was used throughout.

Interferences

The effect of various ions on the determination of copper (5·4 mg), zinc (13·1 mg), cadmium (28·1 mg), mercury (10·0 mg) and nickel (5·9 mg) was examined. The results are shown in Table 1. The criterion for interference was an error greater than 0·5%. Masking agents, where shown, were added in all titrations except those indicated by asterisk.

Procedure

Adjust the pH of a solution containing the requisite amount of metal (Table 2) with 10 ml of acetate buffer (phthalate buffer can also be used in copper titrations). Heat the solution for about 2 min on a water-bath, add 4–6 drops of PTS indicator (followed by 5 ml of alcohol in mercury titrations) and dilute to about 25 ml. Titrate slowly with EDTA solution of appropriate concentration

Table 1.

Foreign ion	Tolerance limits, *mg*, for Copper	Zinc	Cadmium	Mercury	Nickel	Masking agent
F^-	500	500	500	20	500	—
Cl^-	500	500	500	100	500	—
Br^-	500	500	500	500	500	—
I^-	Int.	500	500	Int.	500	—
CN^-	Int	20	10	Int	Int	—
NO_2^-, NO_3^-, ClO_4^-	500	500	500	500	500	—
IO_3^-	Int	500	500	500	500	—
CNS^-	5	500	500	5	500	—
CH_3COO^-	500	500	500	500	500	—
SO_3^{2-}	500	500	500	Int	500	—
SO_4^{2-}	500	500	500	500	500	—
$S_2O_3^{2-}$	Int.	50	200	Int.	30	—
$C_2O_4^{2-}$	Int.	15	500	500	10	—
Tartrate	500	500	500	500	500	—
Thiourea	Int.	500	500	Int.	500	—
Citrate	150	10	500	500	30	—
BO_3^{3-}	100	200	500	50	20	—
PO_4^{3-}	500	Int.	Int	350	Int.	—
Cu^{2+}	—	200	200	Int	200	Thiourea
Ag^+	50	Int	Int.	Int	100	Chloride
Mg^{2+}	500	500	500	100	500	—
Ca^{2+}	50	20	70	30	50	—
Sr^{2+}	500	500	500	100	500	—
Ba^{2+}	500	500	500	400	500	—
Zn^{2+}	500*	—	7	Int	Int.	Citrate
Cd^{2+}	500	Int	—	Int	Int.	—
Hg^{2+}	Int	500	500	—	500	Iodide
Al^{3+}	150	120	80	30*	100*	Fluoride
In^{3+}	2	2	2	1	2	—
Sc^{3+}	70	200*	1*	1*	200*	Fluoride
Pb^{2+}	5*	2*	Int.	Int	100	Sulphate
V^{4+}	Int.	3	25	Int	3	Fluoride
Mn^{2+}	500*	20	13	Int	20*	Fluoride
Fe^{3+}	30	35	56	Int	50	Fluoride
Co^{2+}	5	Int	Int.	Int.	12	—

Molybdenum(IV), nickel(II) and platinum group metal ions interfered when their amounts exceeded 1 mg.

Int. = interference.

* Amounts tolerated without masking agent.

until the reddish colour completely disappears. Heating is not necessary if the solution is let stand for 2–3 min after addition of the indicator and then titrated.

Table 2.

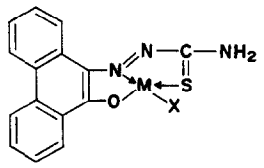
Metal	Requisite concentration	*pH*	Temperature °C
Copper	1 μg–30 mg/ml	0·5–4·0	15–95
Zinc	65 μg-65 mg/ml	4·4–7·5	25–70
Cadmium	20 μg-110 mg/ml	4·8–6·0	40–70
Mercury	40 μg-100 mg/ml	5·3–6·8	30–70
Nickel	12 μg-60 mg/ml	4·5–7·0	20–75

Analysis of alloys

The method was successfully adopted for the analysis of brass and gun metal for copper and Brightray G wire and Monel K wire for nickel after addition of the appropriate masking agents. The errors were within ±0·1%.

Tentative structure

Keeping in view the earlier work on metal complexes with thiosemicarbazones,[1] the following tentative structure is proposed for the metal complexes with PTS:



(where M = Cu, Zn, Cd, Hg or Ni and X = anion present in solution).

Department of Chemistry, A. K. SINGH
University of Delhi, K. C. TRIKHA
Delhi 110007, *India* R. P. SINGH
St. Stephen's College, MOHAN KATYAL
Delhi 110007, *India*

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TALANTA REVIEW*

PLASMA EMISSION SOURCES IN ANALYTICAL SPECTROSCOPY—II

S. GREENFIELD, H. McD. McGEACHIN and P. B. SMITH

Albright & Wilson Limited, Industrial Chemicals Division,
P.O. Box 80, Oldbury, Warley, England

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Summary—The use of microwave plasmas and of capacitively coupled high-frequency plasmas as sources for emission spectrochemical analysis is reviewed.

The first part of this review gave a theoretical background and discussed plasma jets operated with d.c. This part deals with microwave plasmas (by which we mean plasmas operated at frequencies greater than 300 MHz), and with high-frequency (hf) plasmas (at frequencies in the range 1–300 MHz) which are capacitively coupled to the power generator. In the first section we give a survey of the development of these sources as applied to spectrochemical analysis of solutions and solids; the great majority are concerned with solutions. In the second section some aspects of these systems are compared and discussed. The third section lists some specialized applications, mostly with gaseous samples, in gas analysis and isotope analysis, and as detectors in gas chromatography. We have excluded applications of electrodeless discharge lamps to atomic-absorption and atomic-fluorescence spectrometry, where the emission from the plasma does not characterize the sample but rather constitutes the excitation source for it. Happily the confusing literature on the preparation and operation of electrodeless discharge lamps has recently been critically reviewed.[2]

DEVELOPMENT OF PLASMA SOURCES

Capacitively coupled high-frequency plasmas

In 1941, Cristescu and Grigorovici[3] reported their experiments on a discharge produced by applying the output of a high-frequency oscillator to two circular plates which were separated vertically by up to 15 cm. The lower plate had a copper cone with a platinum tip attached to it. The plates formed a condenser which was part of the circuit which determined the frequency of the oscillator, typically in the range 60–90 MHz. A discharge could be formed at the tip by touching it with an isolated conductor which could emit electrons easily when heated by the strong electric field. These electrons gain kinetic energy from the electric field and this energy can be transferred by collision to heat the gas and to produce by ionization the number of electrons necessary for a sustained discharge. A temperature of 4000 K was found when a power of 650 W was supplied. The authors later gave a theoretical treatment[4] of the discharge.

This discharge was utilized in 1956 as a source for spectroscopic gas analysis by Stolov[5] and in 1957 for spectrochemical analysis by Badarau, Giurgea, Giurgea and Truţia.[6] They used a hollow cylinder for the upper electrode and noted that this electrode was not absolutely necessary, but had a useful function in concentrating the lines of force of the electric field. The system is therefore very different from an arc, where a substantial current flows through both electrodes, which are therefore both necessary. The essential electrode is a tip where a very strong electric field is developed. Discussions and applications of one- and two-electrode plasmas of this kind were given by Kapicka,[7,8] Dunken, Mikkeleit and Kniesche,[9] Tappe and van Calker,[10] Dunken, Pforr and Mikkeleit,[11] Trunecek,[12] Dunken and Pforr,[13] and Pforr and Langner.[14] The glow discharge lamp of Vurek and Bowman[15–17] can formally be included in this class, since it has a pointed electrode at which the discharge is formed and an annular electrode surrounding the discharge tube, but the very low power (10 W) applied gives rise to a discharge of much less luminosity.

A new kind of discharge in which a d.c. voltage was superposed on Cristescu and Grigorovici's high-frequency plasma was described by Cristescu[18] in 1960. While the hf voltage was applied across two electrodes as before, these electrodes were held at the same d.c. potential and an adjustable d.c. voltage was applied between them and a third electrode, movable between them. Altering the d.c. voltage so as to vary the d.c. in the range 0·1–1 A changed the apparent excitation temperature and also the appearance of the plasma. Applications to spectrochemical analysis were made,[19–20] and later studies were reported by Zakharov.[21]

In contrast to these systems where the upper electrode, if there is one, acts only as a guide for the

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lines of force and does not conduct a significant current, is the type which is the high-frequency analogue of d.c. arcs or plasma jets, where the electrodes carry a substantial current. Zheenbaev[22–24] developed sources where the discharge space was subjected to hydrodynamic compression, either by sucking air and the discharge products through the central hole of the upper electrode, or by blowing a stream of air along the axis of the discharge. The increased pressure resulted in a higher temperature because of more collisions, and an improvement in sensitivity of one or two orders of magnitude was claimed. The samples were usually aqueous solutions and were continuously vaporized from a Perspex container above the lower electrode by an auxiliary electrode dipping into the solution. Gostkowska and Ekiert[25] used a high-frequency (20 MHz) arc at atmospheric pressure to determine trace impurities in semiconductor materials by fashioning rods out of these solid samples and fixing them to copper electrodes, while Erämetsä and Kukkasjärvi[26] used pelleted samples and graphite electrodes in a helium atmosphere at reduced pressure, to determine bromine, chlorine and tellurium.

Scholz[27] and Roddy and Green[28] designed torches in which a single conductor was used to form both a central electrode and a coaxial coil surrounding it. There is thus both capacitive and inductive coupling to the plasma, which is formed at the tip of the central conductor. Torches of this kind were utilized for spectrochemical analysis by Mavrodineanu and Hughes,[29] who passed the sample aerosol through the hollow conductor, to emerge through small holes at the tip; they found that other methods of introducing a sample aerosol led to partial short-circuiting through liquid films. Other users[10,30,31] did not seem to observe this effect.

Egorova[32–34] used purely capacitive coupling with two external annular electrodes, one at each end of a water-cooled discharge tube. This type of coupling had been used earlier for isotope analysis in plasmas at reduced pressure.[35–37] Egorova's plasma was at atmospheric pressure in argon, which was introduced tangentially, and was viewed along its axis. She found that two kinds of discharge could be excited. The first was a constricted plasma like an arc channel while the second was a continuous diffuse luminescence which filled the tube. Lines of high excitation energy were excited in the first type whereas those of low energy predominated in the second. Both types were useful for analysis and the change from one to the other depended on the concentration and ionization potential of the sample atoms. A plasma excited by a single, water-cooled, external, annular electrode was described by Grigoriev, Frolov and Sanodze.[38] Again the discharge consisted of a thin filament when pure argon was used but changed to a diffuse form when an easily ionized element (an alkali or alkaline earth metal) was introduced at a suitable concentration. The apparatus included two atomizers, one for the sample and the other for the easily ionized element.

Microwave plasmas

Two types of apparatus have been used to excite microwave plasmas. A discharge tube with a central electrode can be used; the electrode is coupled *via* a waveguide to the microwave oscillator and the plasma is formed at the tip, like some of the high-frequency plasmas already discussed. The other method of excitation is to place a discharge tube (with no electrodes) in a resonant cavity.

Most of the sources which use a central electrode are derived from the designs of Cobine and Wilbur[39] and Schmidt,[40] which operate at 2450 MHz. The first application to the analysis of solutions was reported by Mavrodineanu and Hughes[29] in 1963, who used 2 kW power. They found a gas temperature in the range 2900–3300 K by observing that molybdenum could be melted, but not tantalum or tungsten The excitation temperature was much higher. Various working gases were used; hydrogen or helium gave the least background and hydrogen was more effective in volatilizing refractory substances. An incandescent tip, emitting electrons, was required to sustain the discharge in hydrogen. Kessler and his associates studied a similar torch[41,42] and applied it to materials used in the glass industry[43,44] and to general analysis of solutions.[45] Tappe and van Calker[10] reported briefly on sources at frequencies of 461 and 2400 MHz. Yamamoto and Murayama[46] studied a source with a frequency of 520 MHz before using[47] the almost universal microwave frequency of 2400 MHz. Yamamoto and Murayama[46] studied a source with a frequency of 520 MHz before using[47] tions to the analysis of steel have been reported[49–52]

The first successful application to spectrochemical analysis of a microwave discharge formed without electrodes and in a resonant cavity seems to have been the analysis of nitrogen isotopes by Broida and Chapman[53] in 1958. An application to the analysis of solutions was described by Yamamoto.[54] McCormack, Tong and Cooke,[55] in developing a detector for gas chromatography, found that at low pressure it was necessary for the diameter of the discharge tube to be at least 1 cm, for smaller tubes resulted in an unstable plasma; at atmospheric pressure stable and more intense discharges were obtained in tubes as narrow as 1 mm. Runnels and Gibson[56] investigated the use of this type of plasma for the excitation of metals in solution. The low power used (about 25 W), made the introduction of the sample as an aerosol impracticable, since the plasma was easily extinguished by the solvent. The sample was therefore placed on a platinum filament which was heated to give complete sample evaporation outside the discharge. The design of the vaporization chamber had large effects on the sensitivity and reproducibility of the emission; particular attention to the prevention of plating-out was necessary. A number of applications from the same school have appeared[57–59] and the most recent report, by Lichte and Skogerboe,[60] indicated that modifications to the resonant cavity allowed the introduction of desolvated aqueous solutions. This

Table 1. Systems classified by power

Type	Power, *W*	References
Microwave	< 100	56–60, 64, 69, 70
	< 200	46, 61–63, 65, 66
	< 1000	45, 47, 52
	> 1000	29, 41–43, 48, 67, 68
High-frequency	10	15–17
	250	29
	500	30
	1500	32–34
	2000	25

had previously been achieved by other workers with low-power systems.[61–64] Short residence time is a limitation to sensitivity and the possibility of sealing samples in a tube to overcome this has been investigated.[65,66] All the work already mentioned on the use of discharges excited in a cavity was carried out with low-power sources (200 W or less). An exception is the generator used by Tsemko and his associates[67,68] which was capable of supplying more than 2 kW to an argon plasma with tangential flow at atmospheric pressure, the source being viewed either along its axis or at right angles to it.

REVIEW OF SYSTEMS USED FOR ELEMENTAL ANALYSIS OF SOLUTIONS

Plasma generators

A survey of the different types of generator used must be incomplete, since authors frequently do not give details. Even when the power output of the generator is specified we do not usually know how much reaches the plasma. Kessler and Gebhardt's paper[43] is an admirable exception: we are told that of the 2·5 kW available from the magnetron, the maximum they can utilize, because of the gas flows adopted, is 1 kW and that in fact they choose 860 W. Of this, 160 W is reflected, so 700 W are transferred to the plasma. Thus a simple statement that they use a generator of maximum output 2·5 kW would not be very relevant. It is likely that the figures quoted in many instances are for the maximum output (since this figure is supplied by the manufacturer and requires no measurement). These figures are therefore likely to represent only an upper limit for the power actually supplied to the plasma.

For microwave sources where a resonant cavity is used, its design is of great importance in the transfer of power; some designs have been discussed.[60,71,72]

Table 1 shows that there are many applications to the analysis of solutions or solids for which a low-power microwave source is at least sufficiently promising to be thought worth reporting. This is in spite of the restriction to very small samples, necessary for the stability of the discharge. If applications to the analysis of gaseous samples were included here there would be a greater preponderance of these devices. The situation with hf sources is very different; with the exception of Varek and Bowman's glow discharge,[15–17] there are no such systems reported with power of less than 250 W and it is possible to infer that this was considered too small.[29] The impracticability of forming a discharge with a low-power hf oscillator is probably due to the relatively large skin-depth at these frequencies, which means that the power is dissipated in a relatively large volume, giving a power density insufficient to maintain the discharge.

The frequencies reported for the hf sources (with one early exception[36] where it is 150 MHz) lie in the range 6–60 MHz. Apart from commercial availability, reasons are not advanced for the values chosen; it is our opinion that, within fairly wide limits, the choice is not of great importance.

Sample introduction

Table 2 gives a survey of methods used to introduce liquid and solid samples; we exclude cases where a solid sample is placed on, or used as, an electrode. In the cases noted, desolvation was used to prevent plasmas of low power from being extinguished by the solvent. Chemical generation included the production of hydrogen sulphide from cast iron,[57] the reduction of mercury compounds[31,58] and the generation of arsine.[59] Kessler[42] gives a well-justified warning on the necessity of reproducible particle-size and rate of

Table 2. Methods of introducing samples

Method	References
Pneumatic nebulization	6, 7, 9, 10, 19, 29, 32–34, 38, 43–48, 52*, 60*, 61, 62*, 67, 68
Ultrasonic nebulization	11, 13, 14, 30, 32, 33, 64*
Evaporation from heated filament	15–17, 56, 57, 63, 69, 70
Chemical generation of vapour	31, 57–59
In sealed tube	65, 66
As powder	41, 42

* With desolvation.

feed in the quantitative analysis of powders. Ultrasonic nebulization often results in an improvement in sensitivities and detection limits: a comparison is given by Egorova.[32,33] The most convenient method, well suited for automatic analysis of a series of samples on a rotating turntable, is pneumatic nebulization; none of the others is easy to use in this fashion.

Limits of detection

Many of the limits of detection given in the papers reviewed are (following Kaiser[73]) that concentration which is predicted to give a signal of magnitude which is a certain multiple of the standard deviation of the background. The multiplier used is often two, sometimes three and occasionally one. Skogerboe, Heybey and Morrison[74] give what seems to be a technically more correct procedure to take account of the fact that the background and its standard deviation are usually estimated from a small number of readings. The point had not been overlooked by Kaiser, who not only recommended that at least twenty blank analyses be used and that the value of the multiplier should be three but warned against accepting literally the corresponding probability of being in error.

In spite of the fact that the published values are therefore not all comparable, we have made no attempt to adjust them to the same basis, for it seems to us that the differences due to the different methods of estimation are of little consequence to the spectroscopist engaged in practical analysis, because of other factors which affect the limit and may be beyond his control. It seems more important to us that the published limits should have been checked experimentally by analysing known samples having concentration which lie quite near these limits. Extrapolation from concentrations much higher can be misleading; in one case,[66] the discrepancy between extrapolation and experiment pointed the way to an improvement in experimental procedure.

Table 3 lists some of the best values of published limits for most of the elements which have been studied. They are often determined with the use of pure solutions although they are liable to be influenced by the matrix of a real sample. Many other factors, such as the nature and acidity of the solution, gas pressures and flow-rates, available power, type of nebulizer used, and the part of the plasma viewed, also have their effects. If only one element is to be determined these parameters can be optimized if necessary but if the source is used for the simultaneous determination of several elements, either by photography or a multichannel photoelectric system, the conditions will not be optimum for all elements. It seems likely, therefore, that different operating conditions explain the large number of different references cited in Table 3 for the best detection limits; this was brought home to us when compiling the table, when we noted that different systems which might be expected to behave in a similar way frequently gave detection limits differing by factors of perhaps 100, one system favouring some elements, and another others. With the possible exception of systems which are designed and optimized for one element, we would therefore not recommend the blind acceptance of a low detection limit as an indicator of merit of the emission source. The use of ultrasonic nebulization in particular can often make a dramatic improvement.

Matrix effects

One type of matrix effect is due to the presence of refractory radicals; atoms which are not free do not contribute to the atomic spectrum. The intensity of the emission of an element will depend therefore on the concentration in the matrix of other elements with which the element may combine. This effect does not occur if the gas temperature is sufficiently high, because then the radicals are dissociated; freedom from this type of interference is one of the great advantages of working with a high-power source. It is our opinion that the dissipation of several kilowatts in the plasma is necessary to obtain this advantage and that most of the sources reviewed here will therefore be subject to this effect, whether mentioned by the experimenter or not.

The presence of radicals also leads to the emission of band spectra, which are likely to cause spectral interference.

Table 3. Detection limits obtained with microwave and capacitively coupled high-frequency plasma sources

Element	Detection limit, *ppm*	Wavelength, *nm*	Reference	Other references to this element
Aluminium	0·02	396·2	30	6, 8, 10, 13, 14, 22, 25, 29, 32, 33, 38, 42–44, 46–49, 64
Antimony	0·1	231·2	64	25, 29, 33, 47, 63
	0·1	259·8	32, 61	
Arsenic	0·03	193·7	60	25, 29, 47, 48, 59, 61, 63
Barium	0·05	455·4	38	6, 7, 9, 10, 14, 22, 30, 32, 33, 45, 47, 69, 76
Beryllium	0·05	234·9	32	6, 10, 22, 33, 63
Bismuth	1·0	472·3	64	25, 30, 47, 48
Boron	0·01	249·8	60	6, 10, 22, 24, 29, 32, 42, 45, 47, 48, 51, 63, 67, 68
Bromine	500	470·5	26	
Cadmium	2×10^{-7}	228·8	66	10, 16, 21, 30, 32, 33, 45, 47, 48, 60–63, 65, 67–69

Table 3. *Continued*

Element	Detection limit, *ppm*	Wavelength, *nm*	Reference	Other references to this element
Caesium	2	455·5	10	6, 22, 29
Calcium	0·005	422·7	30	9, 10, 13, 14, 16, 17, 22, 25, 29, 34, 38, 42, 44–48, 61, 64, 67, 68
Carbon	100	247·9	42	8
Carbon as CN	4	388·3	42	
Cerium	1·5	413·4	42	6, 22, 48
Chlorine	500		26	
Chromium	0·001	357·9	56	9, 10, 14, 22, 32, 33, 38, 42, 45
Cobalt	0·001	345·4	56	10, 29, 30, 32, 38, 42, 45, 60, 64, 79
Copper	0·0001	324·8	56	8, 10, 16, 25, 29, 30, 32, 38, 45, 48, 61, 63, 64, 67–69
Dysprosium	0·04	396·8	75	29
Erbium				29
Europium	0·01	459·4	38	29
Gadolinium	2	432·6	75	29
Gallium	0·04	417·2	62	47
Germanium	1·5	265·1	47	68
Gold	0·02	267·6	30	10, 25, 29, 32, 33, 47
Hafnium				29
Holmium				29
Indium	10^{-6}	451·1	66	22, 29, 32, 33, 47, 62, 64, 65
Iodine	10	206·2	63	29
Iron	0·001	373·5	56	6, 7, 10, 13, 14, 16, 25, 29, 30, 32, 34, 38, 42–45, 48, 61, 63, 64, 67, 68
Lanthanum				22, 79
Lead	0·005	405·8	60	6, 8, 10, 13, 14, 16, 19, 25, 29, 30, 32, 33, 38, 48, 63–65, 69
Lithium	0·01	670·7	38	10, 14, 30, 45
Magnesium	0·005	285·2	30	10, 13, 14, 16, 22, 25, 32–34, 42–45, 48, 61, 64
Manganese	0·004	403·1	30	9, 10, 13, 14, 25, 32–34, 38, 45–48
Mercury	10^{-5}	253·6	58	10, 16, 29–31, 47, 60–63, 65, 70
Molybdenum	0·045	379·8	45	8, 25, 29, 32, 33, 38, 42, 47, 50
Neodynium	0·3	430·4	75	22, 29
Nickel	0·01	341·5	30	10, 25, 29, 32, 33, 38, 42, 45–47, 67, 68
Niobium	0·5	405·9	52	29, 68
Palladium	0·4	340·6	47	29
Phosphorus	10		68	29, 32, 33, 67
Platinum	0·1	265·9	30	10, 47
Potassium	0·3	769·9	16	6, 7, 10, 14, 15
Praseodymium	0·5	422·5	75	22, 29
Rhenium				29
Rhodium	0·05	369·2	47	
Rubidium	8	420·1	10	22
Samarium	0·2	442·4	75	22, 29
Scandium	20	424·7	32	29
Selenium	0·04	196·0	60	61, 63
Silicon	0·2	251·6	47	25, 29, 67, 68
Silver	0·001	328·1	56	10, 25, 29, 32, 33, 45, 64, 69
Sodium	0·001	589·2	14	10, 13, 15, 16, 25, 29, 42, 44, 45, 61
Strontium	0·0005	460·7	38	9, 10, 22, 24, 30, 67, 68
Sulphur	0·2	216·9	57	29
Tantalum				25, 68
Tellurium	0·2	214·3	61	26, 47
Terbium	1	432·6	75	
Thallium	10^{-6}	377·6	66	10, 25, 29, 30, 32, 38, 65
Thorium	8	401·9	48	
Thulium				29
Tin	0·2	303·4	30	6, 22, 29, 48, 61, 64
Titanium	0·1	365·4	52	10, 48, 68
	0·1	334·9	64	
Tungsten	0·4	429·5	48	8, 10, 47, 50, 68
Uranium				29
Vanadium	0·015	437·9	30	6, 19, 29, 32, 42, 46, 47, 60
Ytterbium	0·5	398·8	32	29
Yttrium	0·03	437·5	75	
Zinc	0·0006	213·9	60	6, 7, 10, 13, 14, 16, 29, 30, 32, 33, 38, 45–48, 61–64, 67–69
Zirconium	1	339·2	42, 52	47, 68

Table 4. Practical applications of microwave and capacitively coupled high-frequency plasma sources

Field of application	Elements determined	References
Clinical chemistry	Ca, Cd, Cu, Fe, Hg, K, Mg, Na, Pb, Zn	15–17
Impurities in semiconductors	Si, Mg, Cu, Mn, Mo, Fe, Al, As, Bi, Tl, Sb, Pb, Ni, Na, Ca	25
Limestone, dolomite	Mg, Fe, Al, Ca, Mn	34, 43, 44
Glass	Na, Ca, Mg, Al, Fe	44
Oil	Fe, Cr, Ni, Ag	45
Steel	Al, W, Mo, B, Nb, Ti, Zr	49–52

Another effect which is liable to occur with apparatus of any power or frequency is a change in emission intensity if an element of low ionization potential is introduced. The immediate result of this is likely to be an increase in electron density, which will move the ionization equilibrium of the other atoms towards the neutral side. This simple consideration is sometimes adequate to explain at least qualitatively the effects observed: these effects are frequently that elements of high ionization potential are not affected, since there are few ions of such species in any case, while those of low ionization potential, which are initially appreciably ionized, will show a noticeable change if the equilibrium is altered. Changes in the spatial distribution of the plasma[32,38] have also been invoked by Murayama[75,76] and other studies have been made by Cristescu and Giurgea,[20] Kitagawa and Takeuchi,[77,78] and Pupyshev and Muzgin.[79] Very pronounced enhancements are sometimes observed; the detection limits for rare earths were improved by factors of up to 1000 by the addition of sodium,[75] but reductions in sensitivity have also long been known.[6]

Applications

Many of the papers mentioned are exploratory and aim at establishing the potential of the technique for the analysis of solutions. Papers referring to specific elements can be traced from Table 3. More substantial practical applications are listed in Table 4.

Plasma parameters

It is reasonable to assume that all the devices mentioned have high excitation temperatures, for otherwise they would be useless as excitation sources. We have already mentioned our opinion that most of the sources reviewed do not have powers sufficiently high to produce a high gas temperature. Most, therefore, will not be in local temperature equilibrium (LTE), which requires the different kinds of temperature to have the same value. Low-pressure plasmas are likely to be still further from LTE, because the lower number of collisions impairs the transfer of energy.

The literature of plasma parameters such as temperatures of various kinds and particle densities of different species is very large. A few papers with relevance to the small plasmas used for laboratory spectrochemical sources are those by Mollwo;[80] van Calker;[81] Lochte-Holtgreven;[82] Lanz, Lochte-Holtgreven and Traving;[83] Jecht and Kessler;[84] Pforr and Kapicka;[85] Kapicka;[86] Egorova;[87] Baltin, Batenin, Goldberg and Tsemko;[88,89] Britske and Sukach;[90] Kapounova;[91] Kapoun;[92] and Busch and Vickers,[93] as well as references[4,6,20,23,29,41,48,62,64,75,77,78] already mentioned in the text.

SPECIALIZED APPLICATIONS

Gas mixtures

Stolov[5] used a high-frequency brush discharge formed at a pointed electrode to analyse binary mixtures of nitrogen and carbon dioxide. This mixture was also studied by Botschkowa, Frisch and Schreider[37] who also undertook trace analysis with their 6-MHz, 350-W source. White, Watkins and Fletcher[94] analysed respiratory gases for oxygen and nitrogen. Vashman, Lipis and Teterina[95] used a microwave (3000-MHz) discharge for the analysis of argon–helium mixtures. Given, Magee and Wilson,[96] and Chakrabarti, Magee and Wilson[97] investigated the possible application of Tesla-type discharges to gas analysis, and also used a 230-MHz source to study argon–carbon dioxide mixtures.[98] An 8-MHz source was evaluated by Boos and Winefordner[99] for the detection of air, CO, CO_2, SO_2, NH_3, NO, NO_2, N_2 and CH_4. The effect of parameters such as gas pressure and power on the spectral intensity of nitrogen–helium mixtures was investigated by Snopov.[100]

Trace impurities in rare gases

Servigne, de Montgareuil and Dominé[101] used a microwave discharge at low pressure to determine nitrogen in the rare gases. Ishida[102] used an hf source for hydrogen and nitrogen in argon. Botschkowa, Frisch and Schreider[37] determined nitrogen, hydrogen, oxygen and carbon monoxide in the rare gases, and traces of rare gases in others, with an hf discharge. Fay, Mohr and Cook[103] studied microwave discharges, Tesla discharges and Geissler tubes before opting for a silent, high-voltage (10-kV) mains-frequency discharge for detecting nitrogen in argon. Gutkina and Maslennikova,[104] however, pointed out the advantages of high frequencies in studying traces of nitrogen in helium. Taylor, Gibson and Skogerboe[105] adapted the system of Runnels and Gibson[56] to the determination of carbon-, oxygen-, nitrogen-, and hydrogen-containing compounds in argon. Penchev, Belchev, Piperov and Belinov[106] analysed helium for traces of neon with a 60-MHz plasma.

Isotope analysis

The spectroscopic analysis of isotopes depends on the shifting, often by as much as 1 Å, of atomic lines

or molecular bands, caused by the different masses of the isotopes. Excitation of the spectra seems to be accomplished very conveniently in high-frequency and microwave discharges.

Nitrogen. The most widely investigated element is nitrogen, perhaps because of the importance of biological experiments with labelled nitrogen, ^{15}N. Hoch and Weisser[35] excited the discharge by applying the output of a diathermy unit of unspecified frequency to aluminium foil wrapped round the ends of a discharge tube. Broida and Chapman[53] experimented with both sealed and unsealed discharges and with frequencies of 150 and 2450 MHz. A sealed tube had the advantage of requiring only a small sample and, although special care was required in filling it, was adopted. The higher frequency was chosen because no tuning was required and it was more sensitive. The pressure in the discharges was chosen to be 1·5 mmHg, and the power supplied was 125 W. Faust[107] used a frequency of about 7 MHz to excite spectra in a capillary tube and measured the intensity ratios with a step-filter rather than a rotating sector. Zaidel, Lazeeva and Petrov[108] applied excitation in a high-frequency electrodeless discharge to the determination of the isotopes of oxygen and nitrogen in metals. Nemets and Petrov[109] reported the simultaneous determination of the isotopes of nitrogen and hydrogen, and of carbon and oxygen isotopes. Sommer and Kick[110] used a 2450-MHz discharge and gave details of their sample handling. Leicknam, Figdor, Keroe and Muehl[111] designed an apparatus of high stability working at 100 MHz, and described suitable detection equipment; operating conditions were discussed by Leicknam, Middelboe and Proksch.[112] With very small (less than 5 μg) samples of nitrogen, the discharge is easily extinguished and Goleb and Middelboe[113] added a mixture of helium and xenon to maintain it. Ferraris and Proksch[114] evaluated commercially available components for constructing a system to excite the spectra and discussed different methods of calculating the isotopic concentrations from the spectra. Kumazawa[115] discussed some practical problems. Keeney and Tedesco[116] developed a method for sample preparation and evaluated a commercially available analyser (Straton, type NOI-4). Middelboe[117] discussed a high-resolution method for the calibration of commercially available analysers. Lloyd-Jones, Hudd and Hill-Cottingham[118] reported instrumental and procedural modifications for the use of the Straton NOI-5 spectrometer and made recommendations on the calculations and sample preparation.

Hydrogen. The analysis of hydrogen–deuterium mixtures was investigated by Broida and Moyer[36] and by Broida and Morgan.[119] Sources at frequencies of 150 and 2450 MHz were tried: the 150-MHz source was preferred since the microwave source showed strong self-absorption. A flow system was used, since with a closed system the calculated concentration decreased with time. (It is interesting to note that the opposite options were later chosen by Broida and Chapman[53] for the analysis of nitrogen, for different but equally pertinent reasons.) A method for the analysis of mixtures with 10–90% hydrogen was reported by Veinberg, Zaidel and Petrov,[120] with small amounts of deuterium by Zaidel and Ostrovskaya[121] and with small amounts of hydrogen by Nemets, Petrov and Shabdukarimov.[122] Nemets and Petrov[109] reported on the simultaneous detection of the isotopes of hydrogen and nitrogen.

Carbon. Isotopic analysis of carbon was described by Zaidel and Ostrovskaya,[123] who used the intensities of carbon monoxide bands. A similar technique was used by Nemets and Petrov.[109]

Uranium. The application of electrodeless discharges to the isotopic analysis of uranium was reported by Capitani and co-workers.[124–126]

Detectors for gas chromatography

Although an hf discharge had been suggested by Karman and Bowman[127] in 1959, and discharge excitation by a Tesla coil by Sternberg and Poulson[128] in 1960, practical applications to chromatographic detection were not reported until 1965. McCormack, Tong and Cooke[55] experimented with high-voltage a.c. and d.c. glow discharges, with a hollow-cathode d.c. discharge, and with electrodeless discharges in argon and helium at 8 and 2450 MHz. They found the intensities of the spectra emitted from the microwave plasma to be significantly higher than those from the others. The spectra emitted from this discharge showed that a variety of organic molecules had been fragmented to atoms or diatomic species; these spectra could be utilized as sensitive detectors of compounds containing carbon, iodine, sulphur, phosphorus, chlorine and fluorine, and applications to other compounds were suggested. An application of this detector by Bache and Lisk[129] to the determination of organophosphorus insecticide residues was published simultaneously. This was the first of a series, subsequent members of which were concerned with the determination of iodinated herbicide residues and metabolites,[130] with the effects of reducing the discharge pressure (which were to enhance by an order of magnitude the emission from phosphorus, but not that from iodine),[131] with the substitution of helium for argon as the discharge gas (which enabled atomic lines of sulphur, chlorine and bromine to be observed and used in place of the band spectra previously utilized),[132] and its application to pesticide analysis,[133–135] and with improved matching of the microwave generator to the discharge cavity[72] and applications to determination of methylmercury salts in fish.[136] Bellet, Westlake and Gunther[137] also used a similar apparatus for the detection of phosphorus.

Moye,[138] having obtained unsatisfactory results in phosphorus detection with a pure argon discharge, studied the effects of mixing nitrogen, carbon dioxide, oxygen and helium with the argon. Only helium proved satisfactory, the non-monatomic gases giving rise to very strong continuum radiation even in trace quantities, and producing very unstable discharges.

Maximum sensitivity was found with a composition of 85% He and 15% Ar. Applications to pesticide residues were reported.

A series of investigations by Dagnall and West with collaborators began with a study of sulphur compounds[139] in which it was pointed out that the response, and wavelength for maximum emission, were dependent on the identity of the sulphur-containing compound, because of incomplete fragmentation; improvements were obtained[140] by restricting the volume of the discharge, by using a platinum catalyst and a different cavity to increase fragmentation, by using all the eluted sample and by stabilizing the discharge pressure. A return to an argon discharge at atmospheric pressure was advocated[141] on the grounds of simplicity, wide application and encouraging performance after optimization for routine analysis. The feasibility of determining interelement ratios was established.[142] Highly selective and sensitive response in the analysis of volatile metal chelates was reported.[143] An emissive helium discharge was used[144] for the determination of carbon monoxide, carbon dioxide, nitrous oxide and sulphur dioxide in air, following separation by gas chromatography.

Luippold and Beauchamp[145] established the feasibility of using a low-pressure microwave discharge in helium to find the ratio of deuterium to hydrogen in order to determine the presence and extent of labelling in hydrocarbons separated by gas chromatography. Houpt and Compaan[146] studied the determination of organic compounds containing phosphorus, sulphur, the halogens or mercury; they developed a method particularly suitable for organomercury compounds in foods, as did Grossman, Eng and Tong.[147] Detection limits for carbon, hydrogen, deuterium, oxygen, nitrogen, fluorine, chlorine, bromine, iodine, sulphur and phosphorus in organic compounds were presented by Lowings:[148] these were less than 0·1 ng/sec, with the exception of oxygen and nitrogen, which were about 3 ng/sec. Almost identical limits were reported by McLean, Stanton and Penketh,[149] who were able to determine atomic ratios and hence empirical formulae of organic compounds. They stress the importance of mixing small quantities of oxygen or nitrogen with the helium working gas, to prevent the deposition of carbon on the wall of the plasma tube. Helium was chosen because the higher energy of a helium plasma gave freedom from band spectra.

An account of the determination of metal chelates (which slightly antedates reference 143) was given by Kawaguchi, Sakamoto and Mizuike.[150]

All the applications listed above use microwave excitation at a frequency of 2450 MHz. West[151] has compared systems operating at 30 and 2450 MHz. He suggests, rather tentatively, that the 30-MHz discharge has the following advantages: (1) it may be somewhat more sensitive; (2) a plasma can be formed in any gas at atmospheric pressure; (3) it is probably somewhat cheaper; (4) it is simpler to adjust and operate; (5) it is less likely to foul the plasma tube. He suggests that the 2450-MHz system has these advantages: (1) it is commercially available; (2) it is perhaps more readily adapted to gas chromatographic systems; (3) it is more easily thermostated; (4) it does not require extensive electrical shielding. It might be thought that West's comparison favours a radiofrequency system; nevertheless the literature shows the overwhelming popularity of microwave excitation for gas chromatographic detectors. This is possibly due to the ready availability of low-power microwave generators intended for therapeutic purposes. The working gases used are argon or helium or a mixture. There is a consensus that with the low power used a stable plasma can be formed at atmospheric pressures only in argon, and that, for stability, helium must be used at reduced pressure.

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EFFECTS OF AUXILIARY COMPLEX-FORMING AGENTS ON THE RATE OF METALLOCHROMIC INDICATOR COLOUR CHANGE—II*

MECHANISM OF THE COLOUR CHANGE OF PAN IN COPPER–EDTA TITRATIONS

GENKICHI NAKAGAWA and HIROKO WADA

Laboratory of Analytical Chemistry, Nagoya Institute of Technology, Showa-ku, Nagoya, Japan

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Summary—The rate of the ligand substitution reaction of copper (II)–PAN (CuR) with EDTA (Y) has been determined spectrophotometrically in 5% v/v dioxan over the pH range 5·0–6·3 at $\mu = 0{\cdot}1$ ($NaClO_4$) and at 25°. In the absence of 1,10-phenanthroline the rate law is expressed as $-d[CuR^+]/dt = 10^{3\cdot2}\,[CuR^+]\,[Y']$, and the release of PAN from the reaction intermediate CuRY is the rate-determining step. In the presence of 1,10-phenanthroline (X), however, copper forms a stable mixed-ligand complex ($CuRX^+$), and the rate of substitution with EDTA is expressed as $-d[CuRX^+]/dt = (10^{6\cdot2}[H^+] + 10^{4\cdot8}[X])\,[CuRX^+]$. The release of PAN from the mixed-ligand complex by H^+ and X is possibly the rate-determining step, with the copper–phenanthroline complexes produced undergoing fast exchange with EDTA. The stability constant of $CuRX^+$ has been determined spectrophotometrically in 5% v/v dioxan at $\mu = 0{\cdot}1$, and at 25° as $[CuRX^+]/[Cu^{2+}]\,[R^-]\,[X] = 10^{21\cdot2}$. The acceleration of the rate of substitution of copper (II)–PAN chelate may be explained by the fact that the Cu–PAN bond in the distorted octahedral mixed-ligand complex CuRX is weaker than in the reaction intermediate CuRY.

In chelatometric titrations with metallochromic indicators, the colour change at the equivalence point occurs by the substitution of the titrant for the indicator in the metal–indicator complex. For a sharp end-point the rate of substitution, as well as the equilibrium condition is extremely important. Some studies of the kinetics of ligand substitution reactions of metal–indicator chelates with EDTA have been reported.[1–3]

In our previous paper[4] it was found that 1,10-phenanthroline accelerates the rate of colour change of 1-(2-pyridylazo)-2-naphthol (PAN) in the copper-(II)–EDTA titration, by forming the mixed-ligand complex Cu–PAN–phenanthroline near the equivalence point. In the present paper the rate of substitution reaction of Cu–PAN and Cu–PAN–phen with EDTA have been studied, and the mechanism of the colour change of PAN at the equivalence point is discussed.

EXPERIMENTAL

Reagents

Copper solution. Metallic copper (99·99% purity) was dissolved in nitric acid and the solution was diluted suitably.

PAN solution. 1-(2-Pyridylazo)-2-naphthol was purified by vacuum sublimation and dissolved in dioxan.

EDTA. EDTA solution was standardized against a standard copper solution, with 4-(2-thiazolylazo) resorcinol as indicator.

1,10-Phenanthroline solution in dioxan.

Sodium perchlorate solution. Prepared by dissolution of sodium carbonate in perchloric acid.

Dioxan. Commercial reagent-grade dioxan was purified by distillation after treatment with potassium iodide and sulphuric acid and refluxing with sodium for more than 20 hr.

Apparatus

A Hitachi Rapid Scan Spectrophotometer type RSP-2, Hitachi Spectrophotometer type 124, Hirama Spectrophotometer type 6, and a Radiometer pH meter type PHM 26c were used.

Procedure for the measurement of the rate of the substitution reaction

In the absence of 1,10-phenanthroline. The solutions A and B were mixed, and the absorbance at 550 nm was recorded as a function of the reaction time. The dead time of mixing was about 20 msec.

Solution A: $Cu = 1{\cdot}01 \times 10^{-5}M$; $PAN = 1{\cdot}00–3{\cdot}02 \times 10^{-5}M$; MES buffer solution[4] = 0·02*M*, pH 5·0–6·3; dioxan = 5% v/v; ionic strength 0·1 ($NaClO_4$). Solution B: $EDTA = 1{\cdot}24–3{\cdot}72 \times 10^{-4}M$; MES buffer solution = 0·02*M*, pH 5·0–6·3; dioxan = 5% v/v; ionic strength: 0·1 ($NaClO_4$).

In the presence of 1,10-phenanthroline. 1,10-Phenanthroline ($1{\cdot}04–2{\cdot}52 \times 10^{-5}M$) was added to solution A, and the absorbance at 545 nm was measured (in the pH range 5·8–6·5) as a function of the reaction time.

RESULTS AND DISCUSSION

The formation constant of Cu–PAN–phen complex

Figure 1 shows the spectra of the Cu–PAN chelate (Curve 1) and Cu–PAN–phen complex (Curves 2–4). The λ_{max} values were 550 and 540 nm, respectively, and the isosbestic point was at 545 nm.

* Part I: see reference 4.

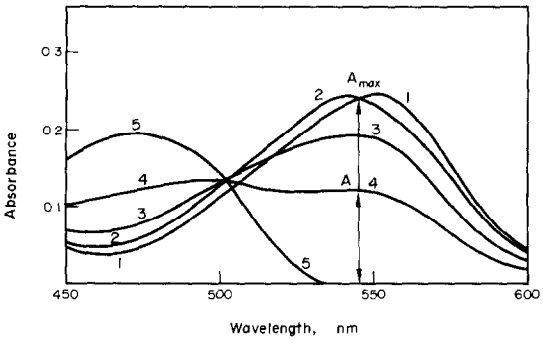

Fig. 1. Spectra of Cu–PAN–phen. C_{Cu}: $2{\cdot}7 \times 10^{-6}M$; C_{PAN}: $2{\cdot}0 \times 10^{-6}M$. C_{phen}: (1) 0 (pH 6); (2) $6{\cdot}8 \times 10^{-6}M$; (3) $1{\cdot}1 \times 10^{-4}M$; (4) $2{\cdot}7 \times 10^{-4}M$; (5) PAN blank. pH 9, 5 cm cell, 5% v/v dioxan.

When copper–PAN complex forms mixed-ligand complexes with 1,10-phenanthroline, the formation constant of mixed-ligand complexes is given by (charges are omitted for simplicity)

$$\beta_{CuRX_n} = \frac{[CuRX_n]}{[CuR][X]^n} \tag{1}$$

and the conditional formation constant of copper–PAN complex is given by

$$K_{(CuR)'} = \frac{[(CuR)']}{[Cu][R]} = K_{CuR}\alpha_{CuR(X)} \tag{2}$$

where R and X represent PAN and 1,10-phenanthroline, respectively, and $\alpha_{CuR(X)}$ is a side-reaction coefficient taking into account the formation of mixed-ligand complexes:

$$\alpha_{CuR(X)} = 1 + \sum_{n=1}^{n} \beta_{CuRX_n}[X]^n. \tag{3}$$

As the total concentration of copper–PAN complexes [(CuR)'] can be obtained from the absorbances at 545 nm, *i.e.*, A_{max} and A in Fig. 1, by equation (4):

$$[(CuR)'] = \frac{A}{A_{max}} C_R, \tag{4}$$

[Cu] and [R] can be calculated by means of equations (5) and (6):

$$[Cu] = \frac{C_{Cu} - [(CuR)']}{\alpha_{Cu(X)}} \tag{5}$$

$$[R] = \frac{C_R - [(CuR)']}{\alpha_{R(H)}} \tag{6}$$

where C_R and C_{Cu} express the initial concentrations of PAN and copper, respectively. $\alpha_{Cu(X)}$ and $\alpha_{R(H)}$ are side-reaction coefficients for the formation of copper–phenanthroline complexes and the protonation of PAN, respectively.* Substitution of the values of [(CuR)'], [Cu] and [R] into equation (2) gives the values of $K_{(CuR)'}$ under the given experimental conditions.

* For the calculation of the α values, $\beta_{CuX_3} = 10^{20.56}$, $K_{HX} = 10^{4\,86}$ and $K_{HR} = 10^{11\,55}$ (5% v/v dioxan, $\mu = 0{\cdot}1$) were used.

The experiments were carried out under the conditions where Cu = $2{\cdot}74 \times 10^{-6}M$, PAN = $2{\cdot}02 \times 10^{-6}M$, 1,10-phenanthroline = $5{\cdot}00 \times 10^{-5}$–$4{\cdot}00 \times 10^{-2}M$, at pH 9·22–11·28, $\mu = 0{\cdot}1$ (KNO_3), and dioxan = 5% v/v. A plot of log $K_{(CuR)'}$ *vs.* log[X] gave a straight line with a slope of 1. Therefore, in the concentration range of 1,10-phenanthroline between 10^{-4} and $10^{-1}M$ one molecule of 1,10-phenanthroline co-ordinates with the Cu–PAN chelate. The formation constant of the mixed-ligand complex was obtained from the value of log$K_{(CuR)'}$ at log[X] = 0:

$$K^{R,X}_{CuRX} = \frac{[CuRX]}{[Cu][R][X]} = 10^{21\,2}$$

The rate of the substitution reaction of Cu–PAN with EDTA

Under the present experimental conditions, the substitution reaction of the Cu–PAN chelate goes to completion and the rate-law can be expressed by

$$\text{Cu–PAN} + \text{EDTA} \rightleftharpoons \text{Cu–EDTA} + \text{PAN}$$

$$-\frac{d[CuR]}{dt} = k_{0(R,Y,H)}[CuR] \tag{7}$$

where $k_{0\,(R,Y,H)}$ is the conditional rate-constant[1] which may depend on the concentrations of PAN, EDTA and hydrogen ion. By representing the absorbances of the reaction system at $t = 0$, t and ∞ as A_0, A_t and A_∞, respectively, we obtain equation (8) from equation (7):

$$\log(A_t - A_\infty) = -\frac{k_{0(R,Y,H)}}{2{\cdot}303} t + \log(A_0 - A_\infty). \tag{8}$$

The plots of $\log(A_t - A_\infty)$ *vs.* t were linear for at least 90% of the reaction, and $k_{0\,(R,Y,H)}$ was obtained from the slopes of the straight lines. The values of $k_{0(R,Y,H)}$ at various concentrations of hydrogen ion, PAN and EDTA are given in Table 1. The data indicate that $k_{0\,(R,Y,H)}$ does not depend on the hydrogen ion and PAN concentrations, but is linearly related to the EDTA concentration. Thus

$$-\frac{d[CuR]}{dt} = k[Y'][CuR] \tag{9}$$

and k was determined as $1{\cdot}7 \times 10^3$ l.mole^{-1}. sec^{-1}. Although in the pH range 5·0–6·3 EDTA is present as HY^{3-} and H_2Y^{2-}, no variation of the rate with varying proportion of these species was observed.

The rate of the substitution reaction of copper (II)–4-(2-pyridylazo) resorcinol (PAR) chelate with (ethyleneglycol) bis (2-aminoethylether)-*N,N,N',N'*-tetraacetic acid (EGTA) was studied by Funahashi *et al.*[2] Under their experimental conditions, *i.e.*, pH 9–10, copper forms a 1:2 complex with PAR, and the following mechanism has been proposed:

$$CuR_2^{2-} + H^+ \rightleftharpoons CuR + HR^-$$

$$CuR + Y' \rightleftharpoons RCuY \xrightarrow{k} CuY^{2-} + HR^- \tag{10}$$

$$k = 8{\cdot}8 \times 10^2 \text{ l.mole}^{-1}\text{. sec}^{-1}.$$

At pH 5–6·3 copper forms a 1:1 complex with PAN and when this is taken into account there is

Table 1. First-order conditional rate constants $k_{0\,(R,Y,H)}$ 25°C, $\mu = 0{\cdot}1$, dioxan 5% v/v, Cu: $5{\cdot}03 \times 10^{-6} M$

$10^5 \times C_{EDTA}$, M	pH	$10^6 \times C_{PAN}$, M	$k_{0\,(R,Y,H)}$, sec^{-1}
6·22	4·94	4·99	0·105
6·22	4·94	9·97	0·103
6·22	5·35	9·97	0·104
9·33	4·94	4·99	0·152
9·33	4·94	9·97	0·151
9·33	5·36	9·97	0·151
9·33	5·55	9·97	0·158
12·4	4·94	9·97	0·204
12·4	4·92	15·1	0·197
12·4	4·94	19·1	0·209
12·4	5·35	9·97	0·205
12·4	5·55	9·97	0·207
12·4	5·78	9·97	0·198
15·6	5·35	9·97	0·260
15·6	5·55	9·97	0·260
15·6	5·78	9·97	0·263
18·6	4·95	9·97	0·324
18·6	6·14	5·03	0·303
18·6	6·28	5·03	0·306

good agreement in the value of k. Thus, the mechanism of substitution may be the same.

The rate of the substitution reaction of Cu–PAN–phen with EDTA

As a mixed-ligand complex Cu–PAN–phen forms completely under the present experimental conditions, the substitution reaction may be written as;

$$\text{Cu–PAN–phen} + \text{EDTA} \rightleftarrows \text{Cu–EDTA} + \text{PAN} + \text{phen} \quad (11)$$

The rate law is expressed by equation (12) or (13).

$$-\frac{d[CuRX]}{dt} = k_{0\,(R,Y,H,X)}[CuRX] \quad (12)$$

$$\log(A_t - A_\infty) = -\frac{k_{0\,(R,Y,H,X)}}{2{\cdot}303} t + \log(A_0 - A_\infty). \quad (13)$$

The plots of $\log(A_t - A_\infty)$ *vs.* t were straight lines for at least 90% of the reaction. The values of $k_{0\,(R,Y,H,X)}$ determined under the various conditions are shown in Table 2. No dependence of $k_{0\,(R,Y,H,X)}$ on the concentrations of PAN and EDTA was found, but a linear relation to the hydrogen ion and 1,10-phenanthroline concentrations was observed.

From these linear relationships the equation

$$k_{0\,(R,Y,H,X)} = k_1[H^+] + k_2[X'] \quad (14)$$

was deduced, where [X'] is the total concentration of 1,10-phenanthroline not combined with copper. From the slopes and the intercepts of the straight lines in plots of $k_{0\,(R,Y,H,X)}$ *vs.* $[H^+]$ or [X'], k_1 and k_2 were calculated. These values are shown in Table 3.

Table 2. First-order conditional rate constants $k_{0\,(R,Y,H,X)}$ 25°C, $\mu = 0{\cdot}1$, dioxan 5% v/v, Cu: $5{\cdot}03 \times 10^{-6} M$

pH	$10^6 \times C_{phen}$, M	$10^6 \times C_{PAN}$, M	$10^5 \times C_{EDTA}$, M	$k_{0\,(R,Y,H,X)}$, sec^{-1}
5·77	5·06	8·48	6·22	2·51
	7·59	8·48	6·22	2·84
	10·1	6·36	6·22	3·02
	10·1	8·48	9·33	3·06
	10·1	8·48	12·4	2·99
	10·1	8·48	15·6	2·97
	10·1	8·48	18·6	2·90
	10·1	10·6	6·22	2·96
	12·6	8·48	6·22	3·06
5·95	5·06	8·48	6·22	1·62
	7·59	8·48	6·22	1·99
	10·1	6·36	6·22	2·09
	10·1	8·48	6·22	2·13
	10·1	8·48	9·33	2·13
	10·1	8·48	12·4	2·13
	10·1	12·6	6·22	2·13
	12·6	8·48	6·22	2·37
6·08	5·06	8·48	6·22	1·35
	7·59	8·48	6·22	1·56
	10·1	8 48	6·22	1·73
	10·1	8·48	9·33	1·75
	10·1	8·48	12·4	1·73
	10·1	8·48	15·6	1·76
	10·1	8·48	18·6	1·74
	12·6	8·48	6·22	1·82
6·45	5·06	8·48	6·22	0·583
	7·59	8·48	6·22	0·824
	10·1	8·48	6·22	0·951
	10·1	8·48	12·4	0·930
	10·1	8·48	15·6	0·930
	10·1	8·48	18·6	0·944
	10·1	10·6	6·22	0·926
	12·6	8·48	6·22	1·01

Table 3. Evaluation of k_1 and k_2

$10^7 \times [H^+]$, M	$10^6 \times [X']$, M	Intercept, sec^{-1}	$10^{-6} \times k_1$, $l.\ mole^{-1}.\ sec^{-1}$	$10^{-4} \times k_2$, $l.\ mole^{-1}.sec^{-1}$
	0	0	1·57	
	2·56	0·19	1·61 *	7·4
	5·07	0·34	1·61	6·7 †
	7·59	0·52	1·62	6·9
16·6		2·59	1·56	7·1
11·2		1·80	1·61 †	6·9
8·31		1·32	1·59	7·1 *
3·55		0·56	1·58	6·5
		average	1·6	6·9

* From slope.
†From intercept.

Thus the reaction mechanism can be expressed as equation (15) and/or (16):

$$CuRX^+ + H^+ \xrightarrow{k_1} CuX^{2+} + HR \qquad (15)$$

$$CuX^{2+} + Y' \rightleftharpoons CuY^{2-} + X'$$

$$CuRX^+ + X' \xrightarrow{k_2} CuX_2^{2+} + R^- \qquad (16)$$

$$CuX_2^{2+} + Y' \rightleftharpoons CuY^{2-} + 2X'$$

The rate-determining steps are the release of PAN from Cu–PAN–phen by attack by hydrogen ion or 1,10-phenanthroline. Then the Cu–phen complex produced undergoes the fast substitution with EDTA.

Comparison of k, k_1 and k_2 shows the rate of substitution of Cu–PAN–phen with EDTA is much faster than that of Cu–PAN. This is probably because copper–PAN bonds in the mixed-ligand complex are weaker than in the Cu–PAN–Y reaction intermediate because of Jahn-Teller distortions. This is suggested by the reduced stability of CuRX compared with CuR (with respect to loss of R):

$$K^R_{CuRX} = \frac{[CuRX]}{[CuX]\,[R]} = 10^{12\cdot2}$$

$$K^R_{CuR} = \frac{[CuR]}{[Cu]\,[R]} = 10^{15\cdot6}.$$

The value for K^R_{CuR} is from reference 5.

Usually copper is titrated at pH 5–6 and the addition of a small amount of 1,10-phenanthroline, *i.e.* 10^{-5}–$10^{-6}M$, is enough to accelerate the rate of colour change of PAN at the equivalence point.[4]

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SUBSTOICHIOMETRIC NEUTRON-ACTIVATION DETERMINATION OF GALLIUM

EXTRACTION FROM HCl WITH TRI-n-OCTYLPHOSPHINE OXIDE IN CYCLOHEXANE

J. W. MITCHELL and J. E. RILEY, JR.

Bell Laboratories, Murray Hill, New Jersey 07974, U.S.A.

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Summary—A highly precise method for the determination of traces of gallium by neutron activation is described. Conditions for the extraction of gallium are reported and general requirements for substoichiometric isolation of cations from HCl with neutral donors are discussed. The mean of determinations of gallium at concentrations of 40 ng/ml in a solution prepared by dissolving a standard reference aluminium alloy was 213·9 ± 1·3 ng. The relative standard deviation and the total error of the method (based on the SRM value) were 0·7 and 10·5% respectively.

Substoichiometric separations have been applied frequently in activation analyses.[1–5] Although most extraction methods described previously have been based on the use of strong chelating agents, several investigators have introduced other extraction systems for this purpose.[6–9] Recently, the range of application of substoichiometric methods was extended by using a substoichiometric amount of a strong neutral donor in the presence of excess of chelating ligand.[10,11] In this approach, elements not capable of forming strong primary chelates can be extracted substoichiometrically. The authors recently reported the use of tri-n-octylphosphine oxide (TOPO) in cyclohexane for the substoichiometric extraction of cations from hydrochloric acid.[12] A method for the determination of Ga^{3+}, based on this extraction system, is described in this paper.

EXPERIMENTAL

Reagents

Tri-n-octylphosphine oxide was used without further purification: fresh 0·10*M* stock solutions were prepared by dissolving the appropriate amount in practical-grade cyclohexane. Gallium (III) solution (2 mg/ml) was prepared by dissolving the zone-refined metal in nitric acid which had been purified by sub-boiling distillation, and was standardized with EDTA. Similar procedures were used to prepare other stock solutions of cations. A 1·0113-g sample of the reference material, SRM 85b, from the National Bureau of Standards, was dissolved in a 1:1 mixture of *aqua regia* and hydrofluoric acid and diluted to 100 ml. ^{72}Ga tracer was made by irradiating suitably diluted aliquots of a gallium nitrate solution for up to 1 hr in the pneumatic-tube facility of the Industrial Reactor Laboratories, Plainsboro, New Jersey.

General extraction and counting procedures

Aqueous phases were prepared by sequentially adding appropriate amounts of hydrochloric acid, gallium tracer and carrier to a series of 10-ml volumetric flasks and diluting to volume with water. The water used was purified by ion-exchange and double distillation from a quartz still. Organic phases (0·001–0·01*M* TOPO) were prepared by diluting aliquots of 0·1*M* stock solution of TOPO with cyclohexane that had previously been equilibrated with appropriate aqueous hydrochloric acid solutions. Five-ml aliquots of each phase were then pipetted into 15-ml centrifuge tubes and extracted by shaking all the tubes simultaneously on a wrist-action shaker for up to 1 hr. Most extractions were complete within 15 min. After centrifugation to separate the phases completely, 4-ml aliquots of each phase were pipetted into 17 × 100 mm polypropylene test-tubes for counting. The 0·835-MeV gamma-ray of ^{72}Ga was monitored by a 3 × 3 in. well-type NaI(Tl) detector in conjunction with a Northern Scientific Model 710 Pulse Height Analyser. Standard procedures were used for photopeak integration and decay correction.

Neutron activation analysis

The dissolved sample of SRM 85b, an aluminium alloy, was diluted with 0·5*M* nitric acid so that the final gallium concentration was 384 ng/ml, based upon the certified value. Five ml of the resulting solution were irradiated for 20 min along with a standard solution of gallium (366 ng/ml). The comparison standard was prepared by exact dilution of an analysed carrier solution.

Following the irradiation, two bulk aqueous phases were made. The reference solution, containing 5·0 ml of the activated SRM solution, 5·5 ml of gallium carrier ($2{\cdot}62 \times 10^{-2}M$), and 28·5 ml of concentrated hydrochloric acid was diluted to 50 ml with water. According to the certified SRM value, the $^{72}Ga^{3+}$ concentration in this aqueous phase was 38·4 ng/ml. The "standard" aqueous phase was prepared by mixing 1·0 ml of activated gallium standard, 5 ml of the non-activated SRM solution ([Ga] = 384 ng/ml), 5·5 ml of gallium carrier, 28·5 ml of concentrated hydrochloric acid, and diluting to 50 ml with water. Five 5-ml aliquots of each bulk solution were extracted for 20 min with 5 ml of $2 \times 10^{-3}M$ TOPO.

THEORY OF SUBSTOICHIOMETRIC EXTRACTION OF CATIONS FROM HYDROCHLORIC ACID WITH TOPO

The necessary conditions for satisfactory substoichiometric extraction of cations that form neutral

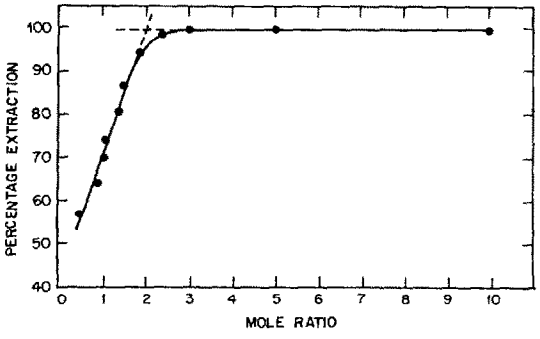

Fig. 1. Dependence of extraction of Ga^{3+} on the mole ratio of TOPO to gallium

chloride complexes of the form MCl_n or $HMCl_{(n+1)}$, where n is the charge on the cation, can be derived in the following way. Only the extraction of MCl_n *via* solvation with a strong oxygen donor, TOPO for example, is treated. The overall extraction constant (K_{ex}) for the two-step process

$$M^{n+} + nCl^- \rightleftharpoons MCl_n \quad (1)$$

$$MCl_n + m\text{TOPO}_{(0)} \rightleftharpoons MCl_n.m\text{TOPO}_{(0)} \quad (2)$$

is given by

$$K_{ex} = \frac{[MCl_n.m\text{TOPO}]_0}{[MCl_n]\,[\text{TOPO}]_0^m} \quad (3)$$

where $[MCl_n.m\text{TOPO}]_0/[MCl_n] = K_D$, the distribution ratio of the cation. It is assumed here that at $[HCl] \gg [M^{n+}]$ (5·0M compared to 0·002M) MCl_n or $HMCl_{(n+1)}$ is predominantly present in the aqueous phase.

At low ($\leq 10^{-1}M$) but excessive concentrations of TOPO in the organic phase, the primary cation-containing species in the organic phase has been shown to be $MCl_n.2\text{TOPO}$ for most bi- and tervalent cations.[13,14] Mole-ratio studies of the extraction of gallium into organic phases containing excess of TOPO showed complete extraction upon formation of the disolvated complex (see Fig. 1).

Under substoichiometric conditions, *i.e.*, $[MCl_n]$ in the aqueous phase > [TOPO] in the organic phase, the monoadduct, $MCl_n.\text{TOPO}$, should be predominantly formed since the stability for the Lewis acid–base reaction

$$MCl_n + \text{TOPO}_{(0)} \rightleftharpoons MCl_n.\text{TOPO}_{(0)} \quad (4)$$

should be considerably larger than the constant for the second reaction

$$MCl_n.\text{TOPO}_{(0)} + \text{TOPO}_{(0)} \rightleftharpoons MCl_n.2\text{TOPO}_{(0)}. \quad (5)$$

If 50% of the stoichiometric amount of TOPO is originally present in the organic phase, and it is reacted to the extent of at least 99%, equation (3) becomes

$$K_{ex} = \frac{1}{0{\cdot}01C_{\text{TOPO}}} \quad (6)$$

where C_{TOPO} is the original organic-phase concentration of the substoichiometric reagent. During activation analysis 1–10 mg of carrier is used which requires $10^{-3} - 10^{-1}M$ solutions of the substoichiometric reagent. K_{ex} must then be $\geq 10^5$ to satisfy the conditions previously mentioned.

The extraction constant for gallium, $\log K_{ex} = 4{\cdot}7$, was determined from the dependence of the distribution ratio on the concentration of TOPO in the range 10^{-4}–$10^{-1}M$. Since the slope of the graph of $\log K_D$ *vs.* $\log$ [TOPO] at a constant hydrochloric acid concentration of 3·0M was measured as 1·7, the K_{ex} value estimated from these data is lower than the actual constant for the diadduct reaction.

Other conditions must be satisfied to achieve substoichiometric extractions. The solubility of $MCl_n.\text{TOPO}$ in the organic phase cannot be exceeded. The solvent should not be appreciably soluble in a hydrochloric acid medium and must not be able to extract MCl_n unless the solvating reagent is present. The primary reaction of TOPO with the metal complex should be sufficiently strong for secondary reactions, for example extraction of hydrogen chloride *via* hydrogen-bonding, not to compete effectively for the adduct.

RESULTS AND DISCUSSION

The substoichiometric extraction curve in Fig. 2 shows a reasonably constant extraction of gallium-(III) from 5·5–7·0M hydrochloric acid. At the optimum acidity of 6·5M, gallium is rapidly extracted under substoichiometric conditions. The γ-ray activity from $^{72}Ga^{3+}$ extracted into the organic phase was 27817, 28320, 27611 and 27525 cpm for 10, 20, 30 and 65 min extraction, respectively. Shaking on a wrist-action mechanical shaker for 15 min was sufficient for equilibrium to be established.

Freshly prepared stock organic and aqueous phases were aged for various periods and equilibrated to determine the stability of the solutions. The γ-ray activity in the organic phase was 13642, 13867, 13953

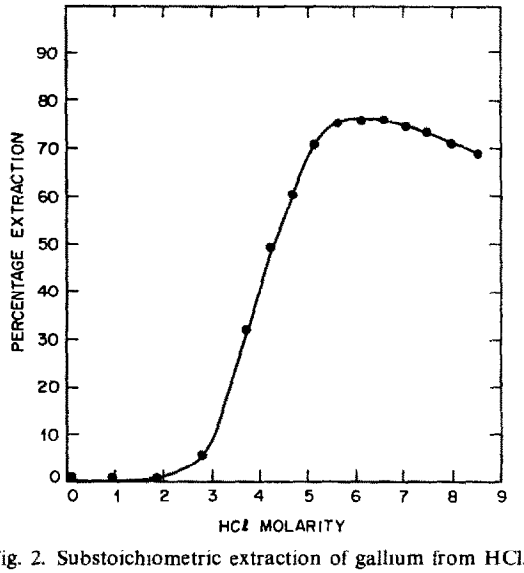

Fig. 2. Substoichiometric extraction of gallium from HCl.

Table 1. Reproducibility of substoichiometric extraction of Ga^{3+}

Tube no.*	^{72}Ga activity isolated in organic phase, *cpm*	Extraction, %
1	101008	21·04
2	104437	21·79
3	102032	21·29
4	102212	21·38
5	101338	21·42
6	99462	21·13
Mean:	101749	21·34
σ:	1641	0·26
Relative σ:	1·6%	1·2%

* $V_{aq} = V_{org} = 5$ ml, $[Ga^{3+}] = 0{\cdot}0037M$, [TOPO] = $0{\cdot}001M$

and 14320 cpm for ages of 0, 0·6, 1·3 and 3·0 hr, respectively.

Precision for the extraction of gallium(III) from a series of aqueous phases of the same volume and initial $[Ga^{3+}]$ is reported in Table 1. When the aqueous phase volume and $[Ga^{3+}]$ were varied, the relative standard deviation increased from 1·6 to 4·3% (see Table 2).

The presence of 10 ppm of various cations in the aqueous phase caused no significant influence on the substoichiometric extraction of gallium, as shown by the interference factors given in Table 3 for 1 and 10 ppm of various cations. By addition of carrier after the neutron activation, the concentration of gallium can easily be adjusted to $\geq$ 100 times the amount of various trace elements present in the sample. In this way, interference from most trace elements can be reduced to an insignificant level during the substoichiometric separation. A large excess of phosphate or arsenate enhances the extraction of gallium. However, in analysis of GaP or GaAs this increased extraction can be compensated for by adding to the standard an amount of non-activated sample equal to that of the irradiated sample undergoing analysis.

Solutions containing known increasing amounts of $^{72}Ga^{3+}$ were extracted substoichiometrically and gave a linear response over a broad concentration range (about 3 orders of magnitude). The accuracy

Table 2. Substoichiometric extraction of Ga^{3+} from aqueous phases of different volumes

Volume of aqueous phase*, *ml*	^{72}Ga activity isolated in organic phase, *cpm*
2	18088
3	17848
4	17939
4·5	19029
5	20062
5·5	17839
6	18000
7	18125
Mean:	18366
σ:	785
Relative σ:	4·3%

* $[Ga^{3+}] = 0{\cdot}007M$, [TOPO] = $0{\cdot}001M$, $V_{org} = 5$ ml.

Table 3. Effect of presence of other ions on the extraction of Ga^{3+}

Cation	Interference factors* 1 ppm†	10 ppm†
Al^{3+}	1·01	1·01
Sc^{3+}	—	0·98
Fe^{3+}	1·00	1·01
Co^{2+}	1·01	1·00
Cu^{2+}	—	1·00
Zn^{2+}	—	1·00
Ge^{4+}	1·00	1·00
As^{5+}	1·00	0·97
Cd^{2+}	—	1·00
In^{3+}	1·01	1·01
Sb^{3+}	0·98	0·98
Tl^{3+}	—	0·99
PO_4^{3-}	1·07§	
AsO_4^{3-}	1·23‡	

* I.F. = the ratio of ^{72}Ga activity in org. phase when test ion was present to ^{72}Ga activity in org. phase when no ion was present in aqueous phase.

† Concentration of cation in aqueous phase; [HCl] = $6{\cdot}5M$, $[Ga^{3+}] = 1000$ ppm ($0{\cdot}01M$).

§ $[PO_4^{3-}] = 0{\cdot}03M$.

‡ $[AsO_4^{3-}] = 0{\cdot}03M$.

of the method was determined by analysing a standard reference material. Following the activation of a solution obtained by dissolving the aluminium alloy, SRM 85b, containing 3·99% Ca, 1·49% Mg, 0·61% Mn, 0·24% Fe, 0·211% Cr, 0·18% Si, 0·084% Ni, 0·030% Zn, 0·022% Ti, 0·021% Pb, 0·019% Ga and 0·006% V, ^{72}Ga and carrier were substoichiometrically extracted. The activities of the organic phases, measured in a well-type sodium iodide detector, are reported in Table 4. Highly precise separations (0·7% relative standard deviation) and good accuracy were obtained. The area under the 0·835-MeV photopeak of ^{72}Ga indicated sensitivity sufficient for determining 2·0 ng of gallium.

The procedure described here can be used to measure low ng/ml concentrations of gallium in samples that require separation of gallium before measurement of the γ-activity from ^{72}Ga. Gallium in buffered solutions (K^+ and Na^+ salts) used during anodic oxidation of gallium phosphide to produce passivating masking or insulating films, can be measured.[15,16] The high precision and accuracy of the method at the trace level suggests that the determination of

Table 4. Determination of gallium in aluminium alloy*

Extraction no	^{72}Ga activity in standards, *cpm*	^{72}Ga activity in samples, *cpm*	Ga found, *ng*	Ga found, %
1	13828	16285	212·3	0·021
2	13864	16348	213·2	0·021
3	13940	16320	212·8	0·021
4	14206	16486	215·0	0·021
5	14338	16567	216·0	0·022
	14035†	16401§		0·021‡

* SRM 85b.

† Mean, $\sigma = 225 = 1{\cdot}6\%$ relative.

§ Mean, $\sigma = 120 = 0{\cdot}7\%$ relative.

‡ Mean error for determination of Ga^{3+} in soln. containing 40 ng/ml = 10·5%.

major amounts of gallium, for example in establishing the amount of gallium in phosphides and arsenides, can be accomplished by a substoichiometric isotope dilution method based on this solvent extraction system.

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DETERMINATION OF LOW-LEVEL CARBON IN TUNGSTEN WIRE BY COMBUSTION GAS CHROMATOGRAPHY

PETER CUKOR®, CARMINE PERSIANI and ARTHUR RUSSELL

General Telephone and Electronics Laboratories, Waltham, Mass. 02154, U.S.A.

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Summary—A combustion gas-chromatographic technique for the determination of trace amounts of carbon in tungsten wire is described. The method involves the oxidation of the tungsten wire in a quartz oven at 1000°. The liberated gases are swept into a cooled sample-loop in a gas-sampling valve. Upon completion of the oxidation process, the contents of the sample loop are introduced into a gas chromatograph. The use of a 3-ft long column of silica gel allows separation of carbon dioxide and oxygen. The presence of oxygen requires that the hot-wire detector used be equipped with filament-protecting circuitry. Calibration curves are constructed by using organic and tungsten carbide standards. A limit of detection of 0·2 μg carbon can be achieved with a precision of better than 10%.

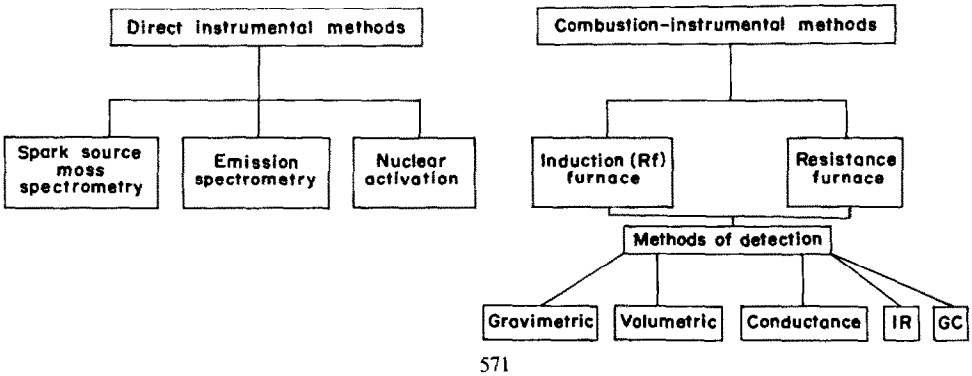
The presence of low level impurities can profoundly affect the chemical and physical properties of tungsten wire and consequently influence its behaviour as a filament in an incandescent lamp. Carbon is an element of particular concern since large amounts of it in the form of graphite or as a viscous organic compound are used to prevent oxidation in the hot drawing of tungsten. The result of this treatment produces a significant carbon deposit on the surface of the wire with the formation of tungsten carbide below the surface. In the subsequent process of converting such tungsten wire into lamp filament, most of the carbon is removed by various heat-treatment operations. It has been shown that large quantities of carbon adversely affect the performance of a filament and reduce its life.[1] It has also been proposed, however, that trace quantities of carbon are beneficial to filament performance because they minimize oxidation and deterioration due to the presence of traces of water vapour in the lamps.[2] In order to investigate the effect of various amounts of carbon on filament performance, a method capable of detecting traces of carbon in tungsten wire and filaments was required. In addition to possessing high sensitivity, this method must be reliable and have the capability of detecting carbon whether it is present as surface contamination or as bulk impurity. It must also be applicable to the analysis of tungsten at each step of the filament manufacturing process.

A literature search indicated that the determination of carbon in metals is normally carried out by methods which employ either direct instrumental analysis or combustion followed by instrumental analysis (see Table 1).

The sensitivity attainable by the spark-source mass spectrometer is extremely high. Unfortunately, the carbon monoxide and dioxide which are to be detected are present either in the residual gases of the vacuum system or as surface contaminants in the mass spectrometer. Thus, the background reduces the sensitivity for carbon detection. Recent work indicates that the background can be reduced considerably by using a cryogenic accessory panel to lower the background noise during measurement.[3]

The emission spectrograph has been shown to be capable of performing carbon determination at the

Table 1. Methods of carbon analysis



10 ppm level. The sample is excited in a d.c. arc and the CN bands are used for measurement.[4] Malamand describes the determination of carbon by measuring the ultraviolet emission spectrum in the region 50–100 nm.[5]

Neutron activation is unsuitable for the determination of carbon because of the element's low neutron-capture cross-section. Charged-particle activation analysis was used, however, by Rook and Schweikert,[6] who reported an ultimate detection limit at the ppM (parts per milliard) level for carbon. This method is essentially restricted to surface analysis because of the limited penetration of a charged particle.

A more attractive nuclear method uses 18-MeV photons to activate carbon. The resultant radioactivity of ^{11}C is measured with a coincidence-counting detector. Lutz and Masters[7] have performed the determinations in high-purity metals and reported carbon values of less than 1 ppm. Some interferences can be encountered if oxygen and other contaminants are present at higher levels.

Combustion methods involve the thermal decomposition of a sample in a stream of oxygen in which the carbon is converted into carbon dioxide, which in turn is measured by a suitable detection system. The combustion apparatus most often used consists of a radiofrequency induction furnace. Sometimes, however, a wire-wound tube furnace is preferred. The more frequently used detection systems are summarized in Table 1.

Gravimetric procedures have been used extensively. The sample, with an appropriate flux, is combusted in a "Globar" or similar type of furnace. The resulting carbon dioxide is collected in an absorption bulb and weighed.[8] This method is mainly suitable for samples containing not less than about 100 ppm of carbon. Volumetric methods employing the collection and measurement of carbon dioxide gas utilize similar combustion techniques, but the carbon dioxide collected is measured manometrically in gas collection vessels of known volumes.[9] The carbon content is calculated by using gas-pressure relationships.

Lower levels of carbon may be determined by using the various instruments manufactured by the Laboratory Equipment Corporation (LECO). In these instruments, combustion takes place in pure oxygen in a crucible heated by high-frequency induction, and the liberated carbon dioxide is measured in various ways. One model of the instrument uses conductometric detection by passing the carbon dioxide through a solution of barium hydroxide and measuring the change in resistivity of the solution due to the formation of barium carbonate. Other LECO models are equipped either with gas-chromatographic detection systems utilizing a thermistor-type Wheatstone bridge as a sensor, or with infrared detection systems employing gas cells. These instruments provide rapid, reliable analysis for carbon at trace level (2 μg) and above in a variety of matrices. One of the problems encountered in applying these instruments to refractory metals is the incomplete loading in a radiofrequency induction coil. As a result, the necessary temperature for complete combustion is not obtained. Accelerators, such as tin or iron, can be used to promote complete combustion; however, these materials always contain some carbon. Thus, a blank is introduced which lowers the sensitivity for carbon detection.

The combustion systems which do not utilize induction furnaces are not subject to these errors, but they are severely limited in terms of the maximum temperature they can attain. For this reason, combustion in a conventionally-heated resistance furnace is usually restricted to the determination of carbon in organic materials. Often the furnace is coupled with a gas chromatograph, to take advantage of the high detection-sensitivity of this instrument.[10]

Tungsten wire and tungsten carbide oxidize at temperatures between 600 and 1000°. It should therefore be possible to use a conventionally heated quartz furnace in conjunction with a gas chromatograph to determine trace amounts of carbon in tungsten wire samples. This paper reports the development of such a method. In its final form, the method can detect 0·2 μg of carbon (in a 0·5-g sample) with a precision of better than 10%.

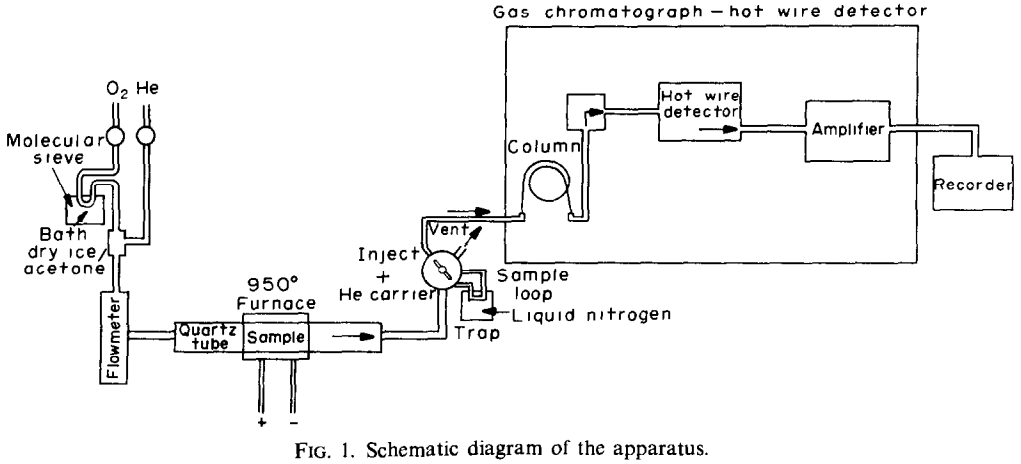


FIG. 1. Schematic diagram of the apparatus.

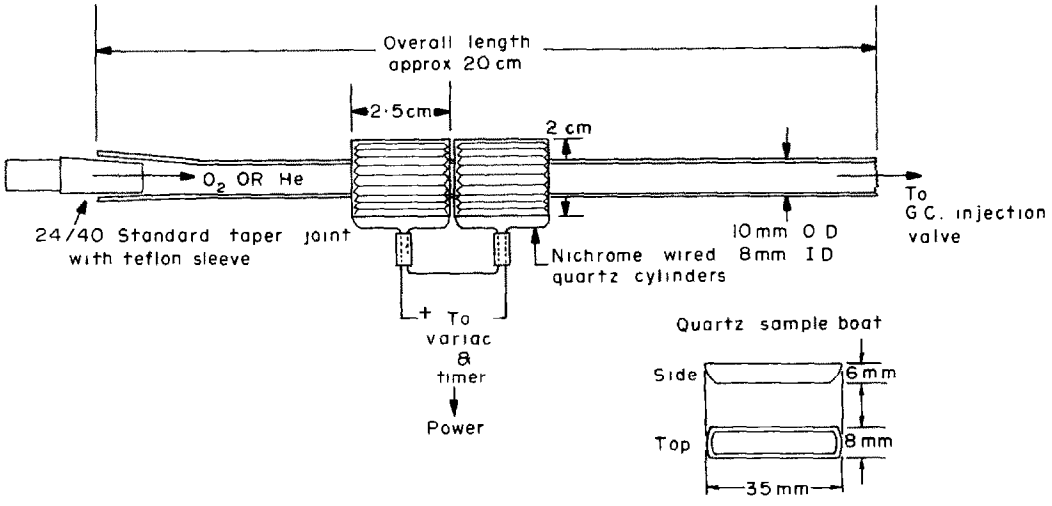


FIG. 2. Detailed drawing of combustion oven.

EXPERIMENTAL

Apparatus

The schematic diagram of the apparatus used is shown in Fig. 1. The combustion tube and boats were fabricated from "Supersil" quartz and are shown in Fig. 2. Heating was accomplished by means of a small tube furnace heated with nichrome wire surrounding the quartz tube and controlled by a "Variac" and timer. Copper tubing with "Swagelock" fittings was used for all connections to the gas-sampling valve and gas chromatograph (GC). Temperature readings were checked with a Leeds & Northrup potentiometer.

Gas-chromatographic analyses were performed with a Perkin–Elmer Model 900 gas chromatograph equipped with a six-port injection valve Model 154-0068 containing a 14-cm long, 0·3-cm bore copper sample-loop. It is absolutely essential that the gas-sampling valve be free from leaks in spite of the extremes in temperatures (from −180 +150 to +50°) it is subjected to during the procedure. An Alltech Associates six-port valve was also evaluated and was found to be reliably leakproof. The GC detector was a hot-wire thermal-conductivity cell equipped with a protective circuit to prevent filament burn-out.

Operating conditions

The column used was a 3-ft long, 3-mm bore, stainless-steel tube packed with Biorad silica gel (100–200 mesh). Injection port temperature: 60°. Column temperature: 60° isothermal. Manifold temperature: 150°. Detector: operated at 150° and 225 mA filament current. Helium carrier-gas flow-rate: 40 ml/min; Oxygen purifier trap: molecular sieve 5A maintained at −75° during operation, purged overnight with helium at 50°. Oxygen flow-rate: 100 ml/min. Helium purge-gas flow-rate: 100 ml/min. Volume of sampling loop: 1 cm^3.

Reagents

Tungsten carbide secondary standard, previously found by classical gravimetric combustion technique to contain 6% carbon. Potassium hydrogen phthalate NBS standard, prepared so as to contain 5 μg of carbon per 100 μl of solution. Etch solution consisting of 50 parts of hydrofluoric acid and 1 part of nitric acid. Matheson "Ultra High Purity Grade" oxygen and "High Purity Grade" helium.

Procedure

Weigh the sample into a quartz boat, put this into the quartz furnace tube and purge for at least 5 min with purified oxygen, venting it through the sample injection valve (see Fig. 1). Cool the sample loop with liquid nitrogen (a polystyrene cup can be used instead of a Dewar flask). After cooling the sample loop, heat the furnace around the combustion boat. The furnace temperature should be above 900° and attained in less than 1 min. Burn the sample for 5 min in oxygen (more or less combustion time may have to be used, depending on sample size, matrix, and oxygen flow). After the heat cycle, immediately purge with helium for 30 sec. Turn the sample valve to the injection position and remove the liquid-nitrogen trap. Heat the sample loop to drive off the sample. The attenuation and detector-current settings will have to be monitored because of the great difference between the amounts of oxygen and carbon dioxide passing through the detector. Upon completion of the run, heat the column at 120° for 10 min. Determine the carbon dioxide from the peak area and calculate the amount of carbon by means of the calibration curve.

Sample preparation

Calibration curves. Aliquots of potassium hydrogen phthalate solution containing 1–20 μg of carbon were transferred by micropipette into quartz boats. The water

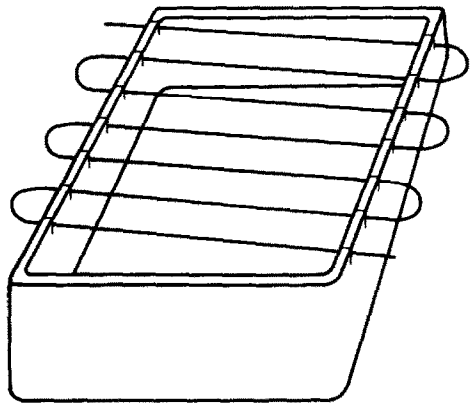


FIG. 3. Plastic holder used in etching tungsten wire (diagrammatic).

was evaporated under an infrared lamp. The boats were placed in the furnace and their contents were combusted and analysed. Various amounts of tungsten carbide powder, from 5 to 20 μg in carbon content, were weighed into quartz boats on a microbalance. The boats were loaded into the furnace and their contents were analysed.

Wire A. The wires were free from splits (hairline cracks) and were chopped to uniform length, blended, etched with potassium hydroxide solution, and electropolished. Etching and electropolishing removed about 20% of the original weight.

Wire B. The wire was heated for 2 min in a reducing atmosphere at 2500°.

Wire C. The wire was etched with a mixture of 50 parts of hydrofluoric acid and 1 part of nitric acid. The amount of material removed was determined by weighing the samples before and after etching. The diameter of the wire was measured with a precision micrometer before and after etching. Etching was accomplished by using a jig prepared by cutting off the top and bottom portions of a square cross-section polyethylene reagent bottle. Equally spaced slots were cut in opposite sides of the jig and a single strand of wire was woven back and forth between them (Fig. 3). The whole assembly was placed in a plastic beaker containing the etching solution. Etching was quenched after the desired time by copious washing with water. The wire was dried and removed from the jig. The portions of wire which were in contact with the plastic during etching were cut out and discarded. This etching procedure yielded considerably better precision than the conventional approach in which small strands of the wire were immersed in the etching solution.

RESULTS AND DISCUSSION

Typical chromatograms are presented in Fig. 4. Figure 4(*a*) shows the separation which can be

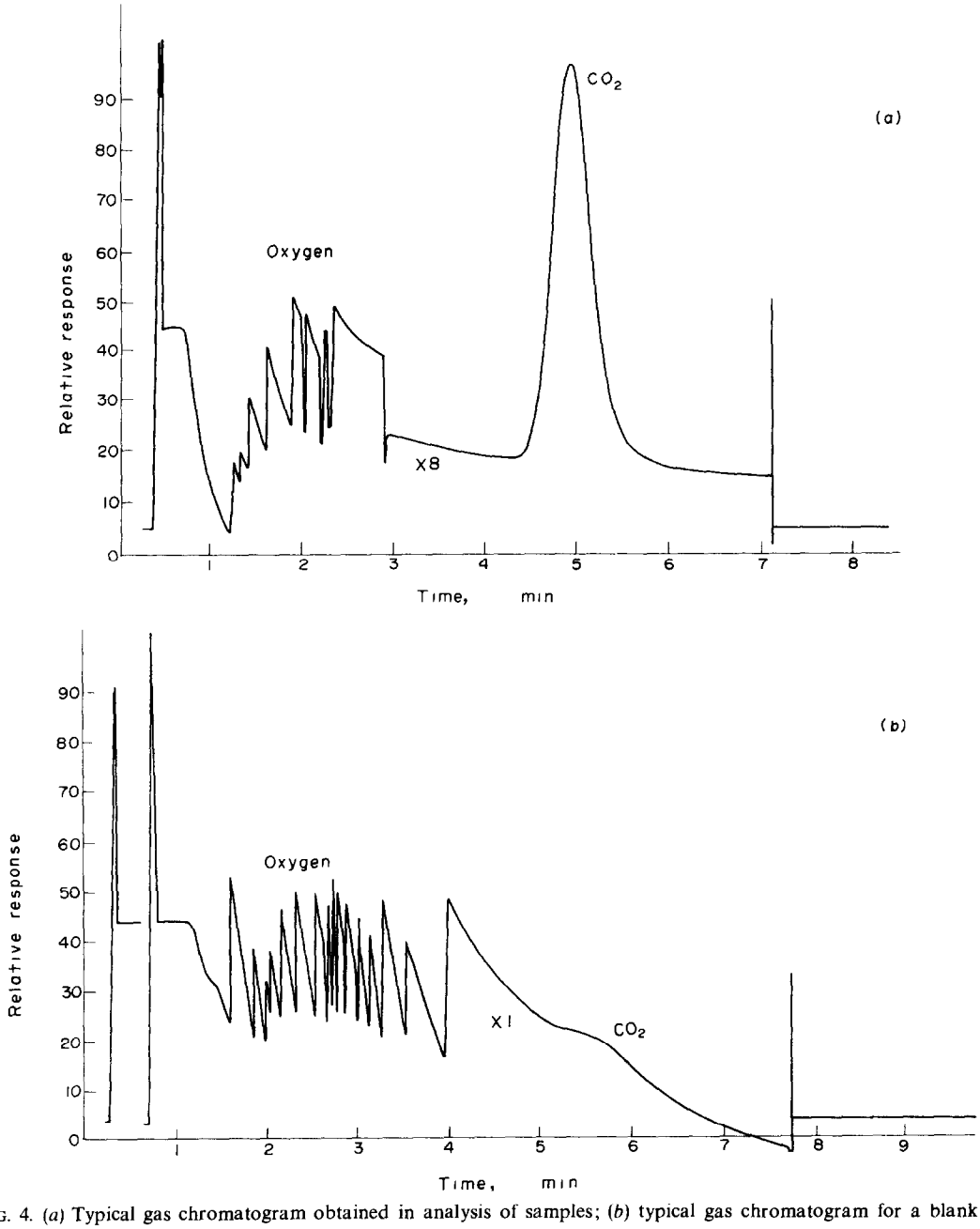


FIG. 4. (*a*) Typical gas chromatogram obtained in analysis of samples; (*b*) typical gas chromatogram for a blank run.

Table 2. Results obtained on typical tungsten samples

Sample	Sample size, *g*	Carbon content, *ppm*	Average, *ppm*
Wire A	0·150	12, 12, 17, 18, 19	15·6
Wire A	0·500	13, 14, 15, 14, 15, 15, 14	14·3
Wire B	0·250	10, 11, 10, 11	10·5
Wire C, unetched	0·100	1400	1400
Wire C, etched	0·100	109, 110, 158	126

achieved between the carbon dioxide and oxygen. The carbon dioxide is readily detected in the presence of a relatively high level of oxygen. Figure 4(*b*) is a chromatogram representing the total background signal of the system. A calibration curve obtained by using tungsten carbide and potassium hydrogen phthalate standards was a straight line passing through the origin and exhibited a slope of 11·5 cm^2 peak area per μg of carbon.

The results of the analyses of wire samples are summarized in Table 2. It can be seen that, for low carbon content, optimum precision is attained when using sample weights of at least 0·25 g. With a sample weight of 0·15 g, the relative standard deviation is 22%, while at sample weights of 0·25 and 0·5 g, it is 6%.

The determination of the carbon content of tungsten wire is complicated by the inhomogeneity of the carbon distribution in the wire, as shown by the dependence on the degree of etching to which the sample has been subjected. It is likely that this circumstance is responsible for discrepancies found in the comparison of analytical results from different laboratories. It is essential that this be understood and that a standardized etching procedure be adopted as part of sample preparation, in order to obtain agreement among different laboratories. Furthermore, agreement must be reached on the extent of etching to be performed before analysis.

In the course of generating the calibration curves, it was found that the background signal corresponded to 0·1 μg of carbon. The limit of detection is often defined as the signal that is twice the noise level. According to this definition, the limit of detection of the method is 0·2 μg of carbon. One very important factor in maintaining the blank at a low level is the low-temperature molecular-sieve trap used to remove organic impurities from the oxygen gas. Mass spectrometric analysis of the oxygen used showed the presence of about 20 ppm of hydrocarbons in the gas. These organic materials are converted into carbon dioxide while passing through the heated oven and yield a high blank having a magnitude proportional to the heating time. The use of a molecular-sieve trap eliminated this large source of background error.

A crucial operating variable was found to be the combustion time. Ignition for too short a time produces low results, probably because of incomplete liberation of the carbon from the tungsten matrix. Heating for a prolonged period also leads to slightly lower results, probably owing to aerosol formation in the sample loop. The optimum heating time has to be determined for each type of sample. Tungsten carbide powder, for instance, yielded a relative response of 73, 110 and 100 when 2·5, 5·0 and 7·0 min heating times were used with similar sample sizes. The optimum heating time for most samples was between 5 and 7 min.

The gas-sampling valve also serves as a preconcentration cold-trap. During combustion, the sample loop is maintained at −180°, while during sample introduction, its temperature is elevated to about 150°. The Perkin–Elmer gas-sampling valve did not give completely leak-free operation when subjected to these extreme temperatures. Alltech Associates manufacture a gas-introduction valve free from O-rings and containing a plastic rotor resistant to high temperatures. At an advanced stage of this project, this valve was evaluated and was found to be superior in performance. The geometry of this valve required the establishment of new optimum operating conditions, *i.e.*, flow-rates, column temperature.

The size and shape of the sample loop has been optimized. The use of larger volume traps yielded larger amounts of condensed oxygen, which was then difficult to separate from the carbon dioxide. Smaller traps did not provide enough volume to condense all the carbon dioxide; consequently, low results were obtained when they were used.

In the course of the development of this method, a sample loop without a packing was found to be optimal, for it produced relatively narrow carbon dioxide peaks. Packed sample loops yielded flat wide peaks. The use of an empty sample loop required the application of liquid-nitrogen cooling. Dry ice–acetone mixture (−80°) failed to condense all the carbon dioxide while ethanol–liquid nitrogen mixture (−110°) did not prove to be reliable in providing constant temperature. The use of liquid-nitrogen cooling resulted in the condensation of some oxygen in the sample loop together with the carbon dioxide. The oxygen–carbon dioxide mixture was subsequently introduced into the gas chromatograph, where the two gases were separated. Passage of the oxygen through the column and detector demanded certain precautions.

The columns found most satisfactory for the separation of oxygen and carbon dioxide were packed either with silica gel or with Porapak T. Either of these columns had a useful life of about 40 determinations but exhibited deterioration. The Porapak T packing, which is a styrene–divinylbenzene copolymer, was slowly attacked by oxygen, and carbon dioxide was formed, leading to an increasingly large blank value. The silica gel column's performance also slowly deteriorated, smaller and smaller responses being obtained for the same size of sample. A set of calibration curves obtained at various times during the useful life of a silica gel column, clearly showed the deterioration. These observations make it mandatory that a working curve be prepared on each day of operation. In our experiments, a new column was

prepared after every forty analyses. It is possible, however, to recondition a column by heating it overnight at 300°.

The hot-wire thermal-conductivity detector used has to be of the type which is equipped with a protective circuit so that relatively large amounts of oxygen passing through it will not burn out the tungsten filaments.

The sensitivity of the method was dramatically increased by using the flame-ionization detector instead of the thermal-conductivity detector. The carbon dioxide formed during combustion was converted into methane, followed by measurement with a flame-ionization detector.[11] The conversion into methane was achieved by using a nickel powder catalyst at 280°. A stainless-steel tube 12·7 cm long and 3 mm in diameter was packed with 100-mesh nickel powder and inserted in the manifold of the Perkin–Elmer 900 GC between the flame-ionization detector and the T-fitting used for mixing the column effluent with the hydrogen detector-gas. The manifold oven was maintained at 280°. Thus, the hydrogen gas served a dual purpose; it reacted with carbon dioxide to form methane and also provided the fuel for the flame jet of the detector. This scheme was, however, abandoned because the oxygen passing through the gas chromatograph poisoned the catalyst after a few determinations, necessitating lengthy regeneration in hydrogen gas. Should the trapped oxygen and carbon dioxide be separated before sample introduction, for instance by gradual elution of the gases from a packed trap, the catalytic conversion approach would become feasible. It should be pointed out, however, that no tungsten sample has so far been found which required greater sensitivity of detection than that attainable with the hot-wire thermal-conductivity detector.

Although this work is primarily concerned with the determination of carbon in tungsten, in principle the method could be extended to the determination of carbon in other matrices. The method in its present form may be used for the analysis of any metal that oxidizes in an oxygen atmosphere at temperatures below 1100°. This maximum temperature may be increased by substituting a platinum-wound alumina furnace for the present combustion tube, provided that the new furnace does not introduce a serious blank problem.

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ANION-EXCHANGE SEPARATION OF PLUTONIUM IN HYDROCHLORIC–HYDROBROMIC ACID MEDIA*

R. P. LARSEN and R. D. OLDHAM

Argonne National Laboratory, Argonne, Illinois 60439, U.S.A

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Summary—Plutonium can be rapidly and selectively separated from the elements that interfere in its radiochemical determination, by the use of hydrobromic acid in a hydrohalic acid anion-exchange separation procedure. Plutonium(IV) and (VI) are adsorbed onto the resin column from 9*M* hydrochloric acid, interfering elements such as americium and thorium are washed from the column with 9*M* hydrochloric acid, and the plutonium is reduced to plutonium(III) and washed from the column with 11*M* hydrobromic acid. Interfering elements such as uranium and neptunium, which are adsorbed onto the column from 9*M* hydrochloric acid, are retained there during the hydrochloric and hydrobromic acid washes. This system would also appear to provide the means for effectively separating plutonium from those elements that commonly interfere in such chemical methods of analysis as redox titration.

In radiochemical determinations of plutonium, the technique most frequently used to separate the plutonium from the other constituents of the sample is anion-exchange, the media most frequently used being nitric and hydrochloric acids. Plutonium(IV) is adsorbed onto a strongly basic anion-resin such as Dowex-1 from strong nitric acid, the resin is washed first with strong nitric acid and then with concentrated hydrochloric acid, and the plutonium is eluted with dilute hydrochloric acid containing a trace of fluoride. This approach is very selective for separation from inert sample constituents but the time required to obtain an adequate separation from most of the other actinide elements is inordinate. Anion-exchange separations of plutonium in these and other media have been reviewed by Coleman.[1]

A selective and rapid anion-exchange separation procedure has been developed for the separation of plutonium from the elements that interfere in radiochemical determinations. The media are hydrochloric and hydrobromic acids. Plutonium(IV) and (VI) are adsorbed onto the resin from concentrated hydrochloric acid, the resin is washed with concentrated hydrochloric acid, and plutonium(IV) and (VI) are reduced to plutonium(III) and eluted from the resin with concentrated hydrobromic acid.

Anion-exchange separations of plutonium in hydrochloric–hydrobromic acid media would also appear to be particularly applicable to the analysis of materials in which plutonium is a major constituent.

EXPERIMENTAL

Column preparation, special reagents, and materials

The ion-exchange resin used in this investigation was Dowex-1 X2, 100–200 mesh (Bio-Rad Laboratories, Richmond, California). The columns used had a bore of 1 cm. The flow-rate was controlled at 1 ml/min, by the use of a capillary stop-cock at the bottom of the column. A small plug of glass wool was used to prevent the resin from entering the stop-cock.

To prepare a column the resin was treated with 9*M* hydrochloric acid for about 5 min and then washed into the column with more acid. After the resin had settled, its height in the column was about 5 cm. To keep the resin bed from being disturbed during operation of the column, glass beads (~1 cm depth, 80–120 mesh) were added to the top of the column.

Reagent grade hydrobromic acid, 9*M*, and hydrogen bromide gas were used to prepare the 11*M* hydrobromic acid. The 9*M* acid was placed in a polyethylene gas-washing tower in an ice-bath, and hydrogen bromide was passed through the system until the gas was no longer being adsorbed. The concentration of the acid produced, (check by titration with alkali) was about 14*M*. This acid was diluted to 11*M*.

Chlorine was used to prevent the reduction of plutonium (IV) to plutonium(III) by the resin in 9*M* hydrochloric acid. The chlorine was formed *in situ* by adding 30% hydrogen peroxide to 9*M* hydrochloric acid, one drop of peroxide per 10 ml of acid, and heating the solution in a covered container for 1 hr at 80–90°.[2] This acid was used to transfer samples and to wash the columns both before and after the addition of the samples.

The behaviour of plutonium, thorium, uranium and neptunium on the anion-exchange columns was established by using the alpha-emitting nuclides ^{238}Pu, ^{230}Th, ^{233}U and ^{237}Np, the activity levels being 10^2, 10^3, 10^5 and 10^2 dpm respectively. The activity measurements were made with a 2π proportional counter. When the activity levels were particularly low, the identity of the alpha-emitter was confirmed by alpha-spectrometry.

Behaviour of plutonium

To establish the effect of hydrobromic acid concentration on the retention of plutonium by the column, individual aliquots of the ^{238}Pu stock solution were evaporated to dryness with 9*M* hydrobromic acid, the plutonium was dissolved in 0·5-ml portions of 6, 9 or 11*M* acid, and transferred to columns that had been pretreated by washing them with acid of the appropriate concentration. The columns were washed with the appropriate acids and 1-ml portions of the effluents were collected,

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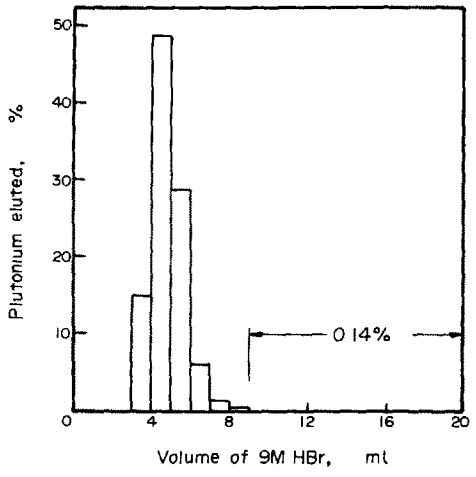

Fig 1. Behaviour of plutonium on a Dowex-1 column when introduced in and washed with 9*M* HBr.

converted into nitrate medium by heating with excess of nitric acid, plated on stainless-steel planchettes, and counted. Figure 1 shows the behaviour of plutonium in 9*M* hydrobromic acid. The behaviour in either 6 or 11*M* hydrobromic acid was not significantly different.

To establish the conditions for eluting plutonium from the column after it had been adsorbed onto the resin from hydrochloric acid, individual aliquots of the ^{238}Pu stock solution were evaporated to dryness and the plutonium was dissolved by adding 1 ml of 9*M* hydrochloric acid and 10 μl of 30% hydrogen peroxide, and heating for 1 hr. The solution was transferred to the column, which was then drained until the liquid level was at the top of the glass bead layer. This operation and three successive washes with the 9*M* hydrochloric acid–chlorine mixture brought the plutonium into contact with the resin. The column was then washed with 30 ml of the hydrochloric acid–chlorine mixture and 5-ml portions of the effluent were collected. The plutonium was eluted from the columns by washing them with 6, 9, and 11*M* hydrobromic acid, respectively, and 1-ml portions of the eluates were collected. The portions of hydrochloric and hydrobromic acid effluents were assayed for their plutonium content. Figure 2 shows the plutonium behaviour when the eluent was 9*M* hydrobromic acid The plutonium behaviour when the eluent was either 6 or 11*M* hydrobromic acid was not significantly different. A comparison of Fig. 1 with Fig. 2 shows that the adsorption of plutonium onto the resin from hydrochloric acid followed by elution with hydrobromic acid leads to tailing. However, experience has shown that more than 90% of the plutonium is always eluted by the first 10 ml of 6, 9 or 11*M* hydrobromic acid.

Behaviour of thorium

To establish the behaviour of thorium on the column, aliquots of a ^{230}Th stock solution were evaporated to dryness, the thorium was dissolved in 9*M* hydrochloric acid, and the solutions were transferred to the columns. The columns were washed with 30 ml of 9*M* hydrochloric acid and 1-ml portions of the effluents were collected and assayed. The behaviour of thorium was identical to that of plutonium in 9*M* hydrobromic acid as shown in Fig. 1. More than 99·9% of thorium was eluted in the first 10 ml of effluent.

Behaviour of uranium

To establish the behaviour of uranium on the column during the hydrochloric and hydrobromic acid washes of the column, aliquots of the ^{233}U stock solution were evaporated to dryness, the uranium was dissolved in 9*M* hydrochloric acid, and the solutions were transferred to the columns. The columns were washed first with 30 ml of 9*M* hydrochloric acid and then with 30 ml of 9*M* hydrobromic acid. 5-ml portions of the effluents being collected and assayed. The amount of uranium in each portion of hydrochloric acid and hydrobromic acid was less than 0·01% of the total. Since the first 10 ml of 9*M* hydrobromic acid contains more than 90% of the plutonium and less than 0·01% of the uranium, the decontamination factor for uranium is about 10^4. When the plutonium is eluted with 11*M* hydrobromic acid, only 0·0003% of the uranium is in the first 10 ml of acid and the decontamination factor is therefore about 3×10^5.

Behaviour of neptunium

To establish the behaviour of neptunium on a Dowex-1 column in hydrobromic acid, aliquots of the stock solution were evaporated to dryness, the neptunium was dissolved in 6, 9 or 11*M* hydrobromic acid, and the solutions were transferred to columns that had been preconditioned by washing them with hydrobromic acid of these concentrations. The columns were then washed with 30 ml of the appropriate acid; 5-ml portions of the effluents were collected and assayed. There was no significant retention of the neptunium by the column from 6 and 9*M* hydrobromic acid; there was complete retention from 11*M* hydrobromic acid. As neptunium(IV) is quantitatively adsorbed onto a Dowex-1 column from 9*M* hydrochloric acid, the adsorption of plutonium(IV) and neptunium(IV) from 9*M* hydrochloric acid followed by a wash with 11*M* hydrobromic acid is an effective means for separating these elements.

It is interesting to note that Nelson and Michaelson[3] have devised a procedure for the separation of neptunium and plutonium in hydrobromic acid media, on the cation-resin Dowex-50. In 6*M* hydrobromic acid plutonium(III) passes through the column rapidly and neptunium(IV) is adsorbed. The neptunium is eluted with 9*M* hydrochloric acid or 0·2*M* hydrofluoric acid in 9*M* hydrobromic acid.

Behaviour of americium

No experimental evaluation of the behaviour of americium was made as it is common practice to separate americium from plutonium by selectively adsorbing Pu(IV) onto a Dowex-1 column from 9*N* hydrochloric acid and washing the Am(III) through the column with this acid.

Behaviour of the elements in the natural decay series

Of the elements in the uranium and thorium natural decay series, only bismuth is not completely separated

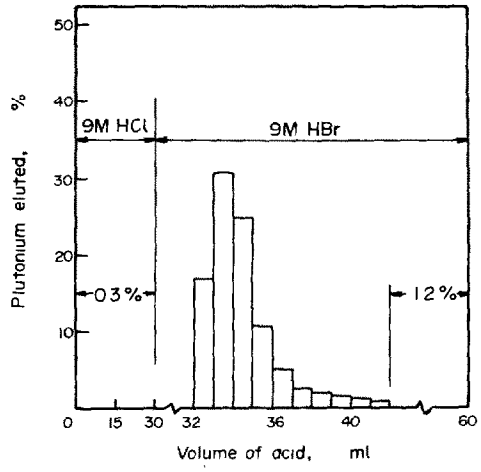

Fig. 2. Behaviour of plutonium on a Dowex-1 column when introduced in 9*M* HCl, and washed with 9*M* HCl and 9*M* HBr.

from plutonium when the plutonium is adsorbed onto the resin from concentrated hydrochloric acid and eluted with concentrated hydrobromic acid. When the plutonium is eluted with 10 ml of 9*M* hydrobromic acid the amount of bismuth eluted with the plutonium is about 5% of that present in the sample. Under a very special set of circumstances this incomplete separation from bismuth will lead to an alpha-spectrogram in which the ^{239}Pu peak is not discernible. The circumstances are a ^{239}Pu activity level that is so low that it can only be established by counting the separated plutonium for a number of days and a very high $^{210}Bi/^{239}Pu$ activity ratio. ^{210}Bi (5·0 d) is the daughter of ^{210}Pb (22 y). The ^{210}Bi which has not been separated will electroplate with the plutonium and will, during the counting period, decay to ^{210}Po (138 d). At very high $^{210}Po/^{239}Pu$ activity ratios, the ^{239}Pu peak, which is at 5·15 MeV, cannot be distinguished from the low-energy tail of the ^{210}Po peak, which is at 5·30 MeV. For samples of this type it is necessary to separate the bismuth from the plutonium on a second anion-exchange column. The hydrobromic acid solution from the first column is evaporated to near dryness, 1*M* hydrobromic acid is added, and this solution is passed through the second column. The bismuth, as well as the polonium that has grown in, is completely adsorbed onto the column and the plutonium passes through rapidly.

DISCUSSION

Chemistry of plutonium in hydrobromic acid and hydrohalic acid mixtures

As one would predict from the standard potentials of the Pu(III)–Pu(IV) and Br(−I)–Br(0) couples, elemental bromine will oxidize Pu(III) to Pu(IV) in 1*M* hydrobromic acid. The values of these potentials are 0·97 and 1·06 V, respectively. The equation for the reaction is:

$$Pu^{3+} + 1/2Br_2 + H_2O \rightarrow PuO^{2+} + Br^- + 2H^+$$

However, owing to the small difference in these potentials and the fact that the reverse reaction has a first-order dependence on the bromide-ion concentration and a second-order dependence on the hydrogen-ion concentration, it is not surprising that Pu(IV) is reduced to Pu(III) in concentrated hydrobromic acid. The fact that elemental bromine reacts strongly with bromide ion to form the tribromide ion, Br_3^- also promotes the reverse reaction. Davidson *et al.*[4] were the first investigators to observe this. When they attempted to prepare $PuBr_4$ by the reaction of PuO_2 with anhydrous hydrogen bromide, the product was not $PuBr_4$, but $PuBr_3$. They subsequently reacted plutonium(IV) hydroxide with 5*M* hydrobromic acid and observed from the colour of the solution (violet) that the plutonium had been reduced to the tervalent state.

The observations that we have made which relate to the reduction of Pu(IV) to Pu(III) by bromide, are that Pu(IV) which has been adsorbed onto a column of Dowex-1 from 9*M* hydrochloric acid, is rapidly eluted with 6, 9 or 11*M* hydrobromic acid but not by 8*M* hydrochloric acid–1*M* hydrobromic acid. From these observations it is concluded that high concentrations of both bromide and hydrogen ions are required to reduce Pu(IV) to Pu(III). It has also been observed that the tribromide ion is strongly adsorbed by the resin. This further promotes the reduction of Pu(IV) to Pu(III) by removing one of the reaction products from solution.

The reduction of both Pu(VI) and Pu(IV) to Pu(III) will, of course, take place in concentrated hydrochloric acid containing a small amount of hydriodic acid and there are a number of published plutonium separation procedures in which the separation from uranium is based on either or both of these reactions. Campbell and Moss[5] use this reagent in their procedure for the determination of plutonium in urine; Marsh *et al.*[6] use it in their procedure for the determination of plutonium in irradiated nuclear fuel.

Hydrobromic acid is superior to a mixture of hydrochloric and hydriodic acid as an eluent for plutonium in anion-exchange separation procedures for two reasons: the separation from other sample constituents is more selective, and hydrobromic acid, unlike hydriodic acid, is not subject to air-oxidation. When a hydrochloric–hydriodic acid mixture is used to elute plutonium from the column, iron, which is a common sample constituent, is reduced from Fe(III) to Fe(II) and is eluted with the plutonium. This does not occur when hydrobromic acid is used. In concentrated hydrochloric acid, iodide is rapidly oxidized by atmospheric oxygen to elemental iodine. For this reason it is necessary to prepare, preserve, and use this reagent under an inert atmosphere. We consider this to be a particular nuisance.

Application to trace constituent analysis

For the analysis of materials in which plutonium is a trace constituent, the principal advantages of an anion-exchange procedure that uses hydrochloric and hydrobromic acids rather than nitric and hydrochloric acids are a significant reduction in analysis time and better decontamination from uranium and thorium. Adsorption of Pu(IV) onto a Dowex-1 column from nitric acid followed by a nitric acid wash is a very effective means of separating plutonium from nearly all the non-actinide constituents of the sample but an inordinately large amount of time is required to separate plutonium from uranium and thorium. (There is some difficulty in separating plutonium from palladium, mercury and bismuth but it would be quite unusual to find significant amounts of these elements in samples for which trace plutonium determinations are needed.) Uranium is not strongly adsorbed onto Dowex-1 from 7*M* nitric acid (the K_D is about 20) but the adsorption is such that uranium can only be removed from the column by washing it with a large volume of acid. Thorium, despite the fact that its adsorption onto the resin from concentrated hydrochloric acid is negligible, is somewhat difficult to wash from the column with this reagent. The K_D in 7*N* nitric acid medium is about 300, and during the extended period in which the column is being washed with this acid, the thorium diffuses into the resin beads. Because of this, extensive washing of the column with hydrochloric acid is required to remove all the thorium.

Adsorption of Pu(IV) and Pu(VI) onto a Dowex-1 column from hydrochloric acid followed by limited-volume washes first with hydrochloric acid and then hydrobromic acid provides a very rapid and specific separation of plutonium from both thorium and uranium. Thorium, because it is not adsorbed onto Dowex-1 from hydrochloric acid, is washed through the column quantitatively and rapidly; uranium, because it is strongly adsorbed onto the resin from both hydrochloric and hydrobromic acids, is retained quantitatively. More than 90% of the plutonium is eluted by a very small volume of hydrobromic acid. This is more than sufficient since the use of an isotopic diluent (^{236}Pu or ^{242}Pu) and alpha-spectrometric assay obviates the need for quantitative recovery.

The separation of plutonium from the non-actinide sample constituents has not been completely investigated but no serious problems are expected. It is expected that the anion-exchange behaviour of most elements in hydrobromic acid will be very similar to their behaviour in hydrochloric acid. Those elements that are not adsorbed onto Dowex-1 from hydrochloric acid will be washed through the column with the thorium; those elements that are adsorbed onto Dowex-1 are probably also adsorbed from hydrobromic acid. However, there are bound to be exceptions, *e.g.*, vanadium(V) is strongly adsorbed from hydrochloric acid, reduced to the quadrivalent state by hydrobromic acid, and eluted as such along with the plutonium. It is expected that such problems can be effectively dealt with in the other steps of the separation procedure that customarily precede the anion-exchange separation, *e.g.*, co-precipitation of the plutonium with ferric hydroxide and/or lanthanum fluoride.

Application to major constituent analysis

In the analytical methods that are used to determine plutonium when it is a major constituent of the sample, the requirement of the separation procedure that has been the most difficult to meet has been that of quantitative recovery. The elements that will interfere in the measurement methods (redox titrations) are few in number, and these elements are not particularly difficult ones to separate by either the nitric–hydrochloric acid or the hydrochloric–hydrobromic acid anion-exchange procedure.

In the anion-exchange procedures where plutonium is adsorbed onto the resin from concentrated nitric acid, washed with nitric and hydrochloric acids, and eluted with dilute hydrochloric acid containing a trace of fluoride, quantitative recovery is thwarted by the oxidation adjustment step before the adsorption step and the difficulty of eluting plutonium from the column once it has been adsorbed. When the sample medium is being changed to nitrate, some plutonium is oxidized to the sexivalent state and if the reduction of this plutonium to the quadrivalent state is not complete, the plutonium(VI) will pass through the column in the nitric acid wash. Elution of the plutonium(IV) is a time-consuming process, because there is significant diffusion into the resin during the nitric acid wash.

The application of the hydrochloric–hydrobromic acid anion-exchange separation procedure to the analysis of samples in which plutonium is a major constituent has not been demonstrated, but the results obtained in this investigation indicate strongly that this approach should be quite superior to the one that uses nitric and hydrochloric acids. To separate uranium and iron, which are the principal interferences in the Pu(III)–Pu(IV) redox titrations, a concentrated hydrobromic acid solution of the sample would be passed through a Dowex-1 column. Uranium and iron, which are both strongly adsorbed onto Dowex-1 from concentrated hydrobromic acid, would be quantitatively retained on the column and the plutonium would be washed through with a limited volume of acid. On the basis of the redox potentials and adsorption characteristics of other elements in hydrochloric acid media, the only ones that would be expected to interfere in the subsequent titration would be vanadium and thallium.

To separate chromium and manganese, the principal interferences in the Pu(VI)–Pu(IV) titrations, concentrated hydrochloric acid solution of the sample would be passed through the column, the column would be washed with a limited volume of hydrochloric acid, and the plutonium eluted with concentrated hydrobromic acid. The particular advantage of this approach over the one that uses nitric and hydrochloric acids is the assurance of complete adsorption onto the column. Both plutonium(IV) and (VI) are strongly adsorbed onto Dowex-1 from concentrated hydrochloric acid; only plutonium(IV) is adsorbed from concentrated nitric acid. Although quantitative elution of plutonium from the resin with concentrated hydrobromic acid requires extensive washing, the fact that the elution is accomplished at a very high acidity and with reduction of plutonium to the tervalent state may be beneficial. Elution of plutonium(IV) with a dilute acid may, despite the fact that fluoride is present, lead to polymerization of plutonium. Polymerized plutonium could be irreversibly adsorbed onto the resin or be intractable in the analysis.

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METALLSALZIMPRÄGNIERUNG VON GRAPHITROHREN ZUR VERBESSERTEN AAS-SILIZIUMBESTIMMUNG

H. M. ORTNER und E. KANTUSCHER

Metallwerk Plansee AG. & Co. KG., A-6600 Reutte, Österreich

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Zusammenfassung—Es werden mehrere Methoden zur Verhinderung der Karbidbildung bei der Siliziumspurenanalyse mittels flammenloser AAS getestet: die Verwendung von Graphitrohren mit eingelegten Wolfram- oder Tantalfolien, von titankarbonitridbeschichteten Rohren und von metallsalzimprägnierten Rohren. Am günstigsten erwies sich der Einsatz tantalsalz- bzw. natriumwolframatgetränkter Rohre. In letzteren lassen sich SiO_2-Mengen von 0·5 bis 100 ng mit einer relativen Standardabweichung von 20 bis 3% bestimmen. Bei Ausschaltung von Umgebungs- und Reagenzienkontamination wäre die Analyse noch wesentlich geringerer SiO_2-Mengen möglich. Die Methode ist u.a. zur Erfassung von SiO_2-Spuren in den Ausgangsmaterialien der pulvermetallurgischen Wolframproduktion geeignet.

Die flammenlose atomabsorptionsspektrophotometrische (AAS) Erfassung von Silizium und Bor wird im Graphitrohr durch die Karbidbildungstendenz dieser Elemente erheblich gestört. Es wurde bereits verschiedentlich versucht, durch diverse Beschichtungsverfahren bzw. durch den Ersatz des Graphits etwa durch Tantal als Rohrmaterial dieser Schwierigkeiten Herr zu werden.[1,2] Die leichte Verletzbarkeit solcher Schichten z.B. durch unterschiedliche thermische Ausdehnungskoeffizienten des Grundmaterials und der Schicht einerseits und die geringe Wandstärke einsetzbarer Metallrohre andererseits verhinderten bis jetzt einen breiteren Einsatz solcher Küvetten. Auch wir untersuchten die Möglichkeit der Verwendung von Graphitrohren mit eingelegten Wolfram- oder Tantalblechstücken an der Einspritzstelle bzw. von Titankarbonitrid-beschichteten Rohren. Als wesentlich günstiger erwies sich die Anwendung natriumwolframatgetränkter Graphitrohre. Eine Imprägnierung mit Metallsalzlösungen anderer IVb bis VIb Nebengruppenmetalle führte zu schlechteren Ergebnissen.

EXPERIMENTELLER TEIL

Geräte

Die Untersuchungen wurden an einem Perkin Elmer Atomabsorptionsspektrophotometer Modell 306 mit Deuteriumuntergrundkompensator in Verbindung mit einer Graphitrohrküvette HGA-72 durchgeführt. Für elektronenmikroskopische Aufnahmen stand ein Rasterelektronenmikroskop Jeol JSM-35R mit energiedispersivem Röntgenfluoreszenzansatz EDAX zur Verfügung. Eichlösungen wurden unter Verwendung des Oxford Mikro-Pipettiersystems hergestellt.

Materialien

Wolframtrioxid und Tantalmetallpulver waren von H. C. Starck, Goslar, BRD, Titanschwamm von Treibacher Chemische Werke, Treibach, Österreich und Hafniumnitrid und Hafniumoxid von Research Organic/Inorganic Chemical Corp., Bellville, N.J., USA.

Silizium-Eichlösungen wurden aus $Na_2SiO_3.9H_2O$ von Baker Chemical Co., N.J., USA hergestellt (pH-Wert 12, eingestellt mit NaOH Suprapur, Merck).

Alle übrigen Reagenzien waren z.A. Reagenzien von Merck, Darmstadt, BRD. Die Tantal- und Wolframfolien stammten aus eigener Produktion.

Graphitrohrimprägnierung

Tantalmetallpulver bzw. Titanschwamm oder Hafniumnitrid wurde (1 g) in 5 ml 40%iger Flußsäure, 10 ml 65%iger Salpetersäure und 10 ml 30%igem Wasserstoffperoxid gelöst, mit 5 ml konz. Schwefelsäure versetzt und bis auf ein Volumen von *ca.* 5 ml eingeengt. Dann wurde mit Wasser auf 100 ml aufgefüllt. Höherprozentige Titan-, Tantal- und Niob-Lösungen sind unbeständig. Hafniumoxid ist in Säuren unlöslich und man ist daher gezwungen, Hafniumnitrid zu verwenden. Zur Natriumwolframat-Imprägnierung wurden entsprechende Lösungen aus $Na_2WO_4.2H_2O$ angesetzt.

Zu imprägnierende Graphitrohre wurden bei Zimmertemperatur 24 Stunden in die entsprechenden Lösungen gelegt, hierauf 12 Stunden bei 120° im Trockenschrank getrocknet. In der HGA-72 wurde zunächst 1 Min bei 120° (40 Einheiten) nachgetrocknet, sodann innerhalb von eineinhalb Minuten von 100 auf 2600° aufgeheizt (Rate 8 ≙ 500,0 Einheiten/Min) und 10 sec auf Maximaltemperatur (999 Einheiten) gebracht. Dieser Zyklus wurde dreimal durchlaufen.

ERGEBNISSE UND DISKUSSION

Einsatz von Graphitrohren mit eingelegtem Tantal- oder Wolframblech

Es wurden Blechstücke von 20 × 10 × 0,025 mm in Graphitrohre eingeschoben und möglichst eng an die innere Graphitrohrwand angelegt. Trotzdem war der Wärmeübergang vom Graphitrohr zum Blech unbefriedigend. Die Aufbringung und Trocknung von mehr als 10 µl Lösung auf Bleche ist problematisch. Dies trifft generell für jegliche glatte Schichten zu und stellt daher eine prinzipielle Schwierigkeit für den Einsatz von Metallküvetten dar. Die Trocknung muß sehr langsam und vorsichtig erfolgen. Überdies verspröden die Bleche recht bald durch Karburierung. Bei Tantal ist dies durch Goldgelbfärbung des Bleches auch optisch zu verfolgen. Tantalbleche verspröden

so schnell, daß sie oft bereits nach zwei bis drei Analysenzyklen Risse bekommen. Daher erscheint Tantal auch als Küvettenmaterial für organische Matrices ungeeignet, zumal nicht nur Kohlenstoff, sondern auch Sauerstoff, Stickstoff, Wasserstoff, Silizium und Bor echt gelöst werden und das Metall schon bei geringen Gehalten an diesen Elementen stark versprödet.

Einsatz von Graphitrohren mit Titankarbonitridbeschichtung

Nach einer von Schintlmeister entwickelten Methode[3,4] wurden Graphitrohre innen mit einer etwa 10-μm starken Titankarbonitridschichte belegt. Die goldgelben Schichten wandelten sich schon beim ersten Ausglühen des Rohres in silbergraue Titankarbidschichten um. Ein Teil des Titans dampfte dabei weg. Trotzdem blieb eine vollkommene Titankarbid-Schicht am Graphitrohr erhalten, welche jedoch bereits nach wenigen Analysen stark porös wurde, wie entsprechende Rasterelektronenmikroskopaufnahmen zeigten. Auch besitzt Titankarbid trotz des hohen Schmelzpunktes ab etwa 1700° einen beträchtlichen Dampfdruck,[5] der bei der Atomisierungstemperatur für Silizium so hoch ist, daß die Strahlung einer Titan-Hohlkathodenlampe vollkommen blockiert wird.

Einsatz imprägnierter Graphitrohre

Schließlich wurde versucht, durch Imprägnierung von Graphitrohren mit Metallsalzlösungen von Metallen der IVb bis VIb Gruppe des Periodensystems eine Verbesserung zu erreichen. Dabei wurde von der Überlegung ausgegangen, daß beim Glühen solcher imprägnierter Graphitrohre in Schutzgasatmosphäre die entsprechenden Karbide günstigenfalls als dünner Film in jenen Bereichen des Graphitrohrs entstehen, welche von der Imprägnierung erfaßt wurden. So hergestellte Metallkarbidschichten sollten die Karbidbildung eingebrachter Probelösungen verhindern, ohne jedoch die relativ rauhe saugfähige Graphitrohroberfläche, welche, wie schon erwähnt, für eine gut reproduzierbare Probenaufbringung und Trocknung von großer Bedeutung ist, wesentlich zu modifizieren. Aus Tabelle 1 geht hervor, daß Hafnium, Tantal und Zirkon die thermodynamisch stabilsten Karbide mit den höchsten Schmelzpunkten bilden. Allerdings ist über die Karbidbildung bei großem Kohlenstoffüberschuß, wie er im Graphitrohr vorliegt, nichts bekannt.

Die Resultate dieser Versuche sind in den Tabellen 2–5 zusammengefaßt. In unbehandelten Rohren ist die Reproduzierbarkeit der Werte erst ab etwa 10 ng SiO_2 ausreichend, um eine Eichfunktion erstellen zu können. Die erreichbare Empfindlichkeit schwankt in gewissen Grenzen von Rohr zu Rohr (unter Empfindlichkeit wird hier wie üblich die Steigung der Eichgeraden verstanden). Bereits durch Zugabe von Natriumwolframatlösung zur Natriumsilikat-Eichlösung tritt eine wesentliche Empfindlichkeitssteigerung ein, wie sie auch anderenorts beobachtet wurde.[6]

Tabelle 1. Normalbildungsenthalpien in kcal/Mol und Schmelzpunkte der wichtigsten Karbide der IVb bis VIb Übergangsmetalle[5]

TiC	VC	$Cr_{23}C_6$
−43,9	−28	−16,4
3160°	2830°	1520° zers
	(V_2C 1890 zers)	Cr_7C_3
		−45,5
		1780° zers
		Cr_3C_2
		−21,0
		1895 zers
ZrC	NbC	Mo_2C
−44,1	−33,7	−4,2
3535°	3500°	2400 zers
	(Nb_2C 3100° zers)	(MoC 2700)
HfC	Ta_2C	WC
−81	−17,0	+8,4
3890° ± 150°	3400° zers	2600 zers
		(W_2C 2700° ± 50)
	TaC	
	−38,5	
	3780°	

Dies ist auf den schon erwähnten Schutzeffekt des sich bildenden Wolframkarbids zurückzuführen, welches offenbar das Silizium weitgehend an der Karbidbildung hindert.

Hafniumgetränkte Rohre. Die Reproduzierbarkeit von Siliziumbestimmungen in hafniumgetränkten Graphitrohren ist schlecht, die Empfindlichkeitssteigerung gegenüber unbehandelten Graphitrohren nicht groß. Die gleichzeitige Aufgabe von Natriumsilikat- und Natriumwolframatlösungen hat eine beinahe dreifache Erhöhung der Extinktion zur Folge. Auch die Reproduzierbarkeit wird wesentlich besser. Dies ist wiederum auf den Schutzeffekt des sich bildenden Wolframkarbids zurückzuführen. Bei Zugabe größerer Natriumwolframat-Mengen sinkt die Extinktion wieder ab. Vermutlich wird die sich ausbildende Wolframkarbidschichte bald so dick, daß sie eine vollständige Atomisierung des Siliziums verhindert. Rasterelektronenmikroskopische Aufnahmen (im folgenden als REM-Aufnahmen bezeichnet) zeigten eine im Vergleich zu natriumwolframatimprägnierten Rohren erhöhte Porosität sowie im Hafnium-Rasterbild eine leichte Inhomogenität der Verteilung. Eine Imprägnierung von Graphitrohren mit Hafniumsalzlösungen erscheint somit nicht vorteilhaft für die Siliziumspurenanalyse (Tabelle 3).

Titangetränkte Rohre. Die in titangetränkten Rohren erhaltenen Extinktionswerte für Silizium liegen beträchtlich unter denen, welche für hafnium-, tantal- und wolframgetränkte Rohre beobachtet werden. Eine Empfindlichkeitssteigerung gegenüber unbehandelten Rohren ist praktisch nicht feststellbar. Die Werte sind außerdem schlecht reproduzierbar. Titan-Rasterbilder zeigen eine sehr inhomogene Titanverteilung. Oft ist Titan körnig im Graphitgrundmaterial eingelagert (Korngröße etwa 1-5 μm). Die bei beschichteten Rohren festgestellte starke Titanverdampfung dürfte auch hier Empfindlichkeit und Reproduzierbarkeit negativ beeinflussen. Damit scheidet auch Titan zur Imprägnierung aus (Tabelle 3).

Tantalgetränkte Rohre. Die mit tantalgetränkten Rohren erreichbare Empfindlichkeit liegt wesentlich

Tabelle 2. Extinktionswerte für SiO_2 in unbehandelten Graphitrohren

SiO_2, *ng*	Extinktionsmittelwert	*s* (Extinktion)	*V*, %	Bemerkungen
	Versuche in unbehandelten Graphitrohren und mit reiner Na_2SiO_3-Lösung			
20	0,070	0,012	17,5	Alle Werte mit dreifacher
50	0,160	0,012	7	Dehnung, ohne Gas-Stop
100	0,264	0,017	6,5	
200	0,483	0,021	4	
	Versuche in unbehandelten Graphitrohren und mit reiner Na_2SiO_3-Lösung; Empfindlichkeitsschwankung von Rohr zu Rohr			
20	0,083	0,010	13	Alle Werte mit dreifacher
50	0,188	0,016	8,5	Dehnung, ohne Gas-Stop
100	0,344	0,043	13	
200	0,652	0,006	1	
	Versuche in unbehandelten Graphitrohren und mit reiner Na_2SiO_3-Lösung; Empfindlichkeitssteigerung durch gleichzeitige Aufgabe von 10 µl Na_2WO_4-Lösung (entsprechend 50 µg W)			
4	0,080	0,010	12,5	Alle Werte mit dreifacher
10	0,163	0,010	6	Dehnung, ohne Gas-Stop
20	0,322	0,020	6,5	
40	0,615	0,053	8,5	

Versuchsbedingungen. Probevolumen jeweils 50 µl für reine Na_2SiO_3-Lösungen. Temperaturprogramm: Trocknen: 35 Einheiten (etwa 100°) 60 sec; thermische Zersetzung: 200 Einheiten (1020°) 45 sec; Atomisierung: 999 Einheiten (>2700°) ohne Gas-Stop 10 sec, mit Gas-Stop 5 sec. Mittelwert, Standardabweichung *s* und Variationskoeffizient *V* beziehen sich jeweils auf fünf Messungen.

Tabelle 3. Versuche mit verschieden imprägnierten Graphitrohren und mit reiner Na_2SiO_3-Lösung

SiO_2, *ng*	Extinktions-mittelwert	*s* (Extinktion)	*V*, %	Bemerkungen
	Imprägnierung mit 1%iger Hafniumsalzlösung			
10	0,115	0,047	41	Alle Werte mit dreifacher Dehnung, ohne
25	0,244	0,044	18	Gas-Stop. Na_2SiO_3-Lösung + 500
25	0,712	0,025	3,5	µg WO_3/50 µl Na_2SiO_3-Lösung + 2500
25	0,284	0,011	4	µg WO_3/100 µl
	Imprägnierung mit 1%iger Titansalzlösung			
50	0,186	0,019	10,5	Alle Werte mit dreifacher Dehnung,
100	0,385	0,018	4,5	ohne Gas-Stop
200	0,886	0,096	11	
	Imprägnierung mit 1%iger Tantalsalzlösung			
5	0,111	0,010	9,5	Alle Werte mit dreifacher Dehnung,
10	0,280	0,044	15,5	ohne Gas-Stop
20	0,453	0,017	4	
25	0,631	0,024	3,5	
	Imprägnierung mit 5%iger Na_2WO_4-Lösung			
5	0,060 (0,180)	0,011	18,5	Alle Werte ohne Dehnung, ohne Gas-Stop
10	0,131 (0,393)	0,026	20	Auf dreifache Dehnung umgerechnete
20	0,235 (0,705)	0,009	4	Extinktionswerte in Klammer
25	0,300 (0,900)	0,005	2	
50	0,562	0,016	3	
	Imprägnierung mit 10%iger Na_2WO_4-Lösung			
2	0,048	0,006	13,5	Alle Werte mit dreifacher Dehnung, ohne
5	0,081	0,011	13,5	Gas-Stop
10	0,184	0,018	10	
20	0,374	0,026	7	
25	0,455	0,007	1,5	
50	0,853	0,019	2	
	Imprägnierung mit 20%iger Na_2WO_4-Lösung			
2	0,064	0,009	13,5	Alle Werte mit dreifacher Dehnung, ohne
5	0,104	0,008	7	Gas-Stop
10	0,229	0,025	11	
20	0,438	0,022	5	
50	0,905	0,024	2,5	

Versuchsbedingungen—siehe Tabelle 2.

höher als die von titan- und hafniumgetränkten Rohren (Tabelle 3). Sie ist vergleichbar mit der Empfindlichkeit in wolframgetränkten Rohren. Auch bezüglich der Reproduzierbarkeit unterscheiden sich tantalgetränkte Rohre nicht von wolframatgetränkten. Die Streuung der Meßwerte um die Eichgerade ist allerdings etwas größer. REM-Aufnahmen zeigen keine Veränderung der ursprünglichen Graphitstruktur. Die Tantalverteilung über die Rohroberfläche ist homogen. Prinzipiell erscheint daher die Verwendung tantalimprägnierter Rohre durchaus günstig und wird von uns weiter verfolgt. Im Hinblick auf die Erfassung von Siliziumspuren in Wolfram erschien es jedoch zweckmäßiger, wolframgetränkte Rohre zu verwenden.

Wolframatgetränkte Rohre. Der Vorteil wolframatgetränkter Rohre liegt zunächst in der überaus einfachen Herstellung auch höher prozentiger Natriumwolframat-Imprägnierungslösungen. Die höchste Empfindlichkeit wurde in mit 5%iger Na_2WO_4-Lösung imprägnierten Rohren beobachtet (Tabelle 3). Die ursprüngliche Graphitstruktur bleibt bei 5%iger Imprägnierung vollkommen erhalten. Bei höherprozentiger Imprägnierung scheinen sich zusätzlich zur Wolframkarbid-Überzugsbildung kleinere Wolframkarbidkriställchen (Durchmesser $< 1\ \mu m$) an den Graphitkörnern abzuscheiden. Die Wolframverteilung ist vor allem bei 5% iger Imprägnierung als sehr homogen zu bezeichnen. Die aus Wolfram-Rasterbildern von Querschnitten 5% wolframatgetränkter Rohre ermittelte Eindringtiefe der Imprägnierung beträgt durchschnittlich 200 μm. Eine Imprägnierung mit 5%iger Na_2WO_4-Lösung erweist sich somit als optimal.

Faßt man die bis jetzt beschriebenen Versuche mit imprägnierten Graphitrohren zusammen, so stellt sich die Frage, warum gerade in wolframatgetränkten Rohren trotz des relativ niedrigen Zersetzungspunktes und der geringen thermodynamischen Stabilität von Wolframkarbid so gute Ergebnisse zu erzielen sind. Weiters überrascht die geringe Empfindlichkeit und schlechte Reproduzierbarkeit in hafnium- und titangetränkten Rohren. Abgesehen von schlechterer Verteilung über die Rohroberfläche dürfte dies mit der Ausbildung ternärer Phasen Metall–Silizium–Kohlenstoff zusammenhängen. Derartige sogenannte Nowotny-Phasen[7] treten besonders bei den IVb Übergangsmetallen auf, während für Wolfram keine Nowotny-Phasen beobachtet wurden (es sind lediglich durch Stickstoff und Sauerstoff zusätzlich stabilisierte Phasen für Wolfram bekannt)[7] Auch für Tantal ist die Stabilität solcher Phasen relativ gering, obwohl eine durch 5 At.-% stabilisierte Nowotny-Phase existiert. Durch die Ausbildung solcher Phasen geht ein Teil des Siliziums für die Atomisierung verloren.

Weitere Versuche in Graphitrohren mit 5%iger Natriumwolframatimprägnierung

Empfindlichkeitsschwankungen und Rohrlebensdauer. Beim Arbeiten mit imprägnierten Graphitrohren treten zwei hauptsächliche Schwierigkeiten auf. Erstens ist für jedes neu verwendete Graphitrohr eine neue Eichfunktion zu erstellen, d.h. die Empfindlichkeit schwankt in gewissen Grenzen von Rohr zu Rohr. Zweitens ist mit einer gewissen Rohralterung zu rechnen. d.h. die Empfindlichkeit sinkt mit der Anzahl der durchgeführten Analysen. Ein Beispiel zu Punkt 1 ergibt sich aus dem Vergleich der entsprechenden Werte von Tabelle 4. Ein Beispiel zu Punkt 2 ist auch in Tabelle 4 angeführt. Es empfiehlt sich daher grundsätzlich, die Eichfunktion nach etwa 15 bis 20 Analysenzyklen zu überprüfen. Die durchschnittliche Lebensdauer eines imprägnierten Graphitrohres bei Anwendung der Gas-Stop-Methode während der Atomisierung (5 sec) beträgt etwa 70 Analysenzyklen, ohne Gas-Stop (Atomisierungsdauer: 10 sec) etwa 120 Analysenzyklen. Der Linearbereich endet für Analysen mit Gas-Stop bei 10 ng SiO_2.

Mengenbereich 0,5 bis 5 ng SiO_2. Die für diesen Bereich erhaltenen Extinktionswerte zeigen, daß die Nachweisstärke der Methode zur Erfassung noch wesentlich kleinerer Mengen ausreichen würde. In einem Industrielaboratorium wie dem unseren ohne die Möglichkeit einer Filterung der Laborluft tritt hier jedoch die Umgebungskontamination als limitierender Faktor auf. Es kommt vor, daß von fünf Werten in diesem Mengenbereich zwei oder drei Werte mit Schreibervollausschlag registriert werden. Dies wird vermutlich durch die Einschleppung von Staubpartikeln in das Rohr selbst oder bereits vorher in die Probelösung verursacht. Bei Bautätigkeit in Labornähe mußten wir den völligen Zusammenbruch der SiO_2-Analyse in diesem Bereich feststellen.

Versuche zum Einsatz der Methode für die SiO_2-Spurenanalyse in Wolframtrioxid. Die in Tabelle 5 aufgeführten Werte zeigen, daß die SiO_2-Analyse in WO_3 im interessierenden Konzentrationsbereich von 10 bis 1000 ppm ohne Schwierigkeiten möglich ist. Allerdings liegt der Blindwert mit 40 bis 60 ppm recht hoch. Dies ist auf das eingesetzte WO_3 zurückzuführen. Versuche zur Drückung des Blindwertes durch den Einsatz aufoxidierten Wolframmetalls und damit zur Erweiterung des Meßbereiches unter 10 ppm werden Gegenstand weiterer Untersuchungen sein. Sowohl die Reproduzierbarkeit als auch das Sinken der Empfindlichkeit bei steigender Analysenzahl werden von der aufgegebenen WO_3-Matrixmenge beeinflußt. Der nicht absublimierende WO_3-Anteil lagert sich—vermutlich als WC—krustenförmig ab, was für das Sinken der Reproduzierbarkeit und der Empfindlichkeit mit steigender Analysenzahl mit verantwortlich sein dürfte. Die Aufgabe von mehr als 100 μg WO_3 pro Analyse ist daher nicht empfehlenswert. Während des Zersetzungsschrittes treten dann auch sehr hohe Peaks unspezifischer Absorption durch WO_3-Verdampfung auf. Die Applikation von 50 μg WO_3 erscheint optimal. Die Methode wird derzeit im Routinebetrieb getestet.

SCHLUSSFOLGERUNG

Von den in Tabelle 1 zusammengestellten Karbidbildnern scheiden die der 4. Periode infolge zu hohen

Tabelle 4. Weitere Versuche in Rohren mit 5%iger Na_2WO_4-Imprägnierung

SiO_2, *ng*	Extinktions-mittelwert	*s* (Extinktion)	*V* %	Bemerkungen
	Reproduzierbarkeit von Rohr zu Rohr, Bereich 2–100 ng SiO_2; reine Na_2SiO_3-Lösungen			
2	0,084	0,014	16,5	Dreifache Dehnung, ohne Gas-Stop
5	0,145	0,006	4	
10	0,288	0,013	4,5	
20	0,548	0,013	2,5	
25	0,688	0,028	4	
50	0,413	0,006	1,5	ohne Dehnung, ohne Gas-Stop
100	0,847	0,035	4	
	Verschiebung der Eichgeraden durch Rohralterung, Bereich 1–20 ng SiO_2; reine Na_2SiO_3-Lösungen			
neues Graphitrohr				
1	0,085	0,018	21	Alle Werte ohne Dehnung, mit Gas-Stop
2	0,131	0,014	11	
5	0,281	0,006	2	
10	0,541	0,045	8,5	
20	0,853	0,025	3	
dasselbe Graphitrohr nach 30 Analysen				
1	0,070	0,017	24,5	Alle Werte ohne Dehnung, mit Gas-Stop
2	0,113	0,026	23,5	
5	0,243	0,006	2,5	
10	0,456	0,040	8,5	
20	0,798	0,021	2,5	
dasselbe Graphitrohr nach 80 Analysen				
1	0,050	0,019	38	Alle Werte ohne Dehnung, mit Gas-Stop
2	0,092	0,025	27	
5	0,195	0,020	10	
10	0,355	0,032	9	
20	0,657	0,028	4	
	SiO_2-Bestimmung im Bereich 0,5–5 ng SiO_2, reine Na_2SiO_3-Lösungen			
0,5	0,040	0,007	18	Alle Werte ohne Dehnung, mit Gas-Stop
1	0,076	0,007	8,5	
2	0,122	0,006	4,5	
4	0,246	0,021	8,5	
5	0,281	0,010	5	

Versuchsbedingungen—siehe Tabelle 2.

Dampfdruckes ihrer Karbide bei der Atomisierungstemperatur des Siliziums aus. Die Metallkarbide der IVb-Gruppe scheiden andererseits aufgrund der Bildung von Nowotny-Phasen zur Siliziumbestimmung aus. Es verbleiben somit die Karbide des Niobs, Molybdäns, Tantals und Wolframs, wobei die Karbide der 6. Periode den niedrigsten Dampfdruck aufweisen. Tatsächlich werden mit tantalsalz- bzw. wolframatgetränkten Rohren sehr befriedigende Ergebnisse erzielt. Die Anwendbarkeit von Nb- und Mo-

Tabelle 5. Bestimmung von SiO_2 in WO_3

SiO_2, *ng*	Extinktions-mittelwert	*s* (Extinktion)	*V*, %	Bemerkungen
	Versuche zur SiO_2-Bestimmung in WO_3, Bereich 50–1000 ppm, Matrix 100 µg WO_3/10 µl. Aufgabe jeweils von 10 µl Matrixlösung und 50 µl Na_2SiO_3-Eichlösung			
0	0,025	0,012	48	Alle Werte ohne Dehnung und ohne Gas-Stop
5	0,071	0,025	35	entspr. 50 ppm SiO_2
10	0,113	0,023	20	entspr. 100 ppm SiO_2
20	0,180	0,027	15	entspr. 200 ppm SiO_2
25	0,231	0,022	9,5	entspr. 250 ppm SiO_2
50	0,420	0,016	3,8	entspr. 500 ppm SiO_2
100	0,783	0,041	5,2	entspr. 1000 ppm SiO_2
	Versuche zur SiO_2-Bestimmung in WO_3, Bereich 10–400 ppm, Matrix 50 µg WO_3/20 µl. Aufgabe jeweils von 20 µl Matrixlösung und 20 µl Na_2SiO_3-Eichlösung			
0	0,149	0,008	5,5	Alle Werte ohne Dehnung, mit Gas-Stop
0,4	0,178	0,013	7	entspr. 8 ppm SiO_2
0,8	0,194	0,018	9	entspr. 16 ppm SiO_2
2,0	0,255	0,013	5	entspr. 40 ppm SiO_2
4,0	0,367	0,031	8,5	entspr. 80 ppm SiO_2
8,0	0,550	0,018	3,5	entspr. 160 ppm SiO_2
10	0,642	0,019	3	entspr. 200 ppm SiO_2
20	0,956	0,018	2	entspr. 400 ppm SiO_2

Versuchsbedingungen—siehe Tabelle 2.

salzgetränkten Rohren wurde bislang noch nicht geprüft.

Weiters seien die Vorteile imprägnierter Graphitrohre gegenüber andersartig beschichteten zusammengefaßt:

(*a*) Es tritt praktisch keine Änderung des elektrischen Widerstandes gegenüber unbehandelten Graphitrohren auf. Eine Temperaturneueichung erübrigt sich daher.

(*b*) Die saugfähige Struktur der Graphitrohroberfläche bleibt vollkommen erhalten. Komplikationen bei der Aufbringung auch relativ großer Lösungsvolumen (100 µl) bzw. bei ihrer Verdampfung treten somit nicht auf.

(*c*) Die Lebensdauer getränkter Graphitrohre ist dieselbe wie die unbehandelter Rohre.

(*d*) Die Imprägnierung ist das bei weitem einfachste Präparationsverfahren für Graphitrohre und kann für jede Rohrart in gleicher Weise vorgenommen werden.

Es ist anzunehmen, daß derartige Imprägnierverfahren bei geeigneter Wahl der Imprägnierlösung nicht nur für Silizium, sondern auch für andere Karbidbildner zu einer wesentlichen Steigerung der Empfindlichkeit und Reproduzierbarkeit bei ihrer Bestimmung durch die flammenlose AAS führen.

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SYNERGIC EXTRACTION OF ZINC, CADMIUM AND LEAD WITH HEXAFLUOROACETYLACETONE AND DI-n-BUTYLSULPHOXIDE AND TRI-n-BUTYL PHOSPHATE, AND THE GAS CHROMATOGRAPHY OF THE ZINC ADDUCT

JEROME W. O'LAUGHLIN and THOMAS P. O'BRIEN

Department of Chemistry, University of Missouri, Columbia, Missouri 65201, U.S.A.

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Summary—The synergic solvent extraction of zinc(II), cadmium(II), and lead(II) with 1,1,1,5,5,5-hexafluoro-2,4-pentanedione,H(HFA), and tri-n-butyl phosphate (TBP) or di-n-butylsulphoxide (DBSO) as neutral donors, into cyclohexane has been investigated. Quantitative extraction occurs at pH 4·5–6·0 in extraction times of 10–30 min, depending on the metal species. The optimum pH, equilibration time, stoichiometry and stability of the extracted species, as well as the effect of fluorinated β-diketone concentration, metal concentration and neutral donor concentration on the extraction are reported. The extracted species was found to be $M(HFA)_2 . 2DBSO$ or $M(HFA)_2 . 2TBP$ by mass-action studies. Thermogravimetric analysis of the complexes is reported. The gas chromatographic behaviour of the ternary complexes of the three metals has also been studied. A calibration plot of peak area *vs.* the amount of zinc injected was linear over the range 40–900 ng of zinc for the $Zn(HFA)_2 . 2DBSO$ species; the cadmium and lead species apparently decomposed on the column and useful chromatographic peaks were not observed. The calibration plot for zinc was determined on the basis of the averages of 3–5 replicate determinations for 14 different concentrations over the range stated. The average relative standard deviation was 2·9%.

The volatility of certain metal chelates, particularly chromium and beryllium chelates with various fluorinated β-diketones, has permitted the determination of these metals by gas chromatography.[1,2] With the use of the electron-capture detector, detection limits as low as 10^{-14} g have been obtained.[3] A problem encountered with many cations is that the co-ordination number is more than twice the number of charges on the cation, and the resulting chelates with the bidentate β-diketones are hydrated or polymeric.[4–6] Belcher *et al.*[4] and Graddon[6] pointed out that this may result in the neutral chelate molecules acting as Lewis acids that form stable base adducts. They expected that these adducts would not be sufficiently volatile to be determined by gas chromatography. The chelates of the lanthanides and several bivalent transition metals with the β-diketones shown this type of behaviour. Several approaches have been taken to surmount this problem.

β-Diketones with bulky terminal groups yield anhydrous chelates in some cases, presumably owing to steric hindrance, and are reported to be superior to 1,1,1,5,5,5-hexafluoro-2,4-pentanedione, H(HFA).[7–9] Ross, Scribner and Sievers[10] reported that cobalt(II) chelates with 1,1,1,2,2,3,3-heptafluoro-6,6-dimethyl-3,5-octanedione, H(FOD), could be determined down to subnanogram levels.

Belcher, Uden and co-workers[4,11] studied monothio-β-diketones as well as bidentate and quadridentate β-ketoamines as ligands that enhanced the thermal stability of the chelates of some metals and reported superior results for copper, nickel, palladium, platinum, cobalt and zinc. Belcher[12] has recently published a review of the determination of metals by gas chromatography.

Another approach taken in the case of the lanthanides, uranium and thorium was the preparation of adducts of metal β-diketonates with neutral donors such as tri-n-butyl phosphate, TBP, or di-n-butylsulphoxide, DBSO. It was reported that these adducts could be separated by gas chromatography without decomposition.[13–18] An advantage of this method is that the ternary complexes can be prepared quite simply by the synergic extraction of the cations.

The synergic extraction and gas chromatography of iron(II) and iron(III) adducts with hexafluoroacetylacetone, H(HFA), and TBP was reported by Tomažič and O'Laughlin.[19] Burgett[20,21] reported that iron(II), cobalt(II), nickel(II) and lead(II) were quantitatively extracted when 0·01*M* solutions of these cations were equilibrated with 0·3*M* H(FHD) (1,1,1,2,2,6,6,7,7,7-decafluoro-3,5-heptanedione) and 0·03*M* DBSO. He reported that all the adducts with the exception of that of lead could be eluted from a gas-chromatographic column.

The present paper reports on the synergic extraction of zinc, cadmium and lead by H(HFA) and either TBP or DBSO. It is shown that these metals can be quantitatively extracted by H(HFA) and either TBP or DBSO in cyclohexane, even when the metals are present in the aqueous phase at trace concentrations. The chromatographic behaviour of the zinc adduct permits the determination of zinc over the range 40–900 ng. Even with all-glass columns, no chromatographic peaks were obtained for either the cadmium or lead ternary complexes.

EXPERIMENTAL

Reagents

The purity of the H(HFA), was checked by infrared, NMR and ultraviolet spectroscopy and by gas chromatography. The TBP and DBSO were commercial products and used without purification.

Dexsil 300 GC, SE-30, Chromosorb W-HP and OV-1 were obtained commercially. Radioactive ^{65}Zn and ^{109}Cd solutions were prepared at the University of Missouri Research Reactor Facility. All other reagents were reagent grade.

Instruments

A Perkin–Elmer Model 403 Atomic Absorption Spectrophotometer equipped with a Perkin–Elmer Model 56 strip-chart recorder was used with an air–acetylene flame to determine lead in the organic and aqueous phases in these studies.

Radioactive tracers were used to follow the partition of zinc and cadmium. A Picker Nuclear Model 5832A Single Channel Analyzer and Scaler equipped with a Picker Nuclear Model 2804 2 × 2 in. NaI scintillation well detector with the window of the analyser adjusted to count the 1·115-MeV and 0·088-MeV gamma-rays for ^{65}Zn and ^{109}Cd, respectively, was used to determine the activity of each phase after extraction.

An Orion Model 801 pH-meter equipped with a Fisher combination electrode was used for all pH measurements.

A Perkin–Elmer Model 180 Infrared Spectrophotometer, a Cary Model 15 Spectrophotometer and a Varian Model A-60 Nuclear Magnetic Resonance Spectrophotometer were used to check the purity of the reagents by comparison of their spectra with those in the literature.

A Bendix Model 2500 gas chromatograph equipped with a flame-ionization detector and a Honeywell Model 194 strip-chart recorder was used. A hydrogen flow-rate of 40 ml/min, an air flow-rate of 150 ml/min and a nitrogen carrier-gas flow-rate of 40 ml/min were used. Glass or stainless-steel columns (1/4-in.o.d.) of various lengths were employed. The columns were packed with 5% Dexsil 300, SE-30 or OV-1 on Chromosorb W-HP. Direct injection was used in all cases. The temperature of the injection port was 210° unless otherwise specified, the column temperature was 170° and the detector temperature was 210°.

The TGA analysis was performed with a DuPont Model 950 Thermogravimetric Analyser equipped with a DuPont Model 900 Differential Analyser and strip-chart recorder with a heating rate of 10°/min and a nitrogen flow-rate of 100 ml/min.

A Burrel wrist-action shaker and an International Model CL Clinical Centrifuge were used in the extraction studies.

Solvent extraction procedure

The stock solutions of the cations were standardized by atomic-absorption spectrophotometry and/or by titration with EDTA with PAN or Xylenol Orange as the indicator.[22] The stock solution of approximately 0·1*M* H(HFA) was prepared by weighing an appropriate amount of H(HFA) into a 1-litre volumetric flask containing 100 ml of a solution of potassium hydroxide (or in a few of the initial experiments sodium hydroxide). The concentration of the base was chosen such that the pH of the resulting solution was 4·0 ± 0·5. The stock solution was kept at this slightly acidic pH to prevent a reverse Claisen condensation. This stock solution was used to prepare more dilute stock solutions ranging in concentration from $1{\cdot}0 \times 10^{-3}$ to $1{\cdot}0 \times 10^{-1}M$. These solutions were prepared the day they were used.

The partition experiments were performed by pipetting 10·00 ml of H(HFA) solution of the appropriate concentration into a Teflon beaker. The pH was checked and always found to be between 4 and 5. Then 10·00 ml of the appropriate stock solution of zinc, cadmium or lead was added. The concentrations of these stock solutions ranged from $1{\cdot}0 \times 10^{-5}$ to $2{\cdot}0 \times 10^{-2}M$. The pH was then adjusted to the desired value with dilute solutions of potassium hydroxide or acetic acid, and the solution diluted to 100 ml. The pH of the aqueous phase was always measured after the equilibration step and this equilibrium pH value is the value reported in subsequent sections dealing with partition studies. Exactly 5·00 ml of the resulting solutions were pipetted into 15-ml screw-capped centrifuge tubes together with 5·00 ml of the appropriate cyclohexane solution of DBSO or TBP, which ranged in concentration from $1{\cdot}0 \times 10^{-2}$ to $1{\cdot}0 \times 10^{-1}M$. The centrifuge tubes were capped with polyethylene-lined caps. The solutions were shaken for 1 hr and then were briefly centrifuged to separate the phases. In the case of lead a 2·00-ml aliquot of each phase was removed and diluted for analysis by atomic absorption. In the cases of zinc and cadmium, the aqueous phases were spiked with radioactive ^{65}Zn and ^{109}Cd before the organic phase was brought into contact with the aqueous phase. After shaking and equilibration, 2·00 ml of each phase were removed for counting.

H(HFA) was used in the aqueous phase to eliminate the possible interferences from the constituents of a buffered aqueous phase in either the extraction step or the subsequent gas-chromatographic study. The use of a sodium acetate–acetic acid buffer in the aqueous phase containing the metal ion, with the β-diketone and neutral donor initially in the organic phase, was also studied. The extraction results were quite similar except for a slight decrease in extraction at high buffer concentrations. Therefore, the former method was used in the remaining studies.

Gas-chromatographic columns

The Chromosorb W-HP was prepared before coating, by a method suggested by Aue.[23] The Chromosorb was placed in a Soxhlet extractor and continuously extracted with refluxing concentrated hydrochloric acid. The acid was replaced periodically and the procedure continued until no trace of yellow developed in the acid. The Chromosorb was then removed and washed with distilled water, followed by an acetone rinse. The Chromosorb was then dried for 24 hr at 110°. The dried product was then silaned with a solution of 5% dimethyldichlorosilane in toluene and rinsed with methanol. The silaned product was then coated with Dexsil 300, SE-30 or OV-1 by preparing a slurry of the product with a chloroform or toluene solution of the appropriate coating material. Excess of solvent was removed by evaporation in a rotary evaporator till the residue was just moist. The product was then removed and dried at 110° with occasional gentle stirring and the dry product placed in a large sintered-glass filtering funnel. A gentle stream of dry nitrogen was passed upwards through the funnel to remove any fines. The resulting product was used to pack the columns, which were conditioned for 24 hr with a nitrogen flow-rate of 5 ml/min at 340° in the case of Dexsil 300 and at 300° in the cases of SE-30 and OV-1.

RESULTS AND DISCUSSION

Solvent extraction

The extraction of zinc, cadmium and lead as a function of pH is presented in Fig. 1. For all three metals quantitative extraction occurred between pH 4·5 and 6·0. Above pH 6·0 there was a decrease in the distribution ratio for all three metals; this is probably due to hydrolysis of the metal ions.

The degree of extraction as a function of equilibration time is shown in Fig. 2. Equilibrium was reached after 10 min for the lead species and within 30 min for zinc and cadmium.

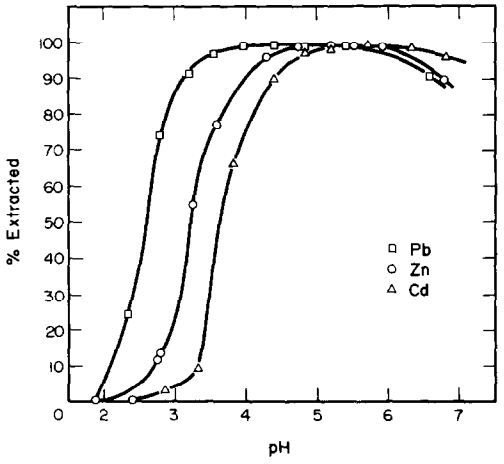

Fig 1. Extraction of bivalent cations with 0·01*M* H(HFA) and 0·05*M* TBP into cyclohexane.

The dependence of extraction on metal ion concentration was studied, and no variation was seen over the concentration range $1{\cdot}79 \times 10^{-6}$–$2{\cdot}03 \times 10^{-3}M$ for zinc; $1{\cdot}16 \times 10^{-6}$–$2{\cdot}00 \times 10^{-3}M$ for cadmium; and $1{\cdot}00 \times 10^{-6}$–$2{\cdot}00 \times 10^{-3}M$ for lead. This suggests the metal species in the organic phase is monomeric.

The overall extraction of ternary species such as $M(HFA)_2S_n$ where M is a bivalent metal and S is a neutral donor can be expressed as $M^{2+}_{(aq)} + 2HFA^{-}_{(aq)} + nS_{(o)} \rightleftharpoons M(HFA)_2S_{n(o)}$. Because a neutral donor such as DBSO or TBP would not be expected to partition appreciably into the aqueous phase, the value of n can be estimated by simple slope analysis from plots of log D *vs.* log $[S]_{(o)}$. Such plots gave slopes of approximately 2 with both DBSO and TBP for all three metals. Electroneutrality considerations would then suggest the species in the organic phase to be $M(HFA)_2S_2$. The fact that H(HFA) partitions between the aqueous and organic phases and the distribution of H(HFA) is a function of pH, the neutral donor concentration and even salt concentration[24] precludes any simple slope analysis of the H(HFA) dependence. An overall equilibrium expression for the extraction can be given as

$$K_e = \frac{[M(HFA)_2S_2]_{(o)}}{[M^{2+}]_{(aq)}[HFA^-]^2_{(aq)}[S]^2_{(aq)}} \qquad (1)$$

where (aq) and (o) refer to species in the aqueous and organic phases. The following assumptions were made in developing the expression above and the subsequent expressions for the dependence of the distribution ratio, D, on the HFA^- concentration.

1. Concentrations can be substituted for activities.
2. The only metal-containing species in the organic phase is $M(HFA)_2S_2$.
3. That the H(HFA) exists mainly as HFA^- in the aqueous phase at the pH of optimum extraction, [pK for H(HFA) 4·6][25], and that at a given pH and neutral donor concentration the fraction of total H(HFA) in the aqueous phase is not a function of the H(HFA) concentration.
4. The neutral donor does not partition appreciably into the aqueous phase.
5. The principal metal species in the aqueous phase are M^{2+} and $M(HFA)^+$.
6. The partition coefficient of $M(HFA)_2S_2$ into the organic phase is large and the concentration of $M(HFA)_2$ in both phases is negligibly small because of the adduct formation.

The distribution ratio, D, can be expressed as

$$D = \frac{[M(HFA)_2S_2]_{(o)}}{[M^{2+}]_{(aq)} + [M(HFA)^+]_{(aq)}} \qquad (2)$$

which on substitution from equation (1) gives

$$D = \frac{K_e[HFA]^2_{(aq)}[S]^2_{(o)}}{1 + K_1[HFA^-]} \qquad (3)$$

Plots of log D *vs.* log $[H(HFA)]_{total}$, as shown in Fig. 3, would be expected to have slopes less than 2 and the observed log D value will be less than those predicted for a slope of 2 by the term $\log[1 + K_1(HFA^-)]$ where K_1 is the formation constant for $M(HFA)^+$.

$$K_1 = \frac{[M(HFA)^+]_{(aq)}}{[M^{2+}]_{(aq)}[HFA^-]_{(aq)}} \qquad (4)$$

The phenomenon of the destruction of synergism at higher H(HFA) concentrations and the difficulty in measuring D values at low H(HFA) concentrations prevent any reliable estimate of K_1 from the present data.

The reported extraction of sodium by H(HFA) and TBP[24] suggested that the presence of the sodium ion might adversely affect the extraction of bivalent metals. The effect of added sodium chloride on the extraction of lead(II) was studied and the results are presented in Table 1. A definite decrease in the distribution ratio was observed, that can be partially attributed to the change in ionic strength. In any event

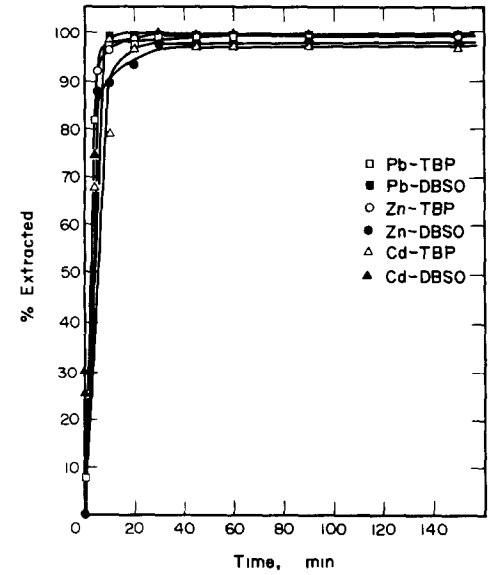

Fig. 2. Dependence of extraction efficiency on time for bivalent cations with 0·01*M* H(HFA), 0·05*M* TBP or 0·05*M* DBSO at pH 5·0–5·6.

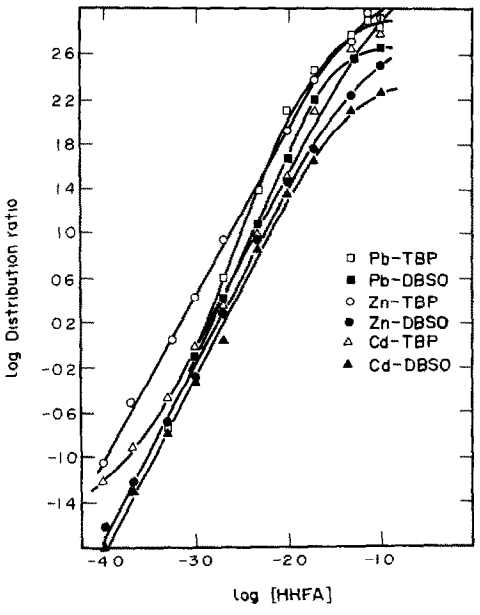

Fig. 3. The extraction of bivalent cations as a function of the concentration of H(HFA): pH 5·0–5·8. [TBP] = [DBSO] = 0·05*M*.

the decrease in the extraction of lead was not sufficiently large to be of concern in the extraction of trace amounts of lead although the extraction of sodium might well have important implications in the subsequent gas-chromatographic determination of ternary complexes prepared by extraction from aqueous media where the sodium ion concentration was moderately large. It has been shown by Belcher, Dudenery and Stephen[26] that the chelates of lithium and sodium with H(HFA) will sublime over a large temperature range above 185° without decomposition. Belcher, Majer, Perry and Stephen[27,28] have also shown that the chelates of lithium, sodium and potassium with 1,1,1,2,2,3,3-heptafluoro-7,7-dimethyl-4,6-heptanedione were eluted (but not separated) from a gas-chromatographic column. These authors[28] have also shown by mass-spectrographic studies that species such as $NaML_4$[where M^{3+} was a tervalent rare-earth ion and L^- one of several β-diketones, including H(HFA)] were volatile.

Thermal properties of the ternary complexes

Eisentraut and Sievers[29] have shown that thermogravimetric analysis (TGA) is helpful in predicting the gas-chromatographic behavior of metal β-diketones. Mitchell and Banks applied TGA as a method to determine the thermal stability of lanthanide–β-diketonate–neutral-donor complexes.[30] Thermograms were obtained for adducts of zinc, cadmium and lead, prepared by extraction of the metal chelates into cyclohexane containing an excess of DBSO. Careful evaporation of the solvent resulted in oils. Elemental analysis for C, H, S and the metal indicated the stoichiometry fell between that of a diadduct, $M(HFA)_2S_2$, and a triadduct, $M(HFA)_2S_3$. As seen from the thermograms in Fig. 4, the zinc complex is more volatile than the lead or cadmium complexes. The residual amount of metal remaining indicates decomposition of the lead complex before complete volatilization, in agreement with the gas-chromatographic behaviour discussed below.

Table 1. Effect of salt concentration on the extraction of lead [0·01*M* H(HFA); 0·05*M* TBP; 100·0 ppm Pb^{2+}; pH ~ 5·10]

$[Na^+]M$	D	E%
0·0	255·4	99·6
0·01	187·5	99·5
0·05	99·9	99·0
0·10	82·6	98·8

Gas chromatography

The elution behaviour of the bivalent metal chelates was studied on both glass and stainless-steel columns that varied from 18 in. to 6 ft. in length. No chromatographic peaks were observed for cadmium or lead even on the short columns and an analysis of the column-packing material on columns into which lead and cadmium adducts had been injected showed lead and cadmium deposits on the front of the column but not further down, indicating almost immediate decomposition. The lead and cadmium were determined on portions of the column packing by atomic absorption after leaching of the packing material with dilute nitric acid.

Initial studies were performed on glass columns packed with 5% OV-1 on Chromosorb W. The OV-1 is intermediate in polarity between SE-30 and Dexsil 300 and nearly the same as SE-30. The elution band for the zinc adduct was broad and not well-resolved from the peak for dibutylsulphoxide. Somewhat sharper peaks were obtained with columns packed with 5% SE-30 on Chromosorb W. The best-formed peaks for the zinc were obtained with the DBSO adduct on 1/4 × 18 in. glass columns, with 5% Dexsil 300 as the stationary phase. Peaks were obtained

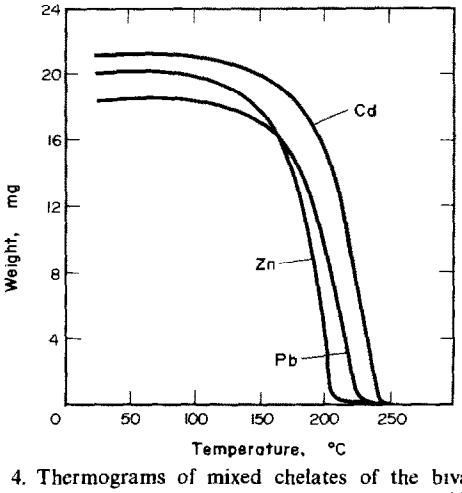

Fig. 4. Thermograms of mixed chelates of the bivalent metals with H(HFA) and DBSO. N_2 flow-rate 100 ml/min; heating rate 10°/min.

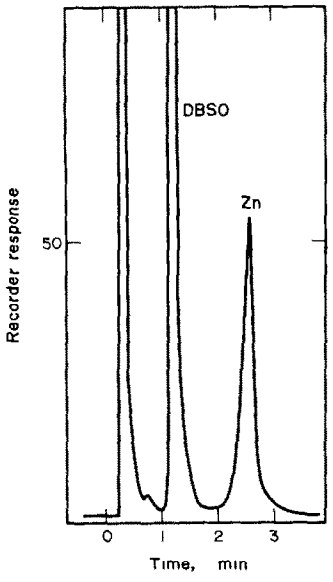

Fig. 5. Chromatogram of $Zn(HFA)_2 . 2DBSO$ at 170° on 18 × 1/4 in. glass column. The stationary phase was 5% Dexsil 300 GC on 100–120 mesh Chromosorb W-HP.

for the zinc adduct with TBP but were not well resolved from the peak due to excess of TBP. A typical chromatographic peak for the DBSO adduct is shown in Fig. 5 which shows the peak for the zinc adduct is well resolved from the peak due to excess of DBSO. A comparison of calibration curves for the zinc adduct on both glass and stainless-steel columns packed with 5% SE-30 or 5% Dexsil 300 on Chromosorb W is shown in Fig. 6.

A calibration plot for the zinc adduct was linear over the range from 40 to 900 ng of zinc. The adduct was prepared by the synergic extraction procedure and 2·00-μl portions of the organic phase were injected into the column. Each point on the plot was the average of 3–5 replicate injections, and 14 different amounts of zinc were used to cover the range.

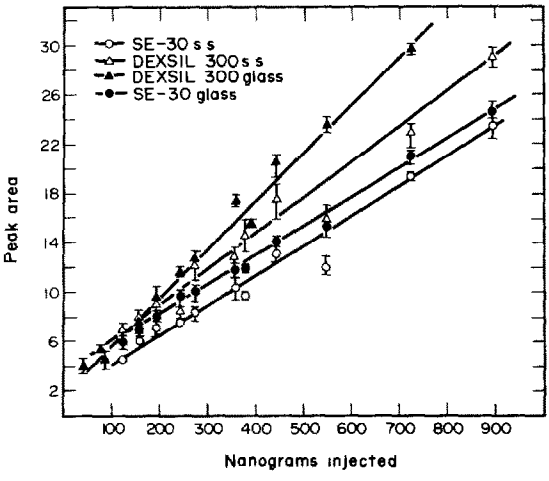

Fig. 6. Dependence of peak area on number of nanograms of $Zn(HFA)_2 . 2DBSO$ injected at 170° on 18 × 1·4 in. glass and stainless-steel columns. The stationary phases were 5% SE-30 or 5% Dexsil 300 on 100–120 mesh Chromosorb W-HP.

The average relative standard deviation was 2·9%. The organic phases containing the zinc adduct were kept for up to 2 months at ambient room temperature (approximately 22°) in small glass vials with polyethylene caps. The peak areas observed when these solutions were chromatographed were the same as those observed immediately after extraction, indicating the stability of the zinc adduct.

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DETERMINATION OF SOLUBLE STYPHNATE AND NITRATE IN WASTE-WATER FROM LEAD STYPHNATE PRIMER PLANTS

GEORGE NORWITZ and HERMAN GORDON

Frankford Arsenal, Philadelphia, Pa. 19137, U.S.A.

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Summary—Methods are proposed for the determination of soluble styphnate and nitrate in waste-water from lead styphnate primer plants. The styphnate is extracted from the waste-water with methylene chloride and is determined by measurement of the absorbance of the methylene chloride solution at 273 nm. The nitrate is determined in the aqueous solution left after the methylene extraction by measurement of the absorbance at 220 nm. For complete extraction of the styphnate by the methylene chloride, the solution must be moderately acidic (about 6% perchloric acid). The acidity for the determination of the nitrate is not critical. Before the determination of the nitrate in the aqueous extract, it is necessary to boil the solution to eliminate residual methylene chloride which would interfere with the determination of nitrate. PETN is extracted by the methylene chloride but does not interfere with the determination of the styphnate, since it shows no interfering peaks. Chloride, sulphate, phosphate, fluoride and carbonate do not interfere with the determination of styphnate or nitrate.

This laboratory undertook the development of methods for the determination of styphnate and nitrate in waste-water from lead styphnate primer plants. No work has previously been reported on the determination of styphnate and nitrate in the presence of each other. Nitrate when present alone has been determined in waste-water by the following methods: spectrophotometrically by use of phenoldisulphonic acid, brucine or chromotropic acid;[1,2] reduction to nitrite, followed by spectrophotometric determination of the nitrite;[1,2] measurement in the ultraviolet region.[1–9] Styphnate interferes with all of these methods. Styphnate when present alone in waste-water could be determined by measurement of the yellow colour of the styphnate ion.

A procedure was developed whereby the styphnate is determined in the waste-water by extraction with methylene chloride and measurement of the absorbance of the methylene chloride solution. The nitrate is then determined in the aqueous solution by measurement in the ultraviolet region.

EXPERIMENTAL

Reagents

Treated methylene chloride. Add about 450 ml of ACS-grade methylene chloride to about 50 ml of 5% perchloric acid in a 500-ml separatory funnel and shake it for 1 min. Drain off the methylene chloride (bottom) layer and store in a dark bottle.

Standard styphnate solution No. 1 (1 ml = 1·0 mg TNR). Dissolve 0·2500 g of trinitroresorcinol (TNR) in treated methylene chloride and dilute to 250 ml in a volumetric flask with treated methylene chloride.

Standard styphnate solution No. 2 (1 ml = 0·1 mg TNR). Dilute 20 ml of standard styphnate solution No. 1 to 200 ml in a volumetric flask with treated methylene chloride.

Standard nitrate solution No. 1 (1 ml = 1·0 mg NO_3^-). Dissolve 0·6853 g of sodium nitrate (previously dried at 150°) in water and dilute to 500 ml in a volumetric flask with water.

Standard nitrate solution No. 2 (1 ml = 0·1 mg NO_3^-). Dilute 20 ml of standard nitrate solution No. 1 to 200 ml in a volumetric flask with water.

Preparation of calibration curves

Styphnate. Transfer 2·0, 5·0, 8·0 and 10·0 ml of standard styphnate solution No. 2 to 100-ml volumetric flasks and dilute to the mark with treated methylene chloride. Measure the absorbance at 273 nm, using treated methylene chloride in the reference cell. Plot absorbance against mg of TNR (per 100 ml).

Nitrate. Transfer 2·0, 5·0, 8·0, 10·0 and 12·0 ml of standard nitrate solution No. 2 to 100-ml volumetric flasks and dilute to about 75 ml with water. Add 6 ml of perchloric acid and dilute to the mark with water. Measure the absorbance at 220 nm, using 6% perchloric acid in the reference cell. Plot absorbance against mg of NO_3^- (per 100 ml).

Procedure

Styphnate. If the solution is not clear, filter it through a sintered-glass crucible of fine porosity but do not wash the filter. Transfer the solution to a clean dry bottle. Pipette an aliquot containing preferably 0·4–1·0 mg of styphnate (but no more than 50 ml) to a 100-ml separatory funnel. Dilute to about 75 ml with water, add 6 ml of perchloric acid and dilute to about 100 ml with water. Extract with three 25-ml portions of treated methylene chloride. Collect the combined extracts in a 100-ml volumetric flask and dilute to the mark with treated methylene chloride. Save the aqueous layer for the determination of nitrate. Measure the absorbance of the methylene chloride solution at 273 nm, using treated methylene chloride in the reference cell.

Nitrate. Wash the aqueous phase from the extraction into a 250-ml beaker and boil down to about 70–80 ml. Cool and dilute to 100 ml with water in a volumetric flask. If the solution contains more than 1·2 mg of NO_3^-, pipette an aliquot containing preferably 0·4–1·0 mg of NO_3^- into a 100-ml volumetric flask and dilute to about 75 ml with water. Add sufficient perchloric acid to bring the total amount of perchloric acid to 6 ml and dilute to the mark with water. Measure the absorbance at 220 nm, using 6% perchloric acid in the reference cell.

The cells should be cleaned daily by soaking them in concentrated sulphuric acid for 15 min.

DISCUSSION AND RESULTS

Much work was devoted to the choice of a solvent for extraction of the styphnate. Obviously the solvent should have the following characteristics: immiscibility with water, high solubility for styphnate, low solubility for nitrate, no absorbance peaks that interfere with the spectrophotometric determination of styphnate, density heavier than water so as to facilitate extraction with a separatory funnel.

There are very few solvents that fulfil these requirements. The first choice was chloroform, but the results obtained were erratic. Attention was therefore turned to methylene chloride. First, absorption spectra were recorded. Technical-grade methylene chloride was used for the preliminary work. It was found that trinitrorescorcinol was quite soluble in the technical-grade solvent but when the solubility was subsequently tested with ACS-grade methylene chloride, it was found the material was rather insoluble in this solvent. This difference in solubility of trinitroresorcinol in the two grades of solvents was so pronounced that it was apparent by visual observation. At first, it was thought that the difference in solubility was due to the effect of impurities (for example, chloroform) present in the technical-grade methylene chloride but not in the ACS-grade. However, after much experimental work, it was ascertained that the cause of the phenomenon was the higher water content of the technical-grade methylene chloride. In order to use ACS-grade methylene chloride in the method, it was concluded that it would be necessary to saturate it with water by shaking with water in a separatory funnel. Rather than use water alone, however, it was found advisable to use dilute perchloric acid (5%), since shaking with water alone caused the methylene chloride to turn slightly yellow (although it still remained clear). The solubility of water in methylene chloride at 20° has been given as 0·14% w/w.[10]

The trinitroresorcinol used was military-grade material (MIL-T-50611, Type I, pale yellow).[11] The assay requirement for the material as determined by titration of the nitro groups is 98·0% minimum (the actual assay was 99·2%).

The absorption spectrum for trinitroresorcinol dissolved in the treated methylene chloride (*vs.* water in the reference cell) is shown in Fig. 1. The spectrum for treated methylene chloride alone is also shown. It is seen that the spectrum of trinitroresorcinol has peaks at 273 and 335 nm (the peak at 273 nm seemed preferable for quantitative work because it was the stronger peak), and that the spectrum of methylene chloride shows no peaks that would interfere with the determination of trinitroresorcinol. A calibration curve, prepared as described above, obeyed Beer's law over the range 0–1·0 mg of TNR per 100 ml.

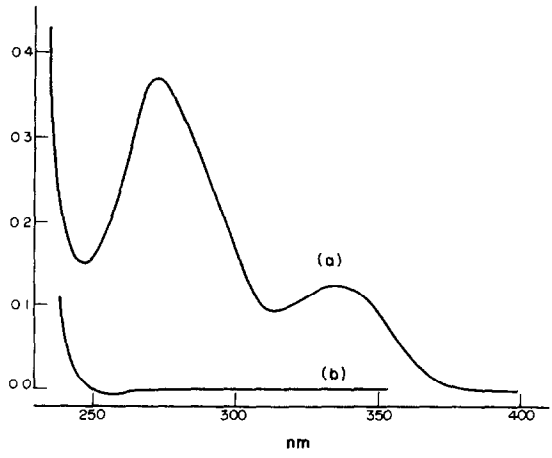

Fig. 1. Absorption spectra for (*a*) trinitroresorcinol dissolved in treated methylene chloride (0·5 mg of TNR per 100 ml) and (*b*) treated methylene chloride.

The effect of acidity on the extraction of styphnate from water by methylene chloride was investigated. For this study, 10-ml portions of a 0·1 mg/ml TNR solution were transferred to 125-ml separatory funnels containing about 50 ml of water, various amounts of perchloric acid were added and the volumes were brought up to about 100 ml. Three extractions were performed with 25-ml portions of methylene chloride and the combined extracts were diluted to 100 ml in volumetric flasks with methylene chloride. The absorbances were measured at 273 nm and the weight of trinitroresorcinol was calculated by referring to the calibration curve. The results (Table 1) show that no trinitroresorcinol is extracted from a neutral solution and that for essentially complete extraction the solution must have a minimum acidity of about 5% perchloric acid. The use of 6% perchloric acid is recommended.

All calculations for styphnate were made on the basis of trinitroresorcinol. Some of the styphnate is present as dissolved lead styphnate but this is converted into trinitroresorcinol by the perchloric acid. The solubility of lead styphnate in water has been given as 0·04%.[12] The method in this paper is designed for the determination of soluble styphnate (this determination by itself is important since the insoluble matter is ordinarily removed by settling or filtration of the waste before its discharge).

The spectrum of nitrate ion in the ultraviolet range shows a strong peak at about 205 nm and a weaker peak at about 303 nm.[13,14] The absorption spectra obtained in this laboratory for nitrate are shown in Fig. 2.

Table 1. Effect of perchloric acid concentration on extraction of trinitroresorcinol by methylene chloride (1·0 mg of trinitroresorcinol present)

Perchloric acid, %	TNR, recovered, *mg*
0	0·00
1	0·88
2	0·90
3	0·95
5	0·98
8	0·98
10	0·97
20	0·98

Table 2. Effect of boiling on the recovery of nitrate

NO_3^- added, *mg*	Volume to which solution was evaporated, *ml*	NO_3^- recovered, *mg*
0·80	80	0·81
0·80	60	0·79
0·80	40	0·80
0·80	20	0·81
8·00*	80	8·10
8·00*	60	8·20
8·00*	40	7·90
8·00*	20	8·00

* 1/10 aliquot taken after boiling.

Ordinarily, it is desirable to measure the absorbance of a peak at the point of maximal absorbance (203 nm in this case). However, it was decided to measure the absorbance at 220 nm as recommended by other investigators[1,2,4–7,9,10] in order to reduce the effect of extraneous organic matter; also, measurement at 220 nm permitted the use of a Beckman Model DU spectrophotometer (measurement at 200–205 nm is not feasible with this instrument on account of errors caused by stray light[13]).

As demonstrated by Bastian *et al.*[13] the acidity is not critical in the determination of nitrate by measurement in the ultraviolet region. These investigators used 5% perchloric acid (in the determination of nitrate in carbonates).

It was found necessary to boil the aqueous solution after the methylene chloride extraction in order to remove the residual methylene chloride that would interfere with the determination of nitrate (the solubility of methylene chloride in water has been given as 2·00% w/w[10]). If the aqueous solution is not boiled for several minutes, high results will be obtained for nitrate. To ascertain whether there is a loss of nitrate as nitric acid, solutions containing 0·80 and 8·00 mg of NO_3^- were transferred to 250-ml beakers. Perchloric acid (6 ml) was added and the solutions were diluted to about 100 ml. The solutions were then boiled down to various volumes and the NO_3^- was determined by measurement at 220 nm. The results (Table 2) show that no loss occurs even when the solutions were boiled down to 20 ml. The nitrate would be almost completely lost if the solutions were boiled until the perchloric acid fumed (at a volume of about 6 ml).

In studying possible interferences with the methods, we considered only the interferences from ingredients from primer mixes made by Frankford Arsenal and other U.S. Army Arsenals. These primer mixes contain such constituents as lead styphnate, barium nitrate, PETN, tetracene, antimony sulphide, aluminium powder, calcium silicide and a binder (a gum such as gum arabic). Tetracene, antimony sulphide, aluminium powder and calcium silicide are insoluble in water and would not interfere since they would be filtered off before the analysis. PETN is only slightly soluble in water and most of it would

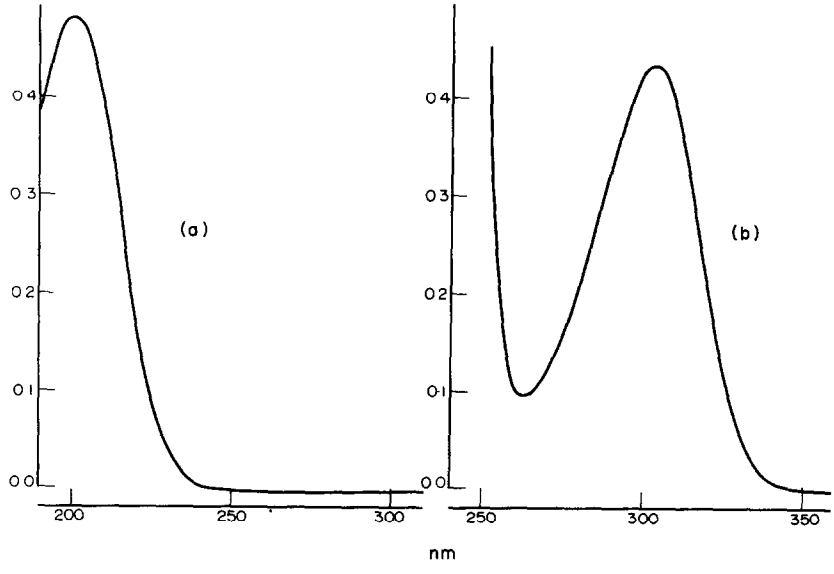

Fig. 2. Absorption spectra for nitrate in 6% perchloric acid. (a) = 1 mg of NO_3^- per 100 ml; (b) = 1000 mg of NO_3^- per 100 ml.

be filtered off; any PETN left in the aqueous solution would be completely extracted by the methylene chloride but would not interfere (the absorption spectrum obtained for 1·0 mg of PETN per 100 ml of methylene chloride was identical with that for methylene chloride alone). The spectrum of gum arabic does not show interfering peaks either for the aqueous solution or the methylene chloride extract (gum arabic is only slightly soluble in methylene chloride).

Chloride, sulphate, phosphate, fluoride and carbonate present in industrial water would not be extracted by the methylene chloride and would not interfere with the method for styphnate. It has been demonstrated by previous investigators[1,2,4–9,13–15] that chloride, sulphate, phosphate and fluoride do not interfere with the method for the determination of nitrate. The interference from carbonate is eliminated by boiling the perchloric acid solution. Nitrite, if present, would be measured as nitrate. Possibly, the interference from nitrite could be eliminated by treatment with such reagents as hydrazine sulphate. This was not investigated.

The problem of interference from extraneous organic matter had no vital bearing on the present problem. However, the question arose as to whether the methylene extraction technique might be used to reduce or eliminate the interference from organic matter with the determination of nitrate in general. Many schemes have been proposed for reducing or eliminating the interference of organic matter in the determination of nitrate in water. The American Public Health Association.[1] Goldman and Jacobs,[4] Hosther,[5] and Hosther and Rackham[6] corrected for the organic matter by measuring the absorbance at 220 nm (or 210 nm) and at 275 nm; they then deducted a multiple of the absorbance at 275 nm from the absorbance at 220 nm (or 210 nm) (the multiple depends on the organic matter present but is ordinarily 2 or 2·5). Navone[9] made the measurements at 210 nm and used a blank obtained by reduction with a copper–zinc couple. Mertens and Massart[7] made the measurements at 210 or 220 nm and used a blank obtained by reduction with Raney nickel. Morries[8] subtracted the average of the increase in absorbance over the intervals 205–210 nm and 225–230 nm from the increase in absorbance between 215 and 220 nm. Armstrong[3] used a blank prepared by reducing the nitrate with hydrazine sulphate (Armstrong's method for determination of the nitrate is unusual in that it involved the addition of an equal volume of sulphuric acid to a dilute hydrochloric acid solution of the nitrate and measurement of the peak at 230 nm, probably due to NOCl). Some interfering organic materials can be removed from solution before the determination of the nitrate, by treatment with aluminium hydroxide.[1]

Table 3. Results for trinitroresorcinol and barium nitrate in synthetic samples

Added, *mg*		Recovered, *mg*	
TNR	$Ba(NO_3)_2$	TNR	$Ba(NO_3)_2$
0·50	4·00	0·49	3·88
0·50	2·00	0·48	1·98
0·50	1·00	0·47	1·00
1·00	4·00	0·97	4·20
1·00	2·00	0·97	2·05
1·00	1·00	0·96	1·02

Table 4. Results for styphnate and barium nitrate in actual samples of waste-water

Sample	TNR *g/l.*	$Ba(NO_3)_2$ *g/l.*
1	0·695 ; 0·700	2·33 ; 2·20
2	0·036 ; 0·033	0·055 ; 0·050
3	1·38 ; 1·40	64·0 ; 60·5

A few experiments with the methylene chloride extraction technique indicated that the interference by such materials as benzene and toluene could be eliminated by a methylene chloride extraction, since these substances are readily extracted. On the other hand, interference from such materials as acetone and pyridine cannot be so eliminated since these substances are not readily extracted.

To check the accuracy of the methods for styphnate and nitrate proposed in this paper, synthetic samples prepared from trinitroresorcinol and barium nitrate were analysed (Table 3). The recoveries were satisfactory. Three waste-samples were also analysed (Table 4).

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INFORMATION THEORY IN ANALYTICAL CHEMISTRY*

BASIC TERMS, DEFINITIONS AND INTERPRETATIONS

ARBEITSKREIS "AUTOMATION IN DER ANALYSE":

Conveners H. MALISSA and J. RENDL†

Institut für Analytische Chemie und Mikrochemie der Technischen Hochschule, 1060 Wien, Getreidemarkt 9, Austria

English version: I. L. MARR

Chemistry Department, University of Aberdeen, Old Aberdeen, Scotland

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Summary—The most important terms in information theory (information, character, code, message and signal) are defined and interpreted with reference to automation in analytical chemistry. The aim of this communication and the earlier one dealing with systems theory,[1] is to facilitate communication and understanding between all specialists working on or with automated systems for analysis.

For further investigation of the problems connected with automation in and with analytical chemistry, it is necessary to follow up the definitions and interpretations of systems theory[1] with a similar clarification and explanation of some terms from the field of information theory, particularly from the point of view of the analytical chemist.

It must first be established that those systems accessible to analytical chemistry, in which thermodynamic and kinetic relationships can be found and precisely determined, are finite with respect to both matter and energy, and must therefore contain within themselves—in their totality—the information sought.

The first step which is relevant to both analytical chemistry and information theory is usually the sampling of the system under investigation.

The sample contains information which is comparable to a certain extent with the information contained by the complete system, but which as a rule is not identical with that information in the sense of being a mathematical model of it. The aim of an optimized sampling technique in analytical chemistry is therefore to minimize the unavoidable differences between the information in the complete system and in the sample taken from it (problems of homogeneity).

On this basis, then, the sample material must carry items of information of which one or more may, through chemical or physical reaction, be released in the form of signals to be transmitted to a detector and then decoded. In the field of automation, which also includes the handling of signals with the help of instrumentation, it is of some importance to define terms such as information, character, code, message, data and signal, since otherwise the interpretation of the analytical measurements is rendered that much more difficult, and communication with computers incomprehensible. In what follows, an attempt has therefore been made to define these terms, based on the DIN Standards 44300 and 44301.

DEFINITIONS AND THEIR INTERPRETATION

Information

Definitions. Colloquially, information is the knowledge of factual content and procedures. In systems theory, information is a system based on elements, called characters, and the relationships between them, called codes. Mathematically, information is the result of correlating a particular event with a probability.

Interpretations. The colloquial definition implies, through the phrase "knowledge of", some human activity. One should, however, attempt to understand a quantity such as information without relating it directly to man. The systems-theory definition achieves this, illustrated in the following examples.

Example 1. Information about the two possible states of a pedestrian crossing is conveyed by the characters "red light" and "green light", and the convention (code) that "red means stop, green means go". The characters would not contain information without the appropriate convention (except that the electricity supply was working!)

Example 2. When we consider Sb as a chemical element, the information is given by the character "Sb" and by the code "Sb means the chemical element

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† Co-workers for this part: Dr. J. T. Clerc, Eidgenössische Technische Hochschule, Zürich; Prof. Dr. G. Gottschalk, Osram Studiengesellschaft, München; Dr. R. Kaiser, Institut für Chromatographie, Bad Dürkheim; Prof. Dr. H. Malissa, Technische Hochschule, Wien; Dr. I. L. Marr, University of Aberdeen; Dr. J. Rendl, Technische Hochschule, Wien; Prof. Dr. E. Schwarz-Bergkampf, Montanistische Hochschule, Leoben; Prof. Dr. H. Spitzy, Technische Hochschule, Graz; Dr. R. D. Werder, CIBA-GEIGY AG, Basel; Dr. H. Zettler, Norddeutsche Affinerie, Hamburg.

antimony, atomic number 51, atomic weight 121·75 *etc.*".

To quantify information, we must be able to link it with the probability $p(x_i)$ of an event x_i, such that

$$I(x_i) = k \cdot \ln p(x_i) \tag{1}$$

i.e., the information I is equal to the probability of the event multiplied by a constant k, the magnitude of which is dependent on the choice of the unit of information. Inasmuch as the unit of information is arrived at when one considers the choice between two equally probable possibilities, then

$$1 = k \ln \tfrac{1}{2} \quad \text{and} \quad k = -1/\ln 2$$

Substituting this value for the constant in the equation (1) we get

$$\begin{aligned} I(x_i) &= -\ln p(x_i)/\ln 2 \\ &= -\log_2 p(x_i) \\ &= \log_2 \{1/p(x_i)\} \end{aligned} \tag{2}$$

One thus arrives at the dimensionless unit called a bit. The smallest quantity of information is given by a yes–no decision and applies when one of two mutually exclusive and equally probable possibilities is chosen.

The tossing of a coin, or the case mentioned in example 1 (as long as the red and green states are equally probable) each gives rise, according to equation (2), to the smallest practical amount of information, *i.e.*, one bit. Example 2 can be considered in terms of the qualitative detection of the element antimony. The answer corresponds to an information content of about 7 bits (see example 5).

The mathematical usage of the term information may lead to non-integral numbers of bits, which are clearly quite meaningful for theoretical or comparative purposes. Experimental verification on the other hand, can involve only integral values.

Information in analytical chemistry must be handled in a similar manner as in communications theory, since we are concerned with realizing information in such a way that a relevant signal which contains that information is obtained from a source (*e.g.*, a system or a sample) by a selection procedure (*e.g.*, a reaction).

For such chemical information to be quantified, it must be modified into a yes–no decision. Qualitative results are in any case already digital and therefore easily convertible into yes–no form. However, in most cases information is obtained in analogue form, as for example, in quantitative results. These results must be digitalized according to some relevant scale of working, in order to quantify the information contained in them.

The following important additional terms are useful for quantifying information.

Maximum information. The maximum information I_0 is given by the choice of one event from n mutually exclusive but equally probable events, *i.e.*,

$$I_0 = \log_2 n \tag{3}$$

As an example we might consider the number of bits required to express one decimal digit:

$$I_0 = \log_2 10 = 3{\cdot}32$$

Similarly, to represent a three-digit number, 9·96 bits are required.

Specific information. The specific information I_i of an event x_i (*e.g.*, the appearance of a particular character) is the logarithm to the base 2 of the reciprocal of the probability $p(x_i)$ of its occurrence.

$$I_i = -\log_2 [1/p(x_i)] \tag{4}$$

If we consider the information content of one letter from our alphabet of 26 plus a space, we arrive at 4·75 bits per letter, as maximum information. But in a piece of written text consisting of words the real information content is much lower, since particular pairs or groups of letters occur rather often, and the individual letters do not all appear with the same frequency, *i.e.*, the probability is not 1/27 for all letters. This raises the point that, making use of experience and knowledge of the language and of the common combinations of letters, we find less information per letter (the specific information) than the maximum information.

Average information. The average information $\bar{I}$ of one event out of a group of n events $x_1 \ldots x_n$ with respective probabilities $p(x_1) \ldots p(x_n)$ is the weighted average of the values of the specific information for each event:

$$\bar{I} = \sum_{i=1}^{n} p(x_i) . \log_2 [1/p(x_i)] \tag{5}$$

Redundance. The redundance is the difference between the maximum I_0 and the mean information $\bar{I}$:

$$R = I_0 - \bar{I} \tag{6}$$

The relative redundance r is the redundance expressed as a fraction of the maximum information:

$$r = R/I_0 = (I_0 - \bar{I})/I_0 \tag{7}$$

These terms will be illustrated by examples, in which the otherwise indefinable and vague concept "analytical experience" will be quantified in the form of statements based on information theory.

Example 3. The copper content of an unknown alloy can in theory lie anywhere between 0%* and 100%. If an analytical procedure with a margin of error of ±1% Cu is used to determine the copper (*i.e.*, error band $\Delta = 2\%$) only $n = 100/2 = 50$ equally probable events (analytical results) can be distinguished. The probability for any one of these events $P_i = 2/100 = 0{\cdot}02$.

The maximum information contained by any one analytical result (the selection procedure mentioned

* From an analytical point of view 0% has no real meaning and cannot be allowed. However, for the sake of this present argument, it will be taken as being the lower limiting value.

previously) such as 36 ± 1% Cu is therefore [according to equation (2)]:

$$I_0 = \log_2(100/2) = 5{\cdot}64$$

Similarly, the maximum information carried by one result from a more precise procedure with a margin of error of only ±0·1% Cu is

$$I_0 = \log_2(100/0{\cdot}2) = 8{\cdot}97$$

In this case the analytical result does indeed tell us "more" than in the first case. The higher information content is a result of the demand for higher accuracy being met by a more critical choice of working conditions or measuring apparatus.

Example 4. When, as a more specific case, brass samples are being routinely analysed in the laboratory of a non-ferrous metal foundry, the statistical frequency of the various possible copper results (still for the present given with a ±1% Cu margin of error) can be estimated from experience. For example for the range 0–50% Cu there are 25 possibilities, each with a probability (based on experience) of 0·001, *i.e.*,

		possibilities
0–50% Cu	$P_1 - P_{25} = 0{\cdot}001$	25
50–60% Cu	$P_{26} - P_{30} = 0{\cdot}01$	5
60–70% Cu	$P_{31} - P_{35} = 0{\cdot}173$	5
70–80% Cu	$P_{36} - P_{40} = 0{\cdot}01$	5
80–100% Cu	$P_{41} - P_{50} = 0{\cdot}001$	10

which satisfies the criterion that

$$\sum_{i=1}^{50} p_i = 1$$

According to these figures, the result 36 ± 1% Cu (range 0–50%) has a probability $p = 0{\cdot}001$ and thus according to equation (4) provides the specific information

$$I_i = \log_2(1/0{\cdot}001) = 9{\cdot}97$$

On the other hand, a result of 65 ± 1% (range 60–70%) with a probability of $p = 0{\cdot}173$, provides only

$$I_i = \log_2(1/0{\cdot}173) = 2{\cdot}53$$

bits of specific information. These different amounts of information are not explicable purely from the result, but from works' experience.

Experience with previous results, suggests that a reasonable result 65 ± 1%, was "to be expected" while a rare and therefore unlikely result of 36 ± 1% points to an error in production, sampling, or analysis. This corresponds of course to the analyst's own feeling simply on looking at the result. The higher information content is here a result of the "improbability" which can be traced back to the statistics—the "input", which is here the existing probability scheme for an idealized concentration range, based on experience.

Example 5. If we now calculate, with the help of equation (5) a weighted mean of all the specific information contents in example 4, we obtain the mean information of one out of these 50 possible results, taking into account the appropriate probabilities.

$$\begin{aligned}\bar{I} &= (25 + 10)0{\cdot}001 \log_2 1000 \\ &\quad + (5 + 5)0{\cdot}01 \log_2 100 \\ &\quad + (5)0{\cdot}173 \log_2 5{\cdot}78 \\ &= 3{\cdot}20 \text{ bits per result}\end{aligned}$$

For the case of equal probability, as in example 3, the mean information is also the maximum information $I_0 = 5{\cdot}64$ bits per result. The more the individual probabilities vary one from another, the smaller is the mean information per result.

Comments on redundance. The redundance is not only the difference between I_0 and $\bar{I}$, it is also a measure of the repetitiousness of an information display. This part of the information is, however, also a measure of the security from interference or falsification when the information is transmitted.

The line emission spectrum of an element A is an example of a presentation of redundant information. One line should suffice for the identification of the element A, but if this line should be masked by a much stronger line from another element B, there still remains the possibility of using a second line for the identification, and overcoming the interference. This would not be possible with a single-line spectrum where there is no redundance.

It is not intended here to go into the terms information-flow, information-volume, and information-content, which deal with the properties of transfer systems (communications systems) and are closely connected with the corresponding practical formulation and realization of such systems, but the reader may be referred to relevant texts.[2,3]

Character

Definition. A character is an element of a finite set of elements agreed on for the representation of information.

Interpretation. The set agreed on is called a character set. A sequence of characters which are taken together in a particular order as a particular entity, is called a word. This is particularly important in electronic data processing, but less so in analytical chemistry when one is concerned primarily with obtaining the signal, and secondarily with handling it. Character is not synonymous with symbol: a symbol is a character or a word to which a meaning is attached.

The interpretations of the terms character, symbol and signal only become clear when these terms are considered in the context of the terminology of automation.[4] Characters represent the abstract content of letters, numerals, punctuation marks, function and command signs (*e.g.*, carriage-return on a typewriter) *etc.* Characters can be reproduced in handwriting, or realized by combinations of holes on a tape, sequences of pulses and so on. In terms of an analytical procedure, characters become of significance when the signal originating in analogue form is digitalized, or for example when only a yes–no decision must

be taken by the analytical apparatus (actual value greater or less than a preselected value).

Code

Definition. A code is a systematic correlation between the respective characters of two character sets.

Interpretation. The ten characters (numerals) of the decimal system can be correlated with the two characters of the binary system through the so-called binary code.

The set of the chemical symbols in the periodic table of the elements is intentionally and unambiguously correlated with the set of the atomic numbers.

Coding has an extended sense, *e.g.*, when the word "iron" and all that is known about the material is correlated with the special character or symbol Fe.

Message

Definition. A message is a particular form of information based on a convention and used for the purposes of transmission.

Interpretation. A message embraces the data or facts being transmitted and can only be understood with reference to a particular communications system (involving transmitter, receiver, operator and machine). For example the information contained in a book becomes a message when the book is read. Reading therefore corresponds to the transmission of information in the form of characters, words, and sentences, and the convention lies in the representation of information by means of characters and words which must be known to both the writer and the reader.

It must be made clear, however, that information can be transmitted in analogue form (as in an analogue computer) as well as in digital form as characters, and it is of course possible to convert from one into the other at any time, although there is quite a difference between, for example, a telegraph message sent in morse code (digital) and a broadcast message sent as amplitude modulation of a carrier frequency (analogue). This matters especially in analytical chemistry, since the message (information obtained from the sample as a result of its interaction with the reagent) is initially always a continuous function (neglecting quantum mechanical considerations). The convention here lies in the connection between information and message, based on a knowledge of the reaction mechanism.

Data are, similarly to messages, a particular form of information based on a convention, but this time used for the purpose of processing rather than transmission.

Signal

Definition. A signal is the physical representation of a message.

Interpretation. The terms discussed so far—information, character and message—are purely abstract concepts, and as such cannot be stored, processed or transmitted. For these purposes they must be imprinted on some kind of physical carrier, and this physical quantity carrying the information is called the signal. It is indispensable for the representation, transmission and storage of a message, but the magnitude of the physical quantity alone is not a signal unless a convention has been agreed. The signal has the dimensions of the particular physical quantity involved, is time-variant, and possesses an information parameter (message) which determines the magnitude of the signal. Two types of display are possible: analogue and digital signals. In the former the information parameter is infinitely variable between given limits, and in the latter it can assume only discrete values. In the case of binary signals the information parameter can take only one of two possible values.

Example 6. Air pressure.

Signal: (physical representation of the pressure) is a column of mercury.

Information parameter: length of the column is the analogue representation of the pressure.

Information: air pressure equals, *e.g.*, 730·0 mmHg.

Example 7. Automatic burette with digital counter.

Signal: position of the piston.

Information parameter: the position of the piston is transformed mechanically into a setting of a digital counter calibrated to read volume, *e.g.*, 14·3 ml.

Information: volume delivered, if two signals (readings), before and after delivery, are recorded.

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ANION-EXCHANGE BEHAVIOUR OF SEVERAL ELEMENTS IN SYSTEMS CONTAINING FORMIC ACID*

S. WAQIF HUSAIN and M. D. CHARANDABI

Analytical Laboratories, Department of Chemistry, Faculty of Science, Azarabadegan University, Tabriz, Iran

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Summary—The anion-exchange characteristics of 27 elements toward the strongly basic anion-exchange resin Amberlite CG-400 in media containing aqueous formic acid and mixtures of formic acid with sodium formate, hydrochloric acid, sodium nitrite, acetone and methanol have been investigated. Possible separations are described and discussed. The quantitative separations achieved are Sr–La, Zn–Cd–Hg, and Ni–Fe.

The most widely used method of separation of metal ions on anion-exchange columns was first developed by Kraus and his co-workers[1] and is based on the different complex formation tendency of metal ions with halide ions. Selective sorption and elution of metal complexes on anion-exchangers has been shown in recent years to be an extremely powerful tool for metal ion separations.[2,3] Formic acid is known to form complexes with many metal ions,[4–10] and use has been made of some of them to facilitate separations.[11,12,13] However, only a few studies on the adsorption of metal formate complexes on anion-exchange resins have been reported.[7] The aim of the present paper was to investigate the adsorption characteristics and separation possibilities of elements in systems containing formic acid. For this purpose the distribution coefficients for 27 metal ions were determined in five systems with a strongly basic anion-exchange resin, resulting in some interesting possibilities for separations. Among these were the quantitative separations Sr–La, Zn–Cd–Hg and Ni–Fe.

EXPERIMENTAL

Reagents

All the chemicals were of analytical grade.

Ion-exchange resin. Amberlite CG-400(100–200 mesh) in the Cl^- form was converted into the $HCOO^-$ form by washing with 0·1 *M* sodium hydroxide, then with demineralized water, shaking with 2*M* formic acid and again washing with demineralized water. It was stored in an air-tight polythene bottle.

Metal ion solutions. Most of the metal ion solutions were 0·05*M* and were prepared in demineralized water or 0·05*M* acid solution from the chlorides or nitrates. Rare-earth metal sesquioxides were first fused with sodium carbonate, then dissolved in the minimum amount of hydrochloric acid and diluted with demineralized water to prepare a 1000-ppm solution (except for neodymium, which was 500 ppm).

Determination of metal ions. All the metal ions were determined titrimetrically with standard 0·002M EDTA. Chromium, vanadium and thallium were determined by back-titration methods.

Apparatus

A temperature-controlled mechanically-shaken water-bath was used for the distribution studies. For separations 10-mm bore glass columns were used.

Determination of distribution coefficients

The batch equilibrium method was used to determine the distribution coefficients according to the relationship:

$$K_d = \frac{\mu g \text{ of element/g of resin}}{\mu g \text{ of element/ml of solution}}$$

Each equilibrium experiment was performed in a 100-ml conical flask containing 30 ml of a mixture of 0·5 ml of the metal ion solution and 29·5 ml of the solvent system. To this mixture 0·5 g of resin in the $HCOO^-$ form was added and the mixture was agitated for 3 hr in the water-bath maintained at 30 ± 1°. The filtered solution was evaporated to remove organic solvents and then it was diluted with water and the metal ion determined.

Separation of metal ions

Strontium and lanthanum. A slurry of 1 g of resin in water was poured into a column. The column was saturated by the passage of 50 ml of solvent number 3 and then the mixture of 0·5 ml each of the strontium and lanthanum solutions in 3 ml of the solvent was added to the column. The strontium was eluted by passing solvent number 3 through the column at a flow-rate of 0·5 ml/min and the effluent was collected in 10-ml fractions. The lanthanum was sorbed on the resin and the strontium passed into the effluent. The lanthanum was eluted with 2·5*M* hydrochloric acid at the same flow-rate.

Zinc, cadmium and mercury. All the conditions were the same as above, except that solvent number 2 was used. The zinc and cadmium were eluted with solvent number 2. The mercury was sorbed on the resin and zinc and cadmium passed into the effluent one after the other. The mercury was stripped by 0·5*M* perchloric acid at a flow-rate of 0·5 ml/min.

Nickel and iron. A slurry of 1·5 g of resin in water was poured into a column. The column was saturated by the passage of 50 ml of solvent number 3 and then the mixture

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of nickel and iron in solvent number 3 was added to the column. The eluent was passed through the column at a flow-rate of 0·25 ml/min and the effluent was collected in 5-ml fractions. Nickel appeared first in the effluent followed by iron in the later fractions.

RESULTS

The anion-exchange behaviour observed for the various elements in different systems is illustrated in Figs. 1–5. The solvent systems used are summarized in Table 1.

Table 1. Solvent systems used in anion-exchange

Solvent number	Solvent system
1	0·01*M* Formic acid
2	0·01*M* Formic acid + 0·1*M* HCl (2:1)
3	0·01*M* Formic acid + 0·2*M* sodium formate (1:2)
4	0·01*M* Formic acid + acetone + 0·1*M* sodium nitrite (1:1:2)
5	0·01*M* Formic acid + methanol + 0·1*M* sodium nitrite (1:1:2)

Quantitative separations

Separations of 2·191 mg of strontium from 500 μg of lanthanum, of 1·632 mg of zinc and 2·810 mg of cadmium from 4·912 mg of mercury, and of 1·467 mg of nickel from 1·935 mg of iron, are illustrated in Figs. 6–8.

DISCUSSION

The adsorption behaviour observed for the various elements in aqueous formic acid is illustrated in Fig. 1 where the variation in K_d values of different metal ions is due to the formation of anionic formate complexes of varying strength. However, when dilute hy-

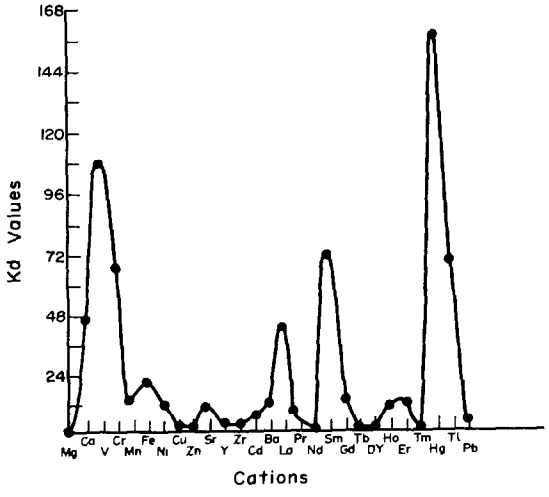

Fig. 1 K_d value of cations. Solvent 0·01*M* aqueous formic acid.

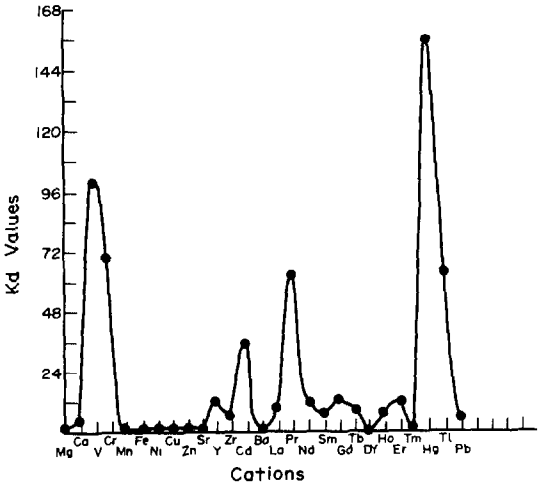

Fig. 2. K_d values of cations. Solvent 0·01*M* formic acid + 0·1*M* hydrochloric acid (2:1).

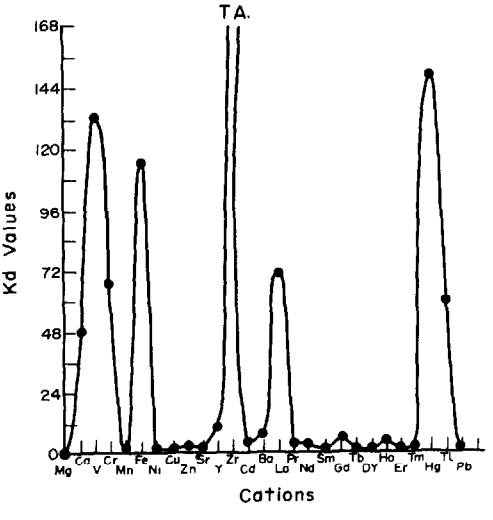

Fig. 3. K_d values of cations. System: 0·01*M* formic acid + 0·2*M* sodium formate (1:2).

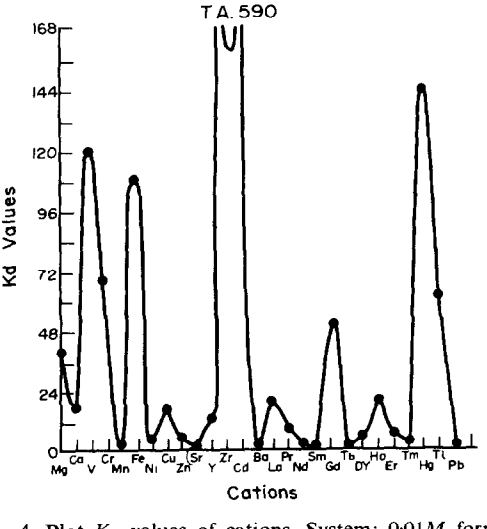

Fig. 4. Plot K_d values of cations. System: 0·01*M* formic acid + acetone + 0·1*M* $NaNO_2$ (1:1.2)

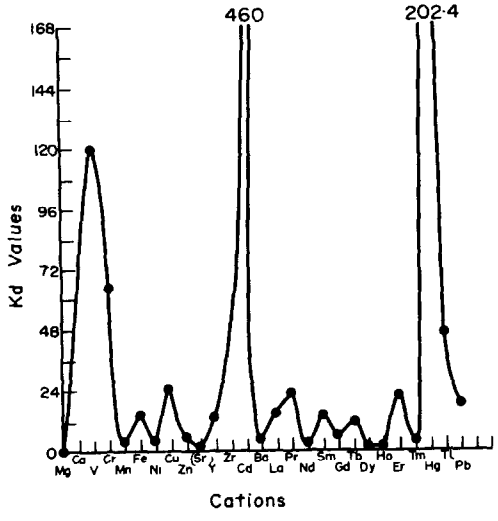

Fig. 5. K_d values of cations. System: 0·01*M* formic acid + methanol + 0·1*M* $NaNO_2$ (1:1:2).

drochloric acid is added to aqueous formic acid (Fig. 2), no pronounced change is found in the anion-exchange behaviour of most of the metal ions except that an increase in the adsorption of cadmium and mercury is observed. This is due to the formation of anionic chloride complexes even at this low concentration of hydrochloric acid.[14] The difference in the K_d values of Zn, Cd and Hg has been used to achieve quantitative separation of these three metal ions (Fig. 7). Mercury, which is strongly adsorbed on the anion-exchange resin, is eluted from the column with perchloric acid.[15] No adsorption of iron, manganese and copper from formic acid solution is observed in the presence of hydrochloric acid (Fig. 2). This is probably due to the fact that weak formate complexes of these elements are unstable in the presence of hydrochloric acid and to the formation of cationic chloride complexes such as $FeCl_2^+$, $MnCl^{2+}$.[14] These species, being positively charged, are not adsorbed on anion-exchange resins. When the concentration of formate ion is increased by adding sodium formate to the solution (solvent 3), considerable increase in the K_d values of some of the cations

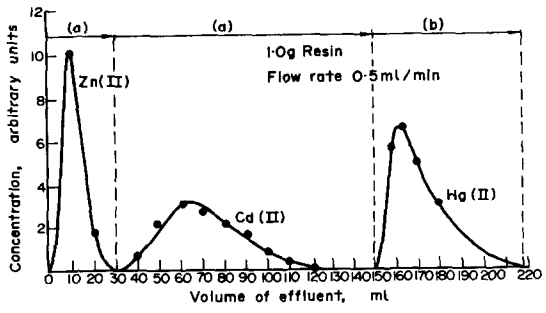

Fig. 7. Elution curve for the separation of Zn(II)–Cd(II)–Hg(II). (a) 0·01*M* formic acid + 0·1*M* hydrochloric acid (2:1), (b) 0·5*M* perchloric acid.

such as iron, chromium, vanadium and zirconium is observed. This is due to the fact that in the presence of excess of formate ion, strongly anionic formate complexes such as $Fe(HCOO)_6^{3-}$ and $Cr(HCOO)_6^{3-}$ are formed[8] which result in the high adsorption of these ions on anion-exchange resins. Zirconium is probably adsorbed as the anionic hydroxide complex, as the pH of this system (as compared to the other systems) is higher. Adsorption of lanthanum has been found to be significantly different[16] from that of other lanthanides on anion-exchange resins from concentrated nitrate solutions. Similarly in systems containing excess of formate ions, lanthanum has a different behaviour from other rare earths and is highly adsorbed. Quantitative separation of strontium and lanthanum (Fig. 6) and nickel and iron (Fig. 8) has been achieved. Other possible separations in this system are Mg(II)–Ca(II), Mn(II)–Fe(III), Y(III)–Zr(IV) and Pb(II)–Hg(II).

The results shown in Fig. 4 where a mixture of formic acid, sodium nitrite and acetone is used, are very interesting. The formate and nitrite anionic complexes of metal ions give a very different adsorption pattern from that of aqueous formic acid (solvent 1) alone. The presence of acetone, an "inert" solvent,[17] interferes in the association between the charged species and having a low dielectric constant it does not solvate them.[13] This system (solvent 4)

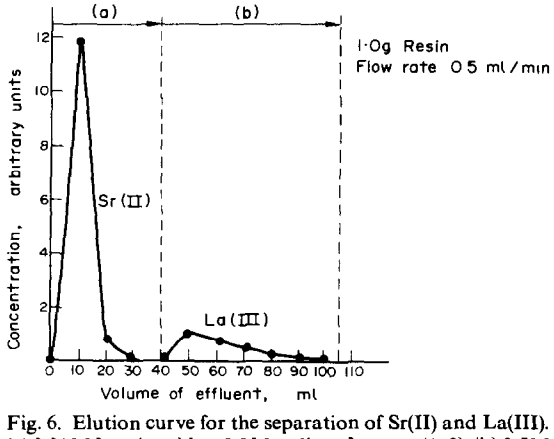

Fig. 6. Elution curve for the separation of Sr(II) and La(III). (a) 0·01*M* formic acid + 0·2*M* sodium formate (1:2), (b) 2·5*M* hydrochloric acid.

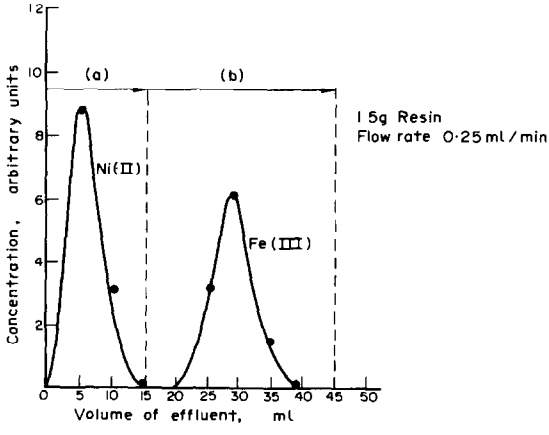

Fig. 8. Elution curve for the separation of Ni(II) and Fe(III). (a) and (b): 0·01*M* formic acid + 0·2*M* sodium formate (1:2).

offers many possibilities of binary and ternary separations such as V–Cr–Fe, Sm–Gd, Pb–Tl–Hg, Tb–Ho, and Ba–Ca–Mg. It is found that when acetone is replaced by methanol (solvent 5) the K_d values of some of the cations are lowered (Fig. 5). If an ion-exchange resin is brought into contact with a mixed solvent system, it is found that after equilibrium has been attained the solvent composition inside the resin may differ considerably from the composition of the external solvent mixture. Generally the resin prefers a more polar solvent to a less polar one. In this way the salting-out of the methanol in anion-exchange systems has been observed in water–methanol mixtures.[18] Having a high dielectric constant compared to that of acetone, it solvates the charged species and reduces their adsorption on the resin. This idea is supported by the higher R_f values reported for some elements in formic acid–methanol systems.[19] The possible separations in this system are Ho–Er, Ba–La, Dy–Er, Ni–Cu–Cd, Mn–Fe–Cu and Ho–Pr.

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SHORT COMMUNICATIONS

NEW COLORIMETRIC METHOD FOR THE DETERMINATION OF NYSTATIN

M. M. AMER

Analytical Chemistry Department, Faculty of Pharmacy, Cairo University, Cairo, Egypt

and

A. A. HABEEB

Drug Research and Control Centre, Cairo, Egypt

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Various colorimetric reagents have been reported for the determination of nystatin, such as phosphoric acid,[1] titanium tetrachloride,[2] aluminium chloride[3] and methanolic hydrochloric acid.[4] Chang *et al.*[5] outlined a procedure involving heating a solution of nystatin in dimethylformamide with 1*M* sodium hydroxide for 2 min, extracting the yellow product with chloroform in presence of a citrate buffer (pH = 2·3) and measuring the absorbance of the chloroform extract at 385 nm. The method was recommended for stability studies of nystatin.

In the present work, the alkaline hydrolysis product of nystatin was found to produce a purple-red colour with *p*-aminoacetophenone in presence of concentrated hydrochloric acid, the colour being a direct measure of the concentration of nystatin. Sugars interfere with the colour-formation, but the presence of alumina in the reaction medium was found to eliminate this interference.

EXPERIMENTAL

Reagents

Standard nystatin solution, 0·1% *w/v*. Prepared by dissolving 100 mg, accurately weighed, of USP reference standard nystatin in 10 ml of pure dimethylformamide and dilution to 100 ml with analytical-reagent grade methanol.

Sodium hydroxide solution, 1M.

p-*Aminoacetophenone solution*, 0·5% w/v in methanol.

Hydrochloric acid, concentrated.

Preparation of samples

Powders, capsules, tablets, vaginal tablets and oral suspension. Weigh an amount of the powdered sample, containing about 100 mg of nystatin, into a 100-ml volumetric flask. Shake with 10 ml of dimethylformamide for 2 min, then dilute to 100 ml with methanol, mix and filter through a dry filter paper; use the filtrate for the determination of nystatin.

Creams. Extract an amount of the cream containing about 100 mg of nystatin by stirring with 10 ml of dimethylformamide, centrifuging if necessary, and transfer the supernatant solution into a 100-ml volumetric flask. Dilute to the mark with methanol, filtering if necessary through a dry filter paper, and use the filtrate for the determination of nystatin.

Procedure

Into a 25-ml volumetric flask, introduce an aliquot of solution containing 0·2–1 mg of nystatin. Add 1 ml of *1M* sodium hydroxide, and in the case of pharmaceutical preparations also add 0·5 g of alumina. Mix well, heat in a boiling water-bath for exactly 2 min with continuous shaking, then cool rapidly for 2 min in an ice-bath. Add 1·5 ml of *p*-aminoacetophenone solution, followed by 1 ml of concentrated hydrochloric acid, mix well and dilute to 25 ml with methanol. Measure the absorbance at 520 nm, in a 1-cm cuvette, against a blank similarly treated.

Calculate the concentration of nystatin from a calibration curve simultaneously prepared by the same procedure, using the standard nystatin solution.

RESULTS

Tables 1 and 2 show the results of analysis of different concentrations of nystatin by the proposed method and by the Chang[5] method. Table 3 contains results for different forms of pharmaceutical preparations, analysed by the two methods.

DISCUSSION

Dilution with methanol does not affect the nature or the intensity of the colour, which has maximum absorption

Table 1. Colorimetric determination of pure nystatin using the proposed *p*-aminoacetophenone method

Nystatin taken, *mg*	Recovery, %
0·2	102·7
0·2	100·5
0·4	103·1
0·4	98·4
0·4	95·8
0·5	98·8
0·5	100·0
0·5	105·0
0·6	101·0
0·6	97·8
0·6	103·7
0·6	103·1
0·8	101·7
0·8	98·6
0·8	100·5
Mean	100·7
Std. devn.	2·5

Table 2. Colorimetric determination of pure nystatin by the Chang method[5]

Nystatin taken, *mg*	Recovery, %
0·5	101·4
0·6	101·2
0·8	98·1
1·2	98·2
1·4	99·5
1·6	97·9
Mean	99·4
Std. devn.	1·6

at 520 nm (Fig.1). The colour is stable over a period of about 15 min.

Since the reaction is mainly dependent on the alkaline hydrolysis of nystatin, the effect of the length of heating-time was studied. Figure 2 shows that the intensity of the colour increases with the time of heating at 100°, reaching a maximum after 2 min, then decreasing rapidly upon further heating. The period of heating is so critical that it is necessary to quench the reaction in an ice-bath after heating for exactly 2 min. A variation of ±10 sec in this heating time causes an error of ~2%.

The colour increases with the concentration of *p*-aminoacetophenone and of concentrated hydrochloric acid, reaching a maximum with 1·2 ml of 5% *p*-aminoacetophenone solution, and 0·6 ml of concentrated hydrochloric acid and remaining constant at higher concentrations; 1·5 ml of the *p*-aminoacetophenone reagent and 1 ml of concentrated hydrochloric acid are therefore used in the proposed procedure.

The colour obeys Beer's law over the range 0·1–1 mg of nystatin. The nature of the coloured product is not definitely known. However, the colour may be due to the condensation of *p*-aminoacetophenone with the carbonyl function of the carboxyl group resulting from the alkaline hydrolysis of nystatin at its ester linkage.

Statistical analysis of the results obtained by the proposed method and that of Chang *et al.*[5] shows that, there is no significant difference between two methods as indicated by Student's *t*-test and the *F*-test; the two methods are thus equally precise and accurate. However, the greater intensity of the purple-red colour produced by *p*-aminoacetophenone (compared with the yellow colour in the Chang procedure) gives a higher sensitivity, allowing determination of much smaller amounts of nystatin, viz. 0·2–1 mg.

Table 3. Colorimetric determination of nystatin in pharmaceutical preparations by the proposed *p*-aminoacetophenone method and the Chang method

Preparation	Recovery, %*	
	Present method	Chang[5] method
Mycostan capsules (Memphis Co.)	103·4	103·4
Nystatin tablets† (Antibiotic works)	81·3	80·8
Mycostan vaginal tablets (Memphis Co.)	104·6	105·1
Memcostan Cream (Memphis Co.)	106·6	107·1
Mycostatin oral suspension, (Squibb Co.)	97·3	98·9

* Assuming that each mg contains 5000 nystatin units.
† Expired sample.

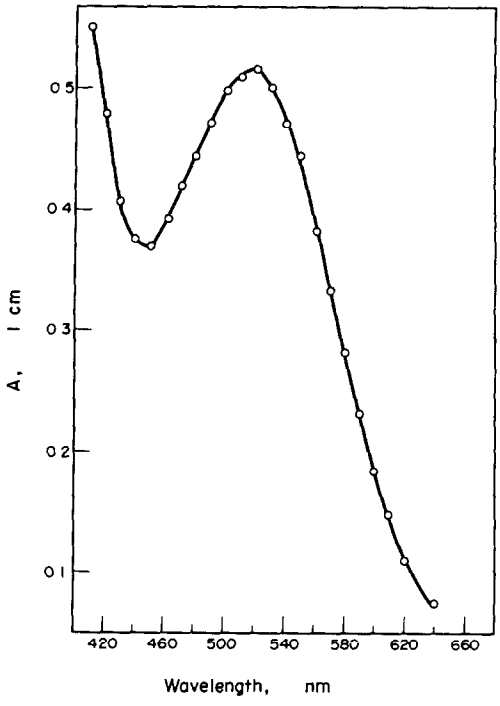

Fig. 1. Absorption spectrum of reaction product of nystatin and *p*-aminoacetophenone (λ_{max} = 520 nm).

Moreover, it does not need an extraction or careful adjustment of pH, as is the case in the Chang method.[5]

However, when the method was applied to the determination of nystatin in pharmaceutical preparations containing lactose or other sugars, it was observed that the purple-red colour formed did not reach its maximum. This problem was solved by including 0·1–0·5 g of alumina in the reaction medium; further addition of alumina does not affect the colour intensity, and the clear supernatant liquid is used for the spectrophotometric measurement. There is no obvious explanation for the role of the alumina, although it has been proved that both the sugar and nystatin were adsorbed on its surface. It is probable that either adsorption of the sugar inhibits its reaction with the coloured *p*-aminoacetophenone product, or that adsorption of nystatin together with *p*-aminoacetophenone allows for a better reaction at the alumina surface.

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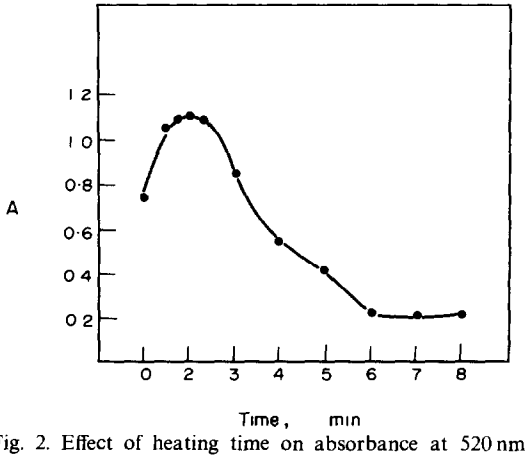

Fig. 2. Effect of heating time on absorbance at 520 nm

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SUR LA SEPARATION DES IONS FLUORURES DES IONS PHOSPHORIQUES SUR RESINES ECHANGEUSES D'IONS, EN VUE DU DOSAGE MICROANALYTIQUE DU FLUOR EN PRESENCE DE PHOSPHORE

MONIQUE POIRIER

Service Central de Microanalyse, du Centre Nationale de la Recherche Scientifique, 2 à 8, rue Henry Dunant, 94320 Thiais, France

(*Reçu le* 4 *décembre* 1974. *Accepté le* 29 *décembre* 1974)

La chromatographie sur résines échangeuses d'ions est devenue une méthode de séparation précise qui est appliquée par de nombreux auteurs dans le cadre de l'analyse chimique organique et inorganique pour la séparation de multiples ions.

Nous avons particulièrement étudié et adapté cette méthode de séparation pour son application au microdosage du fluor dans les composés organiques phosphorés. Ces derniers donnet en effet naissance, après la combustion en fiole à oxygène que nous mettons en oeuvre[1] à des ions phosphoriques, gênant le titrage des ions fluorures par colorimétrie spectrophotométrique; c'est pourquoi nous isolons les ions fluorures des ions gênants par un entraînement intermédiaire, à la vapeur, de l'acide fluosilicique,[2] d'après le principe de Willard et Winter (ce qui exige l'emploi d'un appareillage encombrant et l'augmentation sensible de la durée de la détermination du fluor).

Plusieurs auteurs, visant le remplacement de cette méthode, ont décrit la séparation des ions fluorures d'ions gênants au moyen des résines échangeuses d'ions. Ainsi Coursier et Saulnier[3] ont séparé des traces d'ions fluorures de sels d'aluminium; Newman[4] détermine le fluor contenu dans les minerais de phosphates de calcium; Glasö[5] décrit une méthode de séparation du fluor dans les minerais ferreux et roches phosphatées.

Nous nous sommes proposé de comparer, sur le plan pratique, le principle de séparation des ions fluorures au moyen des échangeurs d'ions à celui de Willard et Winter, en vue de son application dans le domaine de la microanalyse organique.

Principe

Le microdosage du fluor dans les composés organiques fluorés, object du travail décrit dans la présente note, comporte les trois étapes suivantes.

Minéralisation de la substance organique par combustion en fiole de Schöniger, suivant la méthode publiée par Levy et Debal.[1]

Séparation des ions fluorures des ions phosphoriques gênants, par chromatographie sur résine échangeuse d'anions.

Titrage des ions fluorures, dans la solution obtenue par le complexe ferrisulfosalicylique, formation concurrentielle de fluorure ferrique et mesure de la diminution correspondante de la coloration du premier complexe par absorption spectrophotométrique.[1]

Après minéralisation du composé organique, la solution recueillie est chromatographiée sur une colonne de résine anionique, fortement basique, en milieu alcalin. Les conditions opératoires (nature de la résine, dimensions de la colonne, concentration de l'éluant, débit de l'écoulement) ont été déterminées de telle sorte que les coefficients de partage des ions à séparer soient suffisamment différents et le nombre de plateaux théoriques assez élevé.[6]

Ainsi le phosphore et le fluor existant respectivement sous forme des ions PO_4^{3-} et F^-, en milieu alcalin, les premiers sont retenus sur la résine et les seconds, pour lesquels l'affinité de l'échangeur est très faible, sont élués quantitativement de la colonne.

PARTIE EXPERIMENTALE

Appareillage

Colonne de verre Pyrex de 200 mm de hauteur et 7 mm de diamètre surmontée d'un réservoir de 60 ml.

Ouate en chlorofibres Rhovyl, comme support des grains de résine dans la colonne.

Pompe péristaltique Michel, modèle Al-2 vitesse réglable de 0 à 400 tours/min, débit 0,07 ml/tour.

Reactifs

Résine Dowex-2 X10, échangeuse d'anions, du type ammonium quaternaire; 100–200 mesh.

Solutions d'hydroxyde de sodium 3*M* et 0,1*M*.

Solution d'acide chlorhydrique 0,3*M* préparée à partir d'acide chlorhydrique fumant.

2. A. H. Unterman, *Rev. Chim.*, 1961, **12**, 504; *Anal. Abstr.*, 1963, **11**, 3856.
3. O. Stanislova, *Dissertations Pharm.*, 1965, **17**, 3237; *Chem. Abstr.*, 1966, **65**, 573*b*.
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Le microdosage du fluor dans les composés organiques fluorés, object du travail décrit dans la présente note, comporte les trois étapes suivantes.

Minéralisation de la substance organique par combustion en fiole de Schöniger, suivant la méthode publiée par Levy et Debal.[1]

Séparation des ions fluorures des ions phosphoriques gênants, par chromatographie sur résine échangeuse d'anions.

Titrage des ions fluorures, dans la solution obtenue par le complexe ferrisulfosalicylique, formation concurrentielle de fluorure ferrique et mesure de la diminution correspondante de la coloration du premier complexe par absorption spectrophotométrique.[1]

Après minéralisation du composé organique, la solution recueillie est chromatographiée sur une colonne de résine anionique, fortement basique, en milieu alcalin. Les conditions opératoires (nature de la résine, dimensions de la colonne, concentration de l'éluant, débit de l'écoulement) ont été déterminées de telle sorte que les coefficients de partage des ions à séparer soient suffisamment différents et le nombre de plateaux théoriques assez élevé.[6]

Ainsi le phosphore et le fluor existant respectivement sous forme des ions PO_4^{3-} et F^-, en milieu alcalin, les premiers sont retenus sur la résine et les seconds, pour lesquels l'affinité de l'échangeur est très faible, sont élués quantitativement de la colonne.

PARTIE EXPERIMENTALE

Appareillage

Colonne de verre Pyrex de 200 mm de hauteur et 7 mm de diamètre surmontée d'un réservoir de 60 ml.

Ouate en chlorofibres Rhovyl, comme support des grains de résine dans la colonne.

Pompe péristaltique Michel, modèle Al-2 vitesse réglable de 0 à 400 tours/min, débit 0,07 ml/tour.

Reactifs

Résine Dowex-2 X10, échangeuse d'anions, du type ammonium quaternaire; 100–200 mesh.

Solutions d'hydroxyde de sodium 3*M* et 0,1*M*.

Solution d'acide chlorhydrique 0,3*M* préparée à partir d'acide chlorhydrique fumant.

Tableau 1. Acide *p*-fluorobenzoïque; teneur en fluor calculée: F = 13,56%

Prélèvement,		Masse de fluor, μg			Ecart
mg	F/P	calculée	trouvée	F%, corrigé*	F% calc. − F% corr.
6,392		867	858	13,76	+0,20
8,303		1126	1181	13,34	−0,22
6,550		888	862	13,50	−0,06
7,357		998	962	13,40	−0,16
7,791	2	1056	1014	13,34	−0,22
6,768	2	917	902	13,67	+0,11
8,206	2	1113	1083	13,53	−0,03
7,566	2	1026	1008	13,66	+0,10
7,400	2	1003	988	13,69	+0,13
7,758	1,4	1052	1012	13,37	−0,19
7,922	1,3	1074	1044	13,52	−0,04
8,072	1	1095	1078	13,69	+0,13
8,938	0,9	1212	1179	13,53	−0,03
7,258	0,8	984	956	13,51	−0,05
8,097	0,7	1098	1079	13,67	+0,11

* Facteur de correction $\bar{K}$ = 1,026

Mode opératoire

Prétraitement de la résine. La résine anionique, Dowex-2 X10, sous forme chlorurée, est préalablement mise en suspension dans l'eau bidistillée et agitée de façon à en disperser les agglomérats, puis versée dans la colonne de chromatographie où elle subit plusieurs cycles d'échanges. Traitée par une solution d'acide chlorhydrique 0,3*M* jusqu'à saturation en ions Cl^-, puis rincée à l'eau bidistillée déchlorurée, la résine est mise sous forme oxhydrilée par passage d'une solution très alcaline d'hydroxyde de sodium 3*M* et enfin lavée à l'eau bidistillée jusqu'à neutralité de l'effluent. La hauteur du lit de résine ainsi activée, atteint 18 cm. Le débit de l'écoulement est fixé à 1,5 ml/mn.

Elution. L'échantillon mis en solution après la minéralisation est versé dans le réservoir de la colonne de chromatographie qui est connecté à une pompe afin de maintenir le débit de l'écoulement à 1,5 ml/mn. Après fixation sur la résine des ions à séparer, les ions F^- sont déplacés par une solution éluante d'hydroxyde de sodium 0,1*M*. L'éluat est reçu directement dans une fiole jaugée jusqu'à épuisement de la résine en ions F^-. La désorption des ions fluorures dure environ 90 mm.

La résine est régénérée par une solution d'hydroxyde de sodium 3*M* qui entraîne tous les ions phosphoriques fixés par l'échangeur d'ions.

Dosage. Le dosage du fluor est effectué par colorimétrie spectrophotométrique. Toutefois la solution tampon normalement employée pour la formation du complexe coloré est remplacée par une solution d'acide monochloracétique à 75,6 g/l., afin de rétablir le pH acide requis.

RESULTATS

La méthode de séparation par échangeur d'ions a été éprouvée par le microdosage du fluor dans un mélange d'acide parafluorobenzoïque et d'acide benzène phosphonique. Les résultats obtenus, rassemblés dans le tableau ci-joint, ont permis de constater que l'addition de quantités variables de substance organique phosphorée à l'échantillon fluoré (suivant un rapport F/P* variant de 2 à 0,7) n'affecte pas la reproductibilité des valeurs trouvées. Cependant, il est apparu nécessaire de déterminer un coefficient de correction car les résultats obtenus sont systématiquement faibles mais reproductibles. Ce coefficient *K* est calculé avant chaque série à l'aide de plusieurs déterminations effectuées sur une substance-type à teneur connue en fluor:

$$K = \frac{\text{masse de fluor calculée}}{\text{masse de fluor trouvée}}$$

L'écart-type estimé pour l'ensemble des résultats a pour valeur $s = \sqrt{[\Sigma(x_i - \bar{x})^2]/[n-1]} = 0{,}13$ avec x_i = résultat individuel portant sur la teneur F% corrigée, $\bar{x}$ = moyenne arithmétique des résultats individuels x_i, n = nombre de résultats individuels.

Nous avons analysé une autre substance fluorée, la trifluoroacétanilide (dont la teneur en fluor est deux fois plus élevée, F% = 30,14), additionnée d'acide benzène phosphonique, en utilisant le même échangeur d'ions. Les résultats de dosage du fluor, compte tenu du coefficient de correction précédemment déterminé, sont légèrement erronés par défaut†.

DISCUSSION

Les résultats du présent travail d'approche mettent en évidence la possibilité d'utiliser la méthode de séparation sur résines échangeuses d'ions en vue du dosage microanalytique du fluor en présence de phosphore dans les composés organiques. Ces résultats laissent entrevoir de nombreuses applications. En effet, il existe aujourd'hui une grande variété de résines spécifiques,[7] de granulométrie plus fine et plus homogène,[8] dont l'utilisation impliquant un appareillage et une technologie plus élaborés, devrait permettre d'augmenter sensiblement l'efficacité de la colonne et de diminuer simultanément la durée de l'analyse.

Comparativement au principe de séparation par distillation selon Willard et Winter, la méthode mise en oeuvre dans les conditions décrites ne nous permet pas de réduire sensiblement la durée de l'analyse. Elle n'en demeure pas moins perfectible.

Nous remercions vivement Monsieur Rosset pour les conseils qu'il nous a prodigués.

* F/P représente le rapport des masses de fluor et de phosphore en présence.

† Cependant, la méthode normale de dosage du fluor dans la trifluoro-acétanilide (combustion en fiole de Schöniger) fournit également des résultats un peu faibles, cf. réf. 1.

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Résumé—Un exemple de séparation au moyen des échangeurs d'ions est étudié en vue de montrer la possibilité d'application de cette méthode dans le domaine de la microanalyse organique. Des ions fluorures peuvent être séparés d'ions phosphoriques sur résine anionique fortement basique, en milieu alcalin, ce qui permet, notamment, le microdosage du fluor, en présence de phosphore, dans les composés organiques.

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LOCATION OF END-POINTS IN HIGH-PRECISION COULOMETRY

WILLIAM F. KOCH, DONALD P. POE and HARVEY DIEHL
Department of Chemistry, Iowa State University, Ames, Iowa, 50010, U.S.A.

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Location of the end-point is currently the least accurately measured of the variables in high-precision coulometry, the other quantities—weight, potential, resistance, time and molecular weight—being measurable or known to 2 or 3 ppm. The constant current used in such titrations is cut back to a low value, 0·5–10 mA, in the region of the end-point and the problem of detecting the end-point is that commonly experienced when titrating with very dilute solutions, albeit under the favourable circumstance that no increase in volume occurs. In the titration of weak acids or weak bases, the titration curve becomes almost linear in the neighbourhood of the end-point and the location of the point of inflexion by eye assumes the subjective features of a betting game. Although the "placing of equal bets" has received some sanction in the realistic assessment of the error of measurement in work involving the determination of values of the fundamental physical constants,[1] the end-point location problem is obviously one in which application of theoretical and mathematical tools might well prove useful.

Yan[2] in a recent paper refers to Fortuin[3] and the latter in turn supplies a good bibliography to the earlier papers on the subject, principally to works of Kolthoff and of Hahn. The approach of these workers is essentially that of making plots of the first derivative and of obtaining data directly in difference form.

Yan, in the paper just cited, by an elegant finite difference approach based on the assumption that the curve of pH *vs.* moles of titrant could be approximated by a third-order polynomial (cubic equation), developed a neat and rapid numerical method utilizing four sets of data chosen symmetrically about the end-point. Yan selected a cubic equation simply because it is the simplest function having an inflexion point, but this selection has no theoretical justification. It should be noted that although a cubic equation is symmetrical about its point of inflexion, titration curves are not symmetrical, except in a very narrow region. Examination of titration curves (e.g., those shown by Diehl[4]) and a few simple manipulations with tracing paper can show this clearly. Yan's method is a neat procedure and our own feeling, after applying it to end-point data from various high-precision titrations, is that it is considerably better than visual estimation. However, only four data points are used and there is some dependence on the selection of these. Some questions therefore arise. Can a better result be obtained if all the data points are used? Is the cubic equation the best to use? How well does a cubic fit the experimental data?

These questions were tested, using an IBM 360/65 computer, and with the help of the subroutine OPLSPA*, which fits polynomials up to tenth order to experimental data.

The tests were made on data from five different coulometric titrations: of tris(hydroxymethyl)aminomethane (THAM) and of 4-aminopyridine by addition of excess of perchloric acid and back-titration with alkali generated at the cathode; of THAM and 4-aminopyridine with acid generated at the newly devised hydrazine–platinum anode,[5] and titrations of perchloric acid alone with alkali generated at the cathode. Two programs were used, the difference between them being that the independent and dependent variables were reversed.

The fit was excellent for the titrations involving THAM and 4-aminopyridine. The agreement between programs A and B was excellent. Agreement with Yan's method was only fairly good (Table 3). However, the method failed for the titrations of perchloric acid, the calculated equations being not even a reasonably good fit. Fifth-order equations proved no better.

Some dependence was found on the selection of points. The calculated curve fits better when more data points are used and best if the points are disposed symmetrically about the point of inflexion; a considerable latitude is allowable, however. For example, if 25% of the points at one end of the curve are not used, the relative error will be less than 2% (and the value obtained for the point of inflexion even then is better than the value obtained by the Yan method). With the same poor choice of data points, namely, three of the four points being on one side of the point of inflexion, the Yan method yields an absurd result.

It must be pointed out that the data being handled were within 30 μeq of the end-point in titrations involving 30 meq.

* Developed by the Computer Services Group, U.S. Atomic Energy Commission, Ames Laboratory, Ames, Iowa. A similar routine available in the U.K. is NAG. E02ABF, developed by the Numerical Algorithms Group, NAG Central Office, 13 Banbury Road, Oxford, U.K.

4. A. Newman, *ibid.*, 1958, **19**, 47.
5. Ö. Glasö, *ibid.*, 1963, **28**, 543.
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* Developed by the Computer Services Group, U.S. Atomic Energy Commission, Ames Laboratory, Ames, Iowa. A similar routine available in the U.K. is NAG. E02ABF, developed by the Numerical Algorithms Group, NAG Central Office, 13 Banbury Road, Oxford, U.K.

```
C        PROGRAM A
C      THIS PROGRAM FITS TITRATION DATA TO A CUBIC EQUATION,
C      USING A SUBROUTINE DEVISED BY THE AMES LABORATORY
C      COMPUTER SERVICE. THE ENDPOINT IS DETERMINED BY SETTING
C      THE SECOND DERIVATIVE OF THE COMPUTED CUBIC EQUATION
C      EQUAL TO ZERO AND SOLVING FOR THE INDEPENDENT VARIABLE.
C      THE PRINT-OUT INCLUDES: (1) THE COEFFICIENTS OF THE
C      CUBIC, (2) A LISTING OF THE INPUTTED VALUES, (3) A
C      LISTING OF THE CALCULATED VALUES OF THE DEPENDENT
C      VARIABLE FOR EACH DATA POINT, (4) THE TIME AT THE
C      ENDPOINT, (5) THE PH AT THE ENDPOINT, AND (6) THE SLOPE
C      AT THE ENDPOINT.
C      THE FORM OF THE CUBIC EQUATION IS:
C      PH = Q(1) + Q(2)*TIME + Q(3)*TIME**2 + Q(4)*TIME**3
C      NSETS = NUMBER OF SETS OF DATA TO BE READ
C      NAME = IDENTIFICATION OF INDIVIDUAL SETS OF DATA
C
C      OPLSPA SUBROUTINE
C      NDEG = DEGREE OF POLYNOMIAL (1.LT.NDEG.LT.10)
C      NPTS = NUMBER OF DATA POINTS
C      X = TIME IN SECONDS (INDEPENDENT VARIABLE)
C      Y = PH (DEPENDENT VARIABLE)
C      W = WEIGHTING FACTOR
C      Q = THE OUTPUT. A DOUBLE PRECISION ARRAY OF COEFFICIENTS
C      TUNYLO = 0.0 UNLESS LOOP THROUGH DIFFERENT NDEG'S
C      Y = Q(1) + Q(2)X + Q(3)X**2 + Q(4)X**3
C
C
      DIMENSION X(50),Y(50),W(50),YCALC(50),NAME(20)                    1
      DOUBLE PRECISION Q(10)                                            2
      DATA W/50*1.0/                                                    3
      READ(5,120) NSETS                                                 4
  120 FORMAT(I2)                                                        5
      DO 500 K=1,NSETS                                                  6
      READ(5,100)(NAME(I),I=1,20)                                       7
  100 FORMAT(20A4)                                                      8
      WRITE(6,110)(NAME(I),I=1,20)                                      9
  110 FORMAT('1',20A4)                                                 10
      WRITE(6,115)                                                     11
  115 FORMAT(1X,'PH = Q(1) + Q(2)*T + Q(3)*T**2 + Q(4)*T**3')          12
      NDEG=3                                                           13
      NQ=NDEG+1                                                        14
      TUNYLC=0.0                                                       15
      J=0                                                              16
  125 J=J+1                                                            17
      READ(5,130) X(J),Y(J)                                            18
  130 FORMAT(F7.2,F6.3)                                                19
      IF(X(J).LT.0.0) GO TO 140                                        20
      GO TO 125                                                        21
  140 NPTS=J-1                                                         22
      CALL OPLSPA(NDEG,NPTS,X,Y,W,Q,TUNYLO)                            23
      WRITE(6,200)(I,Q(I),I=1,NQ)                                      24


C      PROGRAM B IS IDENTICAL TO PROGRAM A WITH TRANSPOSITION
C      OF VARIABLES. THE FOLLOWING CARD CHANGES SHOULD BE MADE
C      IN PROGRAM A TO CREATE PROGRAM B:
C      STATEMENT 12
  115 FORMAT(1X,'T = Q(1) + Q(2)*PH + Q(3)*PH**2 + Q(4)*PH**3') 128
C      STATEMENT 18
      READ(5,130) Y(J),X(J)                                            188
C      STATEMENT 20
      IF(Y(J).LT.0.0) GO TO 140                                        208
C      STATEMENT 30
  230 FORMAT(1X,' I = ',I2,4X,'PH = ',F6.3,4X,'TIME = ',F7.2,
     &3X,'TCALC = ',F7.2)                                              308
C      STATEMENT 31
      ENDPH=-Q(3)/(3.0*Q(4))                                           318
C      STATEMENT 32
      ENDPT=Q(1)+Q(2)*ENDPH+Q(3)*ENDPH**2+Q(4)*ENDPH**3                328
C      STATEMENT 33
      SLOPE = 1./(Q(2) + 2.0*Q(3)*ENDPH + 3.0*Q(4)*ENDPH**2)           338
C      STATEMENT 36
      CALL GRAPH(NPTS, Y,X,3.7,7.0,5.0,0.0,0.0,0.0,0.0,0.0,0.0,
     &'TIME;','PH;',NAME,'  TIME = F(PH);')                           368
C      STATEMENT 37
      CALL GRAPHS(NPTS,YCALC,X,0.2,' ;')                               378
```

Table 1. Computer print-out for titration of 4-aminopyridine by back-titration of excess of standard perchloric acid with alkali generated at the cathode (pH as a function of time)

```
CATHODIC TITRATION OF 4-AMINOPYRIDINE
PH = Q(1) + Q(2)*T + Q(3)*T**2 + Q(4)*T**3
 Q(1) =  0.406836270 01
 Q(2) = -0.489721410-02
 Q(3) =  0.459390380-04
 Q(4) = -0.703305120-07
 I =  1     TIME =  100.00    PH =  4.010     PHCALC = 4.008
 I =  2     TIME =  139.98    PH =  4.170     PHCALC = 4.168
 I =  3     TIME =  160.13    PH =  4.271     PHCALC = 4.276
 I =  4     TIME =  180.02    PH =  4.390     PHCALC = 4.395
 I =  5     TIME =  199.91    PH =  4.520     PHCALC = 4.523
 I =  6     TIME =  219.82    PH =  4.660     PHCALC = 4.658
 I =  7     TIME =  239.71    PH =  4.801     PHCALC = 4.795
 I =  8     TIME =  259.60    PH =  4.940     PHCALC = 4.932
 I =  9     TIME =  279.55    PH =  5.067     PHCALC = 5.066
 I = 10     TIME =  299.52    PH =  5.192     PHCALC = 5.192
 I = 11     TIME =  319.42    PH =  5.303     PHCALC = 5.307
 I = 12     TIME =  339.40    PH =  5.403     PHCALC = 5.409
 I = 13     TIME =  359.40    PH =  5.488     PHCALC = 5.494
 I = 14     TIME =  379.38    PH =  5.566     PHCALC = 5.558
TIME AT ENDPOINT =  236.09      PH AT ENDPOINT =  4.774

SLOPE AT ENDPOINT =  0.692273E-02PH/SEC
```

Table 2. Computer print-out for titration of 4-aminopyridine by back-titration of excess of standard perchloric acid with alkali generated at the cathode (time as a function of pH)

```
CATHODIC TITRATION OF 4-AMINOPYRIDINE
T = Q(1) + Q(2)*PH + Q(3)*PH**2 + Q(4)*PH**3
 Q(1) = -0.792489110 04
 Q(2) =  0.485468600 04
 Q(3) = -0.988197480 03
 Q(4) =  0.685980590 02
 I =  1     PH =  4.010     TIME =  100.00    TCALC =  101.16
 I =  2     PH =  4.170     TIME =  139.98    TCALC =  138.65
 I =  3     PH =  4.271     TIME =  160.13    TCALC =  158.91
 I =  4     PH =  4.390     TIME =  180.02    TCALC =  180.10
 I =  5     PH =  4.520     TIME =  199.91    TCALC =  200.68
 I =  6     PH =  4.660     TIME =  219.82    TCALC =  220.89
 I =  7     PH =  4.801     TIME =  239.71    TCALC =  240.31
 I =  8     PH =  4.940     TIME =  259.60    TCALC =  259.66
 I =  9     PH =  5.067     TIME =  279.55    TCALC =  278.49
 I = 10     PH =  5.192     TIME =  299.52    TCALC =  298.91
 I = 11     PH =  5.303     TIME =  319.42    TCALC =  319.29
 I = 12     PH =  5.403     TIME =  339.40    TCALC =  339.95
 I = 13     PH =  5.488     TIME =  359.40    TCALC =  359.53
 I = 14     PH =  5.566     TIME =  379.38    TCALC =  379.38
TIME AT ENDPOINT =  236.61      PH AT ENDPOINT =  4.774

SLOPE AT ENDPOINT =  0.729955E-02PH/SEC
```

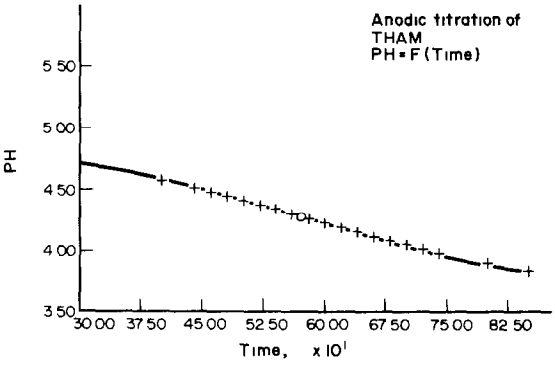

Fig. 1. Titration of tris(hydroxymethyl)aminomethane with acid generated at the hydrazine–platinum anode. Time as a function of pH. +, Experimental data. Solid line, cubic equation fitted by computer. The corresponding plot for pH as a function of time appears identical to the eye.

COMPUTER PRINT-OUT PROGRAMS

In program A, pH is obtained as a cubic function of time:

$$\text{pH} = Q_1 + Q_2(\text{time}) + Q_3(\text{time})^2 + Q_4(\text{time})^3.$$

In program B, time is obtained as a cubic function of pH:

$$\text{time} = Q_1 + Q_2(\text{pH}) + Q_3(\text{pH})^2 + Q_4(\text{pH})^3.$$

In both programs the best values of the coefficients Q_1–Q_4 are determined, the second derivative of the resulting cubic equation is set equal to zero, and the equation is solved for the independent variable. The value found is the point of inflexion. If the calculated cubic equation fits the titration data exactly, then the point of inflexion will indeed be the end-point of the titration (and the equivalence point to the extent that the two are identical). In the computer output are listed: (1) the computed coefficients, (2) the experimental data, (3) the calculated values of the dependent variable for each data point, (4) the computed time at the end-point, (5) the computed pH at the end-point, and (6) the slope of the titration curve at the end-point. A high-level plotting system, SIMPLOTTER, was used to obtain plots showing the calculated cubic equation superimposed on the experimental data points. Representative outputs are shown in Tables 1 and 2 and a typical graph is given in Fig. 1. Comparative results obtained by different methods are given in Table 3. Figure 1 well illustrates the difficulty in determining the end-point by visual inspection.

Table 3. Comparison of end-points obtained by computer programs A and B and method of Yan (data from various titrations)

Titration	End-point, *sec*		
	pH = *f*(time)	Time = *f*(pH)	Yan
4-Aminopyridine, cathodic*	236 69	236 61	230 18
4-Aminopyridine, anodic†	206 90	206 21	208 47
THAM, cathodic*	218 58	218·18	213 91
THAM, anodic†	572 49	573 08	579 09

* Back-titration of excess of standard perchloric acid with alkali generated at a platinum cathode.

† Titration with acid generated at the hydrazine–platinum anode.

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Summary—A computer has been used to fit a cubic equation to experimental data obtained in the region of the end-point in high-precision coulometric titrations of 4-aminopyridine and tris(hydroxymethyl)aminomethane. For these weak bases, the two end-points (points of inflexion calculated by setting the second derivative equal to zero) obtained by choosing first time, and secondly pH, as the independent variable, are in good agreement.

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3-METHYL-2-OXAZOLIDONE AS A SOLVENT FOR ACID–BASE TITRATIONS

JOHN E. TAPHORN III, GARY M. DAVIES and JOSEPH A. CARUSO

Department of Chemistry, University of Cincinnati, Cincinnati, Ohio 45221, U.S.A.

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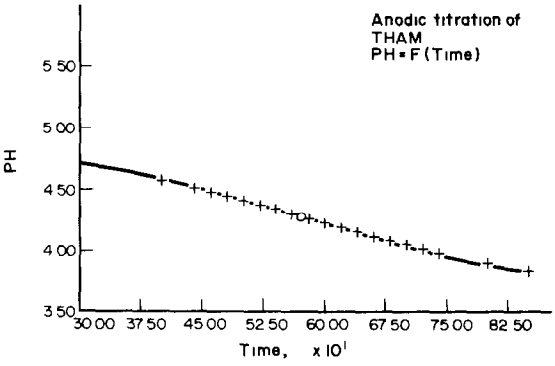
One of the most common problems encountered in non-aqueous titration studies is the lower solubility of ionic species, due in part to the generally low dielectric constants of the most common solvents. The dielectric constant of 3-methyl-2-oxazolidone has been found to be 77·5 (at 25°).[1] This is nearly the same as that for water 78·3 (at 25°),[2] and 3-methyl-2-oxazolidone (3Me2Ox) has been found to have good solvating ability.[3] The molecular struc-



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ture of the compound indicates that it is a dipolar aprotic solvent. This solvent also has been shown to be useful as a titration medium for selected barbiturates and sulpha drugs.[4]

EXPERIMENTAL

Synthesis and purification of 3Me2Ox

The solvent was synthesized by the Homeyer method[5] from diethyl carbonate and methylethanolamine, according to the method of Huffman and Sears,[1] except for certain modifications based on the following observations. A diethyl carbonate–water azeotrope[6] could not be distilled from the reaction mixture. Instead, the by-product, ethanol, began to distil at 0·2–0·3° below its reported boiling point, indicating the probable presence of an ethanol–water azeotrope.[7] The reaction proceeded to approximately 60% completion without the addition of the catalyst, potassium hydroxide. Further distillation, without catalyst, produced copious quantities of decomposition and polymerization products. Addition of the catalyst at the start of the reaction allowed it to proceed to 95–98% completion (based on the stoichiometric amount of ethanol recovered) without excessive decomposition or polymerization. This provided a crude product which could be readily purified. The time required to prepare a 4-l. batch was approximately 18 hr.

The crude solvent was purified by first removing the ethanol and starting materials under vacuum. The solvent was further purified by fractional freezing[8] in a Sargent–Welch Model 43105 incubator–refrigerator controlled to ±0·1°. Before the final stages of purification the infrared and NMR spectral characteristics were determined. A Karl Fischer titration showed the water content to be 0·034%. Purification was continued until the solvent remained solid at 15·5°, 0·4° below its reported melting point.[1] Gas chromatography of this product gave only one peak at the most sensitive attenuation of an F & M, Hewlett Packard Model 700, fitted with a 72 × 1/4 in. column packed with 10% SE-30 silicone on Chromasorb AW support.

The fractional freezing vessel was a 6-litre separatory funnel. The top was fitted with a standard taper joint containing a glass centre core and a stop-cock. The core was used to melt the impurities which collect in the centre of the vessel, and these were removed under vacuum through the stem of the funnel. Nitrogen was admitted through the stop-cock to return the vessel to atmospheric pressure. This procedure allowed the solvent to be permanently stored under a nitrogen atmosphere. The solvent was never in contact with the atmosphere until after use.

Chemicals and equipment

Most of the acids used in this study were recrystallized from suitable solvent systems, vacuum-dried, and stored in a desiccator over "Anhydrone". The phenol was doubly distilled before use.

The titrant used was tetrabutylammonium hydroxide (TBAH) obtained as a 25% solution in methanol. Marple and Fritz have shown that the two most likely impurities are tetrabutylammonium carbonate and tri-n-butylamine.[9] The formation of these impurities was prevented by storage of the reagent at −20° under nitrogen free from carbon dioxide. It has been found in these laboratories that any other storage procedure leads to decomposition products which produce unsatisfactory results. An approximately 0·1*M* solution was prepared by diluting with absolute methanol. Solutions of TBAH in 3Me2Ox were not sufficiently stable to serve as titrant. Quaternary ammonium titrants such as tetra-n-butylammonium compounds prepared in less acidic solvents than isopropyl alcohol are unstable.[10] Tetrabutylammonium hydroxide can undergo Hofmann elimination to give tributylamine, 1-butene and water.[11] The TBAH-methanol solution was standardized against benzoic acid (purified by sublimation) dissolved in 3Me2Ox.

Potential measurements were made with an Orion Model 601 digital readout pH/mV meter equipped with a Model 605 electrode switch. All determinations were made with previously paired Jena glass Sargent 30050-15C electrodes and Sargent 30080-15C calomel reference electrodes. These were chosen because of the low leak-rate (~25 μl/hr) made possible by the porous ceramic junction. Also, to avoid aqueous contamination, the aqueous potassium chloride solution was replaced with a saturated solution of potassium chloride in ethanol. All electrode pairs were soaked in 3Me2Ox for several days before use. Past experience has shown that the potential readings stabilize more readily if the electrodes are soaked in the solvent after each use.

The titrant was dispensed from a Kimax (17110) Class A 5-ml microburette graduated in 0·01-ml steps and read to the third decimal place by means of a Sargent (S-81565) burette reader (magnification up to 5×). Titrations were performed in a 200-ml beaker fitted with a rubber stopper to hold the electrodes in place and to carry a nitrogen purge line and the burette tip. The solution was stirred

Table 1. Carboxylic acids

Acid	Aqueous pK_a[13]	ΔE, mV	Taken, meq	Found, meq	Recovery, %*
3,5-Dinitrobenzoic	2.824	390	0.1306 0.2120 0.2070	0.1312 0.2116 0.2061	99.9 ± 0.3
o-Chlorobenzoic	2.943	379	0.2892 0.3034 0.2706	0.2887 0.3007 0.2700	99.6 ± 0.3
Salicylic	2.996	377	0.1862 0.1574 0.1822	0.1849 0.1577 0.1826	99.9 ± 0.4
m-Nitrobenzoic	3.450	363	0.2159 0.2048 0.2247	0.2154 0.2041 0.2248	99.8 ± 0.1
o-Benzoylbenzoic	3.536	309	0.2050 0.2607 0.2311	0.2035 0.2593 0.2293	99.3 ± 0.1
p-Toluic	4.373	262	0.2179 0.2064 0.2168	0.2190 0.2064 0.2185	100.4 ± 0.3
p-Anisic	4.492	259	0.2832 0.2341 0.3008	0.2822 0.2333 0.3008	99.8 ± 0.2

*Mean deviation based on three reported values.

Table 2. Phenols

Compound	Aqueous pK_a[13]	ΔE, mV	Taken, meq	Found, meq	Recovery, %*
Picric acid	0.29	586	0.1543 0.1551 0.1510	0.1530 0.1547 0.1502	99.4 ± 0.2
2,4-Dinitrophenol	4.11	361	0.2444 0.1608 0.1946	0.2450 0.1601 0.1948	100.0 ± 0.3
Pentachlorophenol	6.70(a)	328	0.1542 0.1665 0.1865	0.1529 0.1662 0.1872	99.8 ± 0.4
p-Nitrophenol	7.149	276	0.1689 0.2254 0.2056	0.1686 0.2254 0.2064	100.1 ± 0.2
p-Hydroxybenzonitrile	7.95	74	0.2613 0.1912 0.2713	0.2611 0.1926 0.2725	100.4 ± 0.3
p-Phenylphenol	9.55	54	0.2277 0.2092 0.1980	0.2268 0.2094 0.1976	99.8 ± 0.2
Phenol	9.998	50	0.2709 0.3026 0.1622	0.2706 0.3037 0.1619	100.0 ± 0.2
p-Methoxyphenol	10.21	37	0.2930 0.2088 0.2831	0.2928 0.2082 0.2834	99.9 ± 0.1

* Mean deviation based on three reported values.

(a) See reference 22

magnetically and thermal insulation from the stirring motor provided by 1/2 in. of polyurethane insulation covered with a 1/4 in. asbestos plate.

A blank titration of the pure solvent with TBAH produced a nearly linear change in e.m.f. with constant volume increments of the titrant. Thus the solvent does not have any acidic properties or impurities. Titration of the solvent (3Me2Ox) in methanol with methanolic sulphuric acid showed the absence of basic impurities. In the review by Dyen and Swern,[12] it was pointed out that oxazolidones are susceptible to oxidation. This precluded the use of perchloric and nitric acids. Also hydrogen chloride and phosphoric acid cause decomposition into the original β-amino-alcohol.

Procedure

For each analysis a separate sample of 20–50 ± 0·1 mg was weighed by difference. This corresponds to about 0·1–0·3 meq of an acid. Approximately 50 ml of 3Me2Ox were added to dissolve the sample. After the addition of the solvent the head space above the solution was continuously flushed with nitrogen which had been scrubbed free from carbon dioxide and moisture by passage through "Ascarite" and "Anhydrone". A stable initial potential was attained in 2–5 min (depending on the rate of dissolution and mixing).

Once the titration was begun, potential readings stabilized (±0·2 mV) in less than 1 min after each addition of titrant. In the immediate vicinity of the end-point 2–3 min were required to achieve potential stability. As the equivalence point was approached, the increments added were decreased to 0·01 ml or less, with the burette tip just immersed in the solution. Since the potential measured stabilized quickly, there was no discernible diffusion of titrant into the solution.

A FORTRAN program was used to compute the end-point volume by means of the first and second derivative procedure. The program was written for the general case and did not require the normal simplifying assumption that all increments added in the region of the end-point were equal. Since one meq of the titrant reacts with one of the acid the stoichiometric equivalence point was taken as the inflection point of the titration curve. Subsequent calculations and statistical evaluations were performed by additional FORTRAN programs.

RESULTS AND DISCUSSION

In this initial evaluation of 3Me2Ox as an acid-base titration medium, determination of exact pK_a values was not attempted. However, it is possible to estimate the relative acid strength by an examination of the potential change in the vicinity of the end-point. By this approach, it was found that the carboxylic acids investigated fall in the same order of acid strength as in water. These results are presented in Table 1. Similar results were obtained for the various phenols titrated (Table 2).

The recovery values obtained in this solvent are comparable to those for other solvents.[10,11,14–21] Phenol behaves in 3Me2Ox much as it does in numerous other solvents.[16–19] Harlow and Bruss titrated weak acids in four inert solvents, with tetrabutylammonium hydroxide in isopropyl alcohol,[17] and pointed out the influence of the structure of various phenols on the shape of the titration curve.

Recently, Eller and Caruso titrated several acids in sulpholane, using much larger samples than in this study.[18] The same acids give equally accurate results when titrated in 3Me2Ox. Morman and Harlow compared three sulpholanes with large potential spans (as high as 1100 mV) as solvents for use in potentiometric titrations with tetrabutylammonium hydroxide.[19] However, the potential range of 800 mV available with 3Me2Ox is probably smaller than the true potential range of the solvent because the methanol in the titrant limits the lower end of the potential scale. Morman and Harlow[19] reported that phthalic acid had to be heated to dissolve it in sulpholanes; no such difficulty was encountered with 3-methyl-2-oxazolidone.

Inspection of the tables shows that the accuracy and precision of these analyses, as given by the computed recoveries, were acceptable, considering the limited sample size. The precision reported as the "±" value was the mean deviation. A range can be seen by inspection of the data.

Several dibasic acids were analysed, as well as tetrazole. The results in Table 3 show that both neutralization steps of dicarboxylic acids and of acids containing a carboxylic

and a phenolic group can be distinguished in titrations in this medium. No attempts were made to titrate mixtures of different acids.

Some of the acids titrated have indicator properties in aqueous systems, but except for picric acid and dinitrobenzoic acid they do not in 3Me2Ox. The picric acid colour change from yellow to amber did coincide with the end-point but appears to be of little value because the colour change is so slight. On the other hand, dinitrobenzoic acid gives a change from yellow to blue which also coincides with the inflection point of the titration curve. Preliminary investigations indicate that other indicators may be available for titrations in 3Me2Ox.

In summary, 3Me2Ox has shown considerable potential for use as a non-aqueous titration medium. Various carboxylic acids, phenols, and dibasic acids can be efficiently titrated in it. The approximate order of acidity of each series resembles that found in aqueous medium. Many organic acids which are sparingly soluble in water dissolve readily in 3Me2Ox. Some compounds exhibit indicator properties.

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Summary—3-Methyl-2-oxazolidone has been evaluated as a solvent for the titration of various weak carboxylic acids and phenols. Its high dielectric constant and wide liquid range contribute to its outstanding solvent properties. Tetrabutylammonium hydroxide was the titrant. End-points were determined potentiometrically with a glass–calomel electrode system. FORTRAN computer programs were used to evaluate the results, and relative acid strengths were determined and related to the aqueous acidity. The accuracies obtained are comparable to those for other solvent media. An 800-mV potential span is available in this solvent, which may allow differentiating titrations to be performed. No titrations of acid mixtures were attempted, but it was found possible to distinguish both neutralization steps for salicylic acid and *o*-phthalic acid.

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2′-HYDROXYCHALCONE AS AN ANALYTICAL REAGENT FOR BERYLLIUM

R. RAGHAVA NAIDU

Department of Chemistry, Sri Venkateswara University College, Tirupati, Andhra Pradesh, India

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Several organic reagents[1–16] have been proposed for the gravimetric determination of beryllium, but very few are available for its determination in presence of aluminium and other interfering elements. Lense *et al.*[17] reported that the *o*-hydroxychalcones are much more reactive with metal ions than the ketones and aldehydes from which they are synthesized, but the literature on their analytical applications is meagre.

and a phenolic group can be distinguished in titrations in this medium. No attempts were made to titrate mixtures of different acids.

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R. RAGHAVA NAIDU

Department of Chemistry, Sri Venkateswara University College, Tirupati, Andhra Pradesh, India

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Several organic reagents[1–16] have been proposed for the gravimetric determination of beryllium, but very few are available for its determination in presence of aluminium and other interfering elements. Lense *et al.*[17] reported that the *o*-hydroxychalcones are much more reactive with metal ions than the ketones and aldehydes from which they are synthesized, but the literature on their analytical applications is meagre.

Eight *o*-hydroxychalcones (2'-hydroxy-,[18] 2,2'-dihydroxy-,[19] 2',4-dihydroxy-,[19] 2',4'-dihydroxy-,[20] 2'-hydroxy-4-methoxy-,2',4'-dihydroxy-4-methoxy-,[21] 2,2',4'-trihydroxy,[19] 2',4',4-trihydroxychalcone[21]) synthesized from benzaldehyde, salicylaldehyde, anisaldehyde and *p*-hydroxybenzaldehyde by condensation with *o*-hydroxyacetophenone and resacetophenone have now been examined for their reactions with beryllium and aluminium ions at pH 8·0–9·0. The first four gave orange-yellow and the remaining four deep yellow precipitates with beryllium, but all eight gave yellow precipitates with aluminium. The precipitates obtained with beryllium were more crystalline and bulky than those with aluminium. None of the reagents showed any specificity either for beryllium or aluminium directly. In the presence of EDTA, however, all of them showed specificity for beryllium. The sensitivities of these reactions were determined according to Feigl's method.[22] The limits of identification and dilution for detection of beryllium were 0·125 μg and $1:4 \times 10^5$ and of aluminium 5·0 μg and $1:10^4$. These results show that all eight chalcones have higher sensitivity for beryllium than aluminium. Reagents which are in use as spot-test reagents for beryllium are morin (0·07 μg; $1:7 \times 10^5$), quinalizarin (0·14 μg; $1:4 \times 10^5$) and *p*-nitrobenzeneazo-orcinol (0·20 μg; $1:2 \times 10^5$). The present investigations revealed that all eight chalcones are much more sensitive reagents than *p*-nitrobenzeneazo-orcinol and quinalizarin, and can be used as spot-test reagents for beryllium in their stead. The effect of complexing agents such as oxalate, fluoride, tartrate, citrate and EDTA was examined. Oxalate was found to be unsuitable because its complexes with both metals were not sufficiently stable, and the hydrous oxides precipitated on addition of ammonia. Fluoride formed a sparingly soluble aluminium complex and it was difficult to keep the aluminium in solution. In the presence of tartrate, citrate or of EDTA, aluminium failed to yield a precipitate with any of the chalcones, but precipitation of beryllium was incomplete in presence of tartrate and citrate; it was complete in the presence of EDTA, however.

2'-Hydroxychalcone, which is readily prepared in a high state of purity by condensing *o*-hydroxyacetophenone and benzaldehyde, gave an orange-yellow precipitate with beryllium at pH 8·0–9·0 and no precipitate with aluminium or iron in presence of EDTA. The complex was soluble in dilute mineral acids, dilute acetic acid, and sparingly soluble in alcohols (methanol, ethanol, n-butanol, isobutyl alcohol, cyclohexanol), ether, or carbon tetrachloride, and moderately soluble in acetylacetone, ethyl acetate, acetone, ethyl methyl ketone, chloroform, benzene, toluene, dimethylformamide and dioxan. Detailed investigations were made of the gravimetric determination of beryllium with this reagent and its separation from aluminium, iron and other elements associated with it in its minerals, and the procedure developed was applied to the gravimetric determination of beryllium in beryl.

EXPERIMENTAL

Reagents

Chalcone solution. A 0·5% solution of 2'-hydroxychalcone in alcohol.

Beryllium solution. A 0·1*M* solution of beryllium sulphate tetrahydrate, standardized by the oxide[23] and pyrophosphate[23] methods. Lower concentrations were prepared by proportionate dilution. A solution containing 0·36 mg of beryllium per ml was used in this investigation.

Ammonia solution, 1·0*M*.

Procedure

A measured volume of beryllium sulphate solution was transferred into a 250-ml beaker and diluted to about 100 ml with distilled water, then 1·0 g of ammonium chloride was added and the solution was heated to about 70°. A small excess of chalcone solution was added and the pH adjusted to 8·0–9·0 with ammonia. The precipitate was digested on a hot water-bath for about 45 min with occasional stirring and then set aside. The cold solution was filtered through a weighed sintered-glass crucible (porosity 4) and the precipitate washed with 5% aqueous alcohol made slightly alkaline with ammonia. The complex was dried to constant weight at 105–110°, cooled and weighed.

For determinations in presence of EDTA, only 0·5 g of ammonium chloride was added, followed by the EDTA and the chalcone solution. The rest of the procedure was then followed.

Determination of beryllium in beryl

A beryl crystal (sample obtained from L.N. Mica Mine, Rapur Taluk of Nellore district, Andhra Pradesh, India) was crushed into coarse powder in a steel mortar, further ground in an agate mortar and finally in a mechanical mortar, then dried at 105–110° and stored in a desiccator.

The finely powdered dry ore (1·0 g) was fused with anhydrous sodium carbonate (6·0 g) and the cold melt dissolved in 4*M* hydrochloric acid. The solution was evaporated to dryness on the water-bath and the residue dried in an oven at 105–110° for 1 hr in order to dehydrate the silica. The residue was moistened with 10–15 ml of concentrated hydrochloric acid, stirred, set aside for 10 min, diluted with 30 ml of distilled water and heated on the water-bath with frequent stirring until only silica remained undissolved. The solution was filtered, then the silica was washed by decantation with hot dilute hydrochloric acid, transferred to the filter and washed with hot water. The filtrate was again evaporated to dryness and the sequence of operations repeated. The filter papers were ignited in a platinum crucible, and the cooled product was treated with 1 ml of water, 3 drops of concentrated sulphuric acid and 5 ml of hydrofluoric acid. The solution was evaporated to dryness on the water-bath, then heated over a sand-bath in a fume-cupboard, and finally over a Méker burner for 15 min. The crucible was cooled and the residue (if any) was fused with sodium carbonate, then extracted with dilute acid, and the solution filtered. Both filtrates were transferred to a 250-ml volumetric flask and the solution made up to the mark. The solution was examined for metals of the hydrogen sulphide group and phosphate, and these were found to be absent.

The beryllium content of the solution was determined (50 ml for each determination) by the oxide and pyrophosphate methods.[24] Another 50 ml of beryl solution were transferred to a 100-ml volumetric flask and diluted to the mark. Portions (15·0, 20·0 and 25·0 ml) of this solution were transferred into 400-ml beakers and the beryllium content determined in presence of EDTA according to the procedure already described.

RESULTS AND DISCUSSION

The gravimetric results show (Table 1) that the chalcone complex can be dried to constant weight and that the

Table 1. Determination of beryllium as the chalcone complex

Wt. of complex, *mg*	Beryllium, *mg* Taken	*Found	Error, *mg*
18·2	0·36	0·36	0·00
36·4	0·72	0·72	0·00
54·6	1·08	1·08	0·00
72·5	1·44	1·43	−0·01
109·4	2·16	2·16	0·00
146·0	2·88	2·89	+0·01
182·2	3·60	3·61	+0·01

* Calculated on the basis of the suggested structure for the complex.

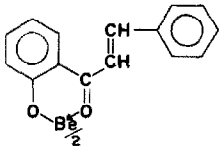
Table 2. Determination of beryllium as chalcone complex in presence of EDTA

Wt. of complex*, *mg*	Beryllium, *mg* Taken	Found	Error, *mg*
145·9 ± 0·1	2·88	2·89	+0·01
72·8 ± 0·1	1·44	1·44	0·00
36·4 ± 0·1	0·72	0·72	0·00

* Average values of three determinations.

results are reproducible. The molecular weight of the chalcone complex is very high (conversion factor 0·01978), so very small amounts of beryllium can be determined with considerable accuracy. These are distinct advantages over several other organic reagents used for the gravimetric determination of beryllium, which require ignition of the complexes to the oxides before weighing.

The ratio of chalcone to beryllium in the complex is 2:1. The structure of the complex is probably



The results obtained in the spectrophotometric study[25] of beryllium with 2'-hydroxychalcone also support this conclusion.

The values reported in Table 2 clearly show that beryllium can be quantitatively precipitated with this chalcone in presence of EDTA.

Interferences

The reaction of the chalcone with various ions which are usually associated with beryllium in minerals and precipitated with it in analysis, were studied at pH 8·0–9·0 in the presence of EDTA. Aluminium, iron(III), chromium(III), vanadium(V), titanium(IV), zirconium, thorium, cerium(IV), manganese(II), magnesium, calcium, strontium and barium do not interfere. The uranyl ion yields a yellow precipitate of ammonium diuranate. Hence, all these metal ions with the exception of UO_2^{2+} can be kept in solution by means of EDTA, and beryllium alone is selectively precipitated by 2'-hydroxychalcone.

The possible interference by aluminium and iron(III) in the presence of EDTA was further studied. It was found that beryllium can be quantitatively precipitated in the presence of ten times its weight of aluminium or iron, and without interference from them.

In the analysis of beryl the chalcone method gave 12·53, 12·52 and 12·53% BeO, the oxide method gave 12·55% and the pyrophosphate method 12·53%.

2'-Hydroxychalcone is a satisfactory reagent for the determination of beryllium in beryl, and the complex can be weighed as such, giving a very favourable conversion factor. The oxide and pyrophosphate methods require removal of aluminium, iron and other elements present in beryl before precipitation of beryllium. The oxide method is not entirely satisfactory owing to the gelatinous nature of the precipitate, its tendency to adhere to the sides of the vessel, and its liability to adsorption and related effects. In the pyrophosphate method, if the conditions of precipitation are not carefully controlled, slight departures from the expected theoretical composition of the ignition product ($Be_2P_2O_7$) may occur, resulting in loss of accuracy.

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Summary—Several *o*-hydroxychalcones were examined to develop specific reagents for the precipitation of beryllium in the presence of elements such as aluminium and iron, which occur in its ores. All these reagents showed specificity only in the presence of EDTA. Among them, the readily obtainable 2'-hydroxychalcone is proposed as a new specific reagent for beryllium. The chalcone complex can be dried to constant weight at 105–110° and the conversion factor is 0·01978. A probable structure for the complex has been suggested. Quantitative separation of beryllium from aluminium and iron carried out by this method gave good results. This method was applied for the gravimetric determination of beryllium in beryl and the results were in good agreement with those obtained by the oxide and pyrophosphate methods.

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8-QUINOLINOL-5-SULPHONIC ACID AS BOTH INDICATOR AND MASKING AGENT—I

THE ZINC-FERROCYANIDE TITRATION

JOHN A. BISHOP

Department of Chemistry, Cedar Crest College, Allentown, Pa. 18104, U.S.A.

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The titration of Zn(II) in acid solution to give a precipitate of $K_2Zn_3[Fe(CN)_6]_2$ by the procedure of Belcher *et al.*[1] has been cited as a student experiment.[2] Lingane and Hartley[3] studied the effect of pH on the reaction by using electrogenerated $K_4Fe(CN)_6$, and decided that the composition of the product depended both on the pH and on the other ions in solution. The method is reviewed in the treatise by Kolthoff and Elving,[4] where it is noted that heavy metal cations must be absent. Much earlier, Willard and Furman[5] suggested that $Zn_2Fe(CN)_6$ was formed as a preliminary to the final precipitate.

In the references cited above, the amount of Zn(II) titrated was normally greater than 1 mg. In the present work, as little as 2 μg of Zn(II), in concentrations as low as about $10^{-6}M$, has been titrated (Table 1) in the presence of Cu(II), Ni(II), Al(III), Fe(III) and U(VI). Cd(II), which forms compounds similar to those of Zn(II), interferes in the titration.

EXPERIMENTAL

Reagents

8-Quinolinol-5-sulphonic acid. A commercially available sample was used without further purification, as an approximately $10^{-3}M$ solution.

Zinc chloride solutions, $10^{-3}M$. Prepared from ACS-certified arsenic-free zinc metal.

Potassium ferrocyanide solution, $10^{-3}M$. The solution was standardized against potassium bromate by an amperometric method.

Potassium hydrogen phthalate, 0·1M solution, pH 4. Other solutions were prepared from common salts.

Procedure

A sample containing the desired amount of ZN(II) was pipetted into a 30-ml beaker containing a magnetic stirring bar. An excess of 8-quinolinol-5-sulphonic acid solution was added, followed by 10 ml of phthalate buffer, and the fluorescence of the solution was measured, using an excitation wavelength of 360 nm and an emission wavelength of 420 nm. The solution was then titrated with $K_4Fe(CN)_6$. As the titration proceeded, samples were removed for a fluorescent measurement, being returned after the measurement. The result of such a titration can be seen in Fig. 1.

In order to determine the amount of 8-quinolinol-5-sulphonic acid needed to provide an excess for the solution being titrated, an initial complexometric titration was done with this reagent. Such a titration is illustrated in Fig. 2. Only the first sample in a batch need be run in this manner, but such a run should be made in any analysis involving other cations in addition to zinc.

A titration such as that shown in Fig. 2 may be used for the determination of cations forming non-fluorescing 8-quinolinol-5-sulphonate complexes.[6] However, van Slageren *et al.*[7] have recently tried to use 8-quinolinol-5-sulphonic acid as a self-indicating titrant, and also as an indicator for titration of Zn(II) with EDTA, and found that there was interference from other cations by formation of 8-quinolinol-5-sulphonate complexes.

When other cations were to be present in addition to Zn(II), they were added after the Zn(II), with the 8-quinolinol-5-sulphonic acid being added before the buffer, to ensure complexation of all the cations. The cation concentration in the solutions prepared for titration was 10^{-5}–$10^{-6}M$, before the titrant was added.

DISCUSSION

Figure 1 shows the results obtained by titrating standard Zn(II) solution with standardized $K_4Fe(CN)_6$. Calculation of the $ZN/Fe(CN)_6$ ratio from 3 runs gave a value of $2·10 \pm 0·14$, indicating a compound $Zn_2Fe(CN)_6$. In calculating the results shown in Table 1, a ratio of 2:1 has been assumed.

Consideration of the formation constants for the 8-quinolinol-5-sulphonate complexes and the solubility pro-

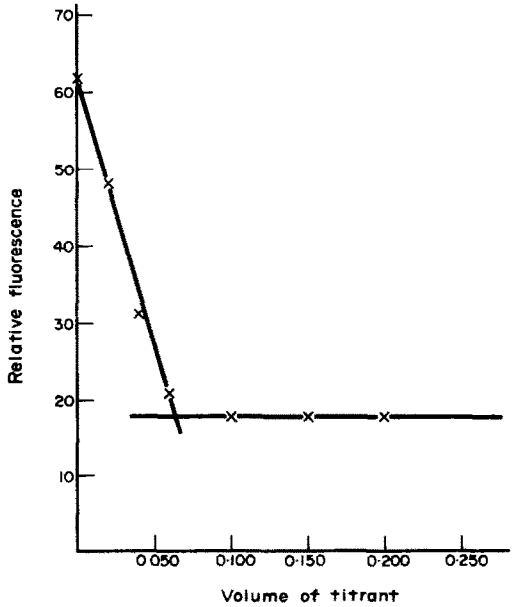

Fig. 1. Titration of Zn(II) with $K_4Fe(CN)_6$ at pH 4. 0·164 μmole of Zn(II) *vs.* $1·21 \times 10^{-3}M$ $K_4Fe(CN)_6$. Starting volume 22·5 ml.

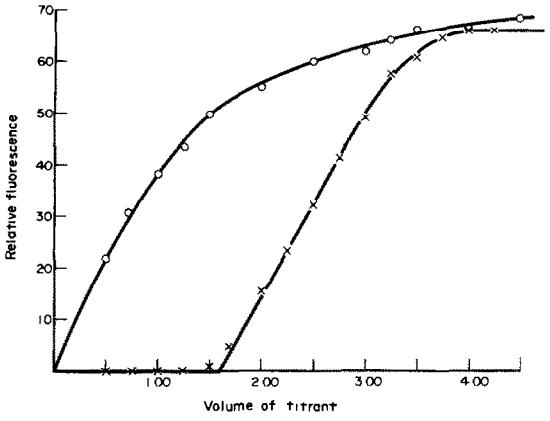

Fig. 2. Titration of solutions of Zn(II) with other cations *vs.* HL. HL = $2 \times 10^{-3}M$ 8-quinolinol-5-sulphonic acid: × = 3·28 μmole of Zn(II) + 2 μmole of Cu(II) in 50 ml; O = 1·64 μmole of Zn(II) + 1 μmole of Al(III).

Table 1. The effect of interfering cations

$[Zn^{2+}]$,* $10^{-6}M$	Cation, μg	Zn, μg Taken	Zn, μg Found	No. of runs	Error, %
7·5	Cu 6·4	10·70	10·30	3	2·8
4·5	Cu 3·8	16·42	6·15	2	4·5
3·0	Cu 1·3	4·28	4·00	2	7·0
13·0	Cu 6·4 Ni 59.	10·70	10·44	2	2·4
5·5	Cu 2·5 Ni 6.	4·28	4·42	2	3·2
2·8	Cu 1·3 Ni 6.	2·14	2·09	3	2 5
8·8	Al 3·1	10·70	10·45	3	2 3
6·5	Fe^{3+} 5·5	10 70	10·20	2	5
3·9	Fe^{3+} 5·5	6·42	6·00	3	4
6·0	Fe^{3+} 5·5	4·28	4·30	3	0·5
3·0	Fe^{3+} 5·5	2·14	2·10	3	2

* The concentration in the sample plus buffer before starting the titration.

ducts of the ferrocyanides,[8] along with the requirements for masking agents,[9] indicated that the reactions given in the present paper might be used in an analytical method.

At pH 4, the reaction for bivalent cations may be taken as

$$H^+ + 2\,ML + HFe(CN)_6^{3-} = M_2Fe(CN)_6 + 2\,HL^- \quad (1)$$

where L is the 8-quinolinol-5-sulphonate ion. ZnL fluoresces but HL^- does not.

The equilibrium constant for this reaction is

$$K = \frac{[HL]^2}{[H^+][ML]^2[HFe(CN)_6^{3-}]} = \frac{K_{HFe(CN)_6^{3-}}}{K_{ML}^2 K_{sp} K_{HL^-}^2} \quad (2)$$

where $K_{HFe(CN)_6^{3-}}$ = the acid dissociation constant for $HFe(CN)_6^{3-}$

K_{HL^-} = the acid dissociation constant for HL^-

K_{ML} = the formation constant for ML

K_{sp} = the solubility product for $M_2Fe(CN)_6$

Substitution of the literature values[8] in equation (2) gives values (rounded off) for pK for a number of cations as: Zn 0; Cd 1; Ni 5; Co 5; Cu 7.

The greater the values of pK the less the chance of interference, since this indicates that the cation will be present predominantly as the ML complex, rather than as a ferrocyanide precipitate or complex.

When Zn(II) is titrated in the presence of other cations which have low pK values, the titration curve is similar to that in Fig. 1, but the position of the horizontal line will vary according to the setting of the instrument, and will depend on whether the other cations form a fluorescent complex ML at pH 4; e.g. Al(III). The results of titrations involving mixtures are also shown in Table 1.

Be(II) and UO_2(II) were titrated at a pH > 7 (where their complexes with 8-quinolinol-5-sulphonic acid fluoresce) with $K_4Fe(CN)_6$ and it was found that the titrant did not affect the fluorescence. It is felt that they may indicate the effect of other light and heavy metals.

Summary—A method has been suggested by which μg amounts of Zn(II) in 10^{-5}–$10^{-6}M$ solution can be titrated with $K_4Fe(CN)_6$ in the presence of heavy metal cations, by using 8-quinolinol-5-sulphonic acid at pH 4 as a combined indicator and masking agent. Cd(II) interferes.

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8-QUINOLINOL-5-SULPHONIC ACID AS BOTH INDICATOR AND MASKING AGENT—II

TITRATION OF PHOSPHATE WITH La(III)

JOHN A. BISHOP and JACKI SOLER

Cedar Crest College, Allentown, Pa. 18104, U.S.A.

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Two common methods for the titrimetric determination of phosphate are discussed by Ayres.[1] Schwarzenbach and Flaschka[2] give an extensive discussion of complexometric procedures in which a precipitating cation is titrated after the filtration and washing of a phosphate precipitate. In the method presented here phosphate is titrated with lanthanum, 8-quinolinol-5-sulphonic acid being used as a fluorescent indicator which also acts as a masking agent.

EXPERIMENTAL

Reagents

8-Quinolinol-5-sulphonic acid solution, $10^{-3}M$. The reagent was used without further purification.

Metal ion solutions, $10^{-3}M$. The solutions were prepared from reagent-grade nitrates, and standardized against DCTA, itself standardized against reagent-grade copper sulphate pentahydrate.

Standard phosphate solution, 0·01*M*. Prepared from NaH_2PO_4, and standardized against carbonate-free sodium hydroxide which had been standardized against potassium hydrogen phthalate. This phosphate solution was used to prepare more dilute solutions.

Procedure

Preliminary experiments showed that there is a fluorescence maximum for the 1:1 La(III)–8-quinolinol-5-sulphonate complex between pH 6·5 and 7·5 (excitation at 360 nm, emission at 520 nm).

The phosphate–lanthanum titrations were performed in small beakers as follows. Pipette a sample of phosphate solution into a beaker containing a small magnetic stirrer bar. Add an excess of 8-quinolinol-5-sulphonic acid solution, followed by sufficient 0·1*M* ammonium acetate (adjusted to pH 7) to bring the pH to 7. Add distilled water and stir the solution: then measure the fluorescence against a water blank. Add an increment of La(III) solution, centrifuge*, measure the fluorescence again, replace the sample in the beaker and continue the titration with another increment of titrant.

DISCUSSION

The anion of fully dissociated 8-quinolinol-5-sulphonic acid will be denoted by L. When equilibrium has been reached the reaction involved is assumed to be

$$LaL^+ + HPO_4^{2-} = LaPO_4 + HL^- \qquad (1)$$

$$K = \frac{[HL]}{[LaL^+][HPO_4^{2-}]} = \frac{K_{HPO_4^{2-}}}{K_1 K_{HL} K_{sp}} \qquad (2)$$

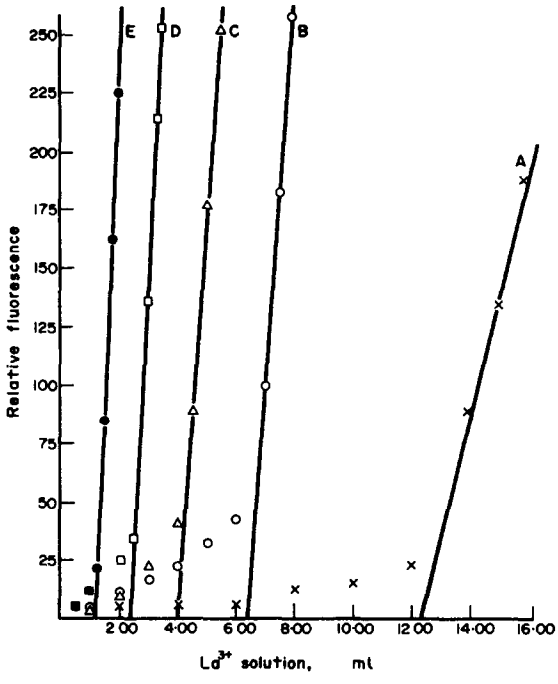

Fig. 1. Titration of HPO_4^{2-} with La^{3+}. (See Table 1—each solution contained 10 ml of $10^{-3}M$ HL^- and 10 ml of pH 7 buffer. Solutions were not centrifuged.)

where $K_{HPO_4^{2-}}$ is the acid dissociation constant for HPO_4^{2-}
K_{HL} that for HL^-
K_1 the formation constant for LaL^+. and
K_{sp} the solubility constant for $LaPO_4$.

At pH 7, the predominant acid species are those shown in equation (1).

The results of the series of titrations shown in Fig. 1 are shown in Table 1. The results found are usually slightly high, and this was also found when much smaller amounts were determined (Table 2).

Table 1. Titration of HPO_4^{2-} with La(III) at pH 7

Sample*	PO_4^{3-} taken, *mg*	PO_4^{3-} found, *mg*	Volume of solution, *ml*
A	3·16	3·32	125
B	1·58	1·72	100
C	0·95	0·97	100
D	0·63	0·64	100
E	0·32	0·32	100

* See Fig. 1.

* Figure 1 shows a curve determined without centrifuging. When the sample is centrifuged, the portion of the curve representing precipitation of $LaPO_4$ is parallel to the *x*-axis.

Table 2. Determination of small amounts of P

P taken, μg	P found, μg
36·4	36·9
18·2	18·6
9·10	9·21
2·72	2·28

La(III) = $1{\cdot}45 \times 10^{-3}M$. Initial volume = 9 ml, containing 0·5 ml of $10^{-3}M$ HL and 2 ml of buffer.

Table 3. Effect of other ions on P determination*

Interfering ion	F^-	Cu^{2+}	Hg^{2+}	Cd^{2+}	Fe^{3+}	Al^{3+}	Bi^{3+}
Concentration, *ppm*	19	33	10	56	276	13	10
P taken, *ppm*	182	943	943	943	806	806	806
P found, *ppm*	198	961	911	942	884	880	880

* All samples were 10·0 ml at the start of titration, including 0·5 ml of $10^{-3}M$ HL and 2 ml of buffer.
La(III) = $1{\cdot}24 \times 10^{-3}M$.

The effect of interference by ions that might form precipitates with either phosphate or La(III) is shown in Table 3 for typical ions that show only slight interference. The fluorescent aluminium complex was corrected for.

Of ions showing greater interference, arsenate, as might be expected, could itself be titrated by the method outlined here for phosphate, and the sum of the two determined. The rare earths and quadrivalent cations would be expected to interfere, so Ce(III), Gd(III) and Th(IV) were tested. With Ce(III) and Gd(III) the extent of interference was proportional to the amount of these ions present, suggesting that they react in the same way as La(III). There was no such simple relationship in the case of Th(IV).

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Summary—The use of 8-quinolinol-5-sulphonic acid as both masking agent and indicator in the titration of phosphate with La(III) has been investigated. The reagent forms complexes with most cations in preference to the formation of their phosphate precipitates at pH 7, but the reverse is the case for the rare earths, which permits the precipitation reaction to be carried out in the presence of these other cations. Amounts of P of the order of 5 μg have been determined at a concentration of 5 ppm.

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TALANTA REVIEW*

THE ANALYSIS OF DETERGENTS

G. F. LONGMAN
7 Bath St., Chester, England

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Summary—A review is made of the analysis of detergents, covering the determination of all classes of component materials.

From time to time reviews have appeared in a number of journals on various aspects of detergent analysis. It is again considered a favourable time for a complete review to appear. The present work considers the procedures for the analysis of anionic, cationic, non-ionic and ampholytic (including zwitterion) surfactants, procedures for the analysis of manufactured products, including methods for the organic components incorporated in formulations for specific purposes, and procedures for the essential and incidental inorganic constituents that are present. Gravimetric procedures are applied only for the major components. The same is normally true for titrimetric methods, but often the only difference between macro, minor and trace level concentrations is a question of dilution of the original sample. This comment also holds for colorimetric procedures and it is not unusual for extensive dilution to allow the application of colorimetric methods to major components. Not infrequently the determination of a particular component depends on its decomposition by hydrolysis or other reactions. The products then have to be determined and identified and their precise nature must be established. In other words the simple analysis for the quantity of each component present will provide insufficient data for the calculation of a reliable composition. Because of the complexity of manufactured products of all types separation procedures are an essential preliminary to the determination of the numerous components and this is equally as essential when instrumental methods are used for their identification. Then with all the data assembled, the composition of the products can be calculated, although in many cases experience in the art is a marked advantage.

Modern manufactured products include commercial washing or laundry products, household powder and liquid products for automatic washing and dishwashing machines, liquid washing-up products, cosmetic preparations, wall and floor cleaners, carpet and furniture shampoos, metal and oven cleaners, leather conditioning products, dye-levelling agents, industrial cleaning preparations, dairy and agricultural cleaning preparations and sprays, insecticide and disinfecting preparations, scouring products and wetting agents. For the manufacture of all these products a variety of detergent raw materials are necessary and methods for their analysis are often required before commencing manufacture. These various products all contribute to present-day pollution problems and this aspect now constitutes an important part of the field of detergent analysis.

The complete analysis of manufactured products is becoming more and more difficult as the complexity of formulations increases. The use of mixtures of surfactants is now a common practice and often as many as four different fluorescent whitening agents may be used.[1] These examples give some indication of the difficulties facing the analyst, and the problems are even greater for newcomers to the field. Even those experienced in the field are finding it vital to carry out research continuously to find new procedures to keep pace with manufacturing advances. Instrumental methods will not as a rule furnish complete quantitative data for calculation of composition, although often liquid–gas chromatography, thin-layer chromatography and sometimes infrared spectroscopy furnish quantitative results. In the main the function of instrumental techniques will be identification after qualitative separations have been achieved.

The recognised publications on the subject are those of Rosen and Goldsmith,[2] Hummel,[3] and Cross,[4] whilst that of Swisher[5] is the accepted text in the biodegradation and pollution field.

ISOLATION PROCEDURES

Modern detergent products may contain a variety of organic and inorganic constituents. These may include unreacted components from surfactant raw materials, lather improvers, fluorescent whitening agents, organic bleaches, low-temperature bleach precursors, suspending agents, anti-tarnishing agents, hydrotropes such as urea and short-chain alkylbenzene sulphonates, free ethanolamines, ethanol or

* For reprints of this Review see Publisher's announcement near the end of this issue.

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methanol, carbonates, perborates, silicates, phosphates, borates, sulphates, EDTA, NTA and chlorides. In order to identify these components it will be necessary to effect separation if possible in the form in which they occur in the product although this may be difficult when mixed inorganic constituents are present. The presence of urea in the product upsets all the normal procedures used for separation and it is essential to destroy it first.

The separation procedures most commonly used are extraction procedures, ion-exchange,[6–8] column chromatography on silica gel,[9] alumina,[10,11] cellulose,[12] Sephadex,[13,14] brine-impregnated cellulose or carbon,[15] but separation by thin-layer chromatography on silica gel,[9] alumina[16] or silaned silica gel,[17–19] paper chromatography[20,21] and sometimes gas–liquid chromatography[22,23] are often used for identification. None of these procedures will be uniformly applicable and it may be necessary sometimes to proceed by trial and error. Chemical separations include extraction with petroleum spirit or diethyl ether from aqueous alcohols or from acidified aqueous solution if soap or sarcosinates are present,[24] with chloroform or carbon tetrachloride from acidified aqueous ethanol,[25] or from dry solids with ethanol,[26] isopropyl alcohol,[27] butanol,[28] chloroform[24,29] or acetone. Often separations can be effected by alkaline or acid hydrolysis. Recent suggestions include Milwidsky's[30] liquid–liquid extraction which by slight modifications enabled free oil, soap fatty acids, non-ionic surfactants and anionic sulphonic and sulphuric acids to be isolated, and Kupfer's,[31] for the separation of mono-, di-, or polysulphonates in alkyl sulphonate preparations. Ali and Laurence[32] used a cellulose column for the separation of long-chain mono-, di- or polysulphonates prepared from aliphatic hydrocarbons, while Milster, Meckel and Schimmering[33] examined the known chromatographic procedures for the separation of anionic and non-ionic surfactants, but they claimed that these failed to give a separation of 7 out of 45 binary mixtures. Ion-exchange has been used by Leschenko and Ishutina[34] but the technique uses essentially the apparatus recommended by Voogt.[8] Riley[35] also used ion-exchange to effect quantitative separations by collecting 10-ml fractions and determining each successive component radiometrically *via* ^{14}C, fluorimetrically or spectrophotometrically. Wickbold[36] has developed an excellent foam-flotation procedure for the isolation of trace quantities of anionic and non-ionic surfactants from sewage and activated sludge liquors. Kinoshita and Oyama[37] report that phosphate-based surfactants can be separated by thin-layer chromatography (TLC) on silica gel, whilst McCoy and Bullock[38] have obtained a good separation of the non-ionic telomers of a non-ionic surfactant by circular TLC of the 3,5-dinitrobenzoyl esters. Every component which had the same number of ethoxylate units appeared in the same ring. Gasparič[39] has published a procedure based on paper electrophoresis which enables surfactants to be separated and identified, but gives no quantitative data. Sahasrabudhe[40] published a silica gel TLC procedure for separating the various types of fractions in sucrose fatty acid ester surfactants and Ludwig[41] described a separation procedure for non-ionic surfactants based on the gas–liquid chromatography (GLC) of their trimethylsilyl esters. Lew[42] has published a phosphoric acid degradation/capillary GLC procedure for the identification of surfactants. It involves controlled high-temperature decomposition followed by separation of the resulting volatile pyrolysis products, aldehydes, saturated and unsaturated hydrocarbons and alkylphenols. The point of cleavage is quite selective and is usually at C–S or C–O, so each type of surfactant gives a characteristic reaction product. The paper claims that the procedure is quantitative for both carbon number and isomer distribution in alkylbenzene sulphonates, semi-quantitative for ethylene oxide derivatives and for branched-chain hydrophobes, and qualitative for hydrotropes and other surfactants.

Analysts will find column chromatography procedures the most useful for separation of essential components. These yield quantitative data and give the most complete separations of components for identification and further analysis. Alumina is the most useful adsorbent although brine-treated cellulose will be found useful, particularly when dealing with non-ionic and amphoteric systems. Foam flotation is particularly useful for sewage, activated sludge, lake and river liquors and waters, for it has the advantage that the surfactant is isolated pure and the effects of natural impurities on colorimetric determinations are eliminated.

Borecký[43] has proposed the use of paper chromatography in the analysis of a variety of surfactant types. He used two parts of propanol–ammonia solution (2:1), butanol–ammonia solution (2:1) or formamide–methanol–water (32:3:3) for the chromatography after the compounds had been hydrolysed with hydrochloric acid and extracted with ethanol. The resultant components were chromatographed as their 3,5-dinitrobenzoates. Compounds containing an aromatic sulphonate group were fused with potassium hydroxide to yield phenols, and were then chromatographed on paper impregnated with dimethylformamide.

THE DETERMINATION OF ANIONIC SURFACTANTS

In the past five years no basically new technique has been proposed for the determination of soaps, anionic, cationic or non-ionic surfactants, but a number of modifications and developments of older methods have appeared. The procedures which the analyst will adopt depend upon whether the composition of the product to be examined is known or unknown. In the latter case it is normally advantageous to use a gravimetric procedure because this gives the product in a form from which its true nature, properties and mean equivalent weight can be deduced.

Gravimetric methods

It is an advantage to know which elements are present in each component of the product. Their quantitative determination will enable the empirical formula and the mean equivalent or molecular weight to be calculated. Before attempting the isolation and determination of the surfactants it is important to isolate the fractions extractable from aqueous alcoholic solution. This involves extraction with petroleum spirit (b.p. 40–60° or 30–40°) and with diethyl ether. These will remove (1) adventitious unsulphated, unsulphonated or unreacted hydrophobes, (2) deliberately introduced components such as fatty alcohols, (3) neutral products such as sulphones formed as by-products during surfactant manufacture, (4) perfume, (5) fatty alkanolamide lather improvers, (6) soaps and (7) any added fatty or waxy component. Some of these components are soluble in petroleum spirit and others such as fatty alkanolamides and monoglycerides in diethyl ether; procedures are detailed in published work.[43] Soap and sarcosinate acids will be removed by petroleum spirit after acidification with sulphuric or hydrochloric acid. The various fractions isolated must be further examined so that the nature and quantity of each constituent can be established.

The gravimetric determination of anionic surfactants can be achieved by ethanol extraction, by hydrolysis with ethanolic or aqueous potassium hydroxide,[44] by acid hydrolysis,[44] by acid hydrolysis under pressure,[44] by dry chloroform extraction,[44] by ethanol–acetone extraction, by wet chloroform extraction,[44] by diethyl ether extraction from concentrated hydrochloric acid solutions,[44] by amyl alcohol extraction,[45] by isolation in ethanol by saturating an aqueous ethanol solution with solid potassium carbonate, by use of chromatography on alumina[44] or by ion-exchange procedures.[8]

No single gravimetric procedure can be recommended for all types of anionic surfactant and the ethanol extraction procedure is a general one for isolation, but it is not recommended for quantitative purposes unless all other procedures fail; the number of corrections[44] to be applied makes accurate assessment very difficult. These comments apply also if the potassium carbonate technique is used. Hydrolysis procedures are applicable to carboxylate ester surfactants or to polyoxyethyleneglycol sulphates, and the dry chloroform extraction procedure is applicable only to alkylbenzene and non-ionic surfactants. Hydrolysable surfactants give rise to components other than fatty derivatives, such as inorganic sulphate, glycerol, monoethanolamine, isethionate, taurine, methyltaurine, *etc.* Each of these must be determined and the nature of the fatty matter established before the content of the hydrolysable component can be deduced. Gravimetric procedures based on alkaline hydrolysis[44] are reserved for carboxylate ester derivatives only; while acid hydrolysis is applicable to both carboxylate and sulphate ester types, and acid hydrolysis under pressure[44] must be used for certain amide derivatives. Their structure is deduced from the nature and amount of the products of hydrolysis. When both ester types are present together it is necessary to hydrolyse first with alkali and then with acid.

The diethyl ether/hydrochloric acid method[44] serves to isolate the true monosulphonates from alkylbenzene sulphonates, while the dry chloroform procedure determines the total mono-, di- and polysulphonates present. Special tests will be necessary to ascertain the precise nature of alkylbenzene sulphonates and often the source of the hydrocarbon used can be deduced. These tests include a mass-spectrometric examination after isolation of the hydrocarbons by the phosphoric acid procedure. The alumina and ion-exchange procedures can be used for quantitative assay of the total anionic surfactant but if hydrolysable components are present then ethanolic hydrochloric acid must not be used to elute the surfactant from the ion-exchange column as decomposition will occur during removal of the solvent.

METHODS FOR ANIONIC SURFACTANTS

Most titrimetric methods use some form of cationic surfactant as titrant. A large number of procedures have been reported and they differ in the choice of indicator and the titration conditions. The earliest procedures were single-phase titrations wherein the disappearance of micelles produced a change in colour. Modern two-phase titrations began with the work of Jones,[46] Epton[47] and Barr.[48] The various methods can use either anionic or cationic dyes as indicator and the effect of using these is to alter the underlying principle. No surfactant/dye complex is formed with an anionic dyestuff. Hence the first excess of cationic titrant will result in the transfer of the titrant/dye salt to the organic solvent. With a cationic dyestuff a surfactant/dye salt is formed, which transfers the colour to the organic phase, and complete transfer of colour back to the aqueous phase should show the end-point. Both these changes are difficult to observe and the former may tend to be prematurely observed. The end-point is therefore normally taken as equal colour intensity in the two phases. This means that anionic dyes give over-titration and cationic dyes give under-titration. This difficulty led Herring[49] to propose the use of mixed indicators, one cationic and the other anionic. He chose dimidium bromide and Disulphine Blue VN150. This modification has been extensively studied by Reid, Longman and Heinerth[50] and has led to a marked improvement in the accuracy of the two-phase titration technique. The outstanding virtues of this modification are that for the first time the titration is stoichiometric and the end-point can be very easily and readily observed. Initially the colour due to the surfactant/dimidium bromide complex is concentrated in the chloroform phase. Near the end-point this colour shifts into the aqueous phase and immediately the anionic/dimidium bromide colour

has disappeared the blue titrant/Disulphine Blue salt shows in the chloroform layer. The end-point is thus a sharp change from pink to blue.

A large number of titrants have been used in the numerous modifications. They include cetylpyridinium bromide (CPB), cetyltrimethylammonium chloride(CTC), cetylbenzyldimethylammonium chloride (CBC) and Hyamine 1622 (*p*-t-octylphenoxyethyldimethylammonium chloride). Careful examination of the different titrants has established that in single-dye procedures the benzene-derived titrants give titrations closer to stoichiometry than do the alkyl-based titrants. Of the benzene derivatives Hyamine 1622 is preferred because of its high solubility in water, its constant composition, its ready purification by recrystallization, and its almost quantitative reaction with a number of different anionic surfactants. It has been established that the normal hydrotropes used, soap, urea, fatty alkanolamides, non-ionic surfactants, bleaches and the inorganic salts normally incorporated do not have a deleterious effect on the titration. There is one other advantage this mixed-indicator system has over single-indicator systems. With the latter it is essential to use a fixed aliquot of titrand and a limited volume (10 ± 0·5 ml) of cationic titrant if reliable results are to be obtained. This is unnecessary with the mixed-indicator system. The aliquot used can vary between 6 and 50 ml and the volume of titrant may vary similarly without accuracy being affected. The titrant must be standardized precisely as described in the publication. In fact the dimidium bromide/Disulphine Blue two-phase titration system[50] is recommended above all others, but it must be remembered that components with a chain length of eight carbon atoms or less will not be titrated quantitatively. This procedure gives an end-point which is very sharp and is easily observed. The procedure can be used under acid or alkaline conditions, but the operator should standardize the titrant for each set of conditions. Single-phase titrations are less accurate.

A very large number of dyes have been proposed. The principal ones are Methylene Blue,[47] Bromophenol Blue,[48] Pontamine Fast Red 8NBL,[51] Rose Bengal,[52] acriflavine,[53] dichlorofluorescein,[54] Bromocresol Green,[55] Methyl Violet,[56] Orange II,[57] tetrabromofluorescein,[58] Thymol Blue[59] and Rhodamine 6G.[60] The procedure using Methyl Violet published by Abramovich[56] is a novel one. It is a single-phase reaction in which the reagent is an aqueous Methyl Violet solution decolorized with sodium sulphite at a pH of 9·5. The addition of this colourless reagent to an anionic surfactant results in the redevelopment of the violet colour, the depth of which is proportional to the concentration of surfactant present. It is thought that the reaction takes place within surfactant micelles from which sodium sulphite is excluded and therefore unable to decolorize the anionic surfactant/Methyl Violet salt formed within the micelle. This however is a colorimetric procedure and it cannot compete for accuracy with the two-phase mixed-indicator system. Alternative titrimetric procedures are those involving the use of benzidine hydrochloride[61] and *p*-toluidine hydrochloride.[62] In the former the benzidine salt of the anionic surfactant acid is precipitated, filtered off, dissolved in ethanol and the free acidity titrated with sodium hydroxide. In the latter the *p*-toluidine surfactant salt is dissolved in diethyl ether and after dilution with ethanol is titrated with sodium hydroxide. The *p*-toluidine procedure is the more satisfactory but neither is as reliable as the mixed-indicator method. Chromniak *et al.*[63] reported a modification of the benzidine hydrochloride technique. The surfactant solution is neutralized with hydrochloric acid and then titrated conductimetrically with benzidine hydrochloride solution, platinum electrodes being used.

Recent developments include the work of Hellsten[64] which uses the sudden breaking of emulsion and the coagulation of the anionic/cationic surfactant salt in a single-phase system and that of Saito[65] which extracts the Rhodamine 6G complex into benzene and measures the absorption at 530 nm. Lewkovich[66] heats the sample in a glass autoclave for 2 hr at 140° with 7 ml of 1·0*N* sulphuric acid. The amount of active detergent is deduced from the increase in amount of 0·5*N* sodium hydroxide needed for the titration with phenolphthalein as indicator. Shapoval *et al.*[67] propose the application of the polarograph to the determination provided the nature of the surfactant is known. Izawa[68] suggests a procedure for the direct assay of anionic surfactant in ternary mixtures of anionic/ampholyic/non-ionic surfactants whereby the anionic surfactant/Methylene Blue colour complex is isolated in chloroform after removal of any ampholyte/Methylene Blue complex on cotton; the anionic surfactant content is measured from its absorbance at 655 nm. Bartha *et al.*[69] used an ultraviolet spectrophotometric method for surfactants containing an aromatic ring, by measuring the absorbance at 220 nm; if aryl anionic surfactants are absent the procedure is applicable to alkylphenol ethoxylates.

It should be noted that reactions involving anionic dyes are performed in alkaline solution, and those with cationic dyes normally in acid solution. The stoichiometry of these different dye reactions vary and this aspect must be examined before any comparison is made between results obtained by different techniques.

DETERMINATION OF CATIONIC SURFACTANTS

The most reliable work on the analysis of cationic surfactants is that due to Cross.[3,70] In his 1965 paper he published a series of titration techniques which enable the cationic surfactants to be differentiated into three classes and each assessed separately. Sodium tetraphenylborate is used as titrant. By use at pH 1·0, pH 10 and pH 13 it classifies (1) alkyl and aryl quaternary ammonium derivatives, (2) pyridinium, quinolinium and biguanidine derivatives and

(3) the tertiary amines present as impurities in quaternary surfactants.

The one general gravimetric procedure is acetone extraction but this cannot be applied directly when any non-ionic surfactant is present. Gravimetric procedures in the main involve the formation of insoluble salts, and are liable to be far from acceptable. This is illustrated by Epton's[47] original dichromate procedure for standardizing cetylpyridinium bromide solutions, where it has since been demonstrated that the solubility of the salt increases with decrease in the molecular weight of the quaternary compound. A large number of precipitating agents have been used. They include potassium ferricyanide[71] and ferrocyanide, phosphotungstic acid,[72] reineckates,[73] Dragendorff's reagent,[36] phosphomolybdic acid and silicotungstic acid. Great care is necessary in the use of precipitating agents for quantitative assay. The reaction is often not stoichiometric and lower molecular weight surfactant components are more readily soluble in the aqueous phase. Careful choice is necessary and if possible the surfactant under examination should be used as a standard. Readers would do well to follow the recommendations of Cross.[3,70]

A more recent quantitative determination as the reineckate by Miyagishi *et al.*,[74] involved a pressed-disc infrared method and absorption measurement at 1250 cm^{-1} but each surfactant required its own calibration curve. Kasai, Yano and Kimura[75] have presented a combined gravimetric and titrimetric procedure. The surfactant solution is titrated in dilute hydrochloric acid solution with phosphotungstic acid and Congo Red as indicator. The molecular weight is deduced from the weight of precipitate and the titration value and this is used to deduce the content of the cationic surfactant.

The two-phase mixed-indicator titration technique already described can be applied equally well to cationic surfactants, but here a standard solution of sodium lauryl sulphate should be used as titrant and the same comments apply as those stressed for anionic surfactants. Some care is necessary in the application of colorimetric procedures to the determination of this type of surfactant. The absorption spectrum of the dye complexes can vary with the concentration of each particular quaternary ammonium halide and with the pH of the solution. For details the reader is referred to Colichman.[76] Few and Ottewill[77] use Orange II dye in their procedure and they measure the extracted colour complex at 485 nm. This was improved on by Scott[78] who used more stringent reaction conditions. Methods for complete examination of dimethyl-di-(long-chain alkyl) quaternary ammonium derivatives are described by Babcock, Terry and Milun.[79]

Recently Jansson, Modin and Schill[80] have discussed the two-phase titration of organic ammonium ions with lauryl sulphate, with Methyl Yellow as indicator. The operating conditions for quaternary ammonium compounds and amines are derived from experimentally-obtained extraction constants for the ion-pairs between lauryl sulphate, Methyl Yellow and the sample. This is an unusual approach to eliminating the difficulties in obtaining stoichiometric endpoints in two-phase titrations. The procedure is too new for extensive examination to have been made of its reliability and reproducibility and until these have been established the author would recommend that the dimidium bromide/Disulphine Blue VN 150 technique[50] be used. One and two-dimensional chromatographic procedures have been developed for identification of cationic surfactants. Neu[81] describes a procedure which enables quaternary ammonium cationic surfactants to be differentiated from amphoteric surfactants by development with a butanol–acetic acid–water (4:1:4) mixture. Murier and Sarrazin[82] report a combination of two-dimensional electrophoresis and TLC for a satisfactory separation of these cationic surfactants. They employ silica gel treated with a pyridine–acetic acid buffer adjusted to pH 6·5.

DETERMINATION OF NON-IONIC SURFACTANTS

Some 20 basic types of non-ionic surfactant are now in use. They are almost all derivatives of ethylene oxide or propylene oxide, or mixed ethylene oxide/propylene oxide derivatives which can exist as block or random co-polymers. These types are manufactured to contain a variable number of alkylene oxide groups and each product contains a large number of telomers which may differ in composition from batch to batch. These products may contain 2–30% of free polyoxyalkylene oxide impurities and these also are present as telomers. They also contain free hydrophobes and the degree to which these impurities are present can affect the performance of the product. This complicated character of individual non-ionic surfactants and the even more complicated nature of mixtures means that their analysis can be a difficult problem, for industry requires to know not only the type of non-ionic surfactant but also the mean chain length of the telomers and often the content of the various telomers present. Some of these non-ionic surfactants are sugar or sorbitan esters.

For the analysis of this type of product some 25 different determinations may be necessary, depending on the particular product being examined. Many of these are conventional tests such as water, ash, refractive index, cloud point, alkalinity, hydroxyl value and ester value. The greatest problem is the determination of the content of total ethylene oxide and/or propylene oxide. The best procedure to adopt depends upon the nature of the products and each is liable to give anomalous results in certain cases. A variety of chemical methods based on hydriodic acid degradation may be used but these are invalid if sulphur, glycerol, glycerides or sugars are present. Moreover, complete decomposition of the alkylene oxide does not result when it is combined through a nitrogen atom; the initial N–C linkage is not destroyed. Nor can the procedures be applied if propylene oxide

forms part of the product of t-butyl or t-octyl groups are present; anomalous results are produced because of degradation of these alkyl groups. Again if the hydriodic acid used is less than 57% w/v low results are obtained. If the alternative Siggia method[83] is employed then it is preferable to use potassium iodide and orthophosphoric acid as the source of hydriodic acid. This procedure suffers from the same failings except that it is not affected by the presence of t-butyl or t-octyl groups. Infrared procedures have been developed for the quantitative assessment of these two groups, but these again can lead to anomalous results. The Voogt[84] procedure makes use of the bands due to the ethoxy group at 2485 or 4030 cm^{-1} but this procedure is more reliable for alkylphenol ethoxylates than for alcohol derivatives. Actually, the 2485-cm^{-1} band is due to $-CH_2O$, not $-CH_2CH_2O-$. Hence the response from alcohol derivatives is different from that of alkylphenol derivatives but even when due allowance is made for this in the standards, anomalous results are still obtained and the procedure is not suitable for reliable work. Far more difficult is the analysis of simple and complex ethylene/oxide propylene oxide co-polymers. Chemical methods cannot be applied. Infrared methods show varying degrees of bias depending on the relative proportions of the two oxides. The great difficulty is that with random co-polymers the instrument fails to detect the presence of a single ethoxy group joined to two propylene oxide groups. The most promising procedure is a differential overtone method using the doublet at 1675 and 1688 cm^{-1} but this can only be used with very expensive instruments and is less reliable for random co-polymers than for block co-polymers. Uno and Miyajima[85] base their procedure for the analysis of these co-polymers on the stretching bands of $-CH_3$ and $-CH_2-$ at 2780 and 2975 cm^{-1}, plotting absorbances against molar % of ethylene oxide. Stead[86] has published a very promising procedure which is applicable to simple alkoxylates or to co-polymers. This he claims is more reliable than the infrared methods which he criticises. His procedure depends on hydrobromic acid degradation of the non-ionic surfactant. The degradation products ethylene dibromide and propylene dibromide are more stable towards heat than are the corresponding di-iodides. The bromides formed are determined by GLC. The fission reaction is not quantitative but Stead has overcome this by using two bracketing standards which span the sample composition within narrow limits and this makes accurate determination possible. The procedure has the advantage that it is applicable both to simple and to complex co-polymers, and has the added advantage that it also assesses any hydrophobe present, It is therefore applicable to simple ethylene oxide or to propylene oxide derivatives and to block and random co-polymers of any type.

The determination of ethylene oxide/propylene oxide or ethylene oxide content is not an easy matter because of the varying accuracy of a given procedure with different types of non-ionic surfactant. Infrared procedures must be applied with great care, for the accuracy is dependent on the type of non-ionic surfactant, the content of ethylene oxide and the ratio of ethylene oxide to propylene oxide. NMR[87] is probably the most reliable method, provided that mixed non-ionic components are not present, and the Stead method[86] is reliable for either ethylene oxide or ethylene oxide/propylene oxide derivatives. Of the chemical procedures for determination of ethylene oxide content, the modified Siggia procedure using potassium iodide and orthophosphoric acid to derive hydriodic acid is recommended.

Both Williams and Graham[88] and Lamendin[89] have used phosphoric acid fission for the analysis of these co-polymers. The latter found that the chemical procedure for the determination of the reaction products was unsuitable. He therefore combined pyrolysis with GLC. A small furnace, in which the fission occurs to give acetaldehyde and propionaldehyde, is attached directly to the chromatograph and the relative proportions of the two are determined after application of standard corrections. This procedure enables simple and co-polymers to be analysed.

NMR has also given good results as exemplified by the procedure of Greff and Flanagan.[87] The hydrophile/hydrophobe ratio can be deduced and the ethylene oxide chain length established; the ratio of ethylene oxide to propylene oxide in simple co-polymers can also be established. This technique is likely to prove one of the most reliable for co-polymers. The hydrophile/lipophile balance is also assessed by gas chromatography by Petrowski and Vanatta.[90] Lamendin[91] has made good use of refractive-index measurements. By plotting refractive index at 50° against n, the mean ethylene oxide chain length, for a variety of different hydrophobe derivatives, he found that each different type had its own specific curve and with a known type he was able then from the refractive index to deduce the value of n; with products of unknown composition, knowing the refractive index and the ethylene oxide content, he could deduce the mean chain length n.

Two techniques are available for the determination of polyoxyethylene glycol in non-ionic surfactants. One is a development of the Weibull[92] procedure. It involves the ethyl acetate extraction of the polyoxyethylene glycol from aqueous solution under carefully controlled temperature and concentration conditions. The glycol remains in the aqueous phase, from which it is extracted with chloroform,[44] and the non-ionic surfactant is recovered quantitatively from the ethyl acetate fraction. This procedure will also enable polyoxyethylene glycol to be isolated from polyoxypropylene glycol, as the latter is soluble in ethyl acetate. The other method is that due to Voogt.[93] This uses reverse-phase chromatography on silaned silica gel; the glycols are eluted first, followed by the removal of the non-ionic surfactant.

Numerous methods have been reported for deducing the telomer distribution within these products. They involve circular TLC, paper chromatography,

GLC and mass spectrometry. The quantitative application of GLC is difficult, as each telomer gives a different degree of response; it is necessary that a correction value be known for each so that a correct quantitative distribution can be calculated. Gildenberg and Trowbridge[94] isolated the first thirteen units of a system as the acetates and the isolation of some 15–20 telomers seems to be the limit at the present time. The polyoxyethylene glycols are even more difficult, although separations of the trimethylsilyl ether derivatives have been effected. Neither paper chromatography nor TLC has proved any more successful. Nonetheless the ability to effect this degree of separation can often be invaluable. Pioneers in this field include Ginn,[95] Patterson[96] and Vaktina *et al.*,[97] all of whom used mixed solvents for development of chromatograms. Konishi and Yamaguchi[98] used circular TLC for the nonylphenol ethoxylates, visualized the chromatogram with iodine and assessed the relative intensities of the photographed stains with a microphotometer. Gauthier and Mangeney[99] chromatographed the 3,5-dinitrobenzoate esters by the Borecký and Gasparič method.[100] These separations showed the same limiting separation of components. Often mixed non-ionic surfactants are used in commercial products. Analysis of these by this technique can then be misleading unless some way can be found of separating the active constituents. Rosen[101] published a column-chromatography procedure using increasingly polar solvents and reported effective separation of the component types from a number of four-component mixtures. There is still much to be done with regard to telomer distribution, for products of mean chain length 30–80 can be encountered in commerce.

Quantitative isolation and determination of non-ionic surfactants from aqueous solution can be effected either by extraction of the dried solids with acetone or preferably by chloroform extraction from aqueous ethanolic solution. If mixed types of surfactant are present it will be necessary to use either alumina-column or ion-exchange separation before attempting the isolation of each surfactant. Fatty acid and sugar esters are best analysed by alkaline or acid hydrolysis; the amount of liberated fatty and/or sugar component can be determined and the content of non-ionic surfactant deduced from this figure. Many precipitation methods have been used, based on phosphotungstic acid,[102] phosphomolybdic acid[103] and silicotungstic acid[104] but for accurate application these procedures require that the actual surfactant present shall be available as a reference standard. Wetterau *et al.*[105] have developed a countercurrent extraction procedure which permits the quantitative isolation in turn of polyoxyethylene glycol, fatty acid monoester of polyoxyethylene glycol, and the corresponding diester.

A number of colorimetric procedures have been reported. These include the use of heteropoly-acids.[102–104,105] ammonium cobaltothiocyanate[107–109] potassium mercuri-iodide, 2,4-dinitrophenylhydrazine,[110] sodium tetraphenylborate,[111] ferrocyanide[112] and dichlorofluorescein.[110] There is one peculiarity with these precipitation and colorimetric procedures and this has been reported by a number of observers.[109,111,113] No ethylene oxide telomer containing less than six EO units will respond to the reaction and as the number of units increases beyond six so the amount of reagent reacting with the molecule increases. The cobaltothiocyanate derivatives of n-dodecanol provide an example. The 6-EO derivative gave a molar absorptivity of 812 $l.mole^{-1}.cm^{-1}$ at 319 nm and the 10-EO derivative a value of $2{\cdot}78 \times 10^3$. Addition to the surfactant molecule occurs at the ether oxygen atom. It is interesting that with the cobaltothiocyanate method, for pure n-alkanol derivatives varying between 4 and 32 in mean molar EO content, the curve of absorbance of the cobaltothiocyanate complex at 319 nm is a parabolic function of the number of EO units, the maximum response being at 25 EO. The corresponding polyoxyethylene glycols give maximum response at about 15 EO.

Free alcohols, free phenols and other free hydrophobes in these products can be determined either by column chromatography on alumina or by GLC procedures. The nature of the hydrophobic group present in non-ionic surfactants can often be deduced by NMR methods but if an NMR instrument is not available then the nature of the group can often be derived by degradation of the alkylene oxide chain by hydriodic acid. Fatty-acid derivatives will give fatty acids, fatty alcohol and fatty thiol derivatives will give an alkyl iodide, and alkylphenol derivatives will give rise to alkylphenol. Sometimes hydrolysis procedures can be used. With ester types it is easier to isolate the hydrophobe fraction after hydrolysis; it will then be possible not only to isolate the hydrophobe but also to extract the resulting polyoxyethylene glycol into chloroform. This procedure will enable the fatty acid or fatty thiol (from thiol ethoxylates) to be isolated and characterized.

If the combined hydrophobe is free from hydroxyl groups then a determination of the hydroxyl value of the surfactant will enable its mean molecular weight to be calculated. The hydroxyl value can be obtained by reacting with phthalic anhydride, stearic anhydride[114] or pyromellitic anhydride. Incidentally, the content of fatty acid, fatty alcohol or iodide, fatty thiol or alkylphenol isolated will enable the mean molecular weight of the surfactant to be calculated.

A scheme for the qualitative identification of non-ionic surfactants was described by Selden and Benedict,[115] based on the isolation of the surfactant by ion-exchange or TLC on silica gel, use of Dragendorff's reagent and tests for reactive groups. Stolzenberg *et al.*[116] isolated the isomers of an alkylphenol ethoxylate by TLC and GLC. The *o*-alkylphenol, *p*-alkylphenol and dialkylphenol monoethoxylate isomers were identified by NMR.

The chloroform or acetone extraction procedures are best used for isolation of the non-ionic surfactants but precise identification is made difficult by the

large number of telomers which are normally present. No procedure for telomer distribution is generally applicable and at present procedures are limited to products containing no component with more than 25 EO units. Of these, that of Gildenberg and Trowbridge[94] is very effective, but the quantitative assessment of telomers is rendered difficult because the response of each telomer to a given reagent increases with increase in the EO chain length in the molecule. When GLC is used for telomer distribution the response of each component falls with increased EO chain length, but this is the better procedure to use because it is easier to assess the relative response of the telomers.

The determination of EO and EO/PO (propylene oxide) content is not an easy matter because of the varying accuracy of a procedure with different types of non-ionic surfactant. No one method is generally applicable. Infrared procedures must be applied with care, for the accuracy is dependent on the type of surfactant, and on the content of EO and of EO and PO. NMR[87] is probably the most reliable as long as mixed surfactants are not present and the Stead[86] method is reliable for EO/PO derivatives. Of the chemical procedures for determination of EO content the modified Siggia procedure[83] is recommended.

Of the colorimetric methods, that involving the use of the Dragendorff reagent[117] is the most reliable, but the determination of the combined bismuth is best made by the West and Coll[118] method which uses EDTA.

DETERMINATION OF AMINE OXIDES

The addition of amine oxides to liquid household detergent products is a recent application although the first patents for their preparation appeared during 1930–5, claiming the use of dimethyldialkylamine oxide as a wetting, cleansing and disinfecting agent. The main asset of this class lies in their power as foam stabilizers and their emollient effect on the skin. They are prepared by the interaction of tertiary amines with hydrogen peroxide and although the oxides are less basic than the parent amines, with strong acids they form salts which show cationic properties but are neutral in alkaline solution.

Amine oxides are determined in the presence of free tertiary amine by two-phase titration with sodium lauryl sulphate in an acid solution. This gives the sum of amine oxide and tertiary amine. The mixture is then reacted with methyl iodide. This converts the free amine into the corresponding quaternary nitrogen base. Two-phase titration in an alkaline medium then determines only the quaternary base. The amine oxide is obtained by difference. Lew[119] has studied the effect of using Bromocresol Green as indicator in an alkaline medium. He found that the amine oxide was not titrated. Hence if a mixture of amine oxide and anionic surfactant is titrated under these conditions only the anionic surfactant is titrated. When the two-phase titration procedure is used in an acid medium the amine oxide reacts with the anionic surfactant and the reduction in titration value is a measure of the amine oxide content. The amine oxide and free tertiary amine can also be determined by potentiometric titration with acid. A simple titration gives the sum of the two components and if the titration is repeated after quaternization with methyl iodide only the amine oxide is titrated. Babcock *et al.*[79] describe methods for the analysis of dialkyldimethylammonium halides. Each of the procedures discussed is reliable but it is essential that the molecular weight of the oxide be known.

THE ANALYSIS OF AMPHOLYTIC AND ZWITTERION SURFACTANTS

The introduction of these types of surfactants is recent and as yet little information has trickled through from industry. A very recent introduction is the zwitterion surfactants. The cost of their production is still high and this limits their application. They contain a quaternary ammonium group and a sulphonic acid group in close proximity in the molecule. This has the effect of rendering the molecule electrically neutral, as distinct from the ampholytes which contain a strong acidic or basic group and a weaker group of opposite charge, so a marked change in pH can alter the chemical properties of the product; Moore and Hardwick[120] define the ampholytes as showing a considerable change from anionic to cationic properties over the pH range 2–12.

The author[44] has investigated methods for the determination of pyridinium sulphobetaines, alkyl quaternary ammonium sulphobetaines, quaternary ammonium hydroxamates, and *N*-hydroxyalkylmethyl taurides, based on five different approaches, namely elemental analysis, TLC on silica gel with absolute methanol and absolute ethanol, acid–base titrations, two-phase mixed-indicator titrations and column chromatography on alumina. Elemental analysis will often indicate the type of product present, *e.g.*, absence of sulphur eliminates the presence of sulphobetaines. Thin-layer chromatography yields important information, *e.g.*, sulphonates show different R_f values in methanol and ethanol. It will differentiate sodium lauryl sulphates, *N*-hydroxyalkylmethyl taurides, pyridinium sulphobetaine, quaternary ammonium sulphobetaines and alkyl quaternary ammonium hydroxamates. By application of chemical reactions before and after the development of the chromatogram, quaternary ammonium salts can be differentiated from the hydroxamates, TLC will also permit the impurities present in the hydroxamate derivatives and in the methyl tauride to be detected. The hydroxamate derivatives are hydrolysed with 50% sulphuric acid and the resulting hydroxylamine can then be determined by reaction with standard bromate solution or by reaction with ferric alum. The zwitterion sulphobetaines give no reaction in two-phase titration either in acidic or alkaline solution. Hydroxyalkylmethyl taurides react as anionic surfactants in an alkaline solution and the hydroxamate derivatives

react only in acidic media and then behave as cationic surfactants. Chromatography on alumina allows elution of tertiary amines by chloroform, of amine oxides, pyridine, alkyl quaternary ammonium compounds and sulphobetaines by absolute ethanol, hydroxyalkylmethyl taurides by 90% aqueous ethanol and anionic surfactant by 50% aqueous ethanol. Alkyl sultones can be removed from the products by diethyl ether extraction. Full details will appear in a forthcoming publication.[44]

MODERN TRENDS

The modern approach to analysis is to use automatic methods. This has progressed rapidly following the appearance of the "Auto-Analyzer." This has revolutionized routine analysis and it makes use of standard procedures. De Jong[121] reported a procedure in which the anionic surfactant was determined as its Methylene Blue complex. Setzkorn *et al.*[122] also used a Methylene Blue procedure, while Brandli and Kelley[123] reported a procedure for alkylbenzene sulphonates. Such techniques are now extensively used in industry.

Nelles[124] has published a series of 52 infrared spectra of surfactants which can be used for identification and these supplement those of Hummel.[2] A number of polarographic and electrochemical procedures have been published. Dietrich[125] gave an a.c. polarography method for the analysis of certain quaternary ammonium, anionic and non-ionic surfactants, and Jehring[126] discussed the value of various electrochemical procedures. Scott[127] used a radiofrequency end-point in an automatic titrimeter for both cationic and anionic surfactants.

SCHEMES FOR THE ANALYSIS AND IDENTIFICATION OF SURFACTANTS

It is useful and usual when examining detergent products to work with some definite scheme of attack. Most industrial concerns have their own special approach but these are rarely published. One of the earliest schemes came in 1945 from Hintermaier[128] but at that time the number of surfactants commercially available was not very numerous. Then came schemes from the American Oil Chemists' Society,[129] the Canadian Government Laboratory,[130] Bergeron *et al.*,[131] and the Society of Public Analysts.[132] In 1955 came the first ASTM standards,[133] Kortland and Dammers's scheme[134] and the Swiss standards.[135] These were followed by recommendations from Holness and Stone,[136] Carlos,[137] the 1958 ASTM standards[138] and a publication from Longman and Hilton.[24] Rosen gives a series of 33 different separation schemes, each varying according to the elements present. This is a complicated plan and is far more complex than any other. Longman prefers to use a system based on the type of component present and full information will be given in a forthcoming publication.[44] It is essential to use an organized approach, particularly for the problem of examining products of unknown composition. Of these schemes the extended one of Longman and Hilton[44] is recommended. This has been developed during years of experience in this field.

The use of such schemes facilitates the subsequent identification of the detergent components, but use of these alone is insufficient for the precise composition to be deduced. At best the schemes can only indicate a type of surfactant and a far greater amount of information is necessary to deduce its precise nature. If the surfactants are hydrolysable to give fatty matter, then the fatty matter must be scrupulously analysed, including mean molecular weight, the degree of unsaturation and if possible the source of the fatty matter. From these data and the complete identification of the components of hydrolysis, the actual content of the surfactant can be calculated. If the surfactant is an alkylbenzene sulphonate, then the original hydrocarbons must be recovered so that their precise nature can be examined by means of the mass spectrometer; some experts can even deduce the manufacturer of the hydrocarbons. The infrared spectrometer, the mass spectrometer and nuclear magnetic resonance are indispensible for the rapid deduction of the nature of the surfactant, but often it will also be necessary to use chemical procedures. Longman has published a scheme for the interpretation of analytical data which was based on chemical behaviour and the elements present. This system is now out of date because of the introduction of new surfactants but this approach can still form the basis for schematic interpretation.

DETERMINATION OF NON-SURFACTANT ORGANIC CONSTITUENTS

There are at least twelve classes of organic component which may be added to formulated products. These include liquid hydrotropes, urea, auxiliary surface-active agents such as lauric monoethanolamide, methyl or ethyl cellulose, sodium carboxymethyl cellulose, anti-tarnishing agents such as ethylene thiourea, fluorescent agents, perborate-stabilizing agents such as *o*-tolyl biguanide, low-temperature bleach precursors, germicidal agents, organic bleaching agents, ethylenediaminetetra-acetic acid (EDTA) and nitrilotriacetic acid (NTA). Each of these may need to be determined before a composition can be calculated.

The volatile alcohols ethanol and isopropyl alcohol can be determined by distillation methods but are best assessed by means of the Conway unit after qualitative tests have established which alcohol is present and also that there is no volatile interfering matter present. This reaction requires a diffusion time of 15 hr but can be performed overnight. The alcohol is collected and oxidized with standard potassium dichromate solution; the nature of the alcohol must be known for the correct conversion factor to be used. Benzyl alcohol may also be used as a hydrotrope; it can be isolated in a Dean and Stark apparatus and the volume measured. The additive most widely

used to solubilize the constituents of liquid preparations is urea. Its presence upsets all the normal schemes for separation and it must be decomposed before any separation or analysis is begun. It can be determined by reaction with urease or with a nitrometer after reaction with sodium hypobromite.

Fatty alkanolamides are best separated and determined gravimetrically by extraction into diethyl ether from aqueous ethanol. They can be identified by instrumental methods, paper chromatography, chemically after acid hydrolysis, or by periodate oxidation when the ratio of ammonia liberated to aldehyde gives the clue for identification. The cellulose ethers and sodium carboxymethyl cellulose are all determined by a modification[44] of the anthrone method but a different reference standard must be used for each particular type; their presence is established by standard qualitative tests, and perborate, if present, must be destroyed before the quantitative determination is commenced. Milwidsky[139] recently published a rapid routine method for the determination of carboxymethyl cellulose and related materials by a colorimetric method in that they are reacted with phenol and concentrated sulphuric acid; the absorbance is measured at 490 nm. A number of different low-temperature bleach precursors have been employed. The function of these is to react with sodium perborate to produce either peracetic acid or perbenzoic acid, either of which will act as a bleaching agent at 60°. For their determination the precursors are reacted at 0° in the presence of excess of sodium perborate in acetic acid solution with potassium iodide.[44] The liberated iodine is a measure of the precursor because perborate does not itself react with the iodide under these conditions. Amide derivatives with the characteristic grouping CO.NH.CO are popular as precursors, although acid anhydrides may also be used.

Anti-tarnishing agents are added primarily to prevent the staining of certain types of cutlery by the phosphates present: benzothiazole and ethylenethiourea have been used. Grote's test is used to detect thiourea and both are determined by precipitating with ammoniacal silver nitrate solution and weighing the residue after ignition. The sequestering agents EDTA and NTA may both be present in detergent products. Triphosphate, when present, must be hydrolysed to orthophosphate before any complexation technique is used for determination of EDTA or NTA, and heavy metals, if present, must be removed. EDTA and NTA are normally titrated with copper in the presence of PAN, tiron or some similar indicator under carefully buffered conditions.[44]

Organic bleaches are beginning to replace sodium perborate, sodium hypochlorite and sodium phosphate–hypochlorite. Recent developments include the use of the chloramine T, dichlorodimethylhydantoin and the salts of the various chlorocyanuric acids; chloro-substituted perbenzoic acid has also been used but must be protected within poly(vinyl alcohol) sachets during shelf-life. The normal iodide techniques are used for their determination. Klotz and Askouris[140] discuss the ultraviolet spectra of the cyanurates and Pettersen *et al.*[141] have used infrared spectroscopy for their identification.

The identification and determination of fluorescent agents is now quite a problem. The earliest fluorescent whitening agents were cotton-substantive and had no effect on man-made fibres. They were derivatives of 4,4′-diaminostilbene-2,2′-disulphonate but now a variety of colourless fluorescing dyes have been developed and all man-made fibres can now be treated with fluorescent agents. Great care must be exercised during determinations. Many of these agents exist in both *cis-* and *trans-* modifications and only the *trans*-form is cotton-substantive. The *trans*-modification can be converted into the *cis-* by exposure to sunlight or ultraviolet light. This means that all work must therefore be performed in a dark-room under red light. Because of the difference in behaviour of these two isomers it is also necessary to separate *trans-* from *cis-* so that only the active and effective form is determined. The cotton-substantive dye can be identified qualitatively from the ultraviolet adsorption spectrum over the range 200–400 nm after adsorption of the dye onto transparent reconstituted cellulose. TLC can also be used to identify the nature of the fluorescent agents present and for their quantitative determination.[44] The various whitening agents present are isolated as individuals, each being removed separately from the plate and eluted with a solvent, diluted to known volume and examined in a direct-reading fluorimeter. They can also be assessed by paper chromatography.

Some twelve or thirteen different germicidal agents have been used but at the present time the use of a number of them is controlled. It is now normal to include more than one agent as mixtures often exhibit a synergistic effect. This means that analysis is more difficult and that identification of the individuals present must precede their determination. They can be identified by TLC but the examination of soap products both for germicides and fluorescent whitening agents is more difficult; solutions should be acidified before development of the chromatogram. Most of the published methods cover specific components but Derry *et al.*[142] separated mixtures on a silaned silica gel column and Jungermann and Beck[143] isolated the germicides in dimethylformamide and studied their ultraviolet absorption spectra in ammoniacal ethanol. Bravo Ordenes and Hermández Alvarado[144] used TLC for identification. These constituents are best isolated by cold dimethylformamide extraction and then the components are eluted in turn from an ion-exchange or alumina column.

Occasionally, certain additives may be incorporated in sachets to preserve them during their shelf-life. There is an ulterior motive in this for the envelope is made from poly(vinyl alcohol) with an inner lining of poly(vinyl acetate). The sachet prevents access of water to the additive but is completely and readily soluble in water, and like carboxymethyl cellulose the solution makes an excellent dirt-suspending agent.

These sachets need to be analysed but their identity can be readily established by infrared spectroscopy.

o-Tolyl biguanide may be incorporated as a preservative for sodium perborate during storage. It prevents the catalytic breakdown of the perborate by metals. It can be identified and determined[44] by a colour reaction characteristic of guanidine or a derivative containing on NH_2-group. The biguanide will react in a strongly alkaline medium with biacetyl and 2-naphthol. The intensity of the red colour developed is a measure of the tolyl biguanide concentration.

DETERMINATION OF INORGANIC CONSTITUENTS

A number of different inorganic salts are likely to be found in detergent products. Of these the most important are the phosphates, sodium perborate, chlorine bleaches and sodium silicates. Three types of phosphate are usually present in powders, Na_2HPO_4, $Na_4P_2O_7$ and $Na_5P_3O_{10}$ and some form of metaphosphate may sometimes be added. Three types of silicate may be present—sodium metasilicate, alkaline sodium silicate ($Na_2O.2SiO_2$) and neutral silicate (Na_2O, $3.27SiO_2$) and the analyst may be called upon to decide which of the three is present in the product. Perborates are prone to some degree of degradation and it is therefore often necessary to analyse the product for total borate in order to deduce the degree of decomposition of the perborate.

Any one of four procedures may be used for the determination of water and the one chosen will depend upon the proportion of inorganic salts present. These are oven drying, drying with acetone, the Dean and Stark method and the Karl Fischer method, but even here it must be realized that perborate, triphosphate and silicate may not release the whole of their water of crystallization. The same comment may hold for the Dean and Stark method but the higher the boiling point of the azeotropic solvent the more effective will be the removal of water. The acetone drying procedure can only be used when the content of inorganic salts is very low. Of the four methods for the determination of water the Karl Fischer will give most satisfaction but there may be times when with low water contents the use of the Dean and Stark method will prove profitable.

The total sulphur content of a product can be determined by a number of different procedures. This figure is often determined so that once the organically combined sulphate is known the inorganic sulphate can be found by difference. Usually either a bomb ignition or an Eschka-mixture ignition is used to destroy the organic matter and to retain the sulphur in a form which is easily oxidized to sulphate. The sulphate can be determined gravimetrically as barium sulphate or by a titrimetric procedure with barium chloride or lead nitrate and using a suitable indicator. Special precautions are necessary when silicates and phosphates are present; it is advisable to remove these first. The author has found the Eschka-mixture method for ignition of the sample perfectly satisfactory for the gravimetric determination of either total sulphur content or the organic sulphur content. The total of free ammonium salts can be determined by simple alkaline distillation into boric acid or standard sulphuric acid. An equally satisfactory determination can be obtained by using a Conway unit and absorbing the diffusing ammonia in standard sulphuric acid. Chlorides can be determined either by potentiometric titration with silver nitrate or by using the Volhard or the Mohr method. Chlorides in soap should be determined after destruction of the soap by the addition of calcium nitrate.

Total silicate may be determined gravimetrically or colorimetrically. The gravimetric procedure is far more reliable but if borates are present it is preferable to remove them with methanol as methyl borate. The sample should be ignited and fused with sodium carbonate before beginning the hydrochloric acid treatment. Miller's[145] method is recommended for the colorimetric determination but in this case any perborate must be decomposed by treatment with potassium permanganate, and interference of phosphates with the silicomolybdate reaction prevented by the addition of citric acid. Many powders contain water-insoluble silica but its content is not easy to determine as the conditions of the test decide the solubility. The conditions should be as near as possible to those likely to be found during washing.

Total phosphates can be determined in a number of ways. For accuracy there is still no better method than precipitation as magnesium ammonium phosphate after hydrolysis of the complex phosphates and weighing as magnesium pyrophosphate, but it is necessary to remove borate as methyl borate, and silicate in the usual manner; when calcium, magnesium or lithium is present the phosphate must be precipitated as ammonium or quinoline phosphomolybdate. Phosphate can be determined by potentiometric titration of NaH_2PO_4 to Na_2HPO_4, after conversion of pyro- and triphosphate into orthophosphate, or alternatively the addition of silver nitrate to NaH_2PO_4 will liberate nitric acid which can then be titrated. The phosphate may also be determined by titration of quinoline phosphomolybdate or colorimetrically by the reduction of phosphomolybdic acid to molybdenum blue.

The relative proportions of the phosphates present in detergent products are extremely important. The performance of a washing powder is controlled by the triphosphate and pyrophosphate contents and their accurate determination is essential. This can be achieved by ion-exchange procedures, paper chromatography or chemical methods. The last named were the first to be used but they have been superseded first by chromatographic methods and then by ion-exchange. Lundgren and Loeb[146] have automated the ion-exchange procedure and now both total phosphate and the proportions of phosphates can be monitored continuously by the Technicon "Auto-Analyzer". This method is recommended if the apparatus is already available. Numerous chromatographic

procedures have been suggested, but that which Longman[44] helped to develop is recommended. It uses a methanol–isopropyl alcohol–water–trichloracetic acid–ammonia solvent in normal developing tanks held at 6°. The position of the phosphates on the chromatogram is visualized by spraying first with ferric chloride solution in acetone and then with sulphosalicylic solution in absolute alcohol–acetone. The various phosphates, including the various metaphosphates, if present, appear as white spots on a pinkish-purple background. The individual phosphates are isolated, dissolved, and determined by the Soyenkoff[147] method which uses the dye 2-(*p*-dimethylaminostyryl)quinoline ethosulphate as reagent. This is a procedure some ten times more sensitive than any molybdenum blue reaction and the pink colour is measured at 520 nm. If this colorimetric procedure is used, then molybdate must not be used as the spraying agent to visualize the chromatogram. The method gives reliable results and is a satisfactory alternative to the "Auto-Analyzer" method.

The ion-exchange determination is performed by downward flow through anion-exchange resins in the chloride form, packed in a borosilicate glass column. The various phosphates are eluted by gradient elution with potassium chloride solution, starting at 0·2*M* and increasing to 1·0*M*. The pattern of elution is orthophosphate, pyrophosphate and triphosphate but this can always be checked by use of known phosphates. In the automated procedure the determination of phosphate is carried out by the Boltz and Mellon method[148] which involves reduction of phosphomolybdate to molybdenum blue. The chemical method, based on a 1937 publication, is a titration procedure. Aliquots are titrated potentiometrically with standard alkali, (1) after addition of sodium nitrate at the end-point at about pH 5 and further titration to an end-point at about pH 8·5, and (2) after addition of excess of silver nitrate at the pH-5 end-point, the liberated nitric acid being titrated to the end-point at about pH 5. From these two titrations and the total P_2O_5 content the proportions of the three phosphates are calculated and reported as Na_2HPO_4, $Na_4P_2O_7$ and $Na_5P_3O_{10}$.

The total alkalinity is determined by direct titration with acid, and carbonates are best determined in a special apparatus in which the liberated carbon dioxide is absorbed and weighed; from the alkali present as carbonate and the amount of carbon dioxide the proportions of sodium bicarbonate and carbonate can be calculated.

The total borate content can be determined by an ion-exchange procedure as outlined in the British Standards Specification but preferably by the accepted methyl borate distillation procedure. In the ion-exchange procedure a solution of the ignited detergent product is passed through Amberlite cation- and anion-exchange resins, leaving only boric acid in solution; this is titrated in the presence of mannitol. A special apparatus[44] is necessary for the distillation procedure because of the high content of inorganic solids; it includes a pressure overflow from the methanol boiler to a special receiver. The content of perborate or percarbonate is determined either from the iodine liberated from acidified potassium iodide or by titration of the available oxygen by potassium permanganate after sequestering any EDTA or NTA by the addition of bismuth nitrate, and detecting the end-point by the disappearance of the colour of the titanyl peroxide complex. If a chlorine bleach is present, the available chlorine content should be determined by means of the reaction with acidified potassium iodide. If it is desired to obtain information on the nature of the hydrates present in any detergent powder product, recourse must be made to thermogravimetric analysis or differential scanning calorimetry. In both cases known standard hydrates must be available in order to obtain comparative data. It will be possible to identify and determine triphosphate hexahydrate, sodium perborate, sodium pyrophosphate decahydrate and sodium sulphate heptahydrate.

Very recently, Al-Sulimany and Townshend[149] reported a polarographic determination of triphosphate and of triphosphate and sodium nitrilotriacetate in admixture. The phosphate was determined from the decrease in height of the cadmium polarographic wave, and in the mixture from this and from the cadmium–NTA wave-height. Akimov *et al.*[150] used a titration procedure for total phosphate in acetone–water medium with nitchromazo (4-nitroso-2-sulpho-2-phenylazo-1,8-dihydroxynaphthalene-3,6-disulphonic acid) as indicator. Herold *et al.*[151] have used an automatic ion-exchange procedure and measured the intensity of the phosphomolybdovanadate colour.

POLLUTION PROBLEMS

Three types of biodegradation are to be distinguished. First, primary biodegradation in which the parent molecules are destroyed regardless of the pollution effect of the decomposition products, secondly biodegradation to an environmentally acceptable level wherein the resulting components do not upset sewage treatment, lead to no pollution, are not toxic to living matter in rivers, lakes or streams and do not cause eutrophication, and thirdly ultimate biodegradation which involves conversion of the substrate into carbon dioxide, water and natural metabolites. The problem is which of the three is most important, and how they affect the analyst.

Manufacturers of detergents are usually satisfied if bacteria effect the removal of the characteristic functional groups irrespective of any pollution effect of resulting intermediates. The manufacturers of finished products are concerned to meet the requirements of the second type of biodegradation. The third type is environmentally desirable but would only be demanded by the idealist.

The problems of analysis of sewage and effluent liquors include the following;

(*i*) Sample preservation and the most suitable procedure to adopt; mercuric chloride, chloroform, fomaldehyde and thymol have been used. Low temperature storage is essential and preferable.

(*ii*) The best method of ensuring representative sampling.

(*iii*) Difficulties due to distribution to the substrate between solid and liquid phases. This will vary with the fat and protein level in the system itself and with adsorption on deposits in the plant.

(*iv*) The effect of mixed surfactants and biodegradation intermediates on the determination.

(*v*) The correct choice of reference standard.

At the present time, Swisher's book "Surfactant Biodegradation" is the accepted work on these problems. The difficulties of analysis have increased in recent years since the marked increase in the use of non-ionic and cationic surfactants. Before this, satisfactory procedures were available for the assessment of anionic surfactants. Nevertheless, Wickbold[117] has shown that more reliable results can be obtained in the determination if the anionic surfactant is isolated by the foam-flotation method, but even this will take no more cognisance of the presence of anionic/cationic surfactant salt than the standard colorimetric procedures will. If a true figure is to be obtained when cationic surfactant is present, then an ion-exchange separation in aqueous alcohol will be necessary, but this aspect seems to be ignored despite the fact that one component of the salt may be destroyed and lead to foam problems.

The behaviour of α-sulpho-fatty acids is peculiar. They show little or poor response when dissolved in distilled water and the preparation of satisfactory standards for their assessment is difficult. The standard addition method is best. Fresh standards must be prepared for each determination as the response varies from sample to sample.

There is as yet no accepted procedure for the determination of cationic surfactants. Naturally any anionic surfactant present will interfere and this should be removed by an ion-exchange treatment. Any amines and amine oxides present will interfere and therefore the determination must be performed in both acid and alkaline solution so that the true cationic surfactant can be deduced by difference. The author has found Disulphine Blue VN 150 a very satisfactory dye for the colorimetric determination. Separate standard curves must be obtained for both media, as the response of a given concentration of cationic surfactant is different in acid and alkaline solutions.

The determination of the non-ionic surfactants in sewage and effluent liquors is far the most difficult, primarily because of the number of different types used and the high number of telomers present in each product. In colorimetric procedures the response to a given dye varies with each non-ionic product. Even if the standard used is identical with the sample being examined there are still difficulties. Preferential biodegradation of certain types of telomer will produce in the effluent a surfactant of different composition from that of the standard. This means that a suitable standard can only be chosen after the telomer distribution of the sample has been deduced. The Wickbold[117] foam-flotation procedure or an equally effective procedure must be used to isolate the surfactant. It is recommended that the subsequent precipitation of the non-ionic surfactant with the Dragendorff reagent be followed as outlined by Wickbold, dissolved in hot ammonium tartrate solution and the combined bismuth in the resulting solution determined by the West and Coll[118] method; this uses the ultraviolet spectrum of the bismuth–EDTA complex.

Since the publication of Wickbold's paper[117] there have been a number of investigations into the foam-flotation procedure. Shirotsuka and Ishiwata[152] give a formula for assessing the efficiency of nitrogen bubbles for removing non-ionic surfactants from aqueous solution. More important is the work of Kucharski and Kuciel[153] who show that the concentration of non-ionic surfactant in foam is increased by decreasing the rate of air flow through the solution and is dependent on the solution concentration. This confirms the present author's observations with nitrogen. Pustovalov and Pushkarov[154] also give a formula to derive the time of removal of C_{12}, C_{14} and C_{16} alkyl sulphates from water.

The foam-flotation procedure separates non-ionic surfactant from poly(oxyethylene glycol) (one of its possible degradation products) and contaminants so that whatever the content of glycols present the residual non-ionic surfactant fraction can be isolated. The biodegradability of different types of poly(oxyethylene glycol) has been examined by Pitter.[155] He shows that acclimatization is more readily achieved the lower the mean molecular weight of the glycol. The highest degradation rate was achieved by using bacteria isolated from PEG 800 cultivated on agar. His infrared study indicated that biodegradation proceeds by gradual loss of terminal ethylene oxide groups.

Patterson[96] has published a TLC procedure which allows the content of non-ionic surfactant to be assessed and then by altering the conditions permits a separation of the telomers present. No method is yet suitable for the determination of mixed non-ionic surfactants.

A procedure for the determination of sodium nitrilotriacetate in sewage and effluent was published by Longman, Stiff and Gardiner,[156] who showed that previous published work on this subject, which had shown high biodegradation to occur, had failed to ensure that the metal–NTA complexes had been destroyed before the determination was begun. Longman *et al.*[156] treated samples with the chelating resin Chelex 100 to remove the metals quantitatively so that a true assessment of the NTA content was possible.

ADVICE TO READERS

Fatty alcohols are sometimes added deliberately; lauryl alcohol to augment lather, and palmityl and/or stearyl alcohols as lather depressants. These are isolated in the non-detergent organic matter soluble in petroleum spirit. Often it will be necessary to examine this non-detergent organic fraction and the diethyl ether fraction thoroughly. This is best done by a column chromatographic technique.[44] Alkanolamide soaps are much less stable than sodium soaps and the analyst may find that the fatty acids can be removed from a neutral or alkaline solution without recourse to acidification.

Many types of surfactant, particularly alkylbenzene sulphonates, non-ionic surfactants and the alkyl or alkylphenol polyethoxylate sulphates are hygroscopic. Vessels must be stoppered immediately heating ceases and the stopper released only to adjust the inside of the flask to atmospheric pressure before weighing. Often fatty acids and fatty alcohols may be released together from different surfactants during acid hydrolysis. The hydrolysis occurs in the oily layer of free acids under conditions which promote the formation of wax esters. The resulting product must be submitted to an alkaline hydrolysis in order to isolate each component quantitatively for weighing. The analyst must also be careful in identifying fatty alcohols. Oleyl alcohol may be wrongly interpreted as lauryl alcohol unless instrumental methods are used for its identification. During the sulphation reaction some of the oleyl alcohol is sulphated at the hydroxyl group and some at both the hydroxyl group and the double bond. The alcohols isolated after acid hydrolysis are therefore a mixture of diols and monohydric alcohols and this mixture can lead to confusion. Teepol (branched-chain secondary alcohol sulphate) cannot be converted quantitatively into alcohol by acid hydrolysis. Some of the surfactant is released as unsaturated hydrocarbon, and a hydroxyl value then gives a high value for the mean equivalent weight. If hydrolysis is to be followed by a Methylene Blue titration then hydrochloric acid must not be used for the hydrolysis. Chlorides cause high and incorrect titrations and in all such cases sulphuric acid should be used for hydrolysis. The higher the chloride content in the final solution, the greater the degree of interference.

A new type of inorganic bleach has been introduced recently under the name of "Elchem". The active component is potassium permonosulphate ($KHSO_5$) in admixture with potassium bisulphate and potassium sulphate. It gives no yellow colour with titanyl salts but it reacts with acidified potassium iodide to yield free iodide. If the presence of potassium bisulphate can also be proved then the product most probably contains "Elchem".

Much of the information (including procedures) quoted in this review will be treated in detail in a text-book by the author[44] to be published shortly by John Wiley and Sons Ltd., to whom the author is grateful for permission to use the information in this review.

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TRIS(HYDROXYMETHYL)AMINOMETHANE—A PRIMARY STANDARD?

WILLIAM F. KOCH, DONALD L. BIGGS and HARVEY DIEHL

Departments of Chemistry and Earth Sciences, Iowa State University, Ames, Iowa 50010, U.S.A.

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Summary—Commercially available "primary standard" grade tris(hydroxymethyl)aminomethane (THAM) may not always be of the requisite quality. Crystals of THAM can contain large amounts of occluded mother liquor. Material which has been ground, dried in vacuum, further ground, sifted through a 100-mesh sieve, and finally dried in vacuum, will approach 100% in purity.

Tris(hydroxymethyl)aminomethane ("THAM", "tris") has frequently been proposed or used as a primary standard base,[1–8] and is sold commercially as such. Our own values for the purity of numerous commercial preparations of "reagent grade" and "primary standard" THAM obtained over the past 15 years, however, have been so generally low and variable that we caution all careful workers to exercise wariness if not downright cynicism toward statements on the labels of bottles of this material. The reason is not hard to find. Crystals of THAM frequently contain large inclusions of mother liquor. Cavities in crystals of THAM are readily seen under the microscope and, in many, meniscuses can be observed (Figs. 1–4). We have found the amount of mother liquor so enclosed to be as much as 0·7%; in contrast, potassium dichromate, SRM 136b of the National Bureau of Standards, has been shown to contain only about 250 ppm of water.[9–11] The only way we have found to obtain pure enough THAM is to grind it, pass it through a 100-mesh sieve and dry it in a vacuum desiccator over anhydrous magnesium perchlorate. Usually, to prevent the formation of a gum, the first grinding must be light and the material dried in a vacuum before further grinding, sieving and drying.

Fig. 1. Two cavities in a single crystal of THAM. Plane of focus is below the surface of the crystal. The tips of the cavities, at left, are in focus; the cavities are inclined down to the right. 100×. Polarized-analysed light.

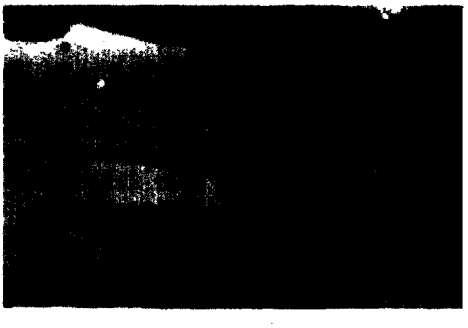

Fig. 2. Same as Fig. 1, but plane of focus lower to bring the meniscus in the upper cavity into focus. Note the inverted meniscus. 100×. Polarized-analysed light.

Fig. 3. Large cavities in a single crystal of THAM. Liquid partially filling the cavities shows darker than the crystalline material. 100×. Polarized-analysed light.

Fig. 4. Single large crystal of THAM showing typical distribution of size of cavities.

EXPERIMENTAL

Examination and reworking of one batch of THAM

Tris(hydroxymethyl)aminomethane, obtained commercially, was titrated with standard acid by the usual volumetric technique, with Methyl Red as indicator; the purity found was 99·3%.

The material was ground, dried in vacuum, then again ground. It was then sifted through a 100-mesh sieve and dried in vacuum at room temperature over anhydrous magnesium perchlorate. The loss in weight in the final drying operation (48 hr) was 0·11%. This material was subjected to high-precision coulometric analysis.[12,13] The purity found by titration with perchloric acid (coulometric titration of excess of acid and coulometric standardization of the acid) was 99·923, 99·911, 99·917, 99·923, 99·913, 99·906, 99·913, average 99·912%, standard deviation $0{\cdot}006_2$%.

Microscopic examination

The cavities in the crystals of THAM formed from water–methanol mixtures are readily seen under the microscope to be numerous, elongated, with rough irregular sides, and frequently partially filled with mother liquor (Figs. 1–4). The meniscus of the mother liquor is convex (resembling that of mercury in a glass tube). When crystals on the microscope slide are covered with a drop of water, the crystals dissolve at an observable rate and when the end of one of the cavities is exposed, water shoots into the cavity with speed. It had been earlier reported by Rose and Van Camp[14] that crystals of THAM lose their birefringence at 135°; we confirmed this, but on our electrically-heated stage the change took place at 149° and reversion at 124°. The crystals were not shattered at these temperatures by the vapour pressure of the trapped mother liquor. Even the crystals of THAM which had passed a 100-mesh sieve were observed to hold cavities.

THAM heated on the microscope stage underwent not only decomposition but also sublimation, forming dendritic growth on the cover glass. The dendritic growths consisted of very small crystals packed closely about a central trunk. Each tiny crystal was birefringent but at different positions of the stage, and the whole gave a pretty, Christmas-tree, effect. The sublimed material was proved by infrared spectroscopy and by X-ray powder diffraction pattern to be THAM and this led directly to the large-scale sublimation experiments described below.

Behaviour on drying

Large crystals of THAM, and material ground and sifted through a 100-mesh sieve, were heated in an oven to successively higher temperatures. The ground material turned yellow at 100° and at 140° had obviously undergone far more extensive deterioration than the coarse crystals. The deterioration was obviously oxidation by air and this proceeded more rapidly with fine than with coarse material.

Sublimation of THAM in nitrogen

The sublimation apparatus used by Koch, Hoyle and Diehl[13] for purifying 4-aminopyridine was used. The flask was embedded in copper shot in an electric heating mantle. At a temperature of 140° the THAM was present as a clear, colourless liquid and a few large crystals formed in the upper portion of the flask, the gooseneck, and the air condenser. The sublimation was very slow, only a very small amount of crystalline sublimate being obtained, and decomposition set in after 20–30 hr, so this approach was given up.

Loss in weight on melting in an atmosphere of nitrogen

A sample of commercial THAM (large crystals, 99·3% pure), held in a weighing bottle, was placed in the flask of the sublimation apparatus mentioned above, the air in the flask was replaced by nitrogen, and the flask heated. The material melted at about 140° (the m.p. reported in the literature[14] and confirmed by our experience with use of a heated microscope stage, is 172°). The material was immediately cooled and weighed. The loss in weight was 0·67%. Traces of THAM appeared as sublimate on the gooseneck and air condenser of the apparatus during this experiment; this was recovered by washing with water. From the pH, 9·4, the volume of the wash-water, and the dissociation constant of THAM, the amount of THAM so sublimed was calculated to be 4·2 mg or 0·02% of the original weight of 22·11 g. Thus, of the loss in weight 0·65% can be attributed to liquid trapped in the crystals.

DISCUSSION

Although the THAM ground and sifted through a 100-mesh sieve, and found to be 99·914% pure, would be satisfactory for standardization in most routine work, it could hardly be considered a primary standard. The impurity is probably still mostly mother liquor and the variability in the results reported above, standard deviation 63 ppm, is further evidence of this (compare the standard deviation of 5·9 ppm for similar concurrent work with 4-aminopyridine[13]).

It would indeed be curious if such a disparity between reality and reputation should have escaped notice completely; even with the limitation of 1 part per 1000 imposed by the use of volumetric burettes by previous workers the discrepancy should have been observed. Actually it had, but it is necessary to read the fine print to find a report of it. In the very first paper on the use of THAM as a primary standard,[1] Fossum, Markunas and Riddick, in describing the purification of THAM, directed that the material should be ground to pass a 50-mesh sieve and be dried at 60° and a pressure lower than 10–15 mmHg for 12 hr or dried over phosphorus pentoxide at < 5 mmHg for 24–36 hr. The consequences of not grinding the material were nowhere pointed out, however, and the abstract accompanying the paper states that the material can be dried by heating at 100–103°, which though true is misleading. The vapour pressure of the mother liquor trapped in the crystals of THAM is not sufficient to shatter the crystals even at the melting point; before that temperature, decomposition sets in, a fact reported by Fossum, Markunas and Riddick[1] (at 110°)—a finding we confirm. Decomposition begins at even lower temperature for 100-mesh material.

Ten years after the publication of the first paper, Riddick, in a review of the virtues of THAM as a primary standard,[5] listed ten merits of the material but failed to display prominently the warning that it must be ground, sifted, and dried. Riddick analysed four commercial preparations of "purified" THAM. Preparations I and II were finely ground materials for which purities of 99·98 and 99·96% were found. Preparations III and IV gave low results until ground. Riddick reported in a footnote that sixteen analyses of preparation IV as received gave results for the purity ranging from 99·32 to 99·79%. In the text Rid-

Table 1. Coulometric titration of SRM 723 Tris(hydroxymethyl)aminomethane, hydrazine–platinum anode method[12]

Titration number	Weight of THAM, *g*	Quantity of electricity, *1969 NBS coulombs*	Electrical equivalent, *1969 NBS coulombs/g*		Purity of THAM, %
1	3·000002	1911·024	796·259		99·9688
2	3·005709	1914·646	796·254		99·9681
3	3·004906	1914·076	796·230		99·9651
				Average	99·9673
				Range	0·0037

Mol. wt. THAM: 121·1372. Faraday: 96,486·69 1969 NBS coulombs/mole.

dick added briefly that in the original study it had been observed that "large crystals analysed low", and "it is believed that solvent is trapped in the large crystals".

While Fossum, Markunas and Riddick may be criticized for not pointing out prominently the need for grinding, others have said nothing about grinding, presumably being unaware of the problem, or ignoring it, or doing what was necessary without comment and assuming that others would do the same. There are at least eight such authors: Whitehead[2] who simply called attention to the existence of the material and compared the titration curves of THAM and sodium carbonate; Williams and Harley[3] who proposed THAM as a primary standard for non-aqueous titrimetry and compared the curves for titration of THAM, potassium hydrogen phthalate and diphenylguanidine with 0·1*M* perchloric acid in acetic acid; Ruch and Critchfield[4] who used it as primary standard for standardizing perchloric acid in "Methyl Cellosolve" (used for the titration of amines); Holler[6] who used it as a standard and titrant in the combustion–acidimetric determination of sulphur; Wilson and Smith[7] who used it as a comparison standard for thermometric titration calorimetry. Even Bates and Hetzer,[15] who laid to rest the false notion that solutions of THAM do not absorb carbon dioxide from the atmosphere, appear to have accepted the idea that THAM need only be dried at 100–103°.

Analyses of the five lots of THAM which became SRM 723 were made by Marinenko[8] at the National Bureau of Standards by the addition of a weighed amount of sulphuric acid, coulometric titration of the excess of sulphuric acid, and coulometric standardization of the sulphuric acid. The average of 30 determinations of the purity was 99·9690% with a standard deviation of 81 ppm. In neither Marinenko's report nor the certificate which accompanies SRM 723 is anything said about grinding the material. Marinenko states that the material taken for analysis was dried at 70° in a vacuum oven, weighed, corrected to weight in vacuum, and titrated; no mention is made of grinding before drying although this was probably done by the manufacturer (Sigma Chemical Company, St. Louis, Missouri). Presumably the same applies to SRM 724a, recommended as a calorimetric standard,[16,17] inasmuch as SRM 724a came from the same lot of material as SRM 723, the basimetric standard.

Our own examination of SRM 723 indicated that although the crystals are small, cavities are present. SRM 723, dried in a vacuum over magnesium perchlorate for two weeks but otherwise analysed as received, was titrated coulometrically with use of the hydrazine–platinum anode developed by Hoyle, Koch and Diehl;[12] the titrations formed part of the sequence of titrations made to establish the efficiency of the hydrazine–platinum anode. The average of the three titrations (Table 1) was 99·9673%; the range, 37 ppm, and the difference between this value and the Marinenko value, 17 ppm, are both less than the standard deviation reported by Marinenko and that reported above for a different lot of THAM.

Still another use of THAM as a calorimetric standard was made by Irving and Wadso[19] who went to considerable trouble to purify their material by the usual water–methanol recrystallization but then used the crystalline material which passed through a 50-mesh sieve but was retained on 100-mesh, and was then dried at 80° and finally in a vacuum; no analyses are reported.

Almost the only workers who have not accepted primary standard status for THAM are Datta, Grzybowski and Weston[20] who by titration found their material to be 99·594 and 99·830%, average 99·71% pure (after recrystallization from water–methanol: 99·870, 99656%, average 99·76%) and took this into consideration in their measurement of the dissociation constant.

In the extensive use of THAM and its hydrochloride as a biological buffer (see for example the various papers published in the Annals of the New York Academy of Science[21] following a conference) it is probably immaterial whether occluded water and methanol are taken into account. Such neglect, however, may not be excusable in careful calibrations of buffers in water and water–methanol mixtures such as those carried out by Bates and co-workers.[22–24]

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SENSITIVE APPARATUS FOR OBTAINING FREEZING CURVES

PURITY OF 4-AMINOPYRIDINE

FREDERICK R. KROEGER and C. A. SWENSON

Ames Laboratory, United States Atomic Energy Commission and Department of Physics, Iowa State University, Ames, Iowa, 50010 U.S.A.

and

WILLIAM C. HOYLE and HARVEY DIEHL

Department of Chemistry, Iowa State University

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Summary—Freezing curves of highly-purified 4-aminopyridine have been obtained with an instrument of new design employing a gold crucible, a platinum resistance thermometer, electrical heating elements on crucible and heat shield, and accessory electrical control devices such that the temperature difference between crucible and shield could be maintained constant within 0·005° while the temperature of the 4-aminopyridine and crucible dropped through the freezing range. No stirring was used. Methods were devised for handling the data as the derivative of temperature with respect to time and of correcting the freezing curve for the heat capacity of the crucible and charge. Although interpretation of the freezing curves obtained on the 4-aminopyridine was confused by attack on the gold by the molten 4-aminopyridine, the initial impurity in the 4-aminopyridine was probably less than the detection limit, 0·001 mole %.

A high-precision coulometric titration of 4-aminopyridine has been carried out by Koch, Hoyle and Diehl[1] in an effort to establish a value for the faraday by a new route. The 4-aminopyridine was purified by sublimation and shown by the spectrographic method to be free from metallic impurities. Because direct methods for the detection and determination of the traces of organic impurities possibly present in such a material were lacking, the total impurity was measured with the freezing-point calorimeter described below. The design of this apparatus and the problems which arose in carrying out experiments with it are described in some detail because they could be applicable to other investigations.

The depression of the melting point T_m of a pure substance caused by a mole-fraction, x_2, of an impurity, is given by

$$\Delta T = T_m - T = (RT_m^2/L_f)x_2 = x_2/A \qquad (1)$$

if the impurity is small in amount and soluble only in the liquid phase to form an ideal solution. In this expression, which was developed first by Washburn,[2] L_f is the latent heat of fusion of the pure substance and $A = L_f/RT_m^2$, the so-called cyroscopic constant, is of the order of 10^{-2} deg^{-1} for many substances.[3] In practice, the temperature T of the two-phase system is monitored continuously during the freezing or melting process, because T_m may not be known accurately in advance, and T_m and ΔT are then calculated from the data; the accuracy of ΔT is then dependent on the precision (sensitivity) with which the temperature is measured, rather than on the absolute accuracy. The freezing-curve method has been most popular, but both methods have been demonstrated to give reliable results for a wide range of total impurity. Witschonke,[3,4] for instance, has described a freezing-point apparatus for the examination of commercial materials melting in the range from −40° to 200° and containing up to 5 mole% of impurity, with a precision of 0·1 mole%. The freezing-point method has been used by Schwab and Wichers[5] to study "single crystal" primary standard benzoic acid with a precision of 10^{-3} mole% and it has been applied with the same precision to highly pure hydrocarbons by Rossini and co-workers[6–9] and by Glasgow and others.[10] The method has even become "official" for determining the purity of hydrocarbons: ASTM Standards D 1015-70[11] and D 1016-55.[12]

The calorimeter used in this work differs from those which have been used for other high-precision melting-curve studies, in a number of ways. The rate of cooling was carefully controlled by utilizing special thermal isolation devices (isothermal heat shield and vacuum jacket), and mechanical stirring was not compatible with these design features and was considered unpeccessary. The crucible was made of gold and numerous thin radial fins were provided to promote thermal equilibrium in the liquid and to furnish maximum area on which the solid could form. Platinum was rejected as material for the crucible because of its much poorer thermal conductivity.

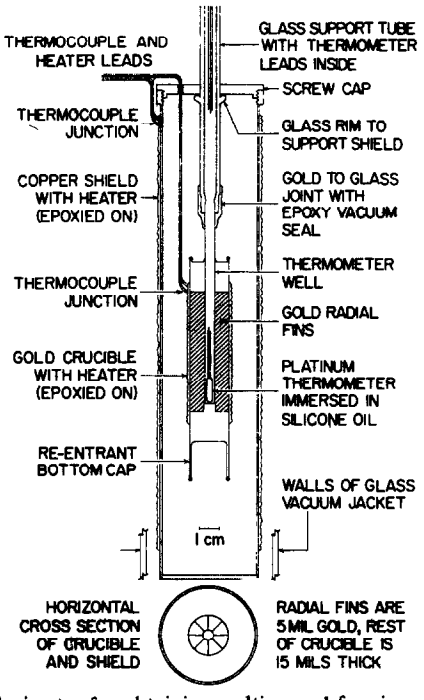

Fig. 1. Calorimeter for obtaining melting and freezing curves.

Possible temperature gradients were also reduced by taking 10–12 hr for the melting or freezing of the 13-g (0·14-mole) samples. Temperatures were measured with a platinum resistance thermometer with a sensitivity of better than 0·0005 K. The heat leak to and from the crucible was controlled very precisely by the use of an isothermal heat shield which completely surrounded the crucible and to which all electrical leads were attached. Two modifications were also made in the method of analysing the data: the heat released by the charged crucible during the freezing was taken into consideration, and the temperature–time curve over an extended range was used in calculating ΔT. This work is described in more detail elsewhere by Hoyle.[13]

EXPERIMENTAL

Calorimeter

Details of the calorimeter are shown in Fig. 1, photographs of the instrument during assembly in Fig. 2, and a block diagram of the electrical components in Fig. 3. The glass tube carrying the crucible was sealed into the top of the vacuum jacket so that no vacuum seal was required for the thermometer leads. The silicone oil provided contact between the thermometer leads and the gold

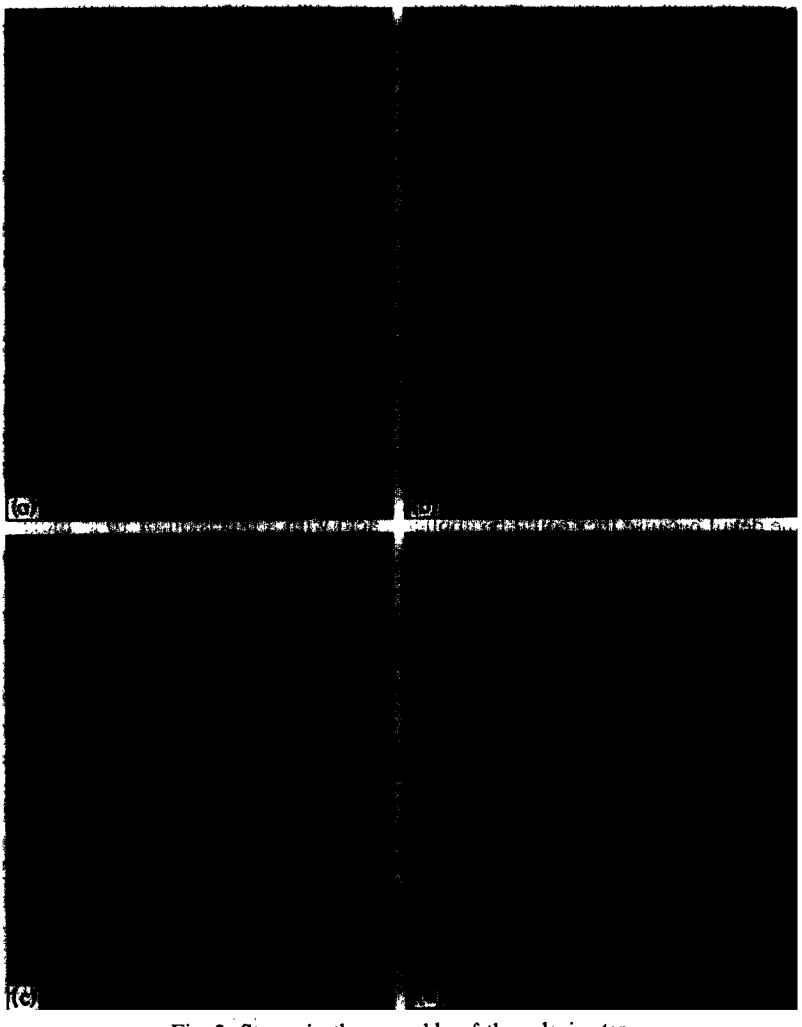

Fig. 2. Stages in the assembly of the calorimeter.

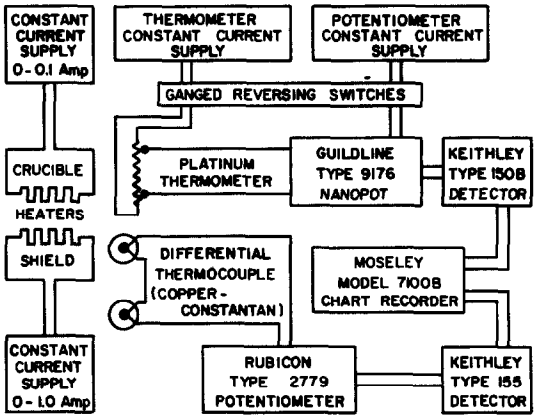

Fig. 3. Components of the electrical system.

thermometer-well and the glass support-tube. The leads to the thermocouple and the heater were brought through a seal in the side of the vacuum jacket. The top and bottom halves of the vacuum jacket were sealed together with an O-ring. Radiation losses were reduced by silvering the inside of the glass vacuum jacket and by wrapping the crucible and the shield with aluminium foil. The vacuum around the calorimeter was never better than 10^{-4} mmHg, but the heat loss due to the residual gas was shown to be negligible in comparison with that due to conduction by the leads and to radiation.

The re-entrant cap of the bottom of the crucible was designed so that the 4-aminopyridine, which was poured in as a powder, would not become overheated during the electron-beam welding of the seal. Loading a new sample in the crucible was a time-consuming task because the glass support tube had to be broken, and all of the crucible wiring, thermocouple and heater, had to be removed so that the crucible could be clamped in a large copper heat-sink in the vacuum system of the electron-beam welder. One result, however, was that the 4-aminopyridine was sealed in under a good vacuum.

The temperature difference between the crucible and the isothermal shield was monitored by observing the emf of the copper–constantan differential thermocouple. Small variations in the emf, which was measured with a Rubicon potentiometer, were recorded by attaching the output of a Keithley 155 detector to one pen of the two-pen chart-recorder (used at a full-scale sensitivity of $\pm 10\ \mu$V). Because the sensitivity of the thermocouple was roughly 40 μV/K, variations in the temperature difference could be observed with a sensitivity of 0·002–0·003 K. The assumption was made that the heat leak into (or from) the crucible would remain constant when this temperature difference, which was typically 5 K, was kept constant. A fine control on the shield power-supply was adjusted manually to keep the temperature difference constant to better than 0·1% during an experiment. All of the current supplies shown in Fig. 2 (for both heaters, the thermometer and the potentiometer) were of the highly stable type described by Kroeger and Rhinehart.[14]

The platinum resistance thermometer was a miniature (3 mm diam.) four-terminal device which is manufactured by MINCO, with a resistance of 41·2 Ω and a sensitivity of 0·1 Ω/K at 432 K. Its resistance was measured by a conventional d.c. comparison method in which the potential drop across the thermometer was compared with the potential drop across a 10-Ω Leeds & Northrup NBS-type standard resistor (not shown in Fig. 2) which was connected in series with it. Simultaneous reversal of the potentiometer and the thermometer currents was used to compensate for the effects of thermal emf's in the potential circuit. The off-balance of the potentiometer, as detected by the Keithley 150B detector, was displayed on the second pen of the chart-recorder to obtain a continuous record of the temperature. Potentiometric methods are usually unsatisfactory for measurements such as these, owing to constant small drifts in the potentiometer and/or thermometer power supplies. However, the electronic supplies which were used in these experiments[14] were found to be stable to roughly 1 ppm over a period of days, so stability was no problem. The chart-recorder display could be operated at $\pm 1\ \mu$V full-scale sensitivity, which corresponds to $\pm 0{\cdot}005$ K at the normal thermometer current of 2 mA. The maximum resolution (0·0001 K) was seldom required in these experiments, and most of the data were obtained at the $\pm 10\ \mu$V full-scale sensitivity of the chart-recorder, with a resolution of 0·0005 K.

An accurate thermometer calibration is not required for purity investigations by experiments of this type, because ΔT [equation (1)] can seldom be determined to better than a few per cent. The absolute melting temperature of the pure compound, T_m, is of some interest, however, so the MINCO platinum resistance thermometer was calibrated by direct comparison with a Leeds & Northrup Type 8164 platinum resistance thermometer which had been calibrated at the National Bureau of Standards. In the course of this calibration, done under thermal conditions similar to those for the determinations, considerable self-heating was found in the MINCO thermometer. This effect amounted to 0·014 K at the melting point of the 4-aminopyridine for the standard current of 2 mA, and is roughly three times the estimated error (0·005 K) in an absolute temperature measurement with the MINCO thermometer. As was mentioned previously, the precision with which temperature changes could be detected and measured was 0·0001 K.

The data for a typical freezing curve were taken as follows. The crucible and shield were warmed to the melting-temperature of the sample, after which the resistance thermometer indicated a relatively constant value until a rapid increase in the heating rate indicated that the sample was completely melted. The crucible temperature was then stabilized at just above the melting temperature while the shield-heater current was reduced to create a predetermined temperature difference (typically 5 K) between the shield and the crucible. After thermal equilibrium had been reached in the system with this temperature difference, the crucible heater current was reduced to zero and the temperature of the crucible and the thermocouple reading were monitored simultaneously on the two chart-recorder channels, with the thermocouple reading being kept constant by manual adjustment of the shield current. When the sample was completely frozen, the temperature of the crucible was kept constant at 5 K or so below the melting-temperature, ready for a further experiment.

Curve B of Fig. 4 represents a typical set of data for one experiment, for which the heater-shield temperature difference was 5 K and the time of freezing just over 11 hr. The initial supercooling was always observed, with a slight amount of superheating (not evident in Fig. 4) being observed for 15–30 min after nucleation. This superheating may be attributed to the large impurity-concentration gradients caused by the sudden freezing when the sample has recovered from the supercooling, and the slow diffusion of the impurities. The extreme rounding of this curve at the right-hand side is due to the increasing concentration of the impurity in the decreasing volume of liquid remaining as the 4-aminopyridine froze. This curve, and the other curves in Fig. 4, are discussed in detail in the next section.

RESULTS AND DISCUSSION

Analysis of data

Because of the way in which the experiment was carried out, it is assumed in the following discussion

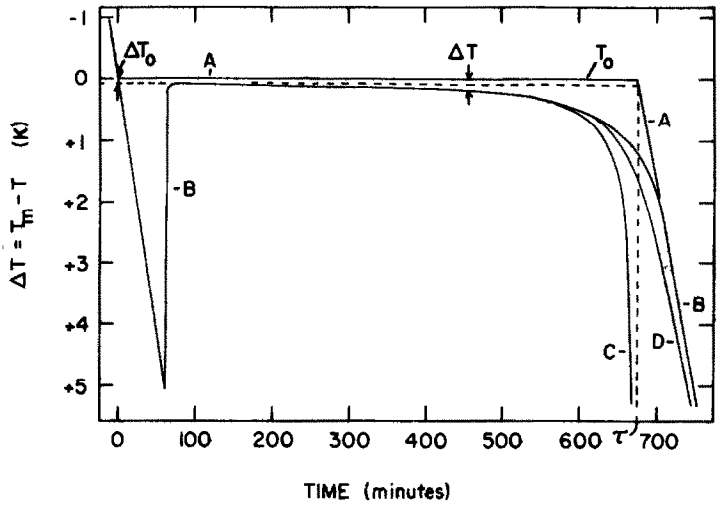

Fig. 4. Freezing curves. (A) Theoretical curve, high-purity material. (B) Experimental curve, Charge I-3. (C) Equation (6), $\Delta T_0 = 0{\cdot}061$ K, $\tau = 676$ min. (D) Equation (7), $\Delta T_0 = 0{\cdot}061$ K, $\tau = 676$ min, $k = 0{\cdot}00132$.

that the rate of cooling remained constant throughout an experiment. The ideal freezing curve of a pure material, $T = T_m$ and $\Delta T = 0$, would resemble curve A of Fig. 4 and would extend over a time τ. In practice, supercooling occurs and T_0 and $t = 0$ are obtained by extrapolation of the horizontal portion of the curve back to the initial rising vertical portion of the curve representing the cooling of the liquid. In a real sample, an impurity will also be present, and the depression of the freezing temperature, ΔT_0, defined by $\Delta T_0 = T_m - T_0$, will be positive. The horizontal portion of the curve is increasingly tilted downward owing to increasing concentration of the impurity in the liquid phase as the major component crystallizes. At $t = \tau/2$, half of the major component will have crystallized, the concentration of the impurity will have doubled, and $T_m - T_0 = 2\Delta T_0$. τ is obtained by extrapolating the cooling curve of the solid back to temperature $T_0 + \Delta T_0$. The last traces of liquid disappear in an actual experiment at times appreciably greater than τ because of the increased depression of the freezing-temperature caused by the increasing concentration of impurities in the liquid. Conformity to equation (1) fails if large concentrations of impurity exist during the last stages (the last 5% or so) of the freezing process. Irregular freezing and entrapment of impurities in small cells of enclosed liquid may also cause deviations from the theoretical curve in the final stages of the freezing. If equation (1) is integrated directly under the assumption of a uniform cooling rate, the equation

$$\Delta T = \Delta T_0/[1 - (t/\tau)] \tag{2}$$

is obtained. This relationship is plotted as curve C in Fig. 4. The agreement between a calculated curve and an experimental curve can be improved by remembering that as the temperature of the filled crucible gradually decreases with time, additional cooling time is required to compensate for heat capacity effects.

The following quantitative discussion is based on the definitions given above of ΔT, ΔT_0, τ (sec) and L_f (J/mole), and of $n(t)$ as the number of moles of solid, n_0 as the total number of moles of material in the crucible, and C as the total heat capacity (J/deg) of the crucible plus the material. The rate at which heat is being lost from the container is given by the definition of τ in Fig. 4 as

$$\begin{aligned}(n_0 L_f/\tau) &= L_f(dn/dt) - C(dT/dt)\\ &= L_f(dn/dt) + C(d\Delta T/dt)\end{aligned} \tag{3}$$

where the terms on the right-hand side represent the heat released by the freezing of the material and the simultaneous cooling of the charged crucible. Equation (1) can be rewritten to give a relation between ΔT and n as

$$\Delta T = \Delta T_0\, n_0/(n_0 - n) \tag{4}$$

which in turn can be differentiated and combined with (3) to rewrite (2) as

$$(\Delta T_0/\tau) = [(\Delta T_0/\Delta T)^2 + k]\,(d\Delta T/dt) \tag{5}$$

where

$$k = (C\Delta T_0/L_f n_0) \tag{6}$$

is a convenient dimensionless parameter.

Equation (5) can be integrated with $\Delta T = \Delta T_0$ at $t = 0$ to obtain the relationship which is plotted as curve D in Fig. 4,

$$\begin{aligned}\Delta T = (\Delta T_0/2k)\{&[(1 - (t/\tau) - k)^2 + 4k]^{1/2}\\ &- (1 - (t/\tau) - k)\}.\end{aligned} \tag{7}$$

This relation reduces to equation (2) when k becomes very small. The rate of cooling at a given time t

can be used to estimate ΔT_0 from

$$d\Delta T/dt = (\Delta T_0/2k\tau)\left\{1 - \frac{(1 - (t/\tau) - k)}{[(1 - (t/\tau) - k)^2 + 4k]^{1/2}}\right\}. \quad (8)$$

Since k is of the order of 10^{-3} for this experiment, it has a small effect for $t \lesssim 0{\cdot}7\,\tau$ and the approximate relation

$$d\Delta T/dt = (\Delta T_0/\tau)[1 - (t/\tau)]^{-2} \quad (9)$$

can be used; it is also the derivative of equation (2).

The parameter k can be evaluated from (5) and estimates of ΔT_0 and τ by noting that $(\Delta T_0/\Delta T)$ [equations (4) and (7)] becomes very small for large times, and indeed must be zero when the sample is completely frozen. In practice, the sample appeared to be completely frozen (curve B, Fig. 4) for $t = 1{\cdot}1\,\tau$, so k could be obtained to within about 1% from the linear portion of curve B. The use of the general relation (7) results in calculated freezing curves which are in quite good agreement with experiment for $t/\tau \sim 0{\cdot}9$.

The determination of ΔT_0, τ and k for a given experimental curve could be accomplished by using a digital computer to fit equation (7) to the data. This would be justified only if freezing-point analyses were to be done on a routine basis. Hence, these quantities (as given in Fig. 4) were determined in the present investigation by successive approximations and refinement of the analysis [beginning with equations (2) and (9)] until a "best" fit to the theoretical curve was achieved over a range of times from $0{\cdot}3\tau$ (where superheating effects had disappeared) to greater than $0{\cdot}9\tau$. In spite of the sensitivity of the thermometry in this experiment, the initial freezing-point depression ΔT_0 could seldom be determined to better than 3–4% for a given run.

Thermodynamic properties of 4-aminopyridine

The latent heat of fusion, L_f, of a material must be known in order to calculate the mole fraction of an impurity from a freezing curve by equation (1). The results of two independent measurements of the latent heat of fusion of 4-aminopyridine are given in Table 1 together with values for the melting-temperature of the pure material, T_m, and the heat capacities of the liquid, C_L, and the solid, C_S.

In one experiment, the latent heat of fusion of 4-aminopyridine and the heat capacity of solid 4-aminopyridine were obtained by using a conventional water-bath calorimeter. This calorimeter was calibrated with a standard sample of metallic copper (NBS 45b) which was heated to a temperature close to the melting temperature of 4-aminopyridine and dropped into the calorimeter. The sample of 4-aminopyridine was sealed in a glass vial for the experiment. Details of this experiment will be found in Hoyle's thesis.[13]

In a second measurement, the 4-aminopyridine was held at a temperature slightly below T_0, in the calorimeter shown in Fig. 1, and the temperature difference between the crucible and the shield was adjusted so that the temperature of the crucible remained constant with no current passing through the crucible heater. The crucible heater current then was turned on to melt the 4-aminopyridine, and as the crucible warmed, the temperature difference between it and the shield was held constant to ensure that the only source of heat to the crucible was its own heater. The temperature of the crucible remained quite constant in the two-phase region, so the latent heat of fusion could be roughly estimated from the power dissipated in the crucible heater and the time of melting (roughly 4 hr), a slight correction being made for the increase in the temperature of the crucible and the 4-aminopyridine during the course of the experiment. A major difficulty was experienced in determining the time of complete melting. After somewhat over 90% of the 4-aminopyridine had melted, erratic temperature changes were observed; periods in which the temperature remained constant were followed by discontinuous temperature increases, or even on occasion, decreases. These effects were ascribed to inhomogeneities in the sample, created during the freezing process required before a melting-curve experiment could be conducted. The true inverse of the freezing curve (curve C of Fig. 4) was never observed. In part, this may have been a consequence of the design of the calorimeter.

The heat capacities of the liquid and solid were obtained from the freezing and melting experiments. The rate of change of temperature in the single-phase regions of the freezing and melting experiments reflected directly the heat capacities of the liquid or

Table 1. Thermodynamic properties of 4-aminopyridine near the melting-temperature

	Weight basis	Mole basis*
Heat capacity, liquid†	$1{\cdot}57(\pm 0{\cdot}06)\,J.g^{-1}.deg^{-1}$	$148(\pm 6)\,J.mole^{-1}.deg^{-1}$
Heat capacity, solid§	$1{\cdot}85(\pm 0{\cdot}03)\,J.g^{-1}.deg^{-1}$	$174(\pm 3)\,J.mole^{-1}.deg^{-1}$
Latent heat of fusion§	$276(\pm 4)$ J/g	$2{\cdot}60(\pm 0{\cdot}04) \times 10^4$ J/mole
Latent heat of fusion†	$285(\pm 14)$ J/g	$2{\cdot}68(\pm 0{\cdot}14) \times 10^4$ J/mole
Melting-temperature, T_m	$159{\cdot}09(\pm 0{\cdot}01)$ °C	$432{\cdot}24(\pm 0{\cdot}01)$ K
Cryoscopic constant, $A = L_f/RT_m^2$	$1{\cdot}67 \times 10^{-2}\ K^{-1}$	

* Molecular weight: 94·117.
† Freezing-curve calorimeter.
§ Water-bath, drop calorimeter.
Figures in parentheses are the estimated errors.

the solid, the heat capacity of the crucible, C_{cr}, being a constant factor:

$$(n_0C_L + C_{cr})(dT/dt)_L = (n_0C_S + C_{cr})(dT/dt)_S. \quad (10)$$

The heat capacity of the 115-g crucible, taken simply as the heat capacity of gold, was estimated to be $C_{cr} = 15$ J/K. The heat capacity of solid 4-aminopyridine was known from the water-bath calorimeter experiment. With 13·2 g (0·14 mole) of 4-aminopyridine in the crucible, the ratio of the slopes was found to be $(dT/dt)_S/(dT/dt)_L = 0{\cdot}91\ (\pm 0{\cdot}02)$ which leads to the value of the heat capacity of the liquid given in Table 1. Because the heat capacity of the total amount of 4-aminopyridine was only about 50% greater than that of the crucible, the result for C_L was relatively sensitive to uncertainties in C_{cr}.

The melting-temperature of pure 4-aminopyridine, T_m, in Table 1 was obtained from T_0 as calculated from freezing curves and from the comparison of the MINCO platinum resistance thermometer with the Leeds & Northrup platinum resistance thermometer calibrated at the National Bureau of Standards (IPTS-68 scale). The self-heating correction (0·014 K) was applied to the MINCO thermometer readings.

Interpretation of the data obtained from freezing curves of 4-aminopyridine

The depression of the freezing-temperature, ΔT_0, was calculated for each of the freezing curves obtained on the highly-purified 4-aminopyridine, by following the procedure given in the preceding section. Each freezing curve resembled curve B of Fig. 4. The values of the depression of the freezing-temperature increased with each successive curve obtained for each of two charges, I and II, of the crucible with 4-aminopyridine. The cumulative time in which the molten 4-aminopyridine was in contact with the gold of the crucible was computed according to

$$t_{cum} = \tfrac{1}{2}t_m + t_s + \tfrac{1}{2}\tau \quad (11)$$

in which t_m is the time required to melt the 4-aminopyridine, t_s is the time required to stabilize the temperature of the liquid 4-aminopyridine, and τ is the time required to freeze the 4-aminopyridine. The values of the depression of the freezing-temperature obtained from the successive curves are given in Table 2 as a function of the cumulative time. Curves I-1 and I-2 were obtained in a relatively short time by using a large temperature difference between the crucible and shield (Table 2). The cumulative time for these two curves is correspondingly small. Curves I-3, I-5, I-6, I-7 and I-8 were taken with the same temperature difference, 5 K. Curves II-1, II-2 and II-3 were also taken with a temperature difference of 5 K; the values obtained for the depression of the freezing-temperature were very close to those obtained with charge I for the same cumulative time. It is thus evident that the instrument was functioning properly and giving consistent results from one charge of 4-aminopyridine to the next. It is apparent, however, from I-4 that the depression of the freezing point observed is greatly dependent on the difference in temperature between the crucible and the shield; for a difference of 10 K, the depression was close to twice that for a 5 K difference (I-3 and I-5). This magnification of the depression at larger temperature differences undoubtedly also affected I-1 and I-2 (25 and 12 K respectively). The value of the depression found from I-1, 0·005 K, is probably too large and the value of the mole fraction of impurity calculated from it, $x_2 = A\Delta T_0 = 1{\cdot}67 \times 10^{-2} \times 0{\cdot}005 = 0{\cdot}008$ mole%, represents only an upper limit for the impurity. It is quite evident also that in I-1 attack on the crucible had been going on from the time of first melting, some 3 hr. It appears valid therefore to conclude that the depression of the freezing-temperature observed is too large. The combination of these two effects makes it likely that the depression of the freezing-temperature observed is too large by at least an order of magnitude and actually is less than can be detected by this instrument, 0·001 K or slightly less. This places great emphasis on a single freezing curve, I-1. Although of short duration, I-1 was normal, that is,

Table 2. Depression of the freezing-temperature, ΔT_0, of 4-aminopyridine as a function of time of contact in the molten state with the gold of the crucible

Freezing curve number	Depression of the freezing point, ΔT_0, K	Time of contact, *min*		Difference in temperature of shield and crucible, °C
		Individual experiment	Cumulative	
Charge I				
I-1	0·005	180	180	25
I-2	0·030	170	350	12
I-3	0·060	400	750	5
I-4	0·160	1250	2000	10
I-5	0·092	1200	3200	5
I-6	0·096	1050	4250	5
I-7	0·097	850	5000	5
I-8	0·103	1000	6000	5
Charge II				
II-1	0·059	500	500	5
II-2	0·070	400	900	5
II-3	0·080	650	1550	5

the temperatures calculated at times $t = 0{\cdot}5\tau$ and $t = 0{\cdot}75\tau$ by using $\Delta T_0 = 0{\cdot}005$ K and equation (3) were very close to the temperatures observed. We conclude that the mole fraction of impurity in the 4-aminopyridine is less than 1×10^{-5} (0·001 mole%).

Gold introduced during the freezing-point experiments

The initial highly-purified 4-aminopyridine and the 4-aminopyridine recovered from the two freezing-point experiments (I and II) were analysed by plasma and spark emission spectroscopy and by neutron-activation. No detectable impurities were present in the initial 4-aminopyridine, the material being in this respect as good as the best grades of spectrographic carbon. A faint trace of copper and a trace of silicon (possibly 10 ppm) and 10–100 ppm of gold were found in I. Neither copper nor silicon was detected in II but the amount of gold was considerable and distributed inhomogeneously: 50, 65 and 150 ppm by the spectrographic method, 3–1200 ppm by activation analysis on 3-mg samples. Optical microscopic examination revealed the presence of obviously different material, in the form of spots, some brown in colour, some of metallic lustre and transparent.

Two mechanisms are suggested for the introduction of gold into the molten 4-aminopyridine. The dissolution of gold by the action of the molten 4-aminopyridine is certainly possible, although in a preliminary experiment, a piece of gold immersed in molten 4-aminopyridine for 48 hr showed no loss in weight. The surface of the gold exposed in the freezing curve experiments was much greater, however, 200 cm^2 or so. As observed, the rate of accumulation of impurity slowed greatly after a certain time, so the contamination process must be confined to a surface layer, quite possibly to the dissolution of a layer of gold oxide. The second mechanism of contamination is simply the decomposition of gold oxide. It is known that gold oxide forms quickly on the surface of reduced gold on the briefest exposure to air[15] and that it is decomposed at about 160°, the melting temperature of 4-aminopyridine.

Implications for the design of freezing-point calorimeters

With the calorimeter described above it appeared possible to determine freezing-point depressions of the order of 0·001 K at 160°, corresponding to a 10^{-5} mole fraction of impurity. Obviously gold was not a sufficiently inert metal for the purpose. Conceivably the offending surface layer of oxide could be removed by heating the crucible in vacuum. The crucible could then be filled with a dry inert gas (helium, argon), and then in a dry-box the sample loaded, the re-entrant cap inserted and the electron-beam welding of the seal made without exposure to air. The problems appear formidable, however, and it would appear that other solutions should be sought to the problem of establishing the purity of an organic amine.

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AN ELECTRODE FOR THE COULOMETRIC GENERATION OF HYDROGEN ION

WILLIAM C. HOYLE, WILLIAM F. KOCH and HARVEY DIEHL

Department of Chemistry, Iowa State University, Ames, Iowa 50010, U.S.A.

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Summary—The anodic generation of hydrogen ion on bright platinum in 1·0*M* sodium perchlorate is not quantitative owing to the formation of a chemical species with oxidizing properties, presumably a peroxydiperchlorate, but 100% current efficiency can be obtained in the anodic generation of hydrogen in 0·25*M* sodium hydrazinium sulphate, $Na(N_2H_5)SO_4$. Five hydrogen ions are formed for each four electrons passed. The efficiency of this "hydrazine–platinum anode" has been demonstrated by the high-precision coulometric titration of tris(hydroxymethyl)aminomethane.

Although a number of high-precision coulometric titrations of acids have now been carried out, high-precision coulometric titrations of bases have been confined to the titration of sodium carbonate.[1,2] Marinenko[3] recently carried out a high-precision titration of tris(hydroxymethyl)aminomethane ("THAM", "tris") by the addition of sulphuric acid and coulometric back-titration and standardization of the latter. He reported that direct coulometric titration of THAM yielded results consistently low by several per cent. He reported also that the literature from 1947 on showed no studies of the electrochemistry of tris(hydroxymethyl)aminomethane and that the evidence in the literature seemed to indicate that attempts to titrate aromatic amines coulometrically failed owing to oxidation of the amines themselves.

In an attempt to establish 4-aminopyridine as a primary standard base, we found this amine to be apparently altered at the anode. To circumvent this, we added the amine after the coulometric generation of the requisite amount of acid in an electrolyte of 1·0*M* sodium perchlorate. The amine was placed in a boat suspended above the electrolyte, 99·95% of the required acid was generated anodically, the 4-aminopyridine added, and the titration finished coulometrically with acid generated at an external "drip" electrode. The apparatus was essentially that described by Eckfeldt and Shaffer[4] as modified somewhat by Knoeck and Diehl[5] and with the addition of the external drip electrode described by Knoeck and Diehl.[6] The results were consistently low, by 2–6%, and it thus became apparent that a primary difficulty in the coulometric tritration of bases lies in the anodic generation of hydrogen ion. The textbooks and treatises are silent on this matter.

Experiments on the solution remaining after anodic generation of hydrogen ion and oxygen on bright platinum in 1*M* sodium perchlorate threw some light on the side-reaction consuming the extra 4% or so of electricity. Tests for hydrogen peroxide failed. A new oxidizing agent was present, however, one that reacted only slowly with ferrous sulphate at room temperature but with speed on the addition of a little silver ion. The Riesenfeld–Liebhafsky[7] test indicated that a true peroxy acid was present. The new oxidizing agent underwent spontaneous decomposition as was shown by indirect iodometric titration of aliquots taken at intervals; some five hours were required for complete decomposition. The phenomena observed resemble, with respect to formation by anodic oxidation and behaviour toward reducing agents and catalysts, those of peroxydisulphuric acid (see for example, Yost and Russell[8]). No hydrogen ion is involved in the anodic formation of the peroxydisulphate anion, $2SO_4^{2-} = S_2O_8^{2-} + 2e^-$. Tentatively we identify the new oxidizing agent as peroxydiperchlorate, Cl_2O_8.

That the hydrogen–oxygen gas-coulometer (sulphuric acid electrolyte) yields low results owing to a shortfall of oxygen was observed by Faraday[9] who confirmed the finding of still earlier workers that a compound, "oxywater", with bleaching power is formed at the anode "even though chlorine and similar bodies were rigidly excluded". That the hydrogen–oxygen gas-coulometer gives low results was rediscovered by Page and Lingane[10] who attributed the extra current required to the formation of hydrogen peroxide and the subsequent reduction of the hydrogen peroxide at the cathode. The nature of the reactions on a platinum electrode in sulphate and perchlorate electrolytes has been studied by several workers and in particular by Johnson, Napp and Bruckenstein[11] who reported that a soluble compound is formed at the anode in addition to oxygen and that the compound is definitely not hydrogen peroxide. For the integration of current varying with time Page and Lingane[10] abandoned the hydrogen–oxygen coulometer and devised another gas-coulometer, the

hydrogen–nitrogen gas-coulometer, employing hydrazine sulphate as the electrolyte, the reactions being

$$N_2H_5^+ = N_2 + 5H^+ + 4e^- \quad (1)$$

and

$$2H^+ + 2e^- = H_2 \quad (2)$$

Page and Lingane reported the results to be somewhat low, presumably because of the loss of gas by solubility.

We have now shown that the bright platinum anode in sodium hydrazinium sulphate [$Na(N_2H_5)SO_4$] solution is 100% efficient in the generation of five hydrogen ions per four electrons [equation (1)]. Moreover, hydrazine is more readily oxidized than is either THAM or 4-aminopyridine so that the titration of these bases may be carried out directly, that is, with the base dissolved in the solution of sodium hydrazinium sulphate.

As experimental proof of the efficiency of this "hydrazine–platinum anode" for the generation of hydrogen ion we offer the direct, high-precision coulometric titration of THAM and a supplementary analysis of this same material by weight-burette titration with perchloric acid, the titration being completed coulometrically and the perchloric acid standardized coulometrically. These titrations were carried out with the same apparatus and essentially concurrently with the titrations of 4-aminopyridine which are reported in another paper.[12] We have also measured the potential of the working sodium hydrazinium sulphate–platinum anode and find it a few millivolts positive to the S.C.E. and thus well over a volt negative to the oxygen over-voltage region.

EXPERIMENTAL

Reagents

Tris(hydroxymethyl)aminomethane. This was obtained in the form of large crystals from a commercial source, was ground, dried in vacuum, again ground, passed through a 100-mesh sieve, and dried in a vacuum over anhydrous magnesium perchlorate. This material was stored over anhydrous magnesium perchlorate; after 2 weeks there was no further loss in weight. Microscopic examination showed the presence of voids, some containing liquid, in this material.[13]

Sodium hydrazinium sulphate [$Na(N_2H_5)SO_4$], 0·25*M*. Commercial hydrazine sulphate ($N_2H_6SO_4$) was recrystallized from 3*M* sulphuric acid and dissolved in 1·0*M* sodium perchlorate; the pH was then brought to 4·5 by the addition of carbonate-free sodium hydroxide. The solution was made 0·25*M* in sodium hydrazinium sulphate by diluting with 1·0*M* sodium perchlorate.

Apparatus

Preliminary work was carried out with the "Coulometric Analyser" of the Leeds & Northrup Company[4] and the modification of the "drip" electrode of Knoeck and Diehl[6] described below. The drip electrode was not used in the work with the new hydrazine–platinum anode.

The high-precision coulometric titrations of THAM were carried out with the apparatus used by Koch, Hoyle and Diehl[12] for the high-precision titration of 4-aminopyridine; the calibrations of the standards of mass, potential resistance, and time were the ones used in that work.

Drip electrode. The external "drip" electrode used in preliminary work was a modification of that of Knoeck and Diehl,[6] Fig. 1. Fine-porosity glass frits were used to separate the three compartments. The level of the electrolyte in the central compartment was maintained above those in the other two compartments so that flow of electrolyte was always outward and diffusion of acid or base from one electrode chamber to the other prevented. The titrant was generated at a platinum wire sealed in glass and the electrolyte was delivered to this platinum wire by means of a wick of glass fibre which passed through a small port in the reservoir and down the outside of the chamber to the platinum wire. Electrolyte flowed slowly down this wick and dripped from the platinum wire, carrying acid (or base) generated on the platinum anode (or cathode). This drip electrode was used in the preliminary investigations of the oxidizing agent formed as a by-product at the anode in a perchlorate solution; it was not necessary in the high-precision titrations of THAM made with either the hydrazine–platinum anode or with perchloric acid.

Titrations of THAM

High-precision titrations of the batch of THAM prepared as described above were carried out in two ways: (1) by using the new hydrazine–platinum anode, and (2) by the addition of a weighed amount of perchloric acid in slight excess and coulometric back-titration at a platinum cathode and coulometric standardization of the perchloric acid. The procedures followed were identical with those used in titrations of high-purity 4-aminopyridine[12] and indeed the titrations were carried out as part of a sequence involving the repeated calibration of the standard of potential and the titrations of the two bases. Weighings were corrected to weight in vacuum, using 1·32 for the specific gravity (found by the pycnometer method using benzene, 1·3184). In calculating the purity of the THAM, the value used for the molecular weight, $C_4H_{11}O_3N$ = 121·1372, was calculated from the atomic weights in the 1961 Table of Atomic Weights (for reasons see ref. 12). The value used for the faraday, F = 96,486·70(±0·54) 1972 NBS coulombs/mole is the current

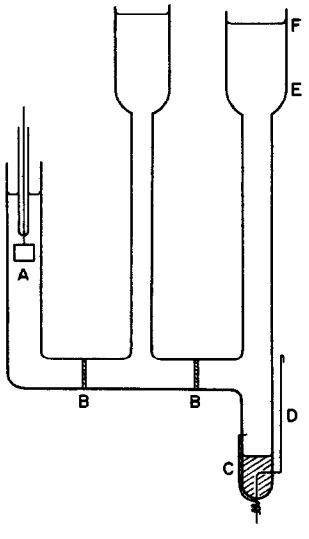

Fig. 1. Details of "drip" electrode: (A) working counter-electrode, bright platinum foil; (B) discs of fritted glass (very fine); (C) glass-fibre wick; (D) platinum-wire working electrode; passes through solid glass (two seals); (E, F) permissible levels of electrolyte during operation; upper level, F, is always below level in central column; the glassware is drawn to scale; the height of the central column is 14 cm.

Table 1. Coulometric titration of tris(hydroxymethyl)aminomethane (THAM) with acid generated at the hydrazine–platinum anode

Titration Number	Weight of THAM, *g*	Quantity of electricity, 1972 *NBS coulombs*	Electrical equivalent per gram = (5/4)*It*/wt, 1972 *NBS coulombs/g*	Purity of THAM, %
1	2·999967	1910·023	795·852	99·9176
2	2·999586	1909·588	795·771	99·9076
3	3·001108	1910·845	795·892	99·9226
4	3·000811	1910·670	795·898	99·9234
5	3·004788	1912·964	795·798	99·9109
6	3·002499	1911·610	795·841	99·9163
			Average	99·9164
			Standard deviation	0·0063

Mol. wt. THAM: 121·1372 Faraday: 96,486·70 1972 NBS coulombs/mole.

value; see the closing discussion in ref. 12 for a review of this. The results of the titrations of THAM are given in Table 1 and 2.

The great attention paid to calibration and technique in this work is not necessary for work in which the allowable error is 1 in 10^3 or 10^4 and the following procedure is written for the more general user of the hydrazine–platinum anode.

Recommended procedure

Use a constant-current source, current-measuring device, and timing device such as those in the Coulometric Analyzer of the Leeds & Northrup Company.[4] Use a partition cell such as the one described by Taylor and Smith[1] or the more convenient one of Eckfeldt and Shaffer[4] and Knoeck and Diehl.[5,6,12] In the titration cell place 100 ml of a solution 0·25*M* in sodium hydrazinium sulphate and 1*M* in sodium perchlorate, and a magnetic stirring bar. Charge the intermediate chamber with 7·5*M* sodium perchlorate and the counter-electrode chamber with 1*M* sodium perchlorate. Pass nitrogen through the liquid and the cell to remove carbon dioxide and oxygen. Electrolyse this solution, making the working electrode anodic or cathodic as required to bring the pH to 4·50. Add the weighed sample of the base to be titrated. Electrolyse anodically, recording the current and time. (Many commercial coulometers have direct read-out of the number of microequivalents passed, making current-time integration unnecessary. However, for high-precision work a current-sensing resistor, potentiometer and an accurate time-interval counter are essential.) When the pH of the solution reaches 5·5, interrupt the titration and rinse the walls of the

Table 2. Titration of tris(hydroxymethyl)aminomethane (THAM) with perchloric acid (coulometric end-point) and standardization of perchloric acid coulometrically

Standardization of perchloric acid

Titration Number	Weight of perchloric acid, *g*	Quantity of electricity, 1972 *NBS coulombs*	Concentration of perchloric acid, 1972 *NBS coulombs/g*
1	25·1721	2190·428	$87·0180_9$
2	25·8985	2253·677	$87·0195_9$
3	25·8424	2248·743	$87·0175_9$
4	30·8234	2682·211	$87·0186_7$
5	20·1659	1754·802	$87·0183_0$
6	20·1630	1754·566	$87·0191_4$
		Average	$87·0185_6$
		Standard deviation	$0·0007_0$

Titration of tris(hydroxymethyl)aminomethane

A Number	*B* g	*C* g	*D* C	*E* C	*F* C	*G* C/g	*H* %
1	2·756568	28·3611	2467·942	274·006	2193·936	795·894	99·9229
2	3·195547	30·2137	2629·152	86·129	2543·024	795·802	99·9114
3	2·953803	28·3733	2469·004	118·234	2350·770	795·845	99·9168
4	2·783250	27·1235	2360·248	145·075	2215·173	795·895	99·9230
5	2·706080	26·7877	2331·027	177·480	2153·548	795·819	99·9135
6	2·768352	25·8580	2250·126	47·180	2202·946	795·761	99·9062
7	3·054527	29·9910	2609·774	178·939	2430·835	795·814	99·9129
						Average	99·9152
						Standard deviation	0·0062

Heading of columns: *A*, Titration number; *B*, Weight of THAM; *C*, Weight of perchloric acid; *D*, Electricity delivered *via* perchloric acid; *E*, Additional electricity to reach end-point; *F*, Total electricity; *G*, Electrical equivalent per gram; *H*, Purity of THAM.

C = 1969 NBS coulombs; Mol. wt. THAM = 121·1372; Faraday = 96,486·70 1972 NBS coulombs/mole.

titration chamber with distilled water. Continue the titration, preferably with a smaller current delivered in increments corresponding to 1 or 2 microequivalents. After each increment of current, allow sufficient time for the solution to equilibrate before reading the pH-meter. The end-point will lie close to pH 4·5. Plot pH *vs.* microequivalents to determine the end-point.

Somewhat better results can be obtained by carrying out the preliminary treatment of the electrolyte as a titration (small current; working electrode anodic) and measuring the number of coulombs passed between the initial and final end-points.

RESULTS AND DISCUSSION

That the hydrazine–platinum anode is completely efficient for the generation of five hydrogen ions for each four electrons passed is borne out by the results obtained in the titration of THAM, Table 1, the purity of the particular lot of THAM analysed having been established by titration with perchloric acid in turn standardized coulometrically, Table 2.

The standard reduction potential for the hydrazine–nitrogen couple [equation (1)] was calculated by Latimer[14] from thermodynamic data to be −0·23 V. Even allowing for variation in the single electrode potential of the anode as the acidity increases, starting from pH 5, during the generation of hydrogen ion this potential is over a volt negative to the region of oxygen overvoltage on bright platinum in sulphate or perchlorate electrolytes; thus, it is highly unlikely that either oxygen or peroxydisulphate will be formed on bright platinum in dihydrazine sulphate solution. A direct measurement of the potential of a bright platinum working electrode in 0·25*M* sodium hydrazinium sulphate was made, at a current density of 2·6 mA/cm^2. The platinum anode was slightly positive to the S.C.E.:

pH	3·75	4·00	4·25	4·50	4·75	4·88	5·00	5·25	5·50	6·60
E. mV	15·6	13·1	11·1	10·8	9·0	8·8	8·0	4·8	1·0	−25·0

These values are in rough agreement with somewhat similar measurements made by Lingane and Jones[15] who used hydrazine as an anodic depolarizer in the controlled cathode-potential deposition of copper from a tartrate solution. The ease with which bases are attacked anodically varies and each candidate for titration must be considered individually. In general the formation of amine oxides and oxidative degradation requires a high potential and it will probably be found that most amines can be titrated successfully with the hydrazine–platinum anode.

To obviate the confusion which appears in the literature on the dissociation constants of hydrazine we adopt the designations

$$N_2H_6^{2+} = N_2H_5^+ + H^+$$

$$K_{a1} = [N_2H_5^+]\,[H^+]/[N_2H_6^{2+}] \qquad pK_{a1} = 1{\cdot}63$$

$$N_2H_5^+ = N_2H_4 + H^+$$

$$K_{a2} = [N_2H_4]\,[H^+]/[N_2H_5^+] \qquad pK_{a2} = 7{\cdot}94$$

The value for K_{a1} was obtained by us from a potentiometric titration of hydrazine sulphate ($N_2H_6SO_4$) with sodium hydroxide; found at mid-point, pH = 1·75, 1·81, average 1·78 (concentration of salt and acid at this point each about 0·10*M*); the value for the dissociation constant was calculated from $[H^+] = K_a(\frac{1}{2}C_o - [H^+])/(\frac{1}{2}C_o + [H^+])$. This is in poor agreement with the value given by Gilbert,[16] expressed as dissociation as a base, of $8{\cdot}9 \times 10^{-6}$, but in fair agreement with that of Kolthoff and Stenger[17] of 3×10^{-13}. The value for K_{a2} is the average of the three best values reported by Bjerrum, Schwarzenbach and Sillén[18] [$8{\cdot}7 \times 10^{-7}$ expressed as dissociation as a base ($pK_{b1} = 6{\cdot}06$)]. Using these values and the usual method of calculating the pH at the equivalence-point in the titration of the first replaceable hydrogen ion of a dibasic acid, the pH at the first equivalence-point should be $(pK_{a1} + pK_{a2})/2 = 4{\cdot}86$. The value found in the precise coulometric titrations was 4·48. The discrepancy is probably due to the high ionic strength of the electrolyte in the coulometric titrations.

The dissociation constant of THAM as an acid is $K_a = 8{\cdot}08$, close to the second ionization constant of hydrazine, $K_{a2} = 7{\cdot}94$. The two bases should be neutralized together on titration. In practice only one end-point was found, at pH 4·31. The hydrazine was present as $N_2H_5^+$ before and after the titration and the hydrogen ion was used to neutralize the THAM. Similarly the dissociation constant of 4-aminopyridine as an acid is 9·37; as with THAM, only one point of inflection was found, falling in various titrations at pH-values between 4·44 and 4·66. In general then, it should be possible to titrate coulometrically with the hydrazine–platinum anode any base having a dissociation constant as a base greater than 10^{-6} or perhaps 10^{-7}.

An intriguing feature of the hydrazine–platinum electrode is the possibility of operating the cell without a partition and thus, providing the cathode reaction is 100% efficient in the utilization of hydrogen ion [equation (2) above], of generating only one hydrogen ion per four electrons passed. Conceivably it could work, although Page and Lingane[10] reported collection of hydrogen plus nitrogen in their hydrogen–nitrogen gas-coulometer to be 0·3% low. We found that it fails in practice by several per cent, undoubtedly because of reduction of the hydrazine at the cathode. The standard reduction potential for this couple $N_2H_5^+ + 3H^+ + 2e^- = 2NH_4^+$, is reported in Latimer[14] to be +1·275 V.

It was pointed out by Knoeck and Diehl[6] in their paper on the high-precision titration of potassium dichromate, that in the generation of hydroxyl ion by the reduction of water at the cathode, $2H_2O + 2e^- = H_2 + 2OH^-$, if the reduction of the perchlorate of the electrolyte occurred as a side-reaction, $ClO_4^- + 2e^- + 2H^+ = ClO_3^- + H_2$ (alternatively: $ClO_4^- + 2e^- + H_2O = ClO_3^- + 2OH^-$), no error would result inasmuch as two hydrogen ions are used up per two electrons. For the problem under investigation it appeared that the presence of chlorate in the 1*M* sodium perchlorate might prove beneficial

in that its oxidation might occur in preference to the formation of peroxydiperchlorate as discussed above, and would release two moles of hydrogen ions per mole of chlorate. By trial it was found that it did not, either admixed with sodium perchlorate or alone, the results for 4-aminopyridine being 103·18 and 105·55% apparent purity, respectively. Sodium chlorate is not readily oxidized to sodium perchlorate. Commercially the reaction is carried out on bright platinum at a very high anode potential. The interesting question now arises as to whether a peroxydichlorate may be formed concurrently with perchlorate and the peroxydiperchlorate postulated above. Commercially the oxidation of sodium chlorate is never carried to above 95–97% completion, to avoid deterioration of the platinum anode which accompanies further oxidation. It seems odd that the large-scale production of sodium perchlorate should have gone on now for a half-century without the peroxydiperchlorate having come to attention. Sodium perchlorate is isolated after the electrolytic oxidation, by boiling to evaporate and concentrate; peroxydiperchlorate and presumably peroxydichlorate if any would be decomposed in the process, and thus it has never caused a problem.

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AN APPLICATION OF THE ZEEMAN EFFECT TO ANALYTICAL ATOMIC SPECTROSCOPY—I

THE CONSTRUCTION OF MAGNETICALLY-STABLE SPECTRAL SOURCES

R. STEPHENS and D. E. RYAN

Trace Analysis Research Centre, Department of Chemistry, Dalhousie University, Halifax, N.S., Canada

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Summary—A design is given for a d.c. discharge lamp which will maintain a stable plasma in a magnetic field. The lamp is of particular use for applications of the Zeeman effect to analytical atomic spectroscopy. Three designs of cathode are described, which cover three different temperature ranges for the m.p. of the elements concerned. The experimental behaviour of lamps at varying magnetic field strengths, filler pressures and operating currents is considered.

There are a number of potentially useful possible applications of the Zeeman effect to atomic spectroscopy.[1–11] However, any such application requires a spectral source capable of stable operation within an intense magnetic field. High-frequency discharge sources are suitable in this respect;[12] thus electrodeless discharge lamps (EDL's), for example, have been used for Zeeman-scanning of atomic line-profiles.[13–15] However, when EDL's are run under such conditions they often apparently show a lack of reliability in operation.[16,17] Currently available d.c. sources such as hollow-cathode lamps are unfortunately unsuitable, since severe plasma–field interactions occur on application of a magnetic field. These interactions have been found to cause an initial focusing of the plasma on the cathode, with subsequent cathode damage, and then instability and extinction of the plasma as the field increases. In addition, commercial hollow-cathode lamps require extremely large and cumbersome magnets to contain their electrode assemblies.

The present work describes a d.c. discharge source which is magnetically stable. The source described has the advantage that it can fit within a very narrow magnet pole-piece, to permit useful Zeeman splitting to be obtained with only a small, low-powered electromagnet.

EXPERIMENTAL

The condition for stability of a d.c. discharge driven by an electric field $\underline{E}$ within an applied magnetic field $\underline{H}$ is that $\underline{H} \wedge \underline{E} = 0$ at all points in the discharge. That is, $\underline{E}$ and $\underline{H}$ must have coincident axes. This condition has been found to be valid even at filler-gas pressures up to 50 mm Hg. and at current densities up to 1 A/cm^2 at the cathode, when ion-trajectories are subject to ion–ion interactions, ion–atom collisional perturbations, *etc.* The design of lamp used in the present studies to satisfy the condition above is shown in Fig. 1.

Lamp construction

General. Asbestos or quartz insulators were used for electrical insulation. Asbestos insulators were first heated strongly until all organic binder had burned away, and were soaked in water before installation, to reduce their mechanical fragility. Aremco Ceramcast 505 refractory cement was used to hold internal components in place. All anodes were made from 0·01-in. copper foil, cut to

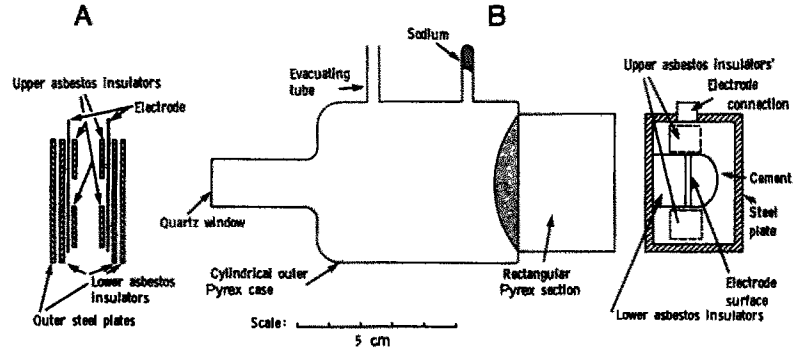

Fig. 1. (A) Front view of the electrode assembly. (B) Side view of the lamp, showing the rear half of the electrode assembly.

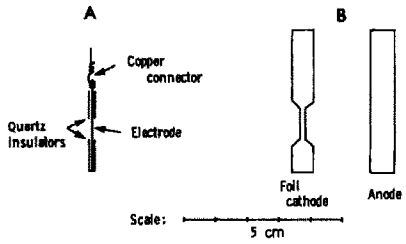

Fig. 2. Electrode structures.

the size shown in Fig. 2B. Cathodes are described in detail later. Electrode metals were obtained from Ventron (Alfa Products) unless otherwise stated.

Assembly. The electrode structure was assembled in two halves, which contained the anode and cathode respectively.

Each anode section was built on a 3 × 4 cm 0·3-mm thick steel plate, which served as the outer side plate of the completed assembly. A 2 × 4·5 cm asbestos insulator was cemented on top of the centre of one face of the steel plate. The anode was placed centrally on top of this insulator. The top and bottom of the anode strip were covered with 1 × 1 cm asbestos insulators (upper insulators), leaving the central portion of the anode exposed to carry the discharge. Insulators and the electrode were cemented in place and unwanted gaps between the insulators were filled with more cement. The area required eventually to form the rear of the completed assembly (*i.e.*, the back of the completed lamp) was built up with more cement to a position flush with the upper asbestos insulators.

Construction of the cathodic section of the assembly was identical to that described above when foil electrodes were used. Wire cathodes were first insulated with tightly fitting quartz capillaries at the top and bottom of the electrode, and the quartz capillary/wire cathode assembly was then mounted in an identical manner to that described for foil electrodes except for the omission of the 1 × 1 cm upper asbestos insulators.

Assembly was completed by joining the two half-sections thus made, compressing them in a hand-vice to the required thickness and baking in a vacuum oven at 200° for 3 hr. The outer plates were then cleaned on a carborundum wheel. Each electrode assembly was joined to the glass case with epoxy resin and made vacuum-tight by covering all the areas between the steel plates with epoxy resin. Quartz windows were sealed onto the case with epoxy resin to complete each lamp.

Conditioning procedure

A 1 × 0·1 cm piece of sodium rod was cleaned in toluene and introduced into the lamp side-arm as shown in Fig. 1. The lamp was then evacuated, with a liquid-nitrogen trap in the vacuum line. Prepurified argon was used as filler gas. Lamps were conditioned by use of a procedure similar to that of Walsh.[18,19] The optimum operating pressure for maximum output intensity was then determined. The lamps were filled to about 0·5 atm pressure of argon, and the sodium heated strongly with a hand-torch. The lamps were then re-evacuated, the sodium being heated as necessary to deposit a heavy film of the metal over the inner surface. The lamps were finally filled with fresh argon to the optimum pressure and sealed off. By use of this procedure a satisfactory lamp-life, frequently in excess of 100 hr operation, can be obtained. No attempt was made to improve this figure by use of, *e.g.*, zirconium as a getter, incorporated into the anode as is done in commercial lamps.

Cathodes

Cathode design depends on the element concerned. Types of cathode assembly have been found to fall roughly into the 3 categories given below. Elements given in parentheses are those which are readily available in the physical form required and for which lamps have been built.

(1) *Elements with a melting point* > 1200° (*Fe, Cr, Ni, Co*). Cathodes for all these elements were made from about 0·6-mm diameter (22 B & S gauge) wire. The wire was contained in two close-fitting quartz capillary insulators, positioned to leave 5 or 6 mm of the wire exposed to act as the cathode surface (Fig. 2A). A length of fine copper wire was wound tightly over one end of the electrode as an electrical connection. the copper–electrode junction was embedded in cement during assembly, and the copper wire led through the outer (expoxy resin) seal. This prevented local overheating of the seal during operation of the lamp.

Owing to the unsuitable mechanical properties of chromium, pure chromium wire of the required diameter is difficult or impossible to obtain. Ordinary chromel wire (Fisher) was, however, found to be satisfactory. Such cathodes were observed to emit lines from both chromium and nickel.

During operation it was found that these electrodes had to be operated at red heat before any atomic emission could be observed. Previous experience showed no difficulty in obtaining emission from easily sputtered elements such as copper or silver. Thus it was felt that a low sputtering rate rather than poor excitation efficiency was responsible for poor emission intensity of the high melting-point elements from a "cold" cathode, and that "thermally assisted" sputtering apparently occurred as the cathode temperature increased. Analogous effects have been reported for heated hollow-cathode lamps in certain instances.[20]

(2) *Elements with melting points between* 600° *and* 1200° (*Cu, Mg, Ag*). Electrodes for these elements may be built from wires as described above, or cut from thin sheets (*e.g.*, 0·01 in.) of the metal as shown in Fig. 2B. The former show a higher intensity; the latter are more electrically robust, with a greater capacity to withstand overloads. The latter type was used in the present work.

(3) *Elements with melting points below* 600° (*Pb, Zn, Cd*). In the present work these elements were coated onto brass strips of the same dimensions as the electrodes shown in Fig. 2B. The brass gives mechanical support and also acts as a heat-sink. Coating was achieved by melting a piece of the required metal over a roughly shaped piece of brass with an oxy-propane flame, with ammonium chloride as a flux. The electrodes were then degassed in a vacuum for about 3 hr at a temperature just above the melting point of the coated metal, and finally cut and filed to the dimensions shown in Fig. 2B. It is also possible to coat these elements onto copper wires, a technique which is particularly advantageous if excitation of a short-wavelength line, such as that of Pb at 217·0 nm, is required.

The spectrometer

The present experiments were carried out with a Varian AA5 spectrometer. The lenses were removed from their original mountings and were replaced in lens holders of adjustable height (Ealing Scientific Ltd). The horizontal supporting grooves cut in the lens supports caused some reduction in the angle of acceptance of the spectrometer optics (see below). An electromagnet was supported on a "lab-jack" at the end of the optical rail of the spectrometer. The instrument was otherwise not modified. Lamps were driven from the AA5 power supply without difficulty.

The magnet was supplied by Scintrex Ltd (222 Snidercroft Road, Concord, Ontario, Canada). The pole-piece of this magnet may be removed in two sections, to permit a lamp to be inserted. When replaced, frictional contact holds the lamp in the required position. The magnet has a weight of about 25 lb and a maximum power consumption of about 200 W, and generates a maximum field of about 17000 Gauss: these data show the highly compact magnet assemblies which can be used to obtain useful Zeeman splitting with the present lamps. The use of a compact

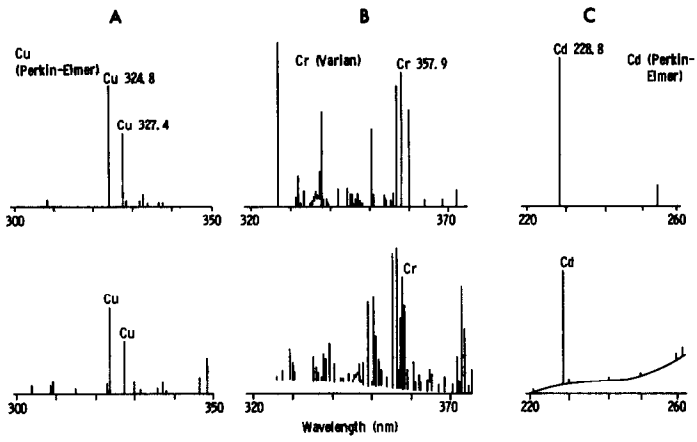

Fig. 3. Spectral scans of Cd, Cu and Cr lamps. Wavelength axis represents zero intensity in all cases. *Upper traces*: Commercial lamps. Photomultiplier voltages and lamp currents were 550, 370, 330 V and 6 mA (each lamp) in A, B, C, respectively. *Lower traces*: Magnetically-stable lamps. Photomultiplier voltage and lamp currents were 600, 650, 550 V and 20, 30, 20 mA in A, B, C, respectively. Monochromator slit-width was 25 μm in all cases.

magnet is permitted by the narrow gap between the pole-pieces (about 4 mm) which allows high field-strengths to be obtained for a low power-dissipation in the windings. It is felt that a 4-mm gap probably represents a lower limit for electrode assemblies of the type described. If the electrode space is reduced further, the cathode becomes very susceptible to mechanical deformation. In extreme cases recrystallization of the metal has been observed, as dendritic growth along the field axis. Such effects usually lead to internal arcing and subsequent lamp-failure.

RESULTS AND DISCUSSION

Chromium (357·9 nm), copper (324·8 nm) and cadmium (228·8 nm) have been selected as typical elements of the 3 groups of cathodes described above. Their behaviour was found to be completely representative of the other elements in their respective groups unless otherwise stated.

Spectral scans of the emission of the three lamps are shown in Fig. 3. These were measured at zero magnetic field and at the maximum power the lamps could safely dissipate for sustained operation. The scans of the corresponding commercial lamps (either Varian or Perkin-Elmer) are also shown in Fig. 3 for comparison, and indicate the relatively poor output and low line-to-background ratios of the sources described in this paper. These deficiencies may be attributable in part to the use of argon rather than neon as a filler gas.[21] The reduced angle of acceptance of the spectrometer optics, mentioned above, gave rise to an image of the plasma at the spectrometer slit approximately 6 mm high for all the lamps used. Thus the relative intensities shown in Fig. 3 *et seq.* were considered to be determined by the emission intensity at the centre of the corresponding plasma irrespective of the (different) optical apertures of the various types of lamp which were examined.

Figure 4 shows magnetic-stability plots for four different lamps. The major factor affecting the magnetic stability of these particular lamps is thought to be the electrode design. If the anode and cathode are not of equal size (*e.g.* as with the chromium or the copper lamp), or are slightly displaced from the magnetic axis, plasma–field interactions will occur. These interactions almost invariably lead to an appreciable enhancement of line intensity at the cost of only a slight change in background, and lamps were usually deliberately designed to make use of this effect to improve their spectral characteristics.

Similar but less marked effects occur if the electrode assembly is moved away from the centre of the magnet pole-piece, into a region of poor field-homogeneity.

Figure 5 shows the effect of increasing the lamp power at various pressures. The results are unusual in that they show only a rather small increase of intensity with increasing power; behaviour which is not normally observed with commercial hollow-cathode lamps.[22] The effect is least apparent for chromium, probably because of the sputtering effects mentioned above. The reason for this behaviour appears to lie in the confinement of the plasma between anode and cathode. This is particularly true at lower pressures, when the cathode glow visibly expands to fill the whole of the interelectrode cavity. The simultaneous electrical effects observed are illustrated in Fig. 6,

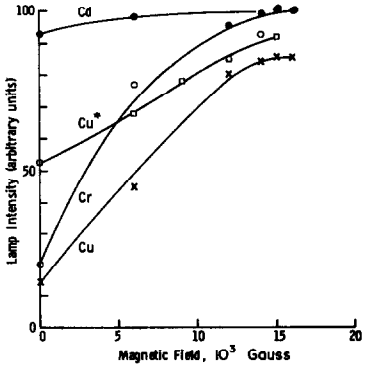

Fig. 4. Line intensities *vs.* magnetic field strength. Cu* and Cd lamps both had symmetrically placed anodes and cathodes of equal area. Cu and Cr lamps had the asymmetric structure described here.

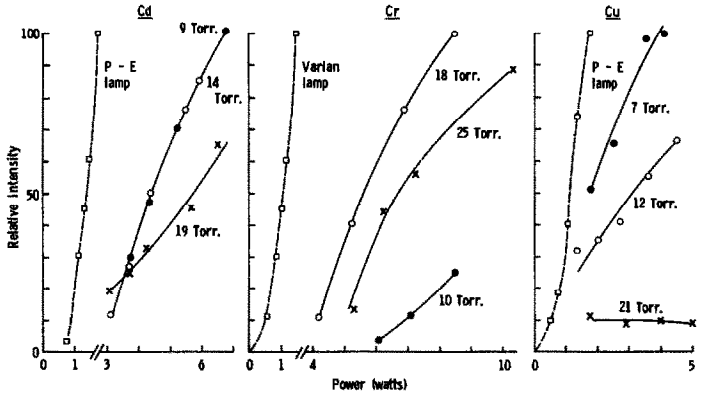

Fig. 5. Dependence of lamp intensity on filler-gas pressure and power. The limits of each plot represent the point of instability of the plasma.

which shows a steady increase in the driving voltage (and hence the power dissipation within the lamp) as the discharge expands with increasing current and decreasing pressure. This behaviour contrasts markedly with that of more conventional low-pressure d.c. discharge devices. Because of this effect, the lamp intensities in Fig. 5 have been plotted *vs.* power, rather than *vs.* current as is more normal for conventional lamps.

CONCLUSIONS

The results obtained in this work are felt to show that useful magnetically-stable spectral sources can be built in the manner described. Although experiments were limited to applied magnetic fields under about 17000 Gauss, owing to saturation of the magnet core, there appears to be no reason why the lamps could not operate in higher fields if required. Considered simply as spectral sources the lamps described are not particularly satisfactory, although their behaviour may be of some interest in relation to the sputtering and excitation processes occurring. It is felt that the relatively poor lamp-performance encountered in this work is not inherent in the design. Recent experiments have led to magnetically-stable lamps of comparable output to their commercial counterparts, although with reduced lifetimes. It is hoped to report on these experiments at a later date.

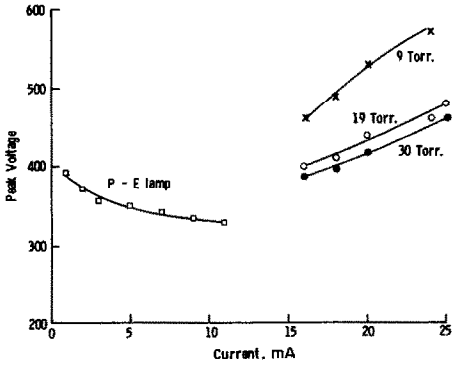

Fig. 6. Voltage *vs.* current variations at different filler-gas pressures for magnetically-stable and Perkin-Elmer Cd lamps.

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AN APPLICATION OF THE ZEEMAN EFFECT TO ANALYTICAL ATOMIC SPECTROSCOPY—II

BACKGROUND CORRECTION

R. STEPHENS and D. E. RYAN

Trace Analysis Research Centre, Department of Chemistry, Dalhousie University, Halifax, N.S., Canada

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Summary—A double-beam atomic-absorption spectrometer is described in which sample and reference beams are generated by Zeeman splitting of the source emission-line. The instrument was found to give satisfactory correction for lamp drift and for background scatter signals. The main advantage of the technique is the simplicity of the optical system used. Analytical sensitivity is found to be generally poorer than that given by single-beam measurements, largely because of the poor spectral characteristics of the lamps used here in comparison to their modern commercial hollow-cathode counterparts.

At suitably high magnetic-field strengths, atomic absorption occurs only at the central component(s) of the Zeeman multiplet of an atomic emission-line, and not at its outer perturbed components. However, spurious wide-band background absorption, due to particle-scatter or molecular absorption, occurs approximately equally at all components. Thus by separately monitoring the inner and outer components of the multiplet it is possible to use the former as a normal atomic-absorption source, and the latter as a correction signal to compensate for non-atomic absorption.[1] This technique has the advantage that corrections are achieved very simply, by using a single spectral source and power supply, and a single-beam optical system. The technique is particularly efficient because the "sample" and "reference" beams are of comparable intensity independent of their wavelength and because their effective wavelength displacement is extremely small (about 0·01 nm) and is controllable. In addition to these characteristics, the intensity ratio of the various components of the Zeeman multiplet is independent of the overall lamp-intensity. Thus the background corrections described above also provide an automatic and simultaneous correction for fluctuations in source intensity.

The application of this technique has already been demonstrated for mercury.[2–4] Its general application, however, has apparently been restricted by the lack of suitable magnetically-stable spectral sources. The present work describes the construction and operation of a spectrometer with Zeeman background correction, which makes use of the magnetically-stable discharge lamps described previously.[5]

EXPERIMENTAL

It is convenient to observe the spectral source in a direction perpendicular to the axis of the applied magnetic field. It is then possible to achieve the required selection of "sample" and "reference" lines from the Zeeman multiplet by their (differing) linear polarizations. This was achieved here by use of the mutually perpendicular quartz reflection polarizers shown in Fig. 1A. Each polarizer was built of a stack of three 3/4-in. diameter 1/16-in. thick quartz discs (Amersil Inc., N.J.). This arrangement gives a reflection efficiency of about 33% at 300 nm.[6] The polarizers were cemented to 1/8-in. diameter brass rods by means of which they were set at the Brewster angle (56° at 300 nm). Subsequent slight adjustments were made to the polarizer angles to obtain maximum radiation intensity on the two photomultipliers (1P28) shown in Fig. 1A, after which the polarizers were fixed in position with black silicone rubber. This optical system gave the required isolation of the different components of the Zeeman multiplet, and the two photomultipliers therefore generated the "sample" and "reference" signals for the spectrometer.

Despite the apparent symmetry of the optical system described above it was found that photomultiplier No. 1 (Fig. 1) had a wider angle of acceptance than No. 2. This was corrected by varying the aperture in front of No. 1 by means of the 8-mm diameter blackened coachbolts shown in Fig. 1B. The bolts were adjusted so that movement of a knife edge in front of the lamp, and approaching the lamp from any direction, caused an equal signal attenuation on both photomultipliers. The bolts were then fixed in position with silicone rubber.

Spectrometer design

A block diagram of the spectrometer is shown in Fig. 2. The magnet used was that described previously.[5] This was supported on a "lab-jack" at the end of a 0·5-m optical rail carrying two 10·2-cm focal-length lenses and a Varian AA5 burner/nebulizer assembly. Optical components were supplied by Ealing Optics, P.Q.

The monochromator was a McKee–Petersen MP1018A fitted with a grating (1180 grooves/mm). The optical assembly shown in Fig. 1 directly replaced the single photomultiplier normally fitted to the MP1018A. The two photomultiplier outputs may be balanced before amplification by the 1M potentiometer shown in Fig. 2, if required.

All electronics were built specifically for the spectrometer (circuit diagrams are available from the authors). High amplification was needed to offset the low

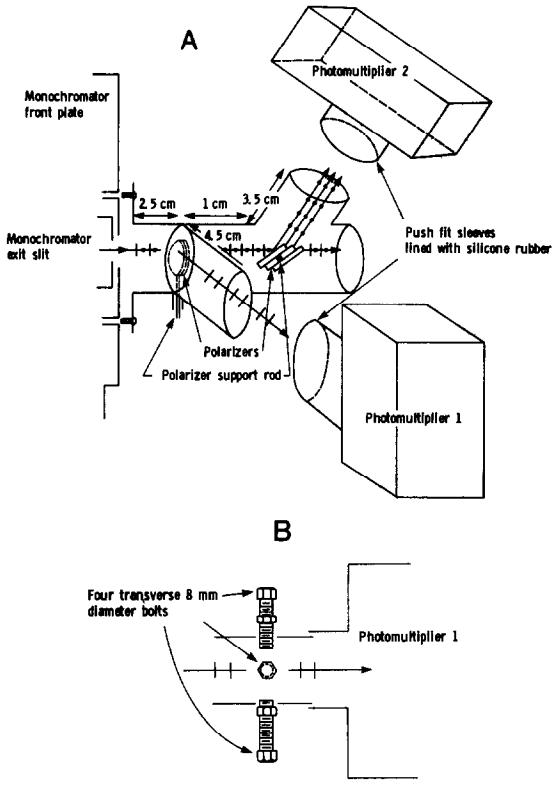

Fig. 1. The polarizing beam-splitter assembly.

lamp-output and radiation losses at the polarizers. This was provided by identical preamplifiers built onto the sockets of each photomultiplier. The main amplifier balanced and subtracted the output of the two preamplifiers, and fed the resulting signal to a tuned amplifier and synchronous detector of conventional design. The main amplifier balance-circuit was infinitely variable to ensure that correction could always be made for the (polarization-dependent) transmission efficiency of the optical components, for variations in photomultiplier efficiency at different light levels, and for variations in sample and reference signal intensities due to anomalous Zeeman splitting (see below). This arrangement also permitted the spectrometer to be used as a conventional single-beam instrument, simply by adjusting the balance control to either extreme so that signals from only one of the preamplifiers would be accepted.

Because of the possible variations in balancing the sample and reference channels mentioned above, flame-emission signals are not necessarily eliminated by subtraction of the sample and reference signals. Thus lamp modulation and synchronous detection are essential for the removal of spurious flame-emission signals, especially with the low-intensity sources used here. Modulation was obtained by driving the lamps from a 0–1 kV current-stabilized supply, square-wave modulated at 1 kHz. This supply provided the reference signal to the synchronous detector *via* a phase-control circuit as usual.

RESULTS AND DISCUSSION

General behaviour of the spectrometer

Figures 3 and 4 show the double-beam capability of the instrument. The results shown in both figures were obtained by simultaneously measuring the output of the sample-channel preamplifier and the Zeeman-corrected output taken off before the filter circuits. The correction for normal lamp-drift is satisfactory; it is not, however, complete, and severe fluctuations in lamp intensity can give small variations in the corrected output, owing to the different response characteristics of the two photomultipliers. The smoke-scatter signal in the uncorrected output appears as noise after correction, probably in part owing to imperfect correction for the different angles

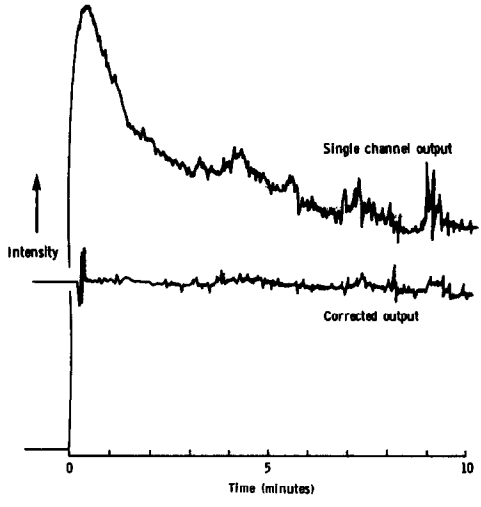

Fig. 3. Comparison of corrected and single-channel signals during lamp warm-up.

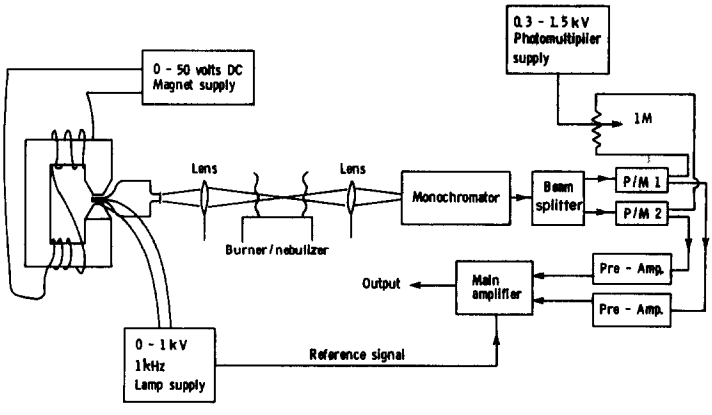

Fig. 2. Block diagram of the spectrometer.

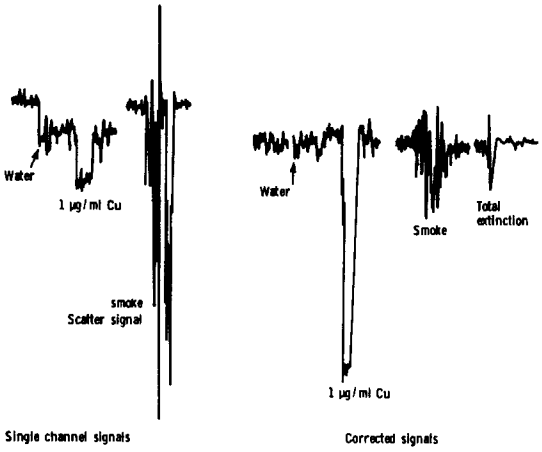

Fig. 4. Comparison of corrected and single-channel signals for a water blank and smoke-scatter signals at 324·8 nm.

of acceptance of the two photomultipliers, mentioned above.

Figure 5 shows calibration curves for copper at various values of the magnetic field-strength, H. These curves are qualitatively typical of those given by the other elements examined here. They initially show normal linear behaviour, but go through a maximum and begin to fall again at high concentrations. This is due to absorption of the reference signal in the wings of the flame absorption-profile at high analyte concentrations. Since the displacement of the reference lines is dependent on H, the positions of the maxima in Fig. 5 also depend on H.

The normal and the anomalous Zeeman effects

Nuclear interactions or isotope splitting, such as occur with the Cd 228·8 nm line, did not appear to influence strongly the present results. The effects of such interactions are not considered in the arguments below.

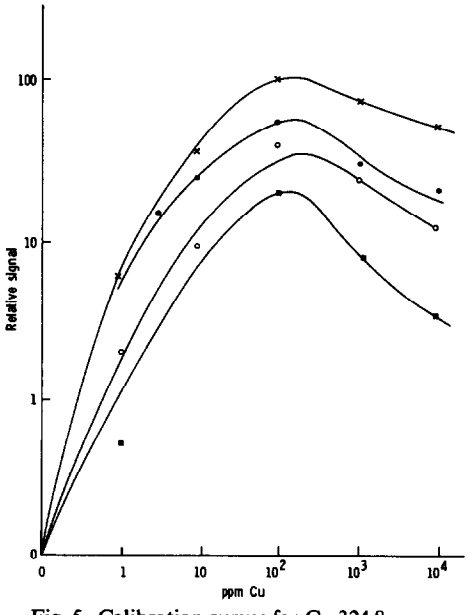

Fig. 5. Calibration curves for Cu 324·8 nm. × 16 × 10^3 Gauss; ● 14 × 10^3 Gauss; ○ 11 × 10^3 Gauss; ■ 7 × 10^3 Gauss.

The normal Zeeman effect is observed for singlet transitions, as a triplet in which the centre component shows no wavelength perturbation[7] and thus acts as the "sample" line irrespective of H. However, other transitions will exhibit in general anomalous Zeeman splitting at the field strengths used here. In such cases the "sample" and "reference" lines all show a wavelength displacement, because of which the absorption sensitivity of the sample channel falls as H increases. The magnitude of this effect depends on the particular element and transition considered. It is illustrated in Fig. 6 for the Cd 228·8 nm ($^1P_1$–$^1S_0$) and Ag 328·1 nm ($^2P_{1\frac{1}{2}}$–$^2S_{\frac{1}{2}}$) lines.

Analytical sensitivity

Table 1 shows a number of instances where "1% absorption" sensitivity is reduced in comparison with the corresponding zero-field values, owing to the effects of anomalous Zeeman splitting discussed above. In principle, this loss of sensitivity could be overcome through the Paschen-Back effect if sufficiently intense magnetic fields were available. The values of H given in Table 1 were determined for optimum sensitivity from plots analogous to those of Fig. 6.

Columns 5, 6 and 8 of Table 1 show the sensitivities and detection limit values given by the present lamps with the spectrometer operated in a conventional single-beam mode (see above). Columns 7 and 9 show the corresponding results given by the spectrometer in single-beam operation with commercial hollow-cathode lamps. Comparison of these data shows the present lamps to be clearly inferior to modern commercial sources, largely because of the high noise-levels of the former. This behaviour appears similar to, although possible more marked than, that of some early hollow-cathode lamps (8).

In general some improvement in the detection limit is given relative to single-beam operation by use of

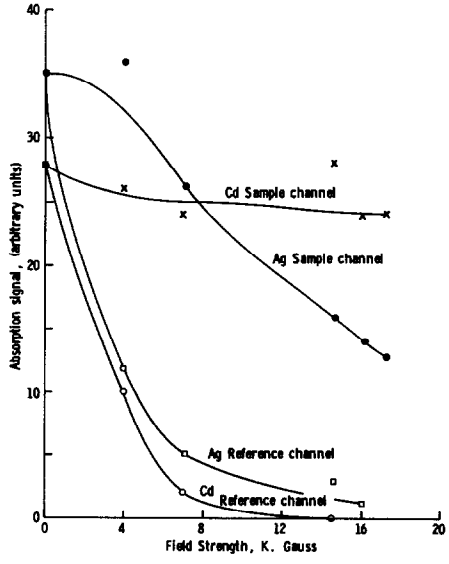

Fig. 6. Comparison of "sample" and "reference" absorption signals with increasing magnetic field for lines showing normal and anomalous Zeeman splitting.

Table 1. Comparison of absorption sensitivity and detection limits for various elements in an air–acetylene flame

Element	Line, nm	H, kGauss	Lamp current, mA	Monochromator slit, μm	Single-beam 1% absorption sensitivity, μg/ml: Zeeman lamp Field on	Zeeman lamp Field off	Hollow cathode lamp	Single-beam detection limit, at a signal: RMS noise ratio of 2:1, μg/ml: Zeeman lamp	Hollow cathode lamp	Zeeman correction detection limit, μg/ml
Ag	328·1	7	20	30	1	0·5	—	0·3	—	0·1
Cd†	228·8*	12	25	40	0·08	0·08	0·04	0·1	0·006	0·08
Cr	357·9	9	20	35	0·5	0·3	0·1	0·3	0·01	0·2
Cu†	324·8	13	20	20	0·5	0·3	0·1	0·2	0·02	0·05
Fe	248·3	7	18	35	0·2	0·2	0·1	0·3	0·007	0·5
Mg	285·2*	9	18	35	0·005	0·004	0·004	0·0008	0·0006	0·0005
Ni†	232·0	9	18	30	0·3	0·2	0·09	0·3	0·02	0·3
	341·5	9	22	30	3	1	0·7	2	0·07	1
Pb	217·0	7	25	50	2	0·5	0·2	0·5	0·05	1
	283·3	9	20	25	5	2	0·7	3	0·07	2
Zn	213·9*	15	25	50	0·1	0·1	—	0·4	—	0·4

† Perkin–Elmer hollow-cathode lamp used.
* Singlet transitions showing normal Zeeman effect.

Zeeman correction, in particular when the effects of anomalous Zeeman splitting are considered. It is felt that this improvement might be usefully enhanced if more intense sources were available. Because of low lamp-output and high transmission-losses, especially at short wavelengths, the photomultipliers were operated at high voltages (typically up to about 800 V maximum) which led directly to correspondingly high levels of photomultiplier noise in addition to the other sources of noise present.

CONCLUSIONS

It is felt that the technique described here offers a very simple simultaneous correction technique for lamp drift and for background absorption. Thus for example it would appear feasible to achieve the conversion of a conventional single-beam instrument simply by addition of the magnet and photomultiplier assembly described here, and the insertion of a balance control between the photomultipliers and the (existing) signal input. It is clear, however, that the technique cannot compete in analytical sensitivity with that currently given by a good single-beam instrument unless marked improvements in lamp intensity and stability can be obtained.

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SURFACE-LAYER PROPERTIES OF GLASS ELECTRODES RESPONSIVE TO SODIUM AND HYDROGEN IONS

ANDERS WIKBY*

Department of Analytical Chemistry, University of Umeå, S-901 87 Umeå, Sweden

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Summary—Cation-sensitive glasses exhibit an alkali-metal ion concentration profile and an electrical conductivity profile which increase smoothly with the distance in towards the bulk glass, as a result of interaction with aqueous solutions. In a pH-sensitive glass, however, a stepwise alkali-metal ion–distance profile is obtained and a low electrical-conductivity region is restricted to a thin film near the gel-layer/bulk-glass transition region. The replacement of silicon by aluminium causes the degree of H^+–M^+ ion-exchange to decrease, and consequently favours alkali-metal ion selectivity of the glass. Lower conductivity is attributed to a low proton-interdiffusion coefficient. The conductivity is lowest where the $\equiv SiOH$ concentration is high, *i.e.*, where the water concentration and the $\equiv SiO^-$ concentrations are low. High conductivity of the gel-layer of pH-sensitive glasses is caused by the presence of water which depolymerizes the glass structure. The network of alkali-sensitive glasses is less affected by water owing to the aluminium decreasing the concentration of terminal oxygen atoms in the structure. A low-conductivity surface layer on the latter glasses contributes to the sluggishness in the response of the electrodes.

Many authors have investigated the effect of the glass composition on the ion-selectivity of electrode glasses. MacInnes and Dole[1] reported the first systematic investigation of glass-electrode properties as a function of composition. Subsequently, the classical pH-responsive Corning 015 glass was developed within the soda–lime–silica system. Shortly thereafter, Sokolof and Passynsky[2] observed that the replacement of Na_2O by Li_2O caused the alkali error to decrease. Modern pH-glasses are therefore made from glass containing SiO_2 and Li_2O as the main components. However, Perley[3] later showed that additions of small amounts of other oxides (BaO, CaO, Cs_2O, TiO_2, La_2O_3, *etc.*) further decreased the potentiometric errors of the electrode glasses.

Lengyel and Blum[4] showed that the replacement of silica by B_2O_3 and/or Al_2O_3 yielded glass electrodes which responded to sodium. The effect of replacing silicon by tervalent ions in glass was systematically investigated by Nikolskii and Shultz[5] and by Eisenman *et al.*[6] Eisenman calculated from atomic models the change in free energy for the reaction

$$Cs^+_{glass} + 1^+_{soln} \rightleftharpoons 1^+_{glass} + Cs^+_{soln}$$

where 1^+ denotes H^+, Li^+, Na^+, K^+ or Rb^+, and concluded that the selectivity order for a silicate site was $H^+ \gg Li^+ > Na^+ > K^+ > Rb^+ > Cs^+$ but the reverse for an aluminosilicate site. An $\equiv SiO^-$ site was considered a high field-strength position since the negative charge is located at a terminal oxygen atom. The absence of terminal oxygen in an $(\equiv AlOSi\equiv)^-$ site lowers the field strength of the ion-exchange group since the negative charge is distributed over four oxygen atoms.

In the works described above, the properties of the glass electrodes were directly related to the original glass structure. As Boksay *et al.*[7] have also pointed out, this relationship has been invalidated by later investigations showing that reactions between typical pH-responsive glasses and aqueous solutions give rise to surface layers with properties differing from those of the bulk glass.[8–17] Two surface regions have been distinguished on the basis of their electrical resistance and by the chemical composition of individual thin surface layers removed by etching. In the outer layer, the gel-layer, the alkali-metal and hydrogen ions interdiffuse readily in a silicate network which is deficient in alkali-metal ions and partly hydrolysed. In towards the bulk glass, the water concentration gradually decreases, and the second layer, the gel-layer/bulk-glass transition layer, occurs where the proton–alkali-metal ion interdiffusion coefficient attains a pronounced minimum value. Since this barrier layer inhibits exchange of species between the adjacent phases, species in the solution must interact predominantly with the gel-layer. Thus the gel coating, rather than the bulk glass, is responsible for the main electrochemical behaviour of pH-responsive glasses. The close correlation between the gel-layer thickness and the magnitude of the potentiometric errors for certain glass electrodes[14] indicates that glasses with thin gel-layers are superior to those with thick layers, since the former prevent the penetration of interfering species more effectively, owing to their more rigid structure.

Although much work on the surface properties of typical pH-responsive glasses has been done during the last 10 years, only a few studies have been made

* Present address: AB Draco, Fack, 221 01 Lund, Sweden.

on the hydration of sodium-sensitive aluminosilicate glasses. Savage and Isard[18,19] have shown that cation-sensitive glasses generally do not respond as rapidly as glasses selective for hydrogen ions, and also that the former exhibit slow drifts of potential. They concluded that gradual hydration of the glass surface, which leaches the surface layer, might account for these undesirable effects.

While working with sodium sensitive glass electrodes, we made similar observations. Subsequent investigation of some chemical and electrical properties of the surface layers of two aluminosilicate glasses and comparison of the behaviour of these glasses with that of pH-sensitive glasses studied earlier provided further information on the sluggishness of the response of aluminosilicate glasses.

EXPERIMENTAL

Composition, preparation and pretreatment of electrode glasses

The compositions of the electrode glasses are shown in Table 1. The sodium aluminosilicate glass (N-glass) was received in a bulb shape from Z. Boksay in Budapest. The glass has been fused at 1350° in a platinum crucible and the bulb blown on a high resistance stem in a gas-oxygen flame. The multicomponent lithium aluminosilicate glass (L-glass) was a commercially available glass electrode (Philips G15-Na) developed by Z. Stefanac and W. Simon in Zürich.[20] The areas of the glass bulbs were about 3 cm^2. Older surface layers were removed by etching for several minutes in 5% hydrofluoric acid.

Leaching procedure

Freshly etched glass bulbs were leached in $2 \times 10^{-4}M$ ammonium bicarbonate at 25·0 ± 0·2°. The leaching baths were renewed daily to avoid accumulation of glass constituents and were analysed for silicon and lithium or sodium.

Measurements of the distribution of alkali-metal ions in the surface layer of leached glasses

Leached glasses were fractionally etched in stirred 0·3–1·0% aqueous hydrofluoric acid baths at room temperature. Each fraction was analysed for alkali metal and silicon as described below.

Analysis for alkali metals and silicon

Lithium and sodium were determined by flame emission spectroscopy using an air–acetylene flame and wavelengths of 670·8 and 589·0 nm respectively. Silicon was determined spectrophotometrically at 815 nm as silicomolybdenum blue.

Response studies

The lithium aluminosilicate glass electrode was placed in a vessel thermostatically controlled at 25°, and containing 25 ml of $2 \times 10^{-4}M$ ammonium bicarbonate. A saturated calomel electrode was used as reference. When the cell had attained a steady emf value, 2·8 ml of a 0·1*M* NaCl solution were rapidly added from a syringe to the stirred solution in the vessel, causing nearly instantaneous sodium ion concentration change from 0 to $10^{-3}M$. The changes in potential were recorded on a Servogor recorder until a steady value was reached. After a few seconds the recorded voltage changes can be taken as a measure of the electrode response rate. Electrodes hydrated for 2 and 16 days were investigated.

Electrical resistance measurements

The electrical resistance of hydrated glass electrodes was measured. Thin surface layers of the glasses were then removed by etching and the resistance was remeasured after each etching. The measurements were usually made in phosphate buffer (pH7), but in a few cases the resistance was measured directly in hydrofluoric acid solution containing chloride ions as described previously.[15] Silver/silver chloride reference electrodes were used on both sides of the bulbs. The electrical resistance was measured essentially as described earlier:[21] a constant current of 515 pA was forced through the electrode chain and the resistance was calculated by means of Ohm's law from the resulting voltage change obtained on a Servogor recorder. The temperature was kept at 25·00 ± 0·02°.

Table 1. Compositions of electrode glasses

Glass	Composition, *mole* %
L-glass	69% SiO_2, 12% Al_2O_3, 6% B_2O_3, 2% Ga_2O_3, 11% Li_2O
N-glass	72·5% SiO_2, 22% Na_2O, 5·5% Al_2O_3
Corning 015	72·2% SiO_2, 21·4% Na_2O, 6·4% CaO

RESULTS

The results shown in Figs. 1 and 2, in which the amounts of alkali-metal ions and silicon leached from the glasses have been plotted *vs.* the leaching time, indicate that the hydrogen-ion alkali-metal ion exchange rate for the N-glass is considerably higher

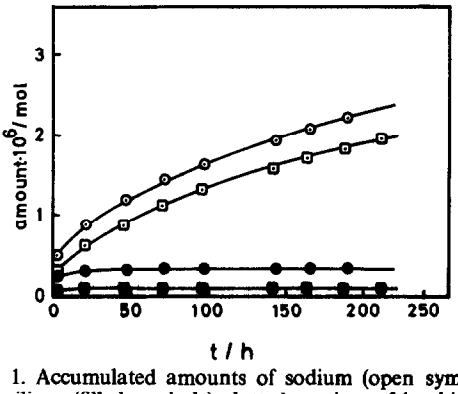

Fig. 1. Accumulated amounts of sodium (open symbols) and silicon (filled symbols) plotted *vs.* time of leaching of the N-glass in $2 \times 10^{-4}M$ NH_4HCO_3 at 25·0°. (⊙, ●) N-glass 1, (⊡, ■) N-glass 2.

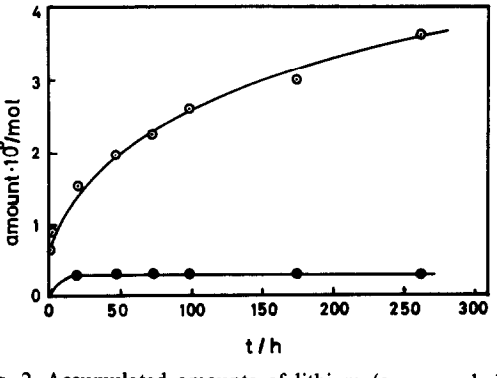

Fig. 2. Accumulated amounts of lithium (open symbols) and silicon (filled symbols) plotted *vs.* time of leaching of L-glass in $2 \times 10^{-4}M$ NH_4HCO_3 at 25·0°.

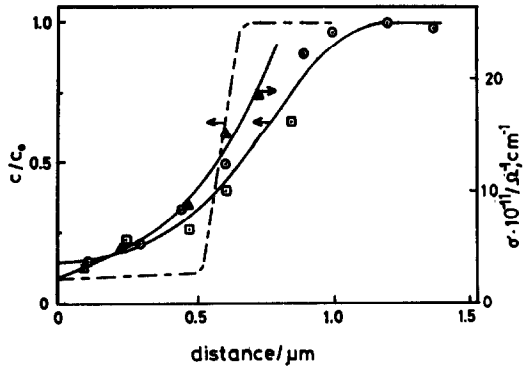

Fig. 3. The electrical conductivity and relative concentration C/C_0 (where C_0 is the bulk-glass conc.) of the sodium ion plotted *vs.* distance in from the glass surface for glasses leached for 8 days. (⊙, ⊡) sodium ion profile for the N-glass, (△) conductivity profile for the N-glass. Dotted curve: Sodium-ion concentration profile for the Corning 015 glass.

than that for the L-glass over the entire hydration period of about 250 hr. The rates gradually decrease with time but a steady value is not reached. The silicon dissolution rate is much slower than the rate of ion-exchange for both glasses, the dissolution of the glass network stopping after a few hours of hydration. The ratio of the alkali-metal concentration in the leach solution, C, to that in the bulk glass, C_0, is plotted *vs.* the distance from the glass surface towards the bulk glass, in Figs. 3 and 4. The depth of etch was calculated from the amount of silicon found in the etch solution, the density of the glass, and the composition. The L-glass reported in Fig. 4 has been hydrated for 260 hr. Although there is a large scatter in the values, it may be concluded that the lithium ion concentration varies smoothly with distance inwards towards the glass bulk. For the N-glass, hydrated for about 200 hr, a much thicker ion-exchanged layer is found (see Fig. 3). For comparison, the sodium-ion concentration profile for the Corning 015 pH-responsive glass studied earlier is also shown. Although there is a small inflexion in the relative concentration–distance curve for the N-glass, a sharply distinguishable gel-layer is not obtained, in contrast to the situation for the pH-sensitive glass.

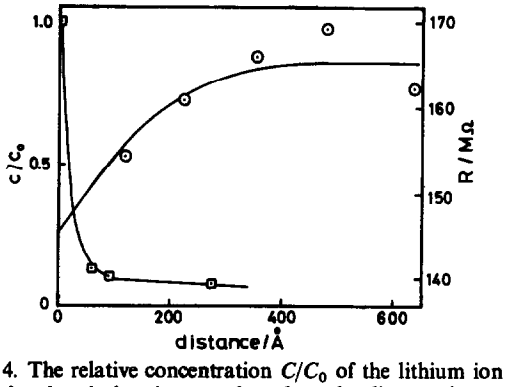

Fig. 4. The relative concentration C/C_0 of the lithium ion and the electrical resistance plotted *vs.* the distance in towards the L-glass. The glass was leached for 11 days. (⊙) lithium-ion profile, (⊡) electrical resistance profile.

The electrical resistivity, which is proportional to the slope of the resistance–distance curve in Fig. 4, is very high close to the surface of the L-glass but decreases rapidly with distance inwards, attaining a constant value near the bulk glass region.The conductivity of the N-glass was calculated as a function of distance. The shape of the conductivity–distance curve (Fig. 3) is similar to that of the sodium-ion concentration–distance curve. In comparison with the bulk glass, the entire ion-exchanged layer constitutes a low-conductivity region. Extremely low conductivity within the surface layers of a pH-responsive glass, however, is limited to a very thin region at the gel-layer/bulk-glass transition region.

In a few experiments it was found that the total electrical resistance of the glass electrodes increased with hydration time. The increase in the resistance is attributed to the surface layer of the glass, *i.e.*, the conductivity of the ion-exchanged layer decreases with time, as does the ion-exchange rate and no steady state is reached within weeks of hydration. Figure 5 shows that the response time of the L-glass increases with longer hydration. The response is considerably slower for an electrode hydrated for 16 days than for one hydrated for 2 days when the sodium-ion concentration is changed from 0 to 1*mM*. Similar curves were obtained when the concentration was changed from 1*mM* to 0·1*M*.

DISCUSSION

For a glass in contact with water, several processes may occur simultaneously, *e.g.*, (*i*) an ion-exchange between alkali-metal ions in the glass and hydrogen ions in the solution, (*ii*) a dissolution of the glass surface by the reaction between the network and water, (*iii*) a depolymerization process caused by the diffusion of water into the surface layer and its subsequent reaction with the glass structure.

The extent of the first process is indicated by the amount of alkali-metal ions leached from the glass into the solution (see Figs. 1 and 2). In comparison with the N-glass, the L-glass exhibits a very low degree of hydrogen ion–alkali-metal ion-exchange, and this can be attributed to the higher concentration of tervalent ions in the L-glass than that in the N-glass. Comparison with the Corning 015 glass shows the degree of ion-exchange to be in the order Corning > N-glass > L-glass. According to reports from other workers,[20,22,23] the hydrogen-ion selectivity decreases in the same order, *e.g.*, the L-glass is superior as a sodium-sensitive electrode. These results are in qualitative agreement with Eisenman's atomic model discussed above.

The rates of leaching of alkali-metal ions and silicon, evaluated as the slopes of the curves in Figs. 1 and 2, indicate that the rates of processes (*i*) and (*ii*) diminish with time and tend towards constant and low values (zero in the case of silicon). When the ion-exchange rate is also zero, a steady state may be assumed. Boksay *et al.*[9,24] showed that under these

conditions and provided that the glass surface is unaffected by depolymerization [process (*iii*)], an exponential profile for the change in alkal-metal ion concentration with distance in towards a potassium silicate glass is consistent with a concentration-independent diffusion coefficient for the ion-exchange process. If, on the other hand, a glass is influenced by process (*iii*), the alkali-metal ion concentration varies almost stepwise with the distance in towards the bulk glass. The profile reflects the formation of a structurally-transformed outer layer, the gel-layer, within which the interdiffusion coefficient may be constant. Within the gel-layer/bulk-glass transition region, however, the interdiffusion coefficient depends on concentration and passes through a pronounced minimum. Thus the sharpness of the inflexion in the concentration–depth curve may provide information on the extent of the depolymerization process in the formation of a surface layer. Comparison of the alkali-metal ion profiles in Figs. 3 and 4 indicates that the glasses are affected by secondary hydrolysis effects in the order L-glass < N-glass < Corning 015. This is in agreement with the well-known fact that the introduction of Al^{3+} increases the chemical durability of the glass. The tervalent aluminium ion replaces the quadrivalent silicon ion as the network former, and thus a negatively charged tetrahedral unit is formed. In this way alkali-metal ions are incorporated into the structure without the creation of terminal negatively-charged oxygen atoms. An increase in the concentration of aluminium ions in the glass will thus decrease the concentration of terminal oxygen atoms and accordingly increase the rigidity of the glass network. According to Boksay and Bouquet,[25] the reactivity of the silicate network decreases when the rigidity increases. They suggest that a five-coordinate silicon atom must be formed for the decomposition of the network to occur. The formation of such groups necessitates distortion of the tetrahedral unit, a process which will be restricted by increased rigidity. Moreover, Charles[26] has suggested that the concentration of terminal oxygen atoms may be of direct importance in the degradation of the glass network by water. The attack may be initiated by the reaction of water with terminal oxygen atoms according to

$$\equiv\text{Si-ONa} + \text{H}_2\text{O} \rightarrow \equiv\text{SiOH} + \text{Na}^+ + \text{OH}^-$$

The hydroxyl ion formed will be more effective than the water molecule in breaking the strong silicon–oxygen bond according to

$$\equiv\text{Si-O-Si}\equiv + \text{OH}^- \rightarrow \equiv\text{SiO}^- + \equiv\text{SiOH}$$

The correlation between the concentration of aluminosilicate sites and the chemical resistance of the net-work is verified by the present work: pH-responsive silicate glasses in contact with water develop typical gel-layers whereas the aluminosilicate glass network sensitive to alkali-metal ions is relatively unaffected by secondary hydrolysis effects, *e.g.*, by process (*iii*) described above.

The measurements of the electrical conductivity of the surface layers support the conclusions drawn above. For the Corning 015 glass, the conductivity of the gel-layer is higher than that of the bulk glass, indicating a less-rigid structure of the layer.[15] The drastic decrease in the conductivity near the gel-layer/bulk-glass boundary, however, indicates that the gel coating is a separate phase with properties different from the bulk. Some additional conclusions about the composition and the location of this barrier layer may be drawn from the distribution of the electrical conductivity of the aluminosilicate glasses (Figs. 3 and 4), in which the low-conductivity region is distributed over the entire ion-exchanged surface layer. The conductivity is at a minimum where the alkali-metal ion concentration is lowest, *i.e.*, where the hydrogen-ion concentration is at a maximum. It is supposed that the conductivity is lowest where the concentrations of water molecules and $\equiv\text{SiO}^-$ are low, since these positions should be the only acceptor sites for the proton. The introduction of aluminium into a silicate network restricts the water influx into the glass and the interdiffusion of protons and alkali metal ions is restricted by a slow diffusion of protons.

In pH-sensitive glasses, the water concentration is high just inside the gel-layer/solution boundary but it decreases towards the gel-layer/bulk-glass boundary.[27] There is a thin region just in front of the latter boundary where both the water and the $\equiv\text{SiO}^-$ concentrations become low, *i.e.*, where the $\equiv\text{SiOH}$ concentration is high. This is the low-conductivity region which has been experimentally verified for many silicate glasses.[12,15] This structure is also compatible with Baucke's results,[17] and is also consistent with surface-conductivity measurements made along leached glass rods.[28]

The sodium-ion selective L-glass exhibits a relatively slow response which becomes even slower when the glass is leached for a long time (Fig. 5). During the leaching, lithium ions in the glass are replaced by hydrogen ions from the solution. For the leached glass, a change in the sodium-ion activity in the solution will affect the ion-exchange equilibrium

$$\text{H}^+_{\text{glass}} + \text{Na}^+_{\text{soln}} \rightleftharpoons \text{H}^+_{\text{soln}} + \text{Na}^+_{\text{glass}}$$

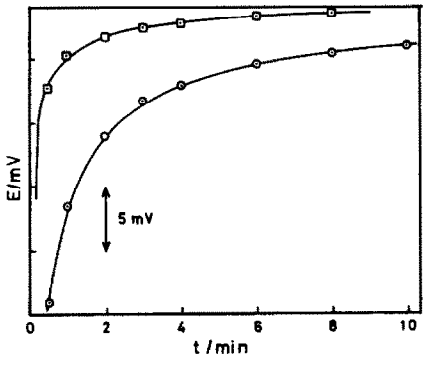

Fig. 5. The sodium-ion response of the L-glass. The sodium ion concentration in a $2 \times 10^{-4}M$ NH_4HCO_3 solution was changed from 0 to $1mM$. The electrodes had been previously hydrated for 2 days (□) or 16 days (○).

The time required for this reaction to attain a steady state is inversely proportional to the interdiffusion coefficient and directly proportional to the square of the distance.[29,30] During the leaching of the glass, and at a fixed distance within the solution/glass boundary, the former parameter will decrease as a consequence of the gradual increase in the proton concentration, while the thickness of the protonated layer increases. The changes in the composition of the surface layer occur very slowly. Thus, as shown in Fig. 5 the electrode response degrades slowly with increasing leaching time.

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ANWENDUNG VON IONENAUSTAUSCHVERFAHREN ZUR BESTIMMUNG VON SPURENELEMENTEN IN NATÜRLICHEN WÄSSERN—VIII

MOLYBDÄN

J. KORKISCH, L. GÖDL und H. GROSS

Analytisches Institut der Universität, Abteilung: Rohmaterialanalyse nuklearer Brennstoffe, Währingerstraße 38, A-1090 Wien, Österreich

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Zusammenfassung—Eine Methode wird beschrieben, die es ermöglicht ppM-Mengen Molybdän aus natürlichen Wässern zu isolieren und der Endbestimmung mittels Atomabsorptionsspektrophotometrie zugänglich zu machen. Die Wasserprobe wird mit Salzsäure angesäuert, filtriert und nach Zugabe von Kaliumthiocyanat und Ascorbinsäure durch eine Säule des stark basischen Anionenaustauschers Dowex-1 X8 (Thiocyanatform) fließen gelassen. Dabei wird das Molybdän als Thiocyanatkomplex quantitativ adsorbiert und kann anschließend durch Anwendung von 2*M* Perchlorsäure–1*M* Salzsäure wieder vollständig eluiert werden. Nach dem Eindampfen des Eluats wird das Molybdän atomabsorptionsspektrophotometrisch bestimmt. Die Methode wurde zur Bestimmung des Molybdäns in österreichischen Gewässern herangezogen wobei Gehalte im Konzentrationsbereich von 0,18 bis 1,4 ppM Molybdän gefunden wurden.

Zur Bestimmung des Molybdäns in natürlichen Wässern, inklusive Meerwasser, werden in der Literatur mehrere Methoden beschrieben, die auf Spektrophotometrie[1–18] und Atomabsorptionsspektrophotometrie[19–22] beruhen. Da es nur bei Anwendung jener spektrophotometrischer Verfahren, die auf katalytisch durch Molybdän induzierte Oxydations–Reduktionsreaktionen basieren,[14–18] möglich ist, das Molybdän direkt in den Wasserproben zu bestimmen, ist es meistens erforderlich eine der Endbestimmung vorangehende Anreicherung des Molybdäns durchzuführen.

Als Isolierungsmethoden werden am Häufigsten die Lösungsmittelextraktion[1,8–13,19,21,22] und die Mitfällung[1–4,6,7,11–13] des Molybdäns herangezogen. Die dazu verwendeten Extraktionssysteme sind: Dithiol (oder Diacetyldithiol[13])–Chloroform[8] (oder Isoamylacetat[9] bzw. Butylacetat[10–12]), 8-Hydroxychinolin–Methylpentylketon[19] (oder Hexon[22]), Benzoin-α-oxim–Chloroform,[9] Ammoniumtetramethylendithiocarbamat–Methylpentylketon,[19] Ammoniumpyrollidin-1-carbodithioat–Hexon[21] und Thiocyanat–Butanol–Chloroform.[1] Einige dieser Reagenzien wie z.B. Dithiol und Thiocyanat sind gleichzeitig auch empfindliche Farbreagenzien, so daß das Molybdän nach Extraktion in die organische Phase direkt in dieser spektrophotometrisch bestimmt werden kann.

Die zur Mitfällung des Molybdäns aus Wässern benützten Verbindungen sind: hydratisiertes Mangandioxid,[1,3,11–13] Eisen(III)-hydroxid,[1,6] Thoriumhydroxid,[4] Benzoin-α-oxim[2] und Aluminiumoxinat.[7] Nach der Mitfällung des Molybdäns wird dann häufig eine weitere Abtrennung des Molybdäns mittels Lösungsmittelextraktion durchgeführt.[1,11–13]

Andere zur Abtrennung des Molybdäns aus Wässern benützte Verfahren beruhen auf Adsorption des Molybdäns auf Chitosan, *p*-Aminobenzylzellulose oder Diäthylaminoäthylzellulose[20] bzw. auf Kationenaustauschern wie Zeo-Karb 225[13] oder Chelex 100.[10] Auch ein Adsorptionsverfahren beruhend auf Kolloidflotation mit Natriumdodecylamin als Surfaktant kann zur Isolierung des Molybdäns herangezogen werden.[6]

In früheren Arbeiten dieser Reihe werden Methoden beschrieben, die es gestatten, die in natürlichen Wässern vorhandenen Spurenelemente Kobalt,[23,24] Cadmium,[24] Uran[24] und Zink,[25] ohne vorangehendes Eindampfen der Analysenproben, durch Anwendung von Anionenaustausch in Thiocyanatsystemen abzutrennen und der spektrophotometrischen,[23,24] fluorometrischen[24] oder atomabsorptionsspektrophotometrischen[25] Endbestimmung zugänglich zu machen. Da auch Molybdän analog zu den oben genannten Elementen einen Thiocyanatkomplex bildet, kann dieses Element, wie in der vorliegenden Arbeit beschrieben wird, direkt aus der Wasserprobe auf dem stark basischen Anionenaustauscher Dowex-1 quantitativ adsorbiert und nach der Elution atomabsorptionsspektrophotometrisch bestimmt werden.

EXPERIMENTELLER TEIL

Lösungen und Reagenzien

Ionenaustauscher. Siehe Beitrag VI dieser Reihe.[25]

Molybdän-Standardlösungen. Ausgehend von Ammoniummolybdattetrahydrat [$(NH_4)_6Mo_7O_{24}.4H_2O$] wurde eine Stammlösung hergestellt die 1,0 mg Mo pro ml 6*M* Salzsäure enthielt. Daraus wurden, durch

Verdünnen mit 6*M* Salzsäure, Lösungen mit Molybdängehalten im Konzentrationsbereich von 1 bis 100 ppm hergestellt.

Vorbehandlungslösung. Siehe Beitrag I dieser Reihe.[23]

Andere Reagenzien. Ferner wurden verwendet: Kaliumthiocyanat, ein Säuregemisch das 2*M* an Perchlorsäure und 1*M* an Salzsäure ist, Schwefelsäure (1 + 1), 6*M* Salzsäure und eine Anzahl der in früheren Arbeiten[24,26] angegebenen Reagenzien.

Apparaturen

Zur Bestimmung des Molybdäns wurde ein Perkin-Elmer 303 Atomabsorptionsspektrophotometer verwendet, und zwar unter Anwendung der in einer früheren Arbeit[26] angegebenen instrumentellen Einstellungen.

Die Ionenaustauschtrennungen wurden in Austauschersäulen eines in einer früheren Arbeit[27] angegebenen Typs ausgeführt.

Bestimmung der Verteilungskoeffizienten

Die Gleichgewichtsverteilungskoeffizienten (K_d-Werte) des Molybdäns wurden unter Anwendung der Batch-Methode bestimmt.[28]

Vorbereitung der Wasserprobe

Die Wasserprobe wird, wie in Beitrag IV dieser Reihe[24] beschrieben, vorbereitet, wobei allerdings nicht 20 g sondern nur 10 g Kaliumthiocyanat pro Liter zugesetzt werden. Sofort nach der Probenahme wurde die Wasserprobe (in einer Polyäthylenflasche) angesäuert und oft erst nach einigen Tagen zur Analyse vorbereitet. Während dieser Zeit war keine Adsorption des Molybdäns an den Gefäßwänden zu beobachten.

Ionenaustauschtrennung

Die vorbereitete Wasserprobe (=Sorptionslösung) wird durch eine mit 4 g des Anionenaustauscherharzes Dowex-1 X8 beschickte Säule (die vorher mit 50 ml der Vorbehandlungslösung gewaschen wurde), mit einer dem Gegendruck des Harzbettes entsprechenden Geschwindigkeit (etwa 120 ml/Stunde) fließen gelassen. Anschließend wird zuerst mit 10 ml dest. Wasser und dann mit 50 ml 6*M* Salzsäure nachgewaschen. Hierauf wird das Molybdän mit 150 ml eines Säuregemisches, welches 2*M* an Perchlorsäure und 1*M* an Salzsäure ist, eluiert (Molybdäneluat).

Quantitative Bestimmung des Molybdäns

Das Molybdäneluat wird auf einem Sandbad oder unter einer Infrarotlampe zur Trockne eingedampft, der Rückstand in 5 ml Schwefelsäure (1 + 1) aufgenommen und die Lösung 3 Stunden (oder länger) am Wasserbad erhitzt, um das Molybdän vollständig in Lösung zu bringen. Danach wird das Molybdän, genauso wie in einer früheren Arbeit[26] angegeben, in Gegenwart von Natriumsulfat atomabsorptionsspektrophotometrisch bestimmt. Beim Eindampfen des 150 ml Molybdäneluate waren keine Molybdänverluste zu verzeichnen.

RESULTATE UND DISKUSSION

Die in der Arbeitsvorschrift beschriebene Methode zur Abtrennung des Molybdäns aus Proben natürlicher Wässer beruht darauf, daß dieses Element, wie bereits früher[24] erwähnt wurde, mit Thiocyanationen einen stabilen Komplex bildet, der aus verdünnt salzsaurer Lösung und in Gegenwart von Ascorbinsäure sehr stark vom Anionenaustauscher Dowex-1 adsorbiert wird. Unter den angegebenen Bedingungen wurde für Molybdän ein Verteilungskoeffizient von $> 5 \times 10^3$ ermittelt, der sowohl bei Zunahme der Salzsäurekonzentration von 0,1*M* auf 1,0*M* als auch der Thiocyanatkonzentration von 5 g auf 20 g KSCN pro Liter keine meßbaren Änderungen erfährt.

Tabelle 1. Resultate von Molybdänbestimmungen im Wiener Trinkwasser

Volumen (in Liter) der zur Analyse verwendeten Wasserprobe*	Molybdängehalt, $\mu g/l$
0,5	nicht meßbar
1,0	nicht meßbar
2,0	<0,3
3,0	<0,3
5,0	<0,2
5,0	0,18†

* Die Probenahme erfolgte am 9. September 1974 im Analytischen Institut der Universität Wien.

† Nach Abzug einer der Wasserprobe zugesetzten Standardmenge von 10 μg Mo.

Auf Grund dieses sehr hohen Verteilungskoeffizienten kann das Molybdän auch aus einem sehr großen Volumen einer Wasserprobe quantitativ abgetrennt werden. Dies ist von großer Bedeutung, da natürliche Wässer in der Regel nur äußerst geringe Molybdängehalte aufweisen. Wie aus den in Tabelle 1 gezeigten Ergebnissen ersichtlich, ist bei Anwendung der im experimentellen Teil beschriebenen Arbeitsmethode zur Trinkwasseranalyse erst dann das Molybdän nachweisbar wenn das Volumen der Wasserprobe 2 Liter oder größer ist.

Wie aus Tabelle 2 ersichtlich ist, ermöglicht es der hohe Verteilungskoeffizient des Molybdäns auch relativ große Molybdänmengen am Austauscher zu adsorbieren.

Eine weitere Folgeerscheinung, die sich aus der sehr starken Adsorption des Molybdäns ergibt ist, daß die Molybdänabtrennung durch Metallionen, die als anionische Thiocyanatkomplexe am Harz adsorbierbar sind,[23–25] nicht gestört wird. Wie aus Tabelle 3 ersichtlich, ist selbst in Gegenwart von 50 mg Eisen keine Verdrängung des Molybdäns zu beobachten. Von den in dieser Tabelle angeführten, koadsorbierten Elementen werden bei dem der Sorption des Molybdäns nachfolgenden Waschen des Anionenaustauschers mit 6*M* Salzsäure nur Kupfer und Kobalt teilweise entfernt. Die Restmengen dieser Elemente

Tabelle 2. Einfluß der Molybdänkonzentration auf die Molybdänausbeute

Der Wasserprobe* zugesetzte Molybdänmenge, μg	Im Eluat wiedergefundene Molybdänmenge, μg
0	nicht meßbar
50	54
100	100
500	515
1000	1020
2000	2060

* Als Wasserprobe wurde jeweils 1 Liter Wiener Trinkwasser verwendet und unter Anwendung der Arbeitsvorschrift analysiert.

Tabelle 3. Einfluß von koadsorbierten Fremdionen auf die Abtrennung des Molybdäns

Der Wasserprobe* zugesetztes Fremdion	Molybdängehalt des Eluats, μg
Fe(III) (50 μg)	98
Fe(III) (500 μg)	98,5
Fe(III) (5000 μg)	101
Fe(III) (50·000 μg)	101
Hg(II) (5000 μg)	97
Ag(I) (500 μg)	100
Zn(II) (5000 μg)	104
Co(II) (5000 μg)	97,5
Cu(II) (5000 μg)	100
V(V) (5000 μg)	104
Cd(II) (5000 μg)	101
UO_2(II) (5000 μg)	105
Ohne Zusatz	99

* Als Wasserprobe wurde jeweils 1 Liter mit 100 μg Molybdän versetztes Wiener Trinkwasser verwendet und unter Anwendung der Arbeitsvorschrift analysiert.

Tabelle 4. Resultate von Molybdänbestimmungen in einer stark salzhaltigen Lösung (Einfluß von hohen Chlorid- und Sulfationenkonzentrationen auf die Molybdänadsorption)

Der Wasserprobe* zugesetzte Molybdänmenge, μg	Im Eluat wiedergefundene Molybdänmenge, μg
0	Nicht meßbar
5	4,85
5	5,1
10	9,85
10	10,4
100	100
100	104

* Zur Anwendung gelangte jeweils 1 Liter Wiener Trinkwasser welches 32 g NaCl und 6,8 g $MgSO_4 . 7H_2O$ enthielt. Diese Lösung weist angenähert dieselbe Zusammensetzung wie Meerwasser auf, und zwar hinsichtlich ihrer Chlorid- und Sulfationenkonzentration (19,4 g Cl^- und 2,7 g SO_4^{2-} pro Liter).

sowie alle anderen koadsorbierten Ionen werden zusammen mit dem Molybdän mittels 2*M* Perchlorsäure–1*M* Salzsäure eluiert (siehe Arbeitsvorschrift), rufen jedoch keinerlei Störungen bei der atomabsorptionsspektrophotometrischen Molybdänbestimmung hervor.

Wie die in Tabelle 4 gezeigten Resultate zeigen, tritt auch in Gegenwart großer Chlorid- und Sulfatkonzentrationen keine Verdrängung des am Harz als Thiocyanatkomplex adsorbierten Molybdäns ein. Diese Tatsache könnte dazu benützt werden, um das Molybdän aus Meerwasserproben zu isolieren und der Messung mittels Atomabsorption zugänglich zu machen.

Untersuchungen hinsichtlich des Elutionsverhaltens des mit Säuren nur schwer zerstör- bzw. -eluierbaren Molybdänthiocyanatkomplexes ergaben die in Tabelle 5 gezeigten Resultate. Aus diesen ist ersichtlich, daß eine quantitative Elution des Molybdäns mittels Perchlorsäure nur möglich ist wenn das Harzbett vorher mit 6*M* Salzsäure behandelt wird, wodurch wahrscheinlich eine "Lockerung" des adsorbierten Molybdäns eintritt. Die zur Elution des als Thiocyanatkomplex adsorbierten Molybdäns von anderen Autoren[29–31] empfohlenen alkalischen Lösungen wie z.B. 0,5*M* NaCl–0,5*M* NaOH erwiesen sich als weniger geeignet. Infolge der großen Stabilität des Molybdänthiocyanatkomplexes war es auch bei Anwendung von methanolischer Salzsäure[26] unmöglich das Molybdän quantitativ zu eluieren.

Von den in der Tabelle 5 angeführten Elutionsmitteln, die eine quantitative Elution des Molybdäns ermöglichen, wurde das System 2*M* $HClO_4$–1*M* HCl näher untersucht, und zwar hinsichtlich der zur vollständigen Elution bestimmter Molybdänmengen erforderlichen Volumina an Elutionsmittel. Die Resultate dieser Elutionsversuche werden in Tabelle 6 gezeigt. Aus ihnen geht hervor, daß mit dem in der Arbeitsvorschrift angegebenen Elutionsmittelvolumen von 150 ml selbst 1 mg Molybdän quantitativ eluierbar ist.

In der Tabelle 7 werden die Ergebnisse von Molybdänbestimmungen in Wasserproben aus einigen österreichischen Gewässern gezeigt. Diese Analysen wurden unter Anwendung der in der Arbeitsvorschrift beschriebenen Methode durchgeführt, und zwar wurde das Molybdän sowohl aus 1 Liter Wasserproben (nach Zugabe einer bekannten Molybdänstandardmenge) als auch aus 1,8 bis 2,8

Tabelle 5. Elutionsverhalten des als Thiocyanatkomplex auf Dowex 1 (4 g Säule) adsorbierten Molybdäns

Lockerungsmittel	Elutionsmittel	Molybdängehalt des Eluats, μg
50 ml 1*N* H_2SO_4	100 ml 1*M* $HClO_4$	460
50 ml 1*N* H_2SO_4	100 ml 2*M* $HClO_4$	390
50 ml 1*N* H_2SO_4	100 ml 4*M* $HClO_4$	410
50 ml 6*M* HCl	100 ml 1*M* $HClO_4$	850
50 ml 6*M* HCl	100 ml 2*M* $HClO_4$	980
50 ml 6*M* HCl	100 ml 4*M* $HClO_4$	1050
50 ml 6*M* HCl	150 ml 2*M* $HClO_4$–2*M* HBr	64
50 ml 6*M* HCl	150 ml 2*M* $HClO_4$–1*M* HCl	1020

* Zur Analyse gelangte jeweils 1 Liter mit 10 ml konz. Salzsäure angesäuertes Wiener Trinkwasser das 10 g Kaliumthiocyanat, 5 g Ascorbinsäure und 1 mg an zugesetzten Molybdän enthielt.

Tabelle 6. Elution des Molybdäns mit 2*M* $HClO_4$–1*M* HCl

Eingesetzte Molybdänmenge, *µg*	Volumen an Elutionsmittel, *ml*	Molybdängehalt des Eluats, *µg*
100	50	65
100	100	94
100	150	99
100	200	104
1000	50	590
1000	100	950
1000	150	1020
1000	200	1020

Literproben am Anionenaustauscher angereichert. Wie ein Vergleich der in Kolonnen A und B angeführten Molybdängehalte zeigt, besteht in allen Fällen eine relativ gute Übereinstimmung der Werte woraus folgt, daß mittels der verwendeten Methode eine quantitative Abtrennung des Molybdäns ermöglicht wird. Dieses Anreicherungsverfahren eignet sich demnach sehr gut zur Bestimmung des Molybdäns in natürlichen Wässern, da diese Molybdängehalte aufweisen, welche bei direkter Anwendung der Atomabsorptionsmethode nicht bestimmbar sind.

Bei Anwendung von größeren Volumina der Wasserproben (z.B. 10–20 Liter) wäre es möglich die Genauigkeit der Molybdänbestimmungen wesentlich zu erhöhen als dies bei Verwendung der in Tabelle 7 angegebenen Volumina der Fall ist (die gemessenen Absorptionen waren sehr gering). Werden jedoch derart große Wasservolumina der beschriebenen Abtrennungsmethode unterworfen, so ist ein zu hoher Reagenzienbedarf erforderlich, der die Analysenkosten wesentlich erhöht.

Zur Molybdänbestimmung in den Eluaten konnten die sehr empfindlichen katalytischen Methoden nicht herangezogen werden, da diese durch miteluiertes Eisen und Kupfer stark gestört werden.

Danksagung. Dem Fonds zur Förderung der wissenschaftlichen Forschung wird an dieser Stelle für die Bereitstellung der zur Durchführung der beschriebenen wissenschaftlichen Arbeit erforderlichen Mittel bestens gedankt.

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Tabelle 7. Resultate von atomabsorptionsspektrophotometrisch bestimmten Molybdängehalten österreichischer Wasserproben

Probenbezeichnung und Datum der Probenahme	Molybdängehalt, *µg/l.* A	B
131. Kalwang, Leitnerbach nördlich des Ortes Treglwang, westlich des Schoberpasses, Steiermark; 31.7.1974.	1,4	1,5 (2,8)
126. Radstatt, Forstaubach 2 km vor Einmündung in die Enns, Ennstal, Salzburg; 16.8.1974.	0,5	0,5 (2,8)
132. Trofaiach, Rötzbach bei der Felsenge im Rötzgraben, oberhalb Trofaiach, Steiermark; 29.7.1974.	1,0	0,9 (2,6)
126. Radstatt, Schreinbach 1 km westlich Forstau an der Straße Radstatt-Forstau, Salzburg; 16.8.1974.	0,5	0,4 (2,8)
126. Radstatt, Forstaubach 5 km südlich Forstau, Schladminger Tauern, Salzburg; 16.8.1974.	1,4	1,2 (2,8)
132. Trofaiach, Laintalbach 7 km oberhalb Einmündung bei Gmeingrube, unterhalb Trofaiach, Steiermark; 29.7.1974.	1,4	1,2 (1,8)
105. Neunkirchen, Göstritzbach 1 km oberhalb Göstritz bei Straße nach Maria-Schutz, Niederösterreich; 7.7.1974.	1,1	1,0 (2,7)
130. Oberzeiring, Lorenzenbach 500 m oberhalb des Ortes St. Lorenzen im Paltental, westlich Trieben, Steiermark; 31.7.1974.	1,0	0,9 (2,7)
104. Mürzzuschlag, Dürrgrabenbach 1 km oberhalb Steinhaus am Semmering, Steiermark; 7.7.1974.	1,1	1,0 (2,5)
127. Schladming, Giglachbach bei Einmündung in den Obertalbach, Obertal, Schladming, Steiermark; 16.8.1974.	1,0	1,0 (2,8)

A = Molybdängehalt ermittelt nach Abtrennung des Molybdäns aus 1 Liter Wasserprobe und nach Abzug einer als Spike vor der Ionenaustauschtrennung zugesetzten Molybdänmenge von 10 µg Mo.

B = Molybdängehalt ermittelt nach Abtrennung des Molybdäns mittels Anionenaustausches. Die Zahl in der Klammer gibt das Volumen (in Liter) an, aus dem das Molybdän abgetrennt wurde.

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A MEASURE FOR ASSESSING CERTIFIED REFERENCE ORES AND RELATED MATERIALS

R. SUTARNO and G. H. FAYE

Mineral Sciences Laboratories, Canada Centre for Mineral and Energy Technology, Department of Energy, Mines and Resources, Ottawa, Canada

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Summary—Experience in the certification of a number of Canadian reference ores and related materials has shown that their quality or usefulness in particular analytical applications can be evaluated objectively in terms of a so-called certification factor. This factor is defined as the ratio of the relative confidence interval of the interlaboratory consensus value for a selected element, expressed as a percentage, to the mean of the within-laboratory coefficient of variation. It is proposed that for a material to be acceptable (certifiable), its certification factor(s) must be $\leqslant 4$.

Since its formation in 1970, the Ores Task Force of the Canadian Certified Reference Materials Project (CCRMP) has prepared and certified nine metallic ores or related materials. In all, "recommended" or "certified" values and their confidence limits have been assigned for seventeen elements. The statistical and other criteria that were used in arriving at these values are described in detail in the documents that are supplied on purchase of each reference.[1–8]

At the outset, the Ores Task Force did not have an objective guide or criterion for assessing the recommended values, and their confidence limits, for a particular element. Therefore, the usefulness of the reference material was judged from a general knowledge of the "state of the art" for the determination of the selected element and how most laboratories would use the materials. However, now that a large amount of information has been accumulated in the interlaboratory programmes, it has become apparent that a "certification factor" can be established, and this permits an objective evaluation to be made of the acceptability of consensus values for certification purposes.

It is desirable to show how this "certification factor" was derived, by describing the nature and the results of CCRMP interlaboratory programme that have led to the certification of a number of reference ores and related materials. Some theoretical considerations are required to put the subject into a suitable context.

THEORETICAL CONSIDERATIONS

Homogeneity of powdered reference materials

The most important property of any reference material (RM) is its homogeneity with respect to the constituents of interest. The homogeneity of RM can be considered as twofold: the long-range homogeneity, *i.e.*, the reproducibility between units (bottles) and the short-range homogeneity, *i.e.*, the homogeneity within each bottle. The long-range homogeneity is essential for any RM; however, the importance of the degree of the short-range homogeneity depends on the use of the material. If it is used for the standardization of an analytical method that requires a relatively large quantity of subsample such as a fire-assay method, the short-range homogeneity is relatively less important than the long-range homogeneity.

In the case of reference ores, homogenization is achieved by grinding and blending; two opposing factors ensue from this process. Statistically, the finer the particle size, the smaller is the subsample required for a desired sampling precision. Thus the finer the material the greater is the probability that it can be made homogeneous. However, from the mineralogical point of view, the finer the material the greater is the chance that it will separate into its mineral constituents, especially if the liberated ore minerals differ substantially in density from those of the gangue. The balance between these factors limits the degree to which the reference ores can be homogenized and this is a principal reason why it is theoretically impossible to assess the "true value" for a selected element or other characteristic. Therefore, the objective of homogenization is to prepare a RM that is sufficiently homogeneous to be useful in a reasonable number of common analytical applications.

Errors associated with characterization procedures

Considering these practical limitations, the characteristic property of an RM (*e.g.*, value of a selected element) can be expressed by its mean and its variance. Because, in most cases, there is no perfect analytical method for the selected element(s), another error will be introduced owing to the imperfection of the method. This error can also be treated in two

parts, a systematic error (the bias) and a random error (the variance).

Ideally, the characterization procedure should be chosen so as to minimize both the bias and the variance; however, technological and economic limitations dictate that a choice be made. This choice should be optimized with respect to the intended use of the RM. For example, if it is intended for use in internal (process) calibration, the bias is relatively unimportant as long as the variance is minimized. However, if the RM is to be used for contractual purposes, in which the "absolute" value is desired, the bias becomes very important.

Choice of interlaboratory characterization schemes

Theoretically, there are two extreme approaches that can be used for certifying a RM. The first is to have the material analysed by a single analyst, using the "best" method available. This method would yield a result with high precision but with unknown bias. The second extreme involves an interlaboratory programme in which the participating laboratories are requested to choose the analytical method(s) that they consider best for the purpose. The result of this type of programme will be most likely to have an acceptable bias, but will have a greater variance.

The choice between these two extreme procedures, or their combination, depends on the intended use of the RM and the type of interlaboratory programmes that can be arranged. The certified reference ores prepared in the CCRM Project are intended for use both by us and by others; therefore, an interlaboratory scheme is used to characterize them. It is to be noted that in these interlaboratory programmes a relatively wide variety of analytical methods is used by the participating laboratories to provide results for certification for each element. This scheme was modified somewhat, in that certain laboratories, within the authors' institution, were requested to carry out more extensive work on each material than that done by other laboratories. Consequently, the contributions of the former carry more weight than those of the latter.

Definition of consensus value

For any laboratory it is assumed that the bias, B_i, is constant; it can only be determined, in theory, by analysing a large number of replicates and knowing the "true value" (μ) for the selected element. Assuming that all the participating laboratories are equally competent to perform a particular analysis, it is also reasonable to assume that B_i is normally distributed with a mean of B_m and variance ω^2. We can now define a "consensus" value to be:

$$c = \mu + B_m$$

and c is the best estimate of the "true value" that can possibly be obtained if a large number of laboratories are each willing to supply a large number of replicate results. With respect to the consensus value, the bias B_i is normally distributed, has an expected value of 0 and variance ω^2, where ω^2 can be defined as the interlaboratory variance. The following model is considered more realistic however:

$$E[x] = c \tag{1}$$

$$V[x] = \delta^2 + \omega^2 + \sigma^2 \tag{2}$$

where x = measured value of a characteristic; $E[x]$ = expected value of x; $V[x]$ = variance of x; δ^2 = inhomogeneity variance; ω^2 = between-laboratory variance; σ^2 = within-laboratory variance.

The principal purpose, then, of an interlaboratory certification programme is to prepare a homogeneous material and to obtain a consensus value, c, having sufficiently narrow confidence limits for the reference material to be useful in a number of realistic analytical applications. When this is the case the consensus value becomes the "recommended" or "certified" value. In this regard, we propose, subsequently in this paper, the use of a quality criterion, or "certification factor", for evaluating objectively the suitability of a reference material for a particular application.

Although this paper deals mainly with programmes to certify base-metal ores, the results of other CCRMP programmes to certify materials rich in precious metals are also discussed.

THE CCRMP INTERLABORATORY PROGRAMME FOR ORES

Physical preparation and testing for homogeneity before distribution

The ore, or related product, is ground in a ball-mill, usually to 200 mesh. The powder is then blended in a rotary conical-shell blender for about 8 hr. Six samples are taken from various parts of the blender and these are tested for homogeneity by X-ray fluorescence determination of one or more elements of importance; five replicate determinations are performed for each sample. A one-way analysis of variance (ANOVA) technique[9] is used to detect the possible differences between samples. If the result shows that the difference is not detectable at the 5% level of significance, the bulk ore is bottled for storage. Randomly selected samples (bottles) are then analysed by chemical methods to confirm the degree of homogeneity.

Distribution of samples to the participating laboratories

The material having been found suitably homogeneous, *i.e.*, that δ is insignificant with respect to σ in equation (2) on the basis of an in-house analyses, the sample is then distributed to the participating laboratories. It is desirable to confirm the insignificance of δ on the basis of the pooled (average) within-laboratory σ. For this reason, two samples, taken at random, are sent to each participating laboratory. Five replicate determinations are requested for each bottle for each element; this number of replicate determinations is considered to strike a balance between excessive work and the required degrees of freedom for the estimates.

Table 1. Summary[4] of the *t*-tests on results between bottles for each laboratory for reference ore HV-1

Lab. No.	Copper	Molybdenum	Lab. No.	Copper	Molybdenum
1	A	R	13	A	A
2	A	A	14	R	A
3	A	A	15	A	R
4	A	A	16	A	A
5	A	A	17	A	A
6	A	R	18	A	A
7	A	A	19	A	A
8	A	A	20	—	—
9	A	A	21	A	A
10	A	A	22	A	A
11	A	A	23	A	A
12	A	A			

A = Null hypothesis accepted, *i.e.*, there is *no* evidence of inhomogeneity.
R = Null hypothesis rejected, *i.e.*, there *is* evidence of inhomogeneity.

Subsample size

The long-range inhomogeneity is influenced by the completeness of blending and the possible effects of the bottling operations. Once the powder has been bottled this factor is fixed and its magnitude can be estimated from the results submitted by the participating laboratories for each of their two bottles. In most cases the magnitude of the within-laboratory variance due to short-range inhomogeneity cannot be estimated experimentally because it cannot be separated from the total analytical error. Previous workers[10,11] have suggested methods of estimating this quantity by using formulae based on the binomial distribution which assume that the material is a mixture of two types of small spherical particles of uniform size and density and which differ only in their concentration of the element of interest. From this estimate the required subsample size is calculated.

While this method is mathematically neat, the basic assumptions are not justified for ore samples. Even if a particular element occurs in a single mineral, the proportion of that mineral in each particle will not be constant. There is also a practical limit to the subsample size for each analytical method; in some cases increasing the subsample size could make the method impractical. Moreover, because the subsampling error is always a part of the total analytical error there is no need to estimate its magnitude. Obviously, however, mixing the contents of the bottle before removal of the subsample will reduce the total error. It is to be noted that in equation (2) σ includes the subsampling error.

In certain cases where the subsampling error is considered to be potentially important (*e.g.*, gold ores), the minimum subsample size, based on analytical and statistical considerations, is suggested to the participating laboratories.

Using submitted results to test homogeneity of reference materials

The initial hypothesis is that the RM is homogeneous, *i.e.*, the between-bottle variance is insignificant with respect to the within-bottle variance. If all the participating laboratories comply exactly with the experimental design, *i.e.*, submit five replicate results for each of the two bottles, the between-laboratory variance can conveniently be estimated by the two-way ANOVA technique. However, there are always inconsistencies in the numbers of results collected from the participants. For this reason, the means of the results reported by each laboratory for each bottle are compared by a *t*-test method at the 5% level of significance. Graphically, the means of the results for the first bottle are plotted against the means of the results for the second. The estimated standard deviations for the two sets of results are represented by cross-bars of corresponding length through these points. Some typical results of these *t*-tests and their graphical representation are illustrated in Table 1 and in Figs. 1 and 2.

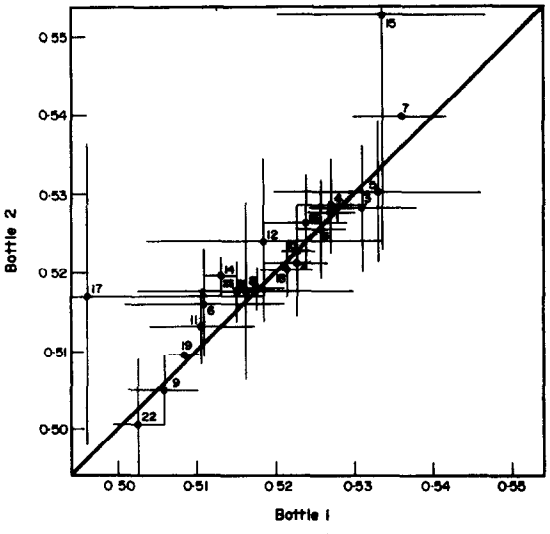

Fig. 1. Average copper analyses (%) for reference ore HV-1 from each participating laboratory.[4] (The crosses indicate one standard deviation on either side of the average for both bottles analysed.)

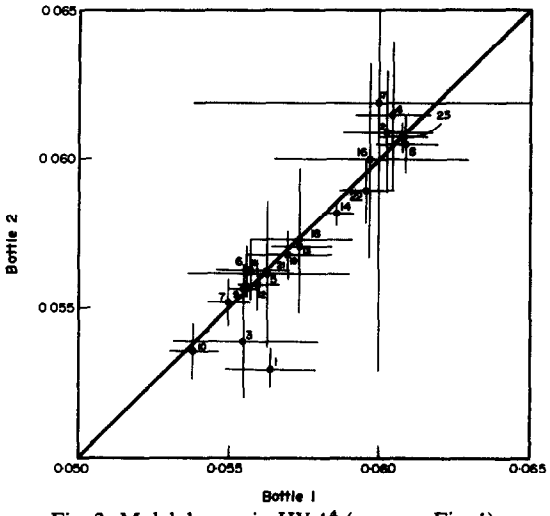

Fig. 2. Molybdenum in HV-1[4] (same as Fig. 1).

Table 2 shows the long-term record of this test, and of 584 tests conducted to date, a total of 61 rejected the hypothesis. This rejection represents about 10% of the total tests, which is higher than the 5% expected. At present, it is not possible to identify the cause of the high rejection rate; it could be a real indicator of inhomogeneity in the RM's, or it could be due to a slight deviation of the results from normal distribution.

The distribution of the analytical results

All the results reported by the participating laboratories for each selected element in a particular reference material are combined and the cumulative distribution of these results is shown graphically in a document supplied with samples of each RM. To characterize the frequency distribution of these results, the following statistical parameters are computed: median, mean, standard deviation, coefficient of variation (relative standard deviation), skewness factor and kurtosis coefficient. The skewness factor is defined as $\alpha_3 = m_3/\sqrt{m_2^3}$ where α_3 is a measure of the symmetry of the frequency distribution curve, and the kurtosis coefficient is defined as $\alpha_4 = m_4/m_2^2$ where α_4 is a measure of the sharpness of the peak of the curve. For a normal distribution the values of α_3 and α_4

Table 2. Long-term results of t-test on the between-bottle variation with respect to the within-bottle variation

Certified reference ore	Elements	No. of t-tests	No. of null hypotheses rejected	Null hypotheses rejected, %
PR-1	Mo	18	1	6
	Bi	16	3	19
	Fe	16	1	6
	S	17	1	6
MP-1	Zn	17	2	12
	Sn	15	1	7
	Cu	15	4	27
	Pb	17	1	6
	Mo	15	1	7
	W	10	1	10
	In	9	2	22
	Bi	11	0	0
	As	17	2	12
	Ag	13	1	8
HV-1	Cu	22	1	4
	Mo	22	3	14
SU-1	Ni	25	2	8
	Cu	25	2	8
	Co	24	3	12
UM-1	Ni	24	1	4
	Cu	24	3	12
	Co	24	3	12
KC-1	Zn	24	3	13
	Pb	30	5	17
	Cu	29	6	21
	Sn	22	2	9
	Ag	27	1	4
PTA	Pb	7	1	14
PTC	Ag	2	1	50
	Au	6	1	17
	Pd	8	1	12
	Pt	6	1	17
	Rh	4	0	0
PTM	Pd	7	0	0
	Pt	6	0	0
	Au	7	0	0
	Rh	3	0	0

Table 3. Statistical parameters computed on the assumption that the analytical results are independent of the reporting

RM	Elements	N *	N †	M% *	M% †	x% *	x% †	s *	s †	Overall c.v. *	Overall c.v. †	α_3 *	α_3 †	α_4 *	α_4 †	Average c.v.
PR-1	Mo	209	200	0·599	0·600	0·594	0·596	0·030	0·024	5·1	4·0	−0·87	−0·22	5·9	3·0	1·5
	Bi	184	173	0·112	0·112	0·111	0·111	0·007	0·006	6·3	5·4	−0·28	−0·24	2·7	2·1	2·6
	Fe	162	156	1·250	1·250	1·244	1·246	0·038	0·029	3·1	2·3	−1·09	−0·09	7·1	3·1	1·1
	S	213	207	0·785	0·784	0·792	0·792	0·027	0·025	3·4	3·2	0·49	0·42	2·3	2·2	1·2
MP-1	Zn	208	193	16·300	16·310	16·289	16·333	0·288	0·212	1·8	1·3	−0·97	−0·30	4·4	3·3	0·5
	Sn	221	215	2·410	2·410	2·424	2·419	0·182	0·166	7·5	6·9	−0·20	−0·05	2·9	2·1	2·2
	Cu	218	208	2·140	2·140	2·137	2·148	0·077	0·060	3·6	2·8	−0·83	−0·30	4·9	3·7	0·8
	Pb	235	22·	1·923	1·920	1·925	1·923	0·074	0·063	3·8	3·3	−0·18	−0·32	3·2	2·8	1·2
	Mo	174	154	0·014	0·013	0·017	0.014	0·009	0·002	54·9	15·3	2·29	1·28	6·8	4·9	7·5
	W	110	106	0·021	0·021	0·022	0·021	0·010	0·008	43·4	38·2	0·94	0·41	3·8	2·0	7·9
	In	113	103	0·072	0·071	0·073	0·071	0·007	0·004	9·7	5·2	1·68	−0·21	5·8	3·1	2·0
	Bi	151	141	0·026	0·026	0·027	0·025	0·007	0·004	27·6	15·0	2·02	−0·59	8·1	5·6	5·5
	As	197	182	0·780	0·780	0·789	0·794	0·062	0·045	7·9	5·7	−0·45	0·64	4·6	3·0	1·6
	Ag (*ppm*)	169	166	·58·0	58·0	58·9	58·8	3·8	3·7	6·5	6·3	0·44	0·42	2·3	2·3	1·5
HV-1	Cu	4·5	3·97	0·522	0·522	0·522	0·521	0·014	0·010	2·6	1·9	0·88	−0·24	8·7	2·7	1·4
	Mo	373	361	0·057	0·057	0·058	0·057	0·003	0·003	5·7	4·7	0·41	0·41	6·7	2·5	3·3
SU-1	Ni	357	333	1·51	1·51	1·50	1·51	0·04	0·03	2·8	2·1	−0·6	−0·1	4·1	2·5	1·3
	Cu	339	319	0·86	0·86	0·86	0·87	0·03	0·02	2·9	2·2	−0·4	0·1	4·5	2·3	1·1
	Co	276	254	0·064	0·064	0·062	0·063	0·006	0·004	9·0	7·1	−0·6	−0·5	3·1	2·9	2·4
UM-1	Ni	336	313	0·88	0·88	0·88	0·88	0·03	0·02	3·3	2·3	−0·6	0·2	5·2	2·7	1·4
	Cu	327	312	0·44	0·43	0·44	0·43	0·02	0·01	4·6	2·9	2·8	−0·5	18·7	3·0	1·6
	Co	286	274	0·034	0·035	0·034	0·035	0·002	0·002	7·1	6·1	−0·6	−0·2	2·9	2·2	2·2
KC-1	Zn	282	266	20·32	20·33	20·34	20·36	0·22	0·16	1·1	0·8	−0·7	0·7	5·9	2·9	0·4
	Pb	334	300	6·98	7·00	6·98	7·01	0·14	0·12	2·1	1·7	−0·2	0·6	4·3	4·0	0·6
	Cu	291	283	0·114	0·114	0·114	0·114	0·005	0·005	4·7	4·2	0·0	−0·1	3·2	2·3	1·7
	Sn§	240	190	0·678	0·680	0·667	0·678	0·049	0·025	7·3	3·6	−0·5	−0·5	4·2	3·8	1·5
	Ag	284	373	0·114	0·114	0·114	0·114	0·005	0·003	4·3	3·0	1·9	−0·2	10·8	3·3	1·1

* All data.

† After rejection of results deviating from the grand mean by more than twice the standard deviation.

§ Some of the results obtained by volumetric methods were rejected on chemical grounds.

are 0 and 3 respectively. In computing these quantities, use is made of the formula

$$m_j = \sum_{i=1}^{i=N} (x_i - \bar{x})^j / N$$

where m_j is the jth moment of the x-values about their mean.

Table 3 shows the distribution parameters for all results collected for the base-metal ores—too few results were available for the parameters to be calculated for the materials containing precious metals. It can be seen that the difference between corresponding medians and the means is small, as are the skewness factors, with the exception of that for iron in PR-1. The kurtosis coefficients are generally larger than the normal value of 3, but they approach this value after rejection of data that deviate from the means by more than two standard deviations. Considering that the results are subject to all the errors associated with the interlaboratory programme, they are remarkably close to a normal distribution.

Computation of the means and their confidence intervals

The model, as expressed by equations (1) and (2), takes into account differences in the between-laboratory results caused by factors such as variations in methods of analysis, the environment of the laboratories, *etc.* Table 3 shows that, in all cases, the average within-laboratory coefficient of variation (c.v.) for each element is smaller than the overall coefficient of variation. Figures 1 and 2 show graphically that the results are obviously dependent on the laboratory; thus it is unrealistic to treat the results as though they are independent variables. Consequently, the model described by equations (1) and (2) is used to compute the means and their confidence intervals. Only in cases where ω is found to be statistically insignificant would the results be treated as independent variables.

When t-tests confirm the insignificance of δ, the following expression can be formulated in terms of the individual results:

$$x_{ij} = c + y_i + e_{ij}$$

where x_{ij} = the jth result reported by laboratory i; c = the consensus value that will be estimated by the overall mean of x; y_i = the discrepancy between the mean of the laboratory i and the consensus value; and e_{ij} = the discrepancy of x_{ij} from the mean of laboratory i.

The assumption in this analysis is that both y_i and e_{ij} are normally distributed with means of zero and variances ω^2 and σ^2, respectively. The existence of ω^2 can be detected by comparing the ratio of "between-laboratory" mean squares to "within-laboratory" mean squares with the F-test at the 95% confidence level and with the appropriate number of degrees of freedom. If the participating laboratories are a random sample of those laboratories regarded as competent in the type of work, then the magnitude of ω can be estimated. Based on this estimate, the confidence interval of c can be computed for each selected element by means of the following formulae:[9]

$$\bar{x}_0 = \sum_{i=1}^{i=k} \sum_{j=1}^{j=n_i} x_{ij} \Big/ \sum_{i=1}^{i=k} n_i \qquad (4)$$

$$V[\bar{x}_0] = \omega^2 \left(\sum_{i=1}^{i=k} n_i^2 \right) \Big/ \left(\sum_{i=1}^{i=k} n_i \right)^2 + \sigma^2 \Big/ \left(\sum_{i=1}^{i=k} n_i \right) \qquad (5)$$

where $\bar{x}_0$ = the overall mean which has an expected

value of c; n_i = the number of results reported by laboratory i; and k = the number of laboratories.

Because the principal parameter to be estimated is the consensus value, c, the 95% confidence interval is calculated for $k-1$ degrees of freedom. This method of computation gives weight to each laboratory in accordance with the number of results submitted.

Other schemes for weighting the data were also considered—these are: weighting the results in inverse proportion to the laboratory variance with respect to the consensus value,[9] and weighting the results in inverse proportion to the square root of the same variance. Experience has shown that these schemes do not greatly alter the grand means, because the major component of the variance is the between-laboratory variance. A further disadvantage of these schemes is that some laboratories report results with apparently zero variance. The results of the method of weighting by the inverse of laboratory variance are also listed in each report. However, so far the consensus or recommended values have been taken from the scheme in which each result is given equal weight.

CERTIFICATION FACTOR

It is desirable to have a criterion with which an RM can be assessed in terms of its analytical usefulness. One approach is to correlate the precision of the consensus value for a selected element with the precision of the results of the various analytical methods used in the certification programme and to assume that these methods are similar to those that will be applied by the users of the reference material. With this in mind, the values assigned to a number of materials certified in the CCRM Project were assessed in relation to their corresponding within-laboratory coefficients of variation; the results are presented in Table 4.

From Table 4 it can be seen that the spread in the values for the selected elements of the precious-metal RM's (PTA, PTC and PTM) are, in general, larger than those of the base-metal RM's. Thus, the consensus values for the precious-metal RM's are estimated with a lower degree of precision than those of other reference materials. In other words, the absolute quality of the former materials is inferior to that of the latter. However, as can be judged from the

Table 4. Certification factor for a number of reference materials

Certified reference ore	Element	Recommended value, %	95% Confidence limits low	high	Spread, % (*A*)	Average of within-lab. c.v., % (*B*)	Certification factor, *A*/*B*
PR-1	Mo	0·594	0·578	0·610	5·38	1·54	3·48
	Bi	0·111	0·107	0·114	6·65	2·60	2·56
	Fe	1·244	1·225	1·263	3·05	1·12	2·72
	S	0·793	0·777	0·809	4·01	1·23	3·27
MP-1	Zn	16·33	16·20	16·45	1·53	0·46	3·36
	Sn	2·50	2·39	2·61	8·80	2·16	4·07
	Cu	2·15	2·12	2·18	2·99	0·82	3·64
	Pb	1·93	1·90	1·96	3·10	1·19	2·60
	Mo	0·14	0·13	0·15	13·16	7·62	1·73
	W*	0·022	0·016	0·029	57·09	7·87	7·25
	In	0·971	0·068	0·074	8·86	2·41	3·68
	Bi	0·025	0·023	0·027	16·02	5·56	2·88
	As	0·791	0·763	0·814	5·71	1·47	3·88
	Ag	59·5 ppm	56·3 ppm	60·6 ppm	7·30	1·50	4·87
HV-1	Cu	0·522	0·517	0·526	1·83	1·37	1·34
	Mo	0·058	0·056	0·059	3·93	3·26	1·21
SU-1	Ni	1·51	1·50	1·52	1·59	1·24	1·29
	Cu	0·87	0·86	0·88	1·88	1·07	1·77
	Co	0·063	0·061	0·065	6·32	2·29	2·64
UM-1	Ni	0·88	0·87	0·89	1·96	1·23	1·59
	Cu	0·43	0·43	0·44	2·29	1·19	1·92
	Co	0·034	0·034	0·035	5·30	2·25	2·35
KC-1	Zn	20·37	20·31	20·43	0·61	0·38	1·61
	Pb	6·98	6·94	7·02	1·22	0·65	1·82
	Cu	0·114	0·112	0·116	3·29	1·69	3·29
	Sn	0·68	0·67	0·69	3·61	1·43	2·53
	Ag	0·114	0·112	0·115	2·24	1·02	2·19
PTA	Pt	3·1 ppm	2·9 ppm	3·2 ppm	8·73	15·70	0·56
PTC	Ag	5·8 "	5·5 "	6·2 "	10·37	11·04	0·94
	Au	0·65 "	0·55 "	0·72 "	27·08	20·17	1·34
	Pd	12·7 "	12·0 "	13·0 "	10·90	7·19	1·52
	Pt	3·0 "	2·8 "	3·2 "	13·28	11·30	1·18
	Rh	0·62 "	0·55 "	0·69 "	18·39	8·37	2·19
PTM	Pd	8·1 "	7·4 "	8·8 "	16·30	7·94	2·05
	Pt	5·8 "	5·5 "	6·2 "	11·21	5·23	2·14
	Au	1·8 "	1·6 "	1·9 "	19·02	9·73	1·96
	Rh	0·88 "	0·73 "	1·03 "	34·79	8·65	4·02
	Ag	66·0 "	59·0 "	73·0 "	21·23	4·49	4·72

means of within-laboratory coefficients of variation, the precision obtainable by the analytical methods for precious-metal ores, is much lower than that for base-metal ores, because only trace-levels of the metals are present, resulting in a high inhomogeneity variance [equation (2)]. Consequently, this field of analysis does not require RM's with such precise consensus values as does the field of base-metal ore analysis. Generally, the same is true for trace constituents in ores and rocks as compared to minor and major constituents.

In Table 4, values for a "certification factor" are given. This is the ratio of the confidence interval of the consensus value, c, for a selected element, expressed as a percentage, to the mean of the within-laboratory coefficient of variation. The certification factor is a measure of the quality of the RM's because it takes into account the degree of precision required for the consensus values of the material in normal applications.

Table 4 shows that the values of the certification factors for the base-metal materials are less than 4, with the exception of those for Sn, Ag and W in ore MP-1*

Therefore, it is arbitrarily proposed that a material be recommended as a reference for a particular element if the element has a certification factor of $\leqslant 4$. This value can be explained on the basis that the confidence interval is twice the product of the value taken from the t-distribution and the magnitude of the coefficient of variation of the consensus value. For a large number of laboratories (approximately 20 or more), at 95% probability, the value of t approaches 2. In other words, a reference material is suitable for use if its consensus value for a selected element has a precision that is equal to or better than the average precision obtainable by the analytical methods that were used in its certification, or are being considered for use in a particular application.

The magnitude of the certification factor is influenced by:

(*a*) the within-laboratory variance, which includes the within-bottle inhomogeneity of the RM and the repeatability of the analytical methods used;

(*b*) the between-laboratory variance, which includes the extent of the agreement between various analytical methods and the between-bottle inhomogeneity of the RM;

(*c*) the number of replicate determinations performed by each laboratory;

(*d*) the number of participating laboratories.

Because these variables are controllable to a certain extent in the interlaboratory programmes, it is often possible to optimize conditions so that a value of $\leqslant 4$ can be achieved for the certification factors.

* MP-1 is not recommended as a reference material for W. Because the certification factors for Sn and Ag are not much greater than 4, their recommended values are useful in certain applications of MP-1. Additional work is now being done to refine the recommended value for Sn and to narrow its confidence interval.

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SHORT COMMUNICATIONS

ATOMIC-ABSORPTION DETERMINATION OF MANGANESE, COBALT AND COPPER IN WHOLE BLOOD AND SERUM, WITH A GRAPHITE ATOMIZER

RICCARDO A. A. MUZZARELLI and ROBERTO ROCCHETTI

Institute of Biochemistry, Faculty of Medicine, University of Ancona, 60100 Ancona, Italy

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Trace elements in blood and other biological fluids are seldom determined, because the methods available are expensive and time-consuming. However, interest in trace manganese, cobalt and copper determinations has recently expanded: the determination of copper is of use in pediatrics,[1–3] gynaecology,[4] dermatology,[5] dietetics,[6,7] gerontology[8] and oncology;[9] for instance the serum copper concentration is clearly related to malignant lymphomas and effectiveness of the therapy.[10]

Cobalt can alter the renal erythropoietic factor[11,12] and its determination is also related to the metabolism of vitamin B_{12}.[13] Cobalt was determined on fish tissues by flame atomic-absorption spectrometry with deuterium background compensation after extraction,[14] and in serum by use of tantalum strips.[15]

Manganese has been determined in urine[16] and in blood serum,[17] but in the latter work no instrumental background compensation was used. Manganese is of interest in clinical chemistry as one of the most accurate indicators of myocardial infarction, when present at high concentration in serum.[18]

Efforts are now being made to achieve rapid determination of trace metals in solid or dried samples by atomic-absorption spectrometry with a graphite atomizer and deuterium background compensation,[19,20] and a multi-element serum standard for neutron activation analysis has been prepared.[21]

We feel that the graphite atomizer method with background compensation can provide a rapid, reliable and sensitive instrumental technique for the determination of manganese, cobalt and copper in biological fluids and tissues; the application of this technique would be an important advance over flame atomic-absorption spectrometry,[22] especially because no manipulations on blood would be required and molecular absorption by smoke would be instrumentally compensated.[23]

EXPERIMENTAL

Blood samples

The blood samples were provided by the "Umberto I" Regional Hospital, Ancona, and by the Associazione Volontari Italiani Sangue, San Benedetto del Tronto, and contained oxalate as anticoagulant: the oxalate and heparin were tested for the metals of interest at the actual dilutions used and the amounts found were below the detection limits. The samples were centrifuged and stored at 4°. Just before the analyses for Mn and Cu, 20 μl of blood or serum were diluted with distilled water, fivefold for Mn or tenfold for Cu, to ensure reproducible delivery

Table 1. Instrumental settings

	Manganese	Cobalt	Copper
Wavelength, *nm*	279·4	240·7	324·7
Slit setting	4	(3)* 4	4
Expansion	1·5/8	1·25/8	0·5/8
Lamp, *mA*	16	26	16
Purging gas	N_2	N_2	N_2
Damping	1	1	1
Programme No.	4 + 7†	7	7
Voltage, *V*	9	9	9
Drying, *sec*	90(Pr.4)†	pre-ashing‡	60
Charring, *sec*	60(Pr.7)†	60	60
Atomization, *sec*	4	5	5
Background, %	~ 5	1	1
Chart speed, *mm/min*	40	20	20

* The cobalt wavelength must be set with slit-setting 3, but the measurements should be carried out with slit-setting 4.

† HGA-70 Programme selection number.

‡ As described under "*Blood samples.*"

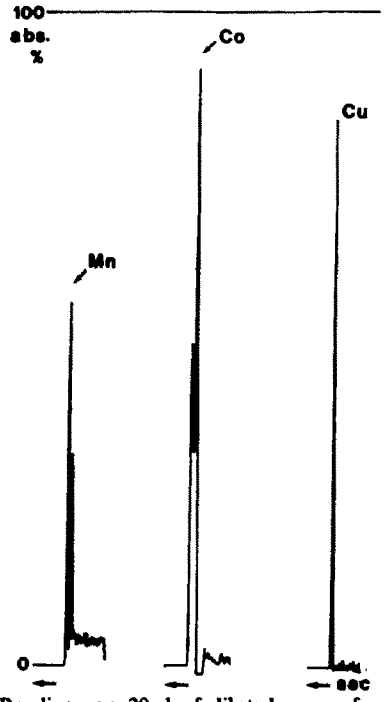

Fig. 1. Readings on 20 µl of diluted serum for Mn and Cu, and on 10 mg of serum ash for Co. The peaks of analytical use are indicated.

with the Eppendorf pipette, to give concentrations on the calibration curves and to avoid carbonaceous crusts in the graphite atomizer that would partially obstruct the light-path. Cobalt was determined on the ash from 0·5 ml of serum, obtained by ashing dried serum at 750° for 5 min. The ash (10–20 mg) was weighed in tantalum boats and introduced into the atomizer with the Perkin–Elmer "spoon".

Instrumentation

A Perkin–Elmer 305 atomic absorption spectrometer, equipped with the HGA-70 graphite atomizer and a deuterium-arc background compensator was used, with a Hitachi P-E 56 recorder. For the determinations of Mn and Cu, a Perkin–Elmer multi-element hollow-cathode lamp was used at 16 mA: above this value the deuterium compensation is not feasible. Cobalt was determined with a single-element lamp at 26 mA. These current values can be adopted only after prolonged warming-up of the lamps; otherwise the current should be 13 and 22 mA respectively and the energy output should be kept in the usual range (red-scale interval) by adjusting the photo-multiplier voltage. This causes a small background signal due to the brightness of the carbon, but this is not detrimental to the measurements. The instrumental settings are given in Table 1.

RESULTS AND DISCUSSION

Figure 1 shows the chart recorder trace for Mn, Co and Cu in serum. Three peaks are present in the manganese reading for blood but only the second is representative

Table 2. Determinations of manganese, cobalt and copper in whole blood and in serum from healthy blood donors

Donor Card No.	Age	Manganese, *ng/ml* blood	serum	Cobalt, *ng/ml* serum	Copper, *µg/ml* blood	serum
59	44	12		7·2	1·3	1·0
97	39	9	5	8·0	1·5	1·4
127	39	11			1·5	
194	30	18	5	9·8	1·3	1·3
226	32	11			1·6	1·4
227	31	9		8·0	1·7	
313	30	21	16	7·9	1·3	1·3
342	40	3		8·0	1·7	
358	41	10	6	6·4	1·3	1·3
360	26	6			1·5	1·4
380	26	6			1·0	
413	41	18		5·6	1·0	
448	23	14		5·6	1·0	
488	22	9	5		1·6	1·4
537	36	10		6·4	1·7	
548	34	9			1·0	
552	37	11	5	9·8	1·2	1·1
612	30	7			1·2	
635	27	12		8·0	1·4	1·3
654	40	20	12	7·9	1·1	1·0
687	38	17			1·1	
725	31	11			1·2	
764	31	6		9·6	1·0	
804	31	6		9·6	1·1	1·2
875	25	16			1·1	
899	53	10		7·2	1·4	1·3
916	21	16	9		1·2	1·1
936	32	9		6·8	1·4	1·3
946	33	11	6		1·3	1·1
949	31	6		6·8	1·3	1·0
1035	24	6			1·2	1·1
1071	36	6			1·4	
1091	22	18			1·0	
Mean values		11	9	7·7	1·3	1·2
Std. deviations		± 4·4	±4·3	± 1·9	± 0·22	± 0·16

of manganese, as is demonstrated by the standard addition method; the third peak is in fact absent in the serum readings. The calibration curves were linear but did not pass through the origin, there being a background contribution from the carbon brightness.

The readings for the metals were also proportional to the volumes of blood submitted to analysis, *i.e.*, 20, 30, 40, 50 and 60 μl of blood or serum introduced into the atomizer and dried for 15 sec per 10 μl in the case of Mn and Cu, or the amount of ash from 0·5, 0·75 and 1·0 ml of serum, for Co. Ten Cu determinations on one serum sample gave a standard deviation of $\pm$ 0·07 ng/ml.

The standard-addition method was applied by adding known volumes of aqueous solutions of the metal ions to diluted blood or serum before the drying; the calibration lines for aqueous solutions and diluted blood were parallel, as expected.

Typical results obtained are shown in Table 2. The ranges observed on samples from blood donors are: Mn 3–21 ng/ml in blood, mean value $\pm$ standard deviation 11 $\pm$ 4·4; 5–16 ng/ml in serum, mean value $\pm$ standard deviation 9 $\pm$ 4·3; Co 5·6–9·8 ng/ml in serum, 7·7 $\pm$ 1·9; Cu, 1·0–1·7 μg/ml in blood, 1·3 $\pm$ 0·22; 1·0–1·4 μg/ml in serum, 1·2 $\pm$ 0·16. They can be taken as normal values for this population, as the blood samples were from healthy blood donors. These values are in agreement with those reported in previous works on copper[10,24] and manganese,[18] while the cobalt concentration corresponds to the one selected for the serum cobalt standard.[21] Preliminary results on sera from patients show that most of them are clearly outside the normal intervals and therefore the metal determinations can provide unequivocal information for diagnostic purposes.[25]

CONCLUSIONS

The instrumental method developed is suitable for the rapid routine determination of manganese, cobalt and copper in whole blood and in serum samples. It requires very little blood or serum, 20 μl for Mn and Cu, and 0·5 ml for Co; it does not require time-consuming manipulations and hence avoids contamination risks. The metal determinations can be carried out on the serum aliquots that usually remain after other chemical tests, and care should then be taken to avoid metal contamination by pipettes, anticoagulant, test-tubes and stoppers. The method is based on the use of commercially available analytical instrumentation and does not require expensive and delicate modifications of the instruments.

These favourable features of the proposed method offer the possibility of collecting a large number of data in a short time and of using the metal concentration values as a new tool in clinical chemistry, environmental hygiene, toxicology, the food sciences and other fields where distinct changes in the metal concentration are diagnostic.

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Summary—A new and rapid method is described for the determination of Mn, Co and Cu by atomic absorption with a graphite atomizer and deuterium compensation, on very small samples of whole blood and serum, with no preliminary manipulations. The metal concentrations in blood serum from healthy donors have been found to be Mn 9 $\pm$ 4·3 ng/ml; Co 7·7 $\pm$ 1·9 ng/ml and Cu 1·2 $\pm$ 0·16 μg/ml.

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CONTRIBUTIONS TO THE BASIC PROBLEMS OF COMPLEXOMETRY—XXV

DETERMINATION OF RARE EARTHS AND PHOSPHATE WITHOUT SEPARATION

RUDOLF PŘIBIL

J. Heyrovský Institute of Physical Chemistry and Electrochemistry, Czechoslovak Academy of Sciences, Prague 1, Jilská 16, Czechoslovakia

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As the phosphates of all rare earths (RE) are soluble only in relatively concentrated nitric acid, their direct determination by EDTA titration is impossible. Indirect determination by back-titration with, for examples, zinc, is also impossible because of displacement of the RE from their EDTA-complexes and their precipitation as the phosphates.[1] Usually separation either of the RE or the phosphate is necessary. Kinnunen and Wennestrand[2] decomposed natural rare-earth phosphates with sodium peroxide, precipitated the RE as the oxalates, ignited these and dissolved the resulting oxides in nitric acid, then determined their sum by direct titration with EDTA at pH 5–5·5, using Xylenol Orange as indicator. Genge and Salmon[3] first precipitated the phosphate as $BiPO_4$ with bismuthyl perchlorate at pH 0·5–1·0 and determined the excess of bismuth in the filtrate by EDTA titration at pH 2; they then determined the RE indirectly by adding excess of EDTA and back-titration with zinc at pH 10. (Traces of Pyrocatechol Violet were used as indicator for the first titration, and Eriochrome Black T for the second).

For these reasons phosphate cannot be determined in the presence of RE by precipitation as $MgNH_4PO_4$ or $ZnNH_4PO_4$, for example. Determination of both RE and phosphate in one solution without any separation would be desirable.

In one of our previous papers[4] we described a very simple method for the determination of RE in the presence of phosphate, based on the fact that the RE form sufficiently stable complexes with diethylenetriaminepentaacetic acid (DTPA) and are not displaced from these complexes by zinc. Knowing that lanthanum is very easily displaced from its EDTA complex by zinc,[1] we have developed a method for the determination of RE as well as phosphate, a problem which had not hitherto been solved satisfactorily with complexometry.

EXPERIMENTAL

Reagents

DTPA solution, 0·05*M*. Prepared by dissolving 19·65 g of the free acid in 100–130 ml of 1*M* sodium hydroxide and diluting to 1 litre. Standardized complexometrically.

Zinc nitrate solution, 0·05*M*. Prepared by dissolving 3·2685 g of pure zinc in sufficient nitric acid (1 + 1) and diluting to 1 litre.

Lanthanum nitrate solution, 0·05*M*. Prepared by dissolving 10·801 g of the hexahydrate in 500 ml of redistilled water.

Lanthanum–EDTA solution, 0·025*M*. Prepared by titration of sufficient 0·05*M* lanthanum nitrate with 0·05*M* EDTA at pH 5–5·5, with Xylenol Orange as indicator. A stock solution can be prepared by mixing equivalent volumes of both solutions. The resulting solution should contain not more than one drop of 0·05*M* lanthanum nitrate in excess (red colour of indicator complex).

Sodium dihydrogen phosphate solution, 0·05*M*. Prepared by dissolving 6·000 g in 1 litre of water.

RE nitrate solutions, 0·05*M*. Prepared by dissolution of appropriate amounts of nitrate or oxide in nitric acid and dilution to 100 ml. RE obtainable from various sources were approx. 98–99% pure.

Procedure

To the sufficiently acid solution containing up to 50 mg of phosphate and up to 20 mg of rare earths in a volume of 30–50 ml add enough 0·05*M* DTPA to complex all cations present, then neutralize with ammonia to pH 4·5. Add 0·5–1·0 g of hydroxylamine hydrochloride or ascorbic acid and boil for 1–2 min. Cool, dilute to 100–150 ml and adjust the pH to 5–5·5 with 20% hexamine solution, add a few drops of 1% Xylenol Orange solution and titrate with 0·05*M* zinc nitrate from yellow to red-violet. The consumption of DTPA corresponds to the sum of rare earths.

To the same solution add an excess of lanthanum–EDTA solution (roughly measured), dilute to 200–300 ml according to the phosphate concentration, warm to 40–50° and titrate slowly with zinc nitrate solution to a red-violet colour which must not fade for at least 2–3 min. The consumption of zinc solution corresponds to the amount of phosphate (Table 1).

Table 1. Determination of RE and phosphate

Taken 0·05*M* RE, *ml*	PO_4^{3-}, *mg*	Found 0·05*M* RE, *ml*	PO_4^{3-}, *mg*	Taken 0·05*M* RE, *ml*	PO_4^{3-}, *mg*	Found 0·05*M* RE, *ml*	PO_4^{3-}, *mg*
1·65 Sm	5·17	1·72 Sm	5·35	1·65 Sm	51·66	1·72 Sm	52·66
0·98 Dy	5·17	0·97 Dy	5·08	9·84 Dy	25·83	9·85 Dy	27·03
5·16 Er	51·66	5·00 Er	53·13	9·00 Gd	36·19	9·05 Ga	36·82
1·93 Tb	10·33	1·99 Tb	10·40	12·40 Yb	51·66	12·23 Yb	52·20

Remarks

Addition of ascorbic acid or hydroxylamine hydrochloride prevents the precipitation of even traces of phosphate. The displacement reaction in the second titration $LaY^- + Zn^{2+} + PO_4^{3-} \rightarrow LaPO_4 + ZbY^{2-}$ is very fast at normal temperature when a large concentration of phosphate is present.[1] When a smaller amount of phosphate is present, the higher temperature of 40–50° is more convenient.

Interferences

All elements forming stable complexes with DTPA under the given conditions are co-titrated. Their sum can be determined (with the exception of aluminium) in a separate aliquot of the solution after masking of RE (and aluminium) with ammonium fluoride. Thorium interferes because it is precipitated as phosphate even in the presence of DTPA. It can be determined in the presence of phosphates if we use TTHA instead of DTPA for its complexation.[5] The procedure is similar to that described above. However, thorium, RE and phosphate cannot *all* be determined by this method, owing to the complicated equilibria between the Th–TTHA complex and the RE–DTPA complexes.

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SPECTROPHOTOMETRIC DETERMINATION OF VANADIUM AND ITS APPLICATION TO GAS-TURBINE FUEL-OILS

SAMARESH BANERJEE, B. P. SINHA and R. K. DUTTA

Research and Control Laboratory, Durgapur Steel Plant, Durgapur-3, West Bengal, India

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The use of liquid-fuel injection in high-pressure boilers and gas turbines is increasing. The high-boiling petroleum fractions obtained as sludges and concentrates from the refineries have very high calorific value and very low ash content. However, some of the minor mineral constituents in the ash are extremely harmful, owing to their corrosive effect, especially vanadium.

Vanadium forms low-melting compounds such as V_2O_5 (m.p. 691°) and causes severe attack on all the high-temperature alloys used for gas-turbine blades. At the 10 ppm level the corrosion rate is 3 times the normal oxidation rate and at 30 ppm it is 13 times the normal oxidation rate,[1] so it is necessary to limit the vanadium content in such fuels to less than 2 ppm.

The determination of vanadium in such oils has become imperative and necessitates a very sensitive and rapid method which is suitable for day to day routine analysis. The ASTM phosphotungstic acid method[1] involves ashing the fuel oil at 525 ± 25°, requires about 1 day and does not appear to be suitable for routine work. Moreover the vanadium must be in the quinquevalent state and the strongest colour is obtained when the molecular ratio of phosphoric acid to sodium tungstate lies in the range 3:1–20:1 and the tungstate concentration is 0·01–0·1*M*.[2] The time for development of the colour is 1 hr. Several organic reagents have been suggested for vanadium. These include pyrocatechol,[3] benzoylphenylhydroxylamine,[4] benzohydroxamic acid,[5] salicylhydroxamic acid,[6] *o*-phenylenediamine[7] and diphenylbenzidine.[8] These reagents are generally used for the determination of vanadium in steels. Benzohydroxamic acid and diphenylbenzidine have been used for the determination of vanadium in petroleum. Spectrographic methods,[9,10] and atomic-absorption spectrophotometry[11] have also been used. We have used tannin and thioglycollic acid as a reagent for the spectrophotometric determination of niobium in stainless steel,[12] and

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have observed that the same reagent can produce an intense indigo-blue colour with vanadium. The reaction can be utilized for a sensitive spectrophotometric determination of vanadium in gas-turbine fuel-oil and navy fuel-oils.

EXPERIMENTAL

Reagents

Standard vanadium solution (0·5 *mg/ml*). Dissolve 1·141 g of pure ammonium vanadate in distilled water in a standard 1-litre flask and make up to volume with distilled water.

Standard vanadium solution (0·025 *mg/ml*). Dilute the 0·5 mg/ml solution 20-fold with distilled water.

Tannic acid–thioglycollic acid mixture. Mix equal volumes of 5% w/v tannic acid and 10% v/v thioglycollic acid solutions. Filter, and store in an amber bottle. Prepare fresh every week.

Acetate buffer pH 4. Dissolve 25 g of ammonium acetate and 200 ml of glacial acetic acid in 1 litre of distilled water.

Table 1. Weight of sample for analysis

Vanadium content, *ppm*	Weight of sample, *g*
<10	10
10	5
20	3
40	2
>60	1

Preparation of standard curve

Into a series of 50-ml standard flasks pipette 0, 2, 4, 6, 8, 10 ml of 0·025 mg/ml vanadium solution, add 20–25 ml of acetate buffer and 5 ml of tannic acid–thioglycollic acid mixture to each and shake well. Dilute to volume with distilled water and after 10 min measure the absorbance of each solution at 600 nm, in a 1-cm cell. Plot the absorbance against the number of mg of vanadium in 50 ml.

Procedure

Prepare the sample according to ASTM[1] and weigh a suitable portion (according to Table 1) into a 100-ml Pyrex beaker and add 5 ml of concentrated sulphuric acid. For a 10-g sample use a 250-ml beaker and 10 ml of sulphuric acid. Place the beaker on a high-temperature hot-plate. Take care to avoid spattering, and heat until the evolution of sulphur trioxide fumes ceases, then ignite with a burner whatever hydrocarbon vapours will burn and continue heating until a dry coke is obtained. Crush any lumps with a flattened-end glass rod and place the beaker in a muffle furnace and continue heating at 600–650° until all carboneceous matter is burnt off. Cool the beaker and add 5 ml of concentrated hydrochloric acid and a few drops of nitric acid and digest the residue on a hot-plate until completely dissolved, boil off nitrous fumes and evaporate until about 1 ml of acid remains. Cool and add 5 ml of distilled water and ammonia solution (1 + 1) drop by drop until the pH of the solution lies between 5 and 5·8 (use narrow-range indicator paper). Transfer the solution quantitatively into a 50-ml standard flask and complete the determination as described for the standard curve. Run a reagent blank.

If the inorganic ash contains silica, this should be removed with hydrofluoric acid in the usual way.

RESULTS AND DISCUSSION

Spectroscopic data

The absorption spectrum for a 3-ppm vanadium solution at pH 4 has a single peak with its absorbance maximum at 600 nm. The absorbance increases with pH from 3 to 4, and is then constant up to pH 5. Beer's law is obeyed over the range 0·5–5 ppm vanadium. The upper limit can be extended by working at lower pH, *e.g.*, to 50 ppm at pH 3.

Table 2. Determination of vanadium

Vanadium, *ppm*	
By ASTM method[1]	By this method
57	55
	58
52	50
	52
40	42
	44
53	52
	55
60	57
	59

The stability of the colour decreases with the increasing pH as well as with concentration of vanadium. Thus a 10-ppm vanadium solution at pH 5 coagulates after 10–15 min and a 5-ppm solution at pH 4 is stable for more than 1 hr; hence measurements are generally made at pH 4.

Effect of diverse ions

The trace metals generally present in the mineral ash of the fuel oils include Ca, Pb, Mg, K, Na and Fe. None of these elements interferes.

Effect of sequestering agents

Complexing anions such as fluoride and oxalate cannot be tolerated. Excess of chloride, sulphate, phosphate or nitrate has no effect, but nitrate interferes. Citrate and tartrate slightly decrease the absorbance. EDTA completely destroys the colour.

Typical results for vanadium in fuel-oil samples are shown in Table 2 and compared with those obtained by the ASTM method.[1]

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Summary—A very sensitive spectrophotometric method for the determination of vanadium in furnace oils is described. The intense indigo-blue colour developed by the reaction of vanadium with tannin and thioglycollic acid is measured at a wavelength of 600 nm at pH 4 and obeys Beer's law between 0·5 and 5 ppm vanadium. The method is applicable to gas-turbine fuel-oil and special navy fuel-oils. The common mineral constituents usually present in such oils do not interfere.

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EQUILIBRIUM EFFECTS IN THE DETERMINATION OF TANTALUM BY ATOMIC-ABSORPTION SPECTROSCOPY

W. F. PICKERING

Department of Chemistry, University of Newcastle, N.S.W., Australia 2308

P. E. THOMAS

Varian Techtron, North Springvale, Victoria, Australia 3171

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Tantalum can be determined by atomic-absorption spectroscopy[1] provided a high-temperature flame (*e.g.*, oxygen, nitrogen–acetylene or fuel-rich nitrous oxide–acetylene) is used and the solution conditions are carefully controlled. The procedure is not sensitive (concentrations of mg/ml are needed for reasonable absorbance values) and several interelement effects have been noted,[1–5] hence when tantalum is present in a complex matrix, preliminary isolation of the element by extraction[6–8] is recommended.

Recent publications on tantalum chemistry permit an interpretation of many of the effects noted in aqueous media.

EXPERIMENTAL

Additional information on interference effects was obtained by adding varying amounts of diluent and analytical-grade reagents to a base solution prepared by dissolving pure tantalum in 1·3*M* nitric acid (1·00 g/l.).

Atomic-absorption measurements were made on a Techtron AA-4 spectrometer, with the 271·5 nm line of the tantalum lamp (15 mA current) and a 100-μm slit.

Both a fuel-rich nitrous oxide–acetylene flame and an oxygen–nitrogen–acetylene flame were used. Results relevant to the discussion are summarized in Fig. 1 and 2.

DISCUSSION

In non-complexing media, tantalum behaves like Zr, Hf, Ti, U (and to a lesser extent Fe, Al) and exists in solution as oxy or hydroxy complexes. These are often polymeric, aggregated in nature, and subject to significant co-precipitation effects. When such solutions are aspirated into a flame, a refractory oxide of high melting point is formed. The fraction of the initial salt converted into atoms is small and for absorption of resonance radiation to be observable the degree of oxide dissociation has to be increased by use of high temperatures and of flame conditions which favour interaction between solute particles and gaseous radical species.

With an oxygen–nitrogen–acetylene flame, maximum absorption by tantalum is observed when oxygen represents 50–55% of the support gas; the sensitivity achieved with a fuel-rich nitrous oxide–acetylene flame is approximately three times as great.[1]

The magnitude of the atom population in the flame can be further enhanced by converting the element of interest into a solute species which is more readily dissociated into atoms. The beneficial role of oxo-fluoro complexes (*i.e.*, metal–fluoride bonds) in this type of operation has been considered in some detail by Sastri *et al.*[2,3]

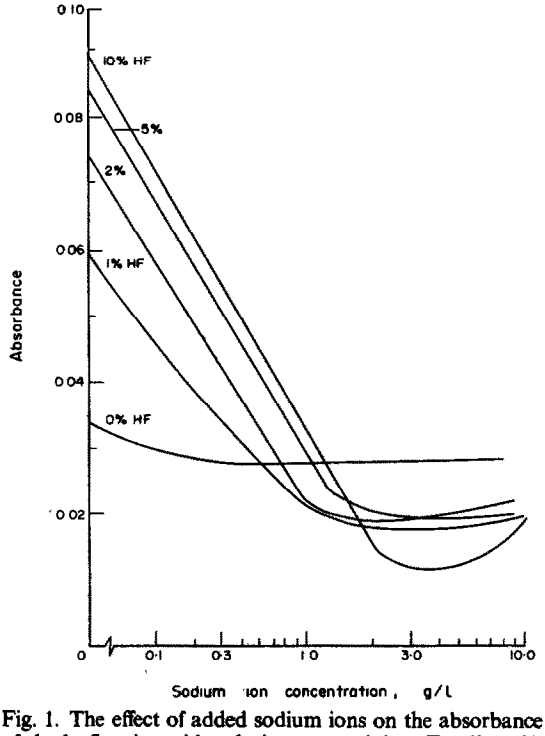

Fig. 1. The effect of added sodium ions on the absorbance of hydrofluoric acid solutions containing Ta (0·4 g/l.). Nitrous oxide–acetylene flame, 3-cm burner.

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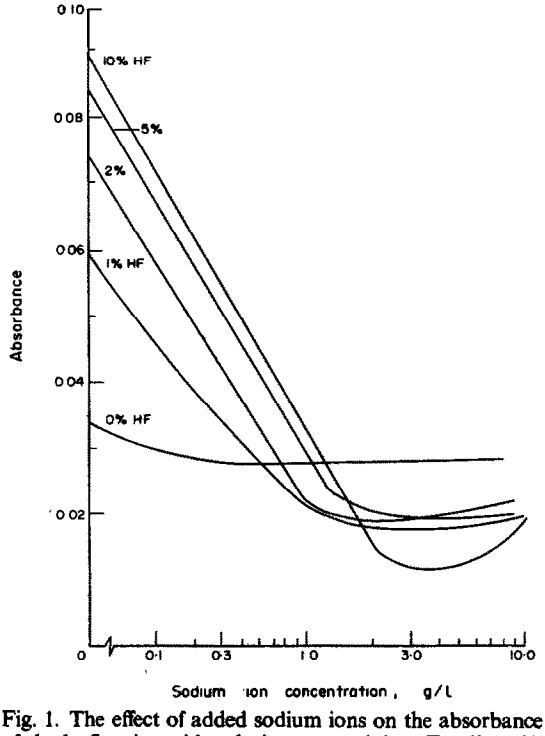

Fig. 1. The effect of added sodium ions on the absorbance of hydrofluoric acid solutions containing Ta (0·4 g/l.). Nitrous oxide–acetylene flame, 3-cm burner.

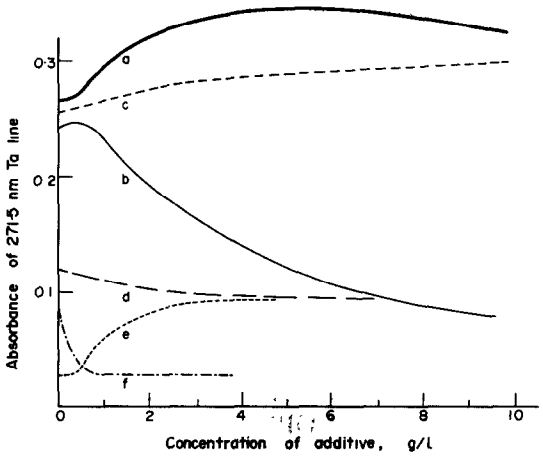

Fig. 2. Diagram showing the variation in absorbance caused by the presence of added solutes. Ta concentration 1 g/l.; nitrous oxide–acetylene flame, burner width 6 cm (*a*, *b*, *c*) or 3 cm (*d*, *e*, *f*). Effect of adding *a*, iron(III) to 5% HF medium; *b*, iron(III) to 0·1% HF medium; *c*, boric acid to 5% HF medium; *d*, boric acid to 0·1% HF medium; *e*, cobalt to 2% HF medium containing sodium (17 g/l.) and tungsten (2 g/l.); *f*, titanium(IV) to 2% HF medium containing sodium (17 g/l.), tungsten (2 g/l.) and cobalt (2 g/l.).

In the absence of alkali metal ions, the addition of hydrofluoric acid to tantalum solutions greatly increases the amount of radiation absorbed; even small amounts (0·1%) produce significant changes.[1,4]

Tantalum forms a series of fluoro species [$Ta(OH)_2F_3$, $Ta(OH)_2F_4^-$, TaF_6^-, TaF_7^{2-}] and calculations based on published[9] equilibrium constants indicate that hydrofluoric acid concentrations greater than $10^{-2}M$ (*i.e.*, >0·02% w/v) would ensure conversion of hydrous tantalum oxide into the trifluorodihydroxy form.

$$[Ta(OH)_5][HF]^3/[Ta(OH)_2F_3] = 1{\cdot}4 \times 10^{-8};$$

$$[Ta(OH)_2^{3+}][HF]^3/[Ta(OH)_2F_3] = 2{\cdot}8 \times 10^{-29}.$$

A highly probable product on flame aspiration of such solutions is TaO_2F; this compound disproportionates at 850° to Ta_3O_7F and TaF_5.[10,11] The melting point of the pentafluoride is quoted as 97° (*cf.* Ta_2O_5, m.p. 1800°) and the increase in absorption at low hydrofluoric acid concentrations could be due to this species.

In solutions containing 6–22% hydrofluoric acid, there is evidence for the formation of both the hexa- and heptafluorotantalate.[10,11]

The proportion of each species present depends[9] on the concentration of fluoride ion $\{[TaF_6^-]/[TaF_7^{2-}] = 7 \times 10^{-4}/[F]\}$ and on the basis of this equation, fluoride concentrations >0·07*M* should ensure almost complete conversion into the heptafluoro form. To achieve fluoride concentrations of this magnitude through dissociation of hydrofluoric acid, acid concentrations >10*M* (*i.e.*, >20% w/v) are required.

The heptafluorotantalate ion combines with cations to form well-defined salts, *e.g.*, with many bivalent metal ions to give[12] compounds having the general formula $MTaF_7.6H_2O$ (M = Ni, Co, Mn, Zn, Cd).

The potassium salt, K_2TaF_7, precipitates from acid solution on the addition of potassium fluoride; the yield varies with potassium fluoride concentration but is independent of hydrofluoric acid concentration.[13] The addition of four moles of sodium fluoride per mole of heptafluorotantalate yields sodium octafluorotantalate. Octafluoro species can also be prepared[10] by fusion of tantalum compounds with alkali metal fluoride (the products include complex compounds such as KTa_2O_5F).

In a flame, some reaction between tantalum species and the molten excess of alkali fluoride can be expected and the marked effect of adding alkali metal ions to hydrofluoric acid solutions is clearly shown in Fig. 1.

Recorded decreases in sensitivity in the presence of some metal ions (*e.g.*, nickel[6]) may be attributed to the formation of bivalent-metal heptafluorotantalates, but these compounds are apparently less stable (thermally) than the alkali metal species since the addition of a metal ion (*e.g.*, cobalt) to a solution containing a high concentration of alkali ions leads to enhanced atomic absorption (Fig. 2, curve *e*).

The nature of the fluorotantalum species formed in solution is a function of both the hydrofluoric acid and fluoride ion concentrations. The latter can be decreased by adding a masking agent such as boric acid or a metal ion which forms stable fluoro complexes (W, Ti, Fe, *etc.*).

A boric acid–hydrofluoric acid mixture has been proposed[14] as a "releasing agent" and Fig. 2, curve *c*, indicates the type of enhancement observed in the presence of excess of boric acid. With higher concentrations of boric acid the signal intensity drops quickly as significant proportions of the fluoride become masked, (*e.g.*, curve *c* falls to a reading of 0·22 with an addition of 50 g/l.). With low initial hydrofluoric acid concentrations (*e.g.*, 0·1% w/v) even small boric acid additions cause a decrease in atomic absorption (curve *d*).

It has been reported[1] that the addition of iron salts enhances tantalum absorption, and this statement is true with high ratios of hydrofluoric acid to iron(III) (*cf.* curve *a*). On the other hand, where the concentrations of additive, tantalum and acid are of the same order (curve *b*) the formation of the iron complex predominates and with increasing additions of iron(III) the tantalum absorption signal tends towards the base-line observed in the absence of fluoride.

Competition between species for both fluoride ions and the fluorotantalate ions can lead to the disappearance of enhancement effects. For example, curve *f* shows how the positive effect of cobalt ions is lost on the addition of titanium(IV).

The analyte used in the studies responsible for curves *e* and *f* contains appreciable amounts of enhancing agents [hydrofluoric acid and cobalt(II)], signal depressant (sodium) and masking agent (tungsten). Such combinations could be encountered in many practical applications, and with so many competitive reactions involved, it is obvious that tantalum determinations by atomic absorption should either be preceded by a "tantalum isolation from matrix" step or be done by a standard addition procedure.

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Summary—The effect of solution variables on the efficiency of tantalum atom formation in hot flames is considered in terms of competing equilibria.

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SPECTROPHOTOMETRIC SOLVENT EXTRACTION STUDIES OF 2-MERCAPTOPYRIDINE-1-OXIDE AND URANYL ION COMPLEX

M. EDRISSI and A. MASSOUMI

Institute of Chemical Engineering, Tehran Polytechnic, Tehran, and
Department of Chemistry, Pahlovi University, Shiruz, Iran

(*Received* 19 *June* 1974. *Revised* 16 *September* 1974; *Accepted* 12 *February* 1975)

2-Mercaptopyridine-1-oxide (thione) has been used for gravimetric and absorptiometric determination of Fe(III), Hg(II), Cu(II) and Pd(II).[1–4] The formation of a soluble thione complex of uranyl ion has also been reported.[5] In the present work the composition and stability constant of this complex are studied and the use of solvent extraction for its separation is reported along with the extraction constant. Use of the complex for spectrophotometric determination of UO_2^{2+} is described.

EXPERIMENTAL

Reagents

The sodium salt of thione was recrystallized twice from a chloroform-ethanol mixture and the purity of the compound (m.p. 251–252°) checked by elemental analysis and by the absorbance (200–780 nm) in methanol solution. A $10^{-2}M$ stock solution was prepared in boiled distilled water. A $10^{-2}M$ stock uranyl nitrate solution was prepared from analytical-grade reagent in boiled distilled water and standardized by redox titration.[6] All other solutions were made from reagent grade chemicals.

Apparatus

A Cary-14 spectrophotometer was used for recording the absorption curves and further measurements were made with a Zeiss Spectrophotometer PMQ II, using 0·5, 1, 2, 4 and 5 cm cells.

General procedure

An aliquot of a sample containing 1–10 mg of UO_2^{2+} was added to a 100-ml volumetric flask and 10 ml of $1M$ sodium perchlorate were added to bring the ionic strength to $0{\cdot}10M$. The solution was diluted to about 85 ml and the pH was adjusted to 4·5 with sodium acetate and acetic acid. The required quantity of thione solution was added and the solution diluted to volume with distilled water. The flask was kept for 30 min in a thermostat at 25° and the absorbance was then measured against a reagent blank.

RESULTS AND DISCUSSION

Complex formation

The absorption spectrum of the complex is shown in Fig. 1, and has absorption peaks at 340 and 490 nm. As neither UO_2^{2+} nor thione shows any absorption at 490 nm this wavelength was chosen for further study of the complex. The composition of the complex was established by the continuous-variation method of Job,[7] the mole-ratio method of Yoe and Jones[8] and the slope-ratio method.[9] All three methods showed that a complex with the composition $UO_2(thione)_3^-$, (thione = $C_5H_4NOS^-$), was formed.

Effects of pH and time

It was observed that the complex is stable over the pH range 3–6·5 and a pH of 4·5 was chosen as optimum.

The colour formation was immediate, but a 30-min wait was allowed to ensure equilibrium was attained. The colour started to fade after about 5 hr.

Stability constant of the complex

The stability constant was determined by the "extinction ratio method" reported by Klausen,[10] from the absorption spectra of solutions with concentration sums of $2C$, C, $C/2$, $C/4$ and $C/5$. It was found that at pH 4·5 the conditional constant of $UO_2(thione)_3^-$ is $2{\cdot}6 \times 10^{12}$. The absolute stability constant of the complex was calculated from the equation (Ringbom[11]) $K' = K/\alpha_{UO_2} \cdot \alpha_{Thione}$. Inclusion of the side-reaction coefficients at the specified pH resulted in the value $K = 5{\cdot}3 \times 10^{12}$. This is according to expectation, as at pH 4·5 not much hydrolysis of UO_2^{2+} takes place[11] and also this pH is very close to the pk_{a_2} of thione.[12]

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M. EDRISSI and A. MASSOUMI

Institute of Chemical Engineering, Tehran Polytechnic, Tehran, and
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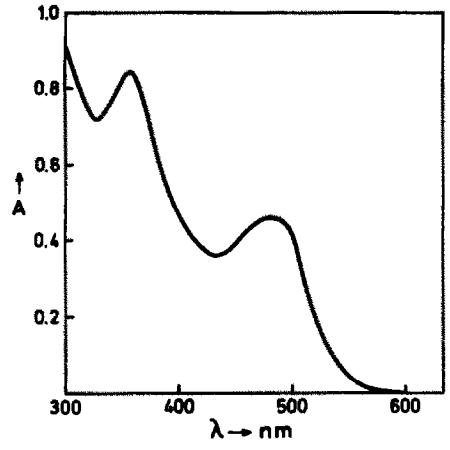

Fig. 1. Absorption spectrum of uranyl thione complex.

Extraction of the complex with organic solvents

Several organic solvents were tested for the extraction of the complex and tributyl phosphate (TBP) was found to be the most efficient. When equal volumes of aqueous phase and TBP were shaken together for 2 min, the volume of the organic phase increased by about 20% at the expense of the aqueous phase, and the absorbance readings had to be corrected accordingly.

The conditional extraction constant of the complex was calculated according to Likussar and Boltz,[13] from the equation:

$$K'_E = 0{\cdot}375 - 3\log K + \log y_{max} - 4\log(1 - y_{max})$$

where K is the concentration sum and y_{max} is the "maximum normalized absorbance term". A value of $K'_E = 8{\cdot}9 \times 10^{12}$ was obtained.

Spectrophotometric determination of uranyl ion

With 1-cm cells, at pH = 4·5, temperature 25° and λ–490 nm, Beer's law is obeyed for solutions of complex containing 1–30 ppm of uranyl ion. The sensitivity of the measurement is fair, 0·04 μg/ml for $A = 0{\cdot}001$. If a 4-cm cell is used, 0·40 ppm of UO_2^{2+} can be determined with an error of 2·1% and a standard deviation of 0·0068 ppm ($n = 6$). Eleven replicate analyses for 13·8 ppm of UO_2^{2+} alone gave a mean of 13·7 μg/ml, standard deviation 0·038 μg/ml, but in the presence of a large amount of other cations the selectivity becomes poor. Ions which form insoluble chelates with thione such as Zr(IV), Bi(III), Cu(II), Hg(II), Ag(I), Pd(II), Fe(III), Ti(IV), V(V), Tl(III), Pb(II), Mo(VI), Co(II), Ni(II), Zn(II), Pt(IV), Sn(II), W(VI), Ga(III), Cd(II) react with the reagent first and seriously interfere; however, if excess of reagent is added the precipitate of these metal ions can be separated from the soluble uranyl complex by centrifugation, or the uranyl complex selectively extracted with tributyl phosphate. Thiocyanate masks the uranyl ion, NO_2^-, SO_2 and H_2O_2 decrease the colour of the complex and iodine reacts with the reagent and must be absent. A 100-fold excess of Al(III), Y(III), Ce(IV), Th(IV), Sb(III), As(III), F^-, PO_4^{3-}, BO_3^{3-}, $C_2O_4^{2-}$, SO_4^{2-} had no appreciable effect on the absorbance of a solution containing 13·8 ppm of uranyl ion.

Summary—The complex formed by uranyl ion with 2-mercaptopyridine-1-oxide (thione) is studied by spectrophotometry. At pH 4·5 and 25° the only complex formed is $UO_2(thione)_3^-$. The conditional stability constant of this complex is $2{\cdot}6 \times 10^{12}$. Tributyl phosphate is used for the extraction of the complex from the aqueous phase and the extraction constant is $8{\cdot}9 \times 10^{12}$. The use of the reagent for the separation and determination of uranyl ion is elaborated.

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ANALYTICAL DATA

MASS SPECTRA OF METAL IODIDES

KOZO MATSUMOTO, NOBUTOSHI KIBA and TSUGIO TAKEUCHI

Department of Synthetic Chemistry, Nagoya University, Nagoya, Japan

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In our laboratory, the quantitative determination of metal halides has been studied by mass spectrometry as a method of determination of trace amounts of metals.

In previous papers mass spectra of several metal chlorides were reported,[1,2,3] but the mass spectra of alkali metal chlorides could not be obtained, because of their low volatility. As the vapour pressure of metal iodides is generally higher than that of the chlorides, attempts were made to measure the mass spectra of alkali metal iodides. It was found possible to record the mass spectra of LiI, NaI, KI, RbI, and CsI as well as those of AsI_3, SbI_3, SnI_4, CuI, and PbI_2.

EXPERIMENTAL

All reagents used were of super pure grade. The instrument used in this study was a JMS-01SG double focusing mass spectrometer, JALCO. The operational conditions were as follows: main slit 20 or 8 μm; acceleration voltage 7 kV; ionization voltage 75 or 20 V; ionization current 200 μA; sample temperatures 100–400°.

RESULTS

Table 1 summarizes the mass spectrum of lithium iodide. In this mass spectrum peaks at *m/e* 7 (Li^+), 127 (I^+), 134 (LiI^+), 141 (Li_2I^+), and 254 (I_2^+) and additional peaks at *m/e* 23 (Na^+, calculated mass; 22·990, observed mass; 22·987), 150 (NaI^+, calculated mass; 149·894, observed mass; 149·895) and 157 ($LiNaI^+$, calculated mass; 156·910, observed mass; 156·906) appeared. The additional peaks were also observed in the mass spectra of other commercial samples of lithium iodide, which suggests that some sodium iodide is contained even in the super pure grade lithium iodide. Table 2 summarizes the mass spectrum of sodium iodide. In addition to the characteristic peaks of sodium iodide, a peak at *m/e* 166 was assigned to KI^+ (calculated mass; 165·868, observed mass; 165·867), which originated from contamination of the sodium iodide.

Table 3 summarizes the mass spectrum of potassium iodide. In this spectrum peaks at *m/e* 39 (K^+), 127 (I^+), 166 (KI^+), 205 (K_2I^+) and 254 (I_2^+) were observed, and other peaks at *m/e* 23 Na^+ (calculated mass; 22·990, observed mass; 22·987), 150 (NaI^+), 189 $NaKI^+$ (calculated mass; 188·858, observed mass; 188·858) and 133 (Cs^+) also appeared.

Table 4 summarizes the mass spectrum of rubidium iodide. In this spectrum peaks at *m/e* 85 (Rb^+), 127 (I^+), 128 (HI^+), 212 (RbI^+), 254 (I_2^+), 297 (Rb_2I^+) and 339 (RbI_2^+) were observed. Other peaks from contamination also appeared at *m/e* 23 (Na^+), 150 (NaI^+), 166 (KI^+), 133 (Cs^+) and 260 (CsI^+).

Table 5 summarizes the mass spectrum of caesium iodide. In this spectrum peaks at *m/e* 63·5 (I^{2+}), 127 (I^+), 133 (Cs^+), 254 (I_2^+), 260 (CsI^+) and 393 (Cs_2I^+) were observed and no other peak appeared.

From these results, it appeared possible to detect various alkali metals by mass spectrometry.

Table 1. Mass spectrum of lithium iodide (sample temperature 380°C)

m/e	Ion	Relative intensity, %
7	Li^+	9·3
23	Na^+	2·2
63·5	I^{2+}	7·3
127	I^+	17·9
128	HI^+	5·1
134	LiI^+	4·6
140	$^6Li^7LiI^+$	100
141	$^7Li_2I^+$	7·9
157	$NaLiI^+$	3·9
254	I_2^+	40·5

Table 2. Mass spectrum of sodium iodide (sample temperature 350°C)

m/e	Ion	Relative intensity, %
23	Na^+	56·4
63·5	I^{2+}	53·3
127	I^+	39·0
128	HI^+	8·2
150	NaI^+	95·4
166	KI^+	35·4
173	Na_2I^+	100
254	I_2^+	44·6

Table 3. Mass spectrum of potassium iodide (sample temperature 420°C)

m/e	Ion	Relative intensity, %
23	Na^+	74·6
39	$^{39}K^+$	47·6
41	$^{41}K^+$	3·4
63·5	I^{2+}	100
85	$^{85}Rb^+$	11·1
87	$^{87}Rb^+$	4·1
127	I^+	79·4
128	HI^+	44·4
133	Cs^+	71·4
150	NaI^+	95·2
166	$^{39}KI^+$	36·6
168	$^{41}KI^+$	3·2
189	$NaIK^+$	38·1
205	$^{39}K_2I^+$	47·6
207	$^{39}K^{41}KI^+$	9·5
254	I_2^+	7·9

Table 4. Mass spectrum of rubidium iodide (sample temperature 380°C)

m/e	Ion	Relative intensity, %
23	Na^+	5·1
85	$^{85}Rb^+$	96·6
87	$^{87}Rb^+$	37·2
127	I^+	97·4
128	HI^+	5·1
133	Cs^+	100
150	NaI^+	7·7
166	KI^+	11·5
212	$^{85}RbI^+$	41·0
214	$^{87}RbI^+$	15·4
254	I_2^+	7·7
260	Cs^+	23·1
297	$^{85}Rb_2I^+$	6·4
299	$^{85}Rb^{87}RbI^+$	5·1
30	$^{87}Rb_2I^+$	1·2
339	$^{85}RbI_2^+$	3·8
341	$^{87}RbI_2^+$	1·5

Table 5. Mass spectrum of caesium iodide (sample temperature 400°C)

m/e	Ion	Relative intensity, %
63·5	I^{2+}	88·3
127	I^+	83·3
133	Cs^+	33·3
254	I_2^+	28·3
260	CsI^+	100
393	Cs_2I^+	11·7

Table 6. Mass spectrum of arsenic tri-iodide (sample temperature 127°C)

m/e	Ion	Relative intensity, %
63·5	I^{2+}	8
127	I^+	100
202	AsI^+	24
254	I_2^+	55
329	AsI_2^+	44
456	AsI_3^+	72

Mass spectra of AsI_3, SbI_3, SnI_4, CuI and PbI_2

Table 6 summarizes the mass spectrum of arsenic tri-iodide. Arsenic is a monoisotopic element, and provides a simple spectrum. Table 7 summarizes the mass spectrum of antimony tri-iodide. Antimony has two natural stable isotopes (^{121}Sb and ^{123}Sb) and this spectrum was more complex. Table 8 summarizes the mass spectrum of tin tetraiodide. Since tin has ten natural stable isotopes, the mass spectrum is even more complex. Table 9 summarizes the mass spectrum of copper(I) iodide. Copper has two natural stable isotopes (^{63}Cu and ^{65}Cu). In this spectrum, peaks at *m/e* values higher than that of CuI^+ were observed. These peaks are due to the ions $Cu_3I_3^+$, $Cu_3I_2^+$,

Table 7. Mass spectrum of antimony tri-iodide (sample temperature 120°C)

m/e	Ion	Relative intensity, %
63·5	I^{2+}	4·4
121	$^{121}Sb^+$	28·6
123	$^{123}Sb^+$	22·0
127	I^+	100
248	$^{121}SbI^+$	24·2
250	$^{123}SbI^+$	18·9
254	I_2^+	6·6
375	$^{121}SbI_2^+$	42·9
377	$^{123}SbI_2^+$	31·9
502	$^{121}SbI_3^+$	36·3
504	$^{123}SbI_3^+$	26·4

Table 8. Mass spectrum of tin tetraiodide (sample temperature 220°C)

m/e	Ion	Relative intensity, %
116	$^{116}Sn^+$	5·3
118	$^{118}Sn^+$	9·9
120	$^{120}Sn^+$	12·5
127	I^+	100
243	$^{116}SnI^+$	8·8
245	$^{118}SnI^+$	13·8
247	$^{120}SnI^+$	18·8
254	I_2^+	100
371	$^{116}SnI_2^+$	2·5
373	$^{118}SnI_2^+$	3·8
375	$^{120}SnI_2^+$	6·3
497	$^{116}SnI_3^+$	8·8
499	$^{118}SnI_3^+$	12·5
501	$^{120}SnI_3^+$	17·5
624	$^{116}SnI_4^+$	7·5
626	$^{118}SnI_4^+$	10·0
628	$^{120}SnI_4^+$	13·8

Table 9. Mass spectrum of copper(I) iodide (sample temperature 280°C)

m/e	Ion	Relative intensity, %
63	$^{63}Cu^+$	41
63·5	I^{2+}	10
65	$^{65}Cu^+$	18
126	$^{63}Cu_2^+$	26
127	I^+	52
128	$^{63}Cu^{65}Cu^+$	15
130	$^{65}Cu_2^+$	7
190	$^{63}CuI^+$	100
192	$^{65}CuI^+$	48
253	$^{63}Cu_2I^+$	76
254	I_2^+	47
255	$^{63}Cu^{65}CuI^+$	65
257	$^{65}Cu_2I^+$	12
380	$^{63}Cu_2I_2^+$	9
382	$^{63}Cu^{65}CuI^+$	7
384	$^{65}Cu_2I_2^+$	2
443	$^{63}Cu_3I_2^+$	44
445	$^{63}Cu_2{}^{65}CuI_2^+$	57
447	$^{63}Cu^{65}Cu_2I_2^+$	25
449	$^{65}Cu_3I_2^+$	3
570	$^{63}Cu_3I_3^+$	66
572	$^{63}Cu_2{}^{65}CuI_3^+$	85
574	$^{63}Cu^{65}Cu_2I_3^+$	38
576	$^{65}Cu_3I_3^+$	5

Table 10. Mass spectrum of lead(II) iodide (sample temperature 260°C)

m/e	Ion	Relative intensity, %
63·5	I^{2+}	8·6
127	I^+	100
128	HI^+	8·6
206	$^{206}Pb^+$	4
207	$^{207}Pb^+$	4
208	$^{208}Pb^+$	10
331	$^{204}PbI^+$	2
333	$^{206}PbI^+$	27
334	$^{207}PbI^+$	23
335	$^{208}PbI^+$	52
458	$^{204}PbI_2^+$	1
460	$^{206}PbI_2^+$	17
461	$^{207}PbI_2^+$	15
462	$^{208}PbI_2^+$	36

$Cu_2I_2^+$, and Cu_2I^+. A peak due to the Cu_2^+ ion also appeared. Table 10 summarizes the mass spectrum of lead(II) iodide. Lead has four natural stable isotopes, but this spectrum was very simple.

The mass spectra of metal iodides were in general simpler than those of the metal chlorides reported earlier, because of the monoisotopic nature of iodine.

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Summary—The mass spectra of LiI, NaI, KI, RbI, CsI, AsI_3, SbI_3, SnI_4, CuI and PbI_2 have been recorded, and trace contaminants in alkali metal iodides detected.

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CORRIGENDUM

On p. 548 of the June issue, the names of two of the authors were inadvertently omitted. The authors' names and addresses should read as follows:

Department of Chemistry,
Lowell Technological Institute,
Lowell, Massachusetts, U.S.A.
V. LAVRAKAS
E. BARRY

New England Nuclear Corp.,
Billerica, Massachusetts
T. GOLENBESKI

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TALANTA MINI-REVIEW*

CELLULAR AND FOAMED PLASTICS AS SEPARATION MEDIA

A NEW GEOMETRICAL FORM OF THE SOLID PHASE IN ANALYTICAL LIQUID–SOLID CONTACT

T. BRAUN and A. B. FARAG†

Institute of Inorganic and Analytical Chemistry, L. Eötvös University, P.O. Box 123, 1443 Budapest, Hungary

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Summary—There has been considerable interest during the last few years in using cellular (foamed) plastics (mainly polyurethanes) either unloaded or as a means of immobilizing hydrophobic organic reagents, powdered ion-exchangers or finely divided precipitates, for the collection and separation of inorganic or organic species from aqueous solution. Foamed plastics with anchored (bonded) functional groups have also been used for the same purpose. It has been realized that the application of cellular plastics is often advantageous not only for quantitative work but also for qualitative and semiquantitative analysis. Methods available on the application of cellular and foamed plastics for the collection, separation and recovery of various inorganic and organic components from aqueous solution are reviewed.

Probably the oldest application of a material of cellular geometry (in the form of sponge) for chemical purposes was the purification of ethyl alcohol by distillation through a sponge impregnated with olive oil. This method, used by Brunschwig[1] more than four centuries ago, can be considered as partition chromatography, the sponge material being the support, olive oil the stationary phase and ethyl alcohol vapour the mobile phase. In 1962 Bayer[2] checked this ancient method and found that it operates well.

Lal *et al.*[3] have described a method for the extraction of trace elements from sea-water, by use of ferric hydroxide supported on natural sponges. Several elements (*e.g.* Si, Be, Al and Ti) were extracted by towing ferric hydroxide impregnated sponge through coastal sea-water.

Recently, however, papers[4–6] have been published describing the possibility of using cellular plastics for gas–solid and gas–liquid chromatographic separations.

Bowen[7] was the first to discover the absorption properties of polyurethane foams toward a number of inorganic and organic species in aqueous solution. Since the appearance of this work several investigators[8–11] have used polyurethane foams for the absorption and recovery of inorganic and organic compounds from aqueous solution.

Braun and Farag[12,13] suggested in 1972 the analytical application of polyurethane foams loaded with hydrophobic extractant. Gesser *et al.*[14] described a method for the collection of pesticides from water by using polyurethane foam coated with chromatographic-grade greases.

Recently, foamed plastics (mainly polyurethanes) immobilizing hydrophobic reagents, powdered ion-exchangers and finely divided precipitates, or bonding certain functional groups, have been recommended for several analytical applications.[15–18]

This review collects the papers published and gives an up-to-date picture of the use of cellular (foamed) plastics as a new geometrical form of the solid phase in analytical liquid–solid extraction processes.

DEFINITION, GEOMETRY AND CELL STRUCTURE OF CELLULAR (FOAMED) PLASTICS

Cellular (foamed) plastics can be defined[19] as plastic materials in which a proportion of solid is replaced by gas in the form of numerous small cells. The gas may be a continuous phase, giving an open cell material, or it may be a discontinuous phase, *i.e.*, in the form of discrete, non-communicating cells.

From the geometrical point of view, if the gas bubbles occupy a volume fraction smaller than 76% of the whole, they may be spherical. If they occupy a volume fraction larger than 76%, they will be distorted into polyhedra[20] (mainly pentagonal dodecahedra). In the latter case the polymer is distributed between the walls of the bubbles and the lines where bubbles intersect. The bubbles are called cells, the lines of intersection strands, and the walls windows (or membranes). In an open-cell flexible foam, at least two windows (from the total) in each cell must be ruptured for fluids to pass freely through the foam.

Cell structure (*i.e.*, the presence or absence of windows in the cells, or the number of windows per cell)

* For reprints of this Review, see Publisher's announcement near end of this issue.

† Present address: National Research Centre, Dokki, Cairo, Egypt.

is a function of the process by which the cellular material is made. It was noted[19] that both rigid and flexible foams may be obtained, with open or closed cells. The structure made up of windowless cells (containing only strands) is called a reticulated foam.[20]

It was reported[19] that flexible and rigid materials generally tend to have open and closed cell structures respectively. However, there are many exceptions and, as the type of cell structure is mainly determined by the method of expansion, some materials which can be made by more than one method can exist in both open and closed cell forms. Furthermore, methods are available by which closed cell structures can be converted into the open cell form by rupture of the windows. Rupturing may be caused mechanically by applying pressure, or chemically by hydrolysis or oxidation.

GENERAL METHODS OF PREPARING CELLULAR PLASTICS

With the highly developed technology for making cellular plastics today,[21] methods exist by which practically every plastic material may be made in cellular form. The general principle for preparing cellular materials is the dispersion of a gas within a liquid to obtain a liquid foam which will then be solidified to a solid cellular plastic. The main methods[19] for uniform dispersion of the gas bubbles are chemical (*e.g.*, thermal decomposition of a chemical blowing agent or blowing by *in situ* chemical reaction); physical (*e.g.*, low-pressure release of dissolved gas, blowing by vapour from a volatile liquid or temporary filler); and mechanical (*e.g.*, mechanical entrainment of gas or the use of microspheres).

Several plastic materials are now commercially available in cellular forms, *e.g.*, poly(vinyl chloride), polyurethane, polymethylmethacrylate, phenol–formaldehyde, urea–formaldehyde, polyethylene, polytetrafluoroethylene.

In the major part of the published work on the application of cellular plastics in analytical chemistry, polyurethane foams have been employed. Consequently, some information about the preparation of polyurethane foam and its physical and chemical properties is briefly given.

Polyurethane foam preparation

Polyurethane foams can be prepared in soft, flexible or rigid forms.[22] They are formed by the reaction of the terminal hydroxyl groups of a polyester or polyether resin and a polyfunctional isocyanate.[23,24] Foams prepared from a wide variety of hydroxyl compounds (polyethers, polyesters or polyols) and isocyanates are now commercially available. In general, polyols in the molecular weight range 400–6000 are employed.[25,26] The most widely used isocyanate compound is toluene di-isocyanate (usually 80/20 and 65/35 mixtures of the 2,4- and 2,6-isomers are used).

Physical and chemical properties of polyurethane foams

Generally, the physical properties of polyurethane foams depend on the method by which they are prepared. For example, the windows may or may not be ruptured in the final stage of expansion, depending on the relative rate of molecular growth (gelation) and gas reaction, giving rise to flexible or rigid foam. The choice of the polyol has a major effect on the foam properties determining its rigidity or flexibility.[22] The cross-link density of the urethane polymer also determines whether the foam will be flexible (low cross-link density) or rigid (high cross-link density). Flexible foams are prepared from polyols of moderately high molecular weight and low degree of branching, while rigid foams are prepared from low molecular weight, highly branched resins.

Also, the chemical properties of polyurethane foams are a function of the preparation process. For example, solvent-resistance of the foam material is increased at higher cross-link density, seems to be unaffected by the type of aromatic di-isocyanate used, and is reduced by the use of a large excess of isocyanate.[21]

Bowen[7] examined the chemical resistance of some batches of flexible polyurethane foam and claimed that they were rather stable and inert. He reported that the foam batches tested were degraded when heated between 180° and 220°, and slowly turned brown in ultraviolet light. They were dissolved by concentrated nitric acid, and reduced alkaline potassium permanganate. They were mostly unaltered, apart from reversible swelling, by water, 6*M* hydrochloric acid, 4*M* sulphuric acid, 2*M* nitric acid, glacial acetic acid, 2*M* ammonia, 2*M* sodium hydroxide and the following solvents: light petroleum, benzene, carbon tetrachloride, chloroform, diethyl ether, di-isopropyl ether, acetone, isobutyl methyl ketone, ethyl acetate, isopentyl acetate, and alcohols. Also it was noted that polyurethane foams could be dissolved in hot arsenic(III) chloride solution.

UNLOADED POLYURETHANE FOAMS

Bowen[7] initiated in 1970 the application of foamed polyurethane for the absorption and recovery of a number of inorganic and organic compounds from aqueous solutions in static (batch) experiments. He measured the surface area of various polyurethane foam samples (of polyether type) and demonstrated that the uptake of different components from aqueous solutions by the foam materials is due to absorption rather than adsorption phenomena.[7,22] The absorption isotherms of some elements have been measured and the distribution ratios and absorption capacities of the foam materials for these elements have been determined.[7] In some cases [*e.g.*, iodine and gold(III)] the absorption was found to be greater at low temperatures than at higher ones, while in others [*e.g.*, Fe(III)] the reverse was observed.

In a subsequent communication Bowen[28] recommended the application of polyurethane foam for the

recovery of gold(III) chloride from mineral wastewaters by the batch technique. The possibility of separating gold(III) chloride from natural waters by polyurethane foams has also been examined by Schiller and Cook.[8] It was claimed[8] that gold at ppM (parts per milliard) level can be quantitatively collected from aqueous solutions by shaking the mixture for 90 min.

Recently, Braun and Farag[10] investigated the recovery of gold–thiourea complex from aqueous solutions containing perchlorate ion, using polyurethane foams in batch operations. Open-cell polyether and polyester type foams were examined. The uptake of the gold–thiourea complex by different samples of the polyether type foam depended to some extent on the cell dimensions and decreased as the cell size decreased. Further, the absorption capacities of the polyether type foams for the gold complex are generally greater than those of the polyester type.[10]

Sukiman[11] described the application of polyurethane foam for the extraction of gold(III) chloride from acidic aqueous solutions and natural waters by the dynamic technique. Gold(III) at trace concentrations (0·02–25 ppM) can be quantitatively collected from aqueous solution by percolating the solution through a short foam column at relatively high flow-rates (10–13 $ml.cm^{-2}.min^{-1}$)*. Acetone has been used for the recovery of gold from the foam column at a flow-rate of 1 $ml.cm^{-2}.min^{-1}$.

On the other hand, Gesser *et al.*[9] studied the possibility of using polyurethane foam columns for the extraction and concentration of organic contaminants from water. The collection of polychlorinated biphenyls at various concentration levels (2–20 ppM) has been successfully achieved by passing the aqueous solution through the foam column at high flow-rates (*ca.* 80 $ml.cm^{-2}.min^{-1}$). Acetone and hexane have been employed for the elution of the biphenyls from the foam column. Further, Gesser *et al.*[29] have shown that polyurethane foam columns can be used to monitor organic matter in drinking water. A certain volume of water (1–2 litres) was percolated through the foam column at a flow-rate of 2–4 $ml.cm^{-2}.min^{-1}$ and the extracted organic compounds were then stripped from the foam material with hexane in a Soxhlet extractor.

POLYURETHANE FOAMS WITH PHYSICALLY IMMOBILIZED HYDROPHOBIC ORGANIC REAGENTS AND EXTRACTANTS

Although unloaded polyurethane foams have successfully been used for the separation and concentration of some inorganic and organic components from aqueous solutions, yet the general applications of foamed polyurethanes are reduced by their limited selectivity towards the absorption of various compounds.[9,17] This directed attention towards the application of polyurethane foam impregnated with certain organic reagents, to provide selective separation methods.

Organic extractants (*e.g.*, tri-n-butyl phosphate) are physically immobilized on the foam matrix by allowing the foam material to swell in solutions of them.[12,13] The hydrophobic character of polyurethane foams together with their high available surface area allowed the immobilization of considerable amounts of a wide variety of organic reagents and extracting agents.[11,12,14,30] Polyurethane foam loaded with tri-n-butyl phosphate (TBP) has been prepared[13] by the above-mentioned method. In this case the foam material can be considered as a support for the TBP, which is actually the stationary phase. Separation methods in which these loaded foams are used in chromatographic columns are called reversed-phase foam chromatography.[13,30] Braun and Farag[13] demonstrated the practical advantages of using TBP-loaded foam for the separation of inorganic species from aqueous solution. They made a comparative investigation of the separation of palladium(II), bismuth(III) and nickel(II) in a thiourea–perchloric acid system on the TBP-loaded foam and on TBP-loaded "Voltalef" (polytrifluorochloroethylene) powder. A polyether foam of open-cell type was found[10,13] to absorb and retain TBP more efficiently than "Voltalef" powder did. The extraction rate of the palladium–thiourea complex on the loaded foam was proved[17] to be faster than on the loaded "Voltalef" powder.

For packing the foam material homogeneously in glass tubes of various lengths and diameters, a vacuum method has been developed.[13] This method was found to produce columns with very good flow characteristics and this vacuum-packing technique proved[31] to be suitable for filling chromatographic columns with granular "Voltalef".

A comparative study on the gravity flow-rate attained for columns packed with polyurethane foam and "Voltalef" powder (0·16–0·25 mm grain-size) has shown that the hydrodynamic properties of the foam columns are much superior.

The chromatographic behaviour of the palladium–thiourea complex on a TBP-loaded foam column has also been examined.[13] The elution curve (with water as eluent) is symmetrical and the peak relatively sharp. The height equivalent to a theoretical plate (HETP) as calculated[32] from the elution curve of palladium was found[17] to be 1·7 and 2·8 mm for foam and "Voltalef" columns, respectively. The breakthrough and overall capacities of foam and "Voltalef" columns have also been measured[17] by using the palladium–thiourea complex solution. In general, the capacity of the TBP-loaded foam is higher than that of the TBP-loaded "Voltalef" (about double).[17] Separation of palladium from bismuth and nickel in a thiourea–perchloric acid system can be achieved on the TBP-loaded foam columns.[13]

Furthermore, the separation and concentration of gold(III) from thiourea–perchloric acid systems on

* We consider it necessary to include the cross-sectional area of the column in specification of the flow-rate, which thus has the dimensions of a linear flow-rate, $cm.min^{-1}$.

TBP-loaded polyurethane foam have also been investigated by the batch and column techniques.[33] The gold–thiourea complex is extracted on the loaded foam from 0·1*M* perchloric acid containing 3% thiourea and 1% sodium perchlorate. The uptake of the gold complex by the loaded foam was claimed[33] to be fast and not appreciably affected by the presence of some interfering elements [*e.g.*, zinc(II), iron(III) or bismuth(III)]. Quantitative separation of trace amounts of gold from high concentrations of Zn^{2+}, Co^{2+}, Ni^{2+}, Fe^{3+}, Sb^{3+}, Cu^{2+}, Bi^{3+} or Pd^{2+} is achieved by using short foam columns and a flow-rate of 10–12 ml.cm^{-2}.min^{-1}.

The chemical enrichment of gold from dilute aqueous solutions has also been investigated.[33] Gold was completely collected on passing the solution through a short foam column at the flow-rate mentioned above. The gold was then recovered from the foam column by dissolving the foam material in hot concentrated nitric acid.

The analytical utility of TBP-loaded polyurethane foam columns for the separation of some metals from hydrochloric acid solution has also been investigated.[34] The distribution of cobalt, copper and iron chlorides in a TBP foam–hydrochloric acid system was measured. Using the TBP-loaded foam columns, it was possible to separate iron from nickel, copper or cobalt, and the suitability of using the loaded foam columns for the separation of ^{58}Co and ^{59}Fe isotopes has been demonstrated.

Polyurethane foam columns immobilizing finely divided tetrachlorohydroquinone were proved[30] to be suitable for the reduction of some metal ions in their higher valency state. Reduction of cerium(IV), vanadium(V) and iron(III) on foam-redox columns has been examined. The effect of flow-rate and temperature on the reduction efficiency for each metal ion was investigated. Cerium(IV) can be reduced quantitatively on passing its aqueous solution through the foam column at flow-rates of 1–6 ml.cm^{-2}.min^{-1} and room temperature. The reduction of vanadium(V) and iron(III) was, however, slower. At 35° a relatively high flow-rate could be used without affecting the completeness of the reduction.

The application of polyurethane foam immobilizing tetrachlorohydroquinone in a finely divided state or in chlorobenzene solution and packed in a syringe (pulsed column) has been described[35] for the reduction of Ce(IV), V(V) and Fe(III). The reduction of the metal ion is simply achieved by pressing and releasing the plunger of the flexible-foam pulsed column several times, with the tip in the test solution. The reduction efficiency of pulsed columns packed with swollen foam materials (*i.e.*, immobilizing the redox reagent in chlorobenzene solution) was found to be better than that of pulsed columns packed with dry foam (*i.e.*, immobilizing the redox reagent in a finely divided state). The reduction of Ce(IV), V(V) and Fe(III) was more effective if the aqueous metal ion solution was heated to about 80° before use of the pulsed column. Various amounts (2–20 mg) of the three metal ions have been determined by this method.

Polyurethane foams immobilizing methyl isobutyl ketone, diethyl ether, isopropyl ether or ethyl acetate have also been examined[11] for the extraction of gold(III) chloride from aqueous solutions. For the rapid collection of gold at trace concentrations (0·06–25 ppm) the percolation of the aqueous solution through short columns packed with these foams at relatively high flow-rates (10–13 ml.cm^{-2}.min^{-1}) was recommended. The gold was then eluted from the foam column with acetone.

All the methods mentioned previously describe the possibility of using polyurethane foam immobilizing various organic reagents. However, polyurethane foams were also proved[18,36] to be suitable for the immobilization of inorganic reagents. Immobilized finely divided silver sulphide or metallic copper have been suggested for isotope and redox exchange separations, respectively. The silver sulphide foam was prepared[18] by loading a heterogeneous cation-exchange foam[37] with ionic silver and subsequent precipitation of silver sulphide in the foam matrix with sodium sulphide solution. Similarly, foam containing copper was prepared[36] by loading the heterogeneous cation-exchange foam with copper ions and then reducing the ionic copper to the metallic form with sodium hydrosulphite solution. Static and dynamic isotope and redox exchange separations of radiosilver on silver sulphide foam and copper foam, respectively, have been investigated. Columns packed with silver sulphide foam were suitable for the collection of various levels of radiosilver (0·1–100 μg of Ag^+) from nitric acid solution, at relatively high flow-rates (20 ml.cm^{-2}.min^{-1}).

Quantitative collection of radiosilver at various concentrations (in 2*M* nitric acid) by redox exchange reaction on columns packed with copper foam has also been reported, the flow-rate being 10–12 ml.cm^{-2}.min^{-1}.

The possibility of using polyurethane foam immobilizing chromatographic-grade greases (preferably DC-200) for the collection of trace concentrations of organo-chlorine pesticides from water or aqueous suspensions has also been investigated.[14] The grease-loaded foam is prepared by dipping the foam material in a 5% solution of the grease in a suitable solvent.

The extraction efficiencies of different grease-loaded foam columns for ten different organo-chlorine pesticides have been tested. In the collection of the different pesticides from water, fast flow-rates (*ca.* 80 ml.cm^{-2}.min^{-1}) could be employed. However, in the case of collection from suspensions, low flow-rates (*ca.* 10 ml.cm^{-2}.min^{-1}) were recommended.[14]

Generally, foam columns (loaded with DC-200) grease) are able to extract all the ten pesticides from water almost quantitatively. However in the case of suspensions some pesticides (*e.g.*, *p,p'*-DDE) are not extracted completely. This was attributed to their ability to adsorb on the suspension.

PLASTICIZED REAGENT FOAMS

Plasticizers can be defined as non-volatile liquids used to modify synthetic resins.[38] Plasticizing of a polymer is a process in which plasticizer molecules neutralize (reduce) the secondary valence forces (van der Waals) between the polymeric chains, thus increasing the mobility of the molecular segments and decreasing the glass-transition temperature of the system. Above the glass-transition temperature the mobility of plasticizer molecules within the polymeric network is apparently quite high.[39]

The preparation of plasticized reagent foams has recently been studied[16,40,41] by dissolving hydrophobic organic reagents in a plasticizer solution and then immobilizing the solution on an open-cell type polyurethane foam by swelling. Several hydrophobic organic reagents (*e.g.*, dithizone, 1-nitroso-2-naphthol and diethylammonium diethyldithiocarbamate) were found to dissolve in various plasticizers (*e.g.*, TBP, α-di-n-nonyl phthalate, di-n-octyl phthalate or dibutyl adipate). Accordingly, plasticized zinc dithizonate,[16,40] 1-nitroso-2-naphthol[41] and diethylammonium diethyldithiocarbamate[41] foams with reasonable capacities and suitable for the preconcentration of metal ions from aqueous solutions have been prepared. The mobilities of metal ions in the plasticized reagent foam were proved to be quite high and consequently their collection proceeded rapidly. This makes the applications of relatively high flow-rates in column operations possible without any appreciable loss in collection efficiency.

The collection of traces of silver(I) or mercury(II) on zinc dithizonate foam has been examined.[16,40] It was proved that the collection rates with plasticized zinc dithizonate foams are generally better than with the unplasticized ones. Small amounts of silver or mercury from extremely dilute solutions (*e.g.*, 1 ppM) are collected by percolating the aqueous metal ion solution through the plasticized foam column at a flow-rate of 8–12 $ml.cm^{-2}.min^{-1}$. Quantitative recoveries of silver and mercury from the plasticized zinc dithizonate foam are obtained by elution with sodium thiosulphate solution.[16,40]

Complete collection of silver was possible in presence of 10^6 times as much lead or copper.[16]

Traces of cobalt(II) are collected on plasticized 1-nitroso-2-naphthol and diethylammonium diethyldithiocarbamate foams.[41] The optimal pH-values of the aqueous solutions for the collection are 6·6–9·0 and 4·5–5·5 for 1-nitroso-2-naphthol and diethylammonium diethyldithiocarbamate foams respectively. Various amounts of cobalt(II) (1–1000 μg) are quantitatively collected from aqueous solutions on foam columns at a flow-rate of 5–6 $ml.cm^{-2}.min^{-1}$.

Recently, the preparation of plasticized iodine and silver dithizonate foams suitable for isotope exchange separations of radioactive isotopes has been described.[42] The exchange of radioiodide on the iodine foam was found[42] to be very fast in batch experiments. The highest exchange yield is obtained from aqueous solutions at pH-values lower than 1. It was proved[42] that the mobility of the iodide ion in the plasticized foam material is quite high and consequently equilibrium is attained rapidly. Complete separation (by exchange) of radioiodide from a large excess of sodium, potassium, chloride and bromide ions, which are known to interfere seriously in the determination of iodine in biological materials by activation analysis,[43] was achieved.

Quantitative collection of radiosilver (0·01–1 μg) from 0·1*M* nitric acid was realized on columns packed with plasticized polyurethane foam immobilizing primary silver dithizonate.[42]

On the other hand, plasticized polyurethane foams immobilizing chromogenic hydrophobic organic reagents have been suggested[44] for rapid detection and semiquantitative determination of very low concentrations of metal ions in aqueous solution. The name "chromofoam" was proposed for these reagent foams. It was claimed[44] that the organic reagent solution, which is homogeneously distributed on the large available surface area of the plasticized reagent foam (chromofoam), can function as an effective collector for metal ion traces from relatively high volumes of aqueous solution. This together with the greater possibility of observing the reaction products on the surface of the foam material allows the detection of traces of metal ions with a chromofoam by shaking one small cube of it with one or more ml of the aqueous solution in a test-tube.

Detection and semiquantitative determination of zinc(II) or lead(II) with plasticized dithizone foam and of copper(II) and cobalt(II) with rubeanic acid and Amberlite LA-1 foams, respectively, have been investigated.[44] Generally, the sensitivity of the foam test is better than or equal to that of the usual spot-tests on a spot-plate or filter paper. Also, the detection of cobalt(II) with Amberlite LA-1 foam in the presence of thiocyanate ions was proved[44] to be more sensitive than the resin spot-tests.[45] The selectivity of the chromofoam test has been examined in the case of cobalt by studying the detection of 1 μg of cobalt in the presence of up to 10 mg of more than 40 elements. The chromofoam test was found to be quite selective.

A further advantage of chromofoams is that columns packed with them can be used for the detection and semiquantitative determination of metal ions at the ppM level. This is simply achieved by passing large volumes of the aqueous solution through the reagent foam column at a flow-rate of 10–15 $ml.cm^{-2}.min^{-1}$ and measuring (in comparison with a standard) the length of the coloured zone.

POLYURETHANE FOAMS WITH ANCHORED (BONDED) FUNCTIONAL GROUPS

The preparation of cellular (foamed) plastics to which specific functional groups are chemically bonded has also been attempted.[15,37] Gesser *et al.*[15] described a method for the preparation of SH–polyur-

ethane foam. Columns packed with the SH-foam were evaluated for the adsorption of mercuric chloride and methylmercuric chloride from extremely dilute aqueous solution. It was found that mercury at concentrations ranging between 0·4 and 0·0004 ppm can be quantitatively collected on the foam columns when 100 ml of the aqueous solution are allowed to pass through them at a flow-rate of about 13 $ml.cm^{-2}.min^{-1}$. At higher mercury concentrations (*e.g.*, 4 ppM) the retention efficiency of the foam columns is decreased because of oversaturation.

In general, the effective capacity of the foam columns for mercury was much lower for methylmercuric chloride than for mercuric chloride. This was attributed to the probable steric hindrance effect of the methyl group. The fraction of mercury adsorbed on the foam column was generally increased as the concentration of mercury decreased.

The recovery of mercury from the SH-foam has also been investigated, the foam material being extracted with 2*M* hydrochloric acid in a Soxhlet extractor.

On the other hand, Braun *et al.*,[37] during their studies on the preparation of ion-exchange foams, described various methods suitable for the direct and indirect introduction of functional groups (ionogenic groups) in the foamed skeleton structure. They prepared phenol–formaldehyde resin foam to which sulphonic acid groups were chemically bonded by direct sulphonation of a commercially available phenol–formaldehyde foam. It was reported that the mechanical properties of the original phenol–formaldehyde foam were not much changed by sulphonation. Also, the ion-exchange capacity of the foams was reasonable (1·85 meq/g).

Indirect introduction of the ionogenic groups into the foam material has also been described. Two different methods are used. The first method is based on carrying out a polymer analogue reaction after joining the foam to an easily transformable polymer. Styrene–polyurethane interpolymer foam was prepared by this method and the anion-exchange groups then introduced by chloromethylation and amination. The mechanical properties of the foams depended on the polymerization conditions and the quality of the initiator used.

The second method for the indirect introduction of ionogenic groups into the foam matrix was based on the radiation grafting of a monomer with ionogenic groups. The radiation grafting of open-cell polyurethane and closed-cell polyethylene foams with methacrylic acid has been investigated.[37] Foams with excellent properties and good ion-exchange capacities (4 meq/g) have been prepared.

In our opinion, the analytical use of foamed plastics with bonded functional groups is a very promising field. Foam materials with very selective properties should be obtained by anchoring functional groups to the foam skeleton, and could become very important if suitable methods could be developed for the preparation of such foams.

HOMOGENEOUS AND HETEROGENEOUS ION-EXCHANGE FOAMS

Homogeneous ion-exchange foams are prepared by[37,46] (*i*) physical immobilization of liquid ion-exchangers on or in flexible polyether-type polyurethane foam, (*ii*) direct anchoring of ion-exchange groups on previously prepared phenol–formaldehyde foam, (*iii*) indirect introduction of the ionogenic groups into polyurethane or polyethylene foams.

The direct and indirect introduction of the ionogenic groups into the different foams has been described in the previous section. Physical immobilization of a benzene solution of tri-n-octylamine (TNOA), liquid anion-exchanger on polyurethane foam was found[46] to be possible by allowing the foam material to swell in a TNOA–benzene solution. The analytical utility of the foam was tested by investigating the separation of cobalt(II) and nickel(II) in hydrochloric acid media. Columns packed with foam materials containing 11·4 and 17·7% w/w of TNOA in benzene were found[46] to be the most suitable for the quantitative retention (and subsequent elution) of cobalt from hydrochloric acid solution. Separation of nickel and cobalt at different relative concentrations was achieved by using 8*M* and 1*M* hydrochloric acid for the elution of nickel and cobalt respectively.

Plasticized polyurethane foam immobilizing Amberlite LA-1 (liquid anion-exchanger) has also been prepared.[44] The application of this foam material for rapid and selective detection and semiquantitative determination of cobalt(II) in batch and column operations was described above.

A method for the preparation of a heterogeneous cation-exchange foam has also been reported.[37] This method is based on foaming a very finely ground powder of a commercially available cation-exchanger (Varion KS) with the precursors of open-cell polyether-type polyurethane foam. The possibility of using this cation-exchange foam for rapid separations in aqueous and alcoholic solutions has been investigated.[47] Sorption of metal ions (*e.g.*, Cu^{2+}) on the cation-exchange foam took place in one rapid step, *i.e.*, gel diffusion was not the rate-controlling step as in common ion-exchange beads. The $t_{1/2}$ value for equilibrium[48] sorption on the cation-exchange foam, as calculated from the rate-curve for copper(II), was found[47] to be 0·6 min. However, the capacity of the cation-exchange foam is much higher than that of surface-sulphonated resin beads.

A comparison between the efficiency of cation-exchange beads (Varion KS) and the cation-exchange foam for the elution of copper(II) with hydroxylammonium chloride solution shows that flow-rates as high as $3\ ml.cm^{-2}.min^{-1}$ could be applied in the case of foam columns without any considerable loss in column performance, while in the case of bead columns quantitative elution is only obtained at a flow-rate of $1\ ml.cm^{-2}.min^{-1}$. The selectivity of the cation-exchange foam was proved to be more or less the same as that of the original cation-exchange beads.

SPECIALLY TREATED POLYURETHANE FOAMS

Bauman *et al.*[19,50] reported that open-cell polyurethane foam can be used as a support for starch gel containing enzymes. They described a method for the preparation of immobilized horse-serum cholinesterase products in which the enzyme in the starch gel is physically entrapped on the surface of open-cell polyurethane foam pads. This immobilized enzyme pad is used to monitor water and air continuously for atmospheric pollutants which are enzymic inhibitors of cholinesterase.

Goodson *et al.*[51] have recently described an improved method for the preparation of polyurethane foam coated with horse-serum cholinesterase. They suggested the adsorption of the horse-serum cholinesterase on aluminium hydroxide gel before the starch-gel preparation. Portions of this foam were found[51] to be suitable for the detection of low concentrations of anticholinesterase substances in air, by use of a special cell in which the enzyme activity of the foam pad is observed electrochemically.

On the other hand, Evans *et al.*[52] examined the possibility of using open-cell polyurethane foam in the immunoadsorption of cells. Reticulated polyurethane foam of the polyester-type to which the antibody is coupled was found[52] to serve as a matrix for the immunological binding of erythrocytes.

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PHOSPHORIMETRY, A SPECTROCHEMICAL METHOD OF ANALYSIS*

J. J. AARON† and J. D. WINEFORDNER

Department of Chemistry, University of Florida, Gainesville, Florida 32611, U.S.A.

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Summary—A review is given of the various phosphorimetric techniques, now available, together with their analytical applications.

Phosphorimetry is a method of spectrochemical analysis that has been developed rather recently. In this technique, a sample containing organic molecules is excited at low temperature by ultraviolet or visible radiation; the excited molecules emit radiation of lower energy but of relatively long lifetime known as phosphorescence, which is measured by the detection system.

Although the use of phosphorescence as an analytical method was proposed in 1944 by Lewis and Kasha,[1] it was not until 1957 that the analytical usefulness of phosphorimetry was established by Keirs, Britt and Wentworth.[2] In the 1960's, numerous papers describing the instrumentation and the qualitative and quantitative uses of phosphorimetry in non-aqueous solvents were published, and their content has been summarized in several recent reviews.[3–8]

Most of these studies were performed with clear glasses of organic solvents, *e.g.*, pure ethanol, and EPA (EPA is a mixture of ethanol, isopentane and ether, 2:5:5 v/v) at 77 K. In 1970, quantitative analytical determinations utilizing phosphorescence spectra were extended to organic compounds in cracked or snowed matrices of organic solvents.[9] Since that date, phosphorimetry of organic compounds has been studied with snowed matrices of aqueous or partially aqueous solvents.[8–19] Progress has also recently been reported on the analysis of organic compounds and their mixtures by time-resolved and phase-resolved phosphorimetry.[20–25] Room-temperature phosphorescence of ionic organic compounds has been also recently proposed as an analytical technique.[26]

In the present paper, we wish to review briefly the fundamental aspects, the instrumentation, and the analytical applications of phosphorimetry in snowed media, and of time-resolved and phase-resolved phosphorimetry.

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† Present address: Consultate Général de France, 920 Esperson Building, Houston, Texas 77002.

CONVENTIONAL PHOSPHORIMETRY IN SNOWED MEDIA

Up to 1970, low-temperature phosphorescence analysis had to be carried out with organic solvents forming a clear and rigid glass at 77 K (b.p. of liquid nitrogen, generally used as coolant).[27] The use of cracked glasses and snowed matrices was proposed by Zweidinger and Winefordner.[9]

Theoretical aspects

Expressions for the intensity of phosphorescence in optically inhomogeneous and homogeneous matrices, are given in Table 1. They are obtained by the integration of the Kubelka and Munk[28] differential equations of diffuse reflectance, used to calculate the transmittance, T, and diffuse reflectance, R, of the analyte in these media. Basic assumptions are that the sample is an ideal diffuser, planar, and illuminated on one surface with diffuse monochromatic light. For more thorough discussion and complete integration, the reader should refer to Zweidinger and Winefordner.[9]

From the expressions of Table 1, some analytically useful conclusions can be drawn:

(*i*) for a clear glass (homogeneous matrices), all analytical curves ($\log I_p$ *vs.* $\log C$) have a slope of unity at low concentrations and a slope of zero at high concentrations of analyte;

(*ii*) for an optically inhomogeneous medium, *e.g.*, a snow or densely cracked glass, analytical curves should have a slope of unity at low concentrations, a slope of 0·5 at intermediate concentration, and a slope of zero at high analyte concentrations.

Instrumentation

The basic system used for phosphorimetry consists of a spectrophotofluorimeter with a phosphoroscope attachment, and a specially-designed quartz Dewar flask for low-temperature measurements. Two types of phosphoroscopes are used:

(*i*) the Becquerel phosphoroscope, in which the sample tube is placed between two circular rotating

Table 1. Phosphorescence intensity expressions

Homogeneous or inhomogeneous matrices	$I_p = 2\phi_p \beta I_0 \left[\frac{(1+\beta)\exp(\kappa\bar{b}) + (1-\beta)\exp(-\kappa\bar{b}) - 2}{(1+\beta)^2\exp(\kappa\bar{b}) - (1-\beta)^2\exp(-\kappa\bar{b})}\right]$	
Clear glass ($s = 0$)	$I_p = \phi_p . I_0 [1 - \exp(-kb)]$	
	Low concentrations $I_p = \phi_p I_0 kb$	*High concentrations* $I_p = \phi_p I_0$
Optically inhomogeneous matrix (snow or densely cracked glass) ($s = 0$)	*Low concentrations*	*High concentrations*
	$I_p = 2\phi_p I_0 kb\left(\frac{1}{1+2sb}\right)$	$I_p = 2\phi_p I_0\left(\frac{\sqrt{k}}{\sqrt{k}+2s+\sqrt{k}}\right)$

I_p = phosphorescence intensity, in J (actually a flux); ϕ_p = phosphorescence power efficiency, no units; I_0 = incident intensity, in J; $\beta = k/(\sqrt{k} + 2s)$ where k, the fraction of radiation absorbed per average path-length, is given by $k = 2{\cdot}303\epsilon C$ in cm^{-1} (ϵ is the molar absorptivity of the analyte in $l.mole^{-1}\ cm^{-1}$, and C is the concentration of analyte, in mole/l.); s is the fraction of radiation scattered per average path-length and independent of analyte concentration for all analytical concentrations of the analyte, no units; $\bar{b}$ is the average cell path-length for diffuse reflectance, in cm; $\kappa = \sqrt{k(k+2s)}$.

disks in a straight-through arrangement [this arrangement is less common than (*ii*)];

(*ii*) the Aminco-Keirs phosphoroscope, more widely used, in which the sample tube is placed in the middle of a rotating cylinder with two diametrically opposite apertures; emission light is usually collected at right angles to the excitation light.

Detailed description of several types of commercial spectrophosphorimeters has been given in recent reviews.[3,5,6,8] However, important improvements of the technique have been recently reported.[7,9–12] They mainly concern the modification of the sample cell and the sensitivity of the detector system.

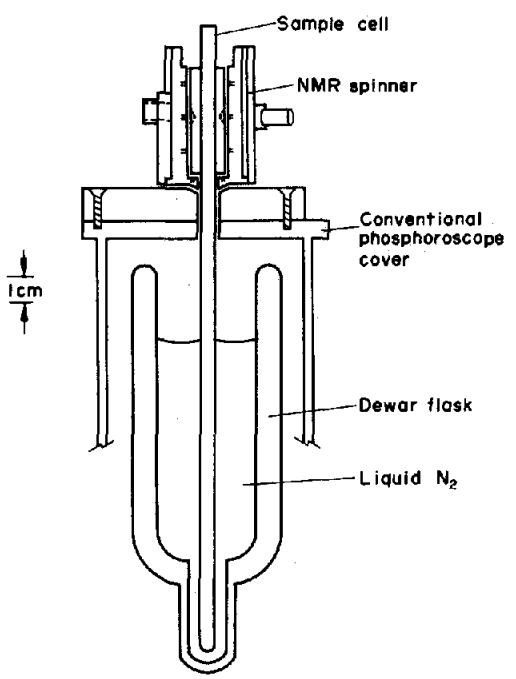

Fig. 1. Schematic diagram of rotating sample-cell assembly.[9] (Reprinted with permission from *Anal. Chem.*, 1970, **42**, 639. Copyright by the American Chemical Society.)

Sample cell. In Fig. 1, the rotating sample-cell assembly is schematically shown, as described by Hollifield and Winefordner,[29] and modified by Zweidinger and Winefordner.[9] It consists of a Varian A60-A High Resolution Nuclear Magnetic Resonance Spectrometer Spinner Assembly mounted on a sample-compartment light-cover. The fluctuations of signal resulting from inhomogeneities in the snowed media and irregularities in the diameter of the sample tube are minimized by the rotation of the sample cell (average speed from 450 to 1400 rpm), which is generally a long thin-walled quartz tube. Other properties of the rotating sample-cell are:

(*i*) the inner-filter effect is reduced;

(*ii*) sampling is simpler and more rapid;

(*iii*) precision of measurement of the phosphorescence signal is improved.

A new type of rotating sample-cell is suitable for aqueous solvents. It consists of an open-ended quartz capillary tube.[10,12] The use of a capillary tube permits quantitative phosphorimetric measurements of organic compounds in frozen aqueous solutions, with the following advantages:

(*i*) shattering of the sample cell by the strain caused by expansion of water at 77 K, is prevented by the thick walls of the capillary tube;

(*ii*) the sampling procedure is much simpler and more convenient than previously reported procedures;

(*iii*) the inherent photoluminescence of the capillary tube material is minimized by the use of film polarizers;[12]

(*iv*) the sample size is reduced to about 20 μl.

Detector system. Phototube signals of very low intensity are measured by analogue means with a low-noise nanoammeter described by O'Haver and Winefordner[30] or by digital means with a photon counter.

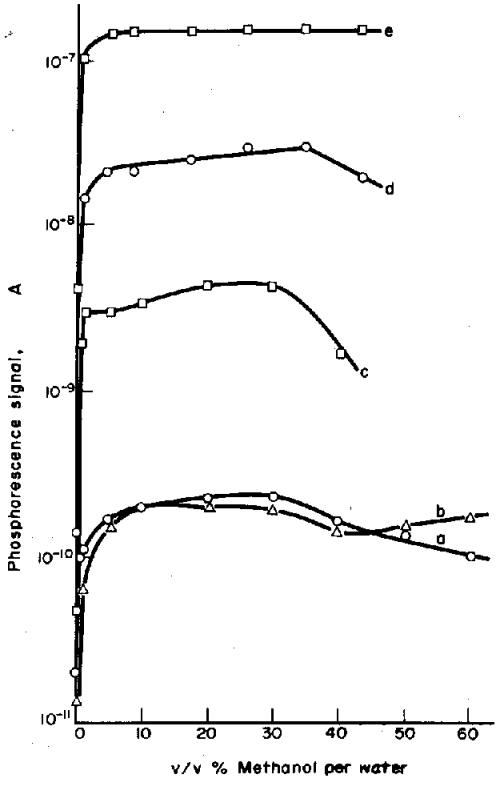

Fig. 2. Phosphorescence signal as a function of solvent composition (methanol/water solution); (*a*) $20 \times 10^{-6}M$ indol-3-ylacetic acid; (*b*) $4{\cdot}7 \times 10^{-6}M$ hippuric acid; (*c*) $1{\cdot}7 \times 10^{-6}M$ thioacetamide; (*d*) $1{\cdot}0 \times 10^{-4}M$ purine; (*e*) $1{\cdot}0 \times 10^{-4}M$ adenine.

Analytical studies

Solvent matrix effect. The effect of change in composition of methanol–water mixtures on the phosphorescence signal has been studied in detail in the case of several biologically-important organic compunds.[11,14] As shown in Fig. 2, the dependence on solvent composition is similar for all compounds tested, and the optimum composition for sensitivity and accuracy of phosphorimetric measurements is between 10 and 30% v/v methanol. In this region, the matrix is mainly snowed, and relatively homogeneous, which results in a reproducible and nearly constant phosphorescence signal.

A similar effect is obtained with various amounts of sodium chloride, bromide, and iodide, added to pure water, which indicates the importance of the physical matrix effect, in increasing phosphorescence signal.[11]

External heavy-atom effect. Several studies have shown recently the importance of the effect of a heavy-atom solvent on the phosphorescence intensity, which results in better sensitivity.[11,12,16–18,31,32]

It has been demonstrated that it is advantageous to use alkali metal halide solutions as solvents for phosphorimetric analysis of organic molecules. Indeed, alkali metal halides (especially the bromide and iodide) may be obtained in ultrapure form, and thus the phosphorescence background may be reduced to extremely low levels. Also, the heavy-atom effect enhances the phosphorescence signal by virtue of increasing the rate of intersystem crossing to the triplet manifold. Decay-time measurements indicate that the phosphorescence decay is considerably shorter in aqueous sodium iodide solutions than in methanol–water solutions (Table 2). These results are consistent with the heavy-atom perturbation theory.[33]

The heavy-atom effect on the phosphorescence intensity, defined as the ratio I_p^{NaX}/I_p of the phosphorescence intensity in methanol–water–sodium halide solutions (I_p^{NaX}) and in methanol–water (I_p), may vary widely with the phosphorescence quantum yield and the structure of the organic molecules.

In Table 3, the heavy-atom enhancement factors of sodium isodide are given for a number of organic compounds. In the case of monosubstituted benzenes, the values of the enhancement factors are correlated with the phosphorescence relative quantum yields ϕ_s, as proposed by Aaron, Mousa and Winefordner:[17]

$$\log \phi_s = -2{\cdot}06 \log I_p^{NaI}/I_p + 0{\cdot}22$$

This relation would allow the prediction, within an error of about 25%, of the magnitude of the analytical heavy-atom effect and therefore, evaluation of this effect for the improvement of sensitivity.[17] It is clear that the increase in the phosphorescence signal resulting from the effect of sodium iodide should be at least 2–3 times the normal signal if it is to be analytically useful.

Limits of detection and analytical curves. In Table 4, a comparison is given of the best experimental limits of detection for several organic compounds measured by phosphorimetry, fluorimetry and colorimetry. As far as sensitivity is concerned, the results in Table 4 indicate that phosphorimetry compares favourably with other commonly used spectrometric methods. In some cases, of course, fluorimetry is a

Table 2. Typical data for the sodium iodide effect on phosphorescence decay times

Compound	τ, sec*†	τ, msec*§	Ref.
Anisole	3·4 (3·0)	10·7	17
Benzene	7·0 (7·0)	58	17
Benzoic acid	2·7 (2·5)	5·8	17
Benzyl alcohol	6·2	13·7	17
N, N-Dimethylaniline	2·3	36·0	17
Ethylbenzene	8·8	5·8	17
Phenol	2·8 (2·9)	122	17
Toluene	8·2 (8·8)	30·2	17
Acetophenone	0·0041 (0·004)	4·9	17
Benzaldehyde	0·0035 (0·0023)	4·9	17
Propiophenone	0·37	15·5	17
Indol-3-ylacetic acid	7·0	900‡	11
Thioacetamide	1·7	830‡	11
Hippuric acid	3·0	970‡	11

* Lifetime: error ± 10%. Times are in msec for the solvent containing NaI. Values in parentheses are for EPA media, and taken from R. S. Becker, *Theory and Interpretation of Fluorescence and Phosphorescence*, Wiley, New York, 1969.

† Solvent 10% v/v methanol–water.

§ Solvent 10% methanol–water–0·75*M* NaI, except where otherwise noted.

‡ Solvent 1*M* aqueous NaI.

Table 3. Heavy-atom enchancement factors in phosphorimetry

Compound	Enhancement factor,* I_p^{NaI}/I_p	Ref.
Anisole	2·8	17
Benzene	8·3	17
Benzoic acid	1·7	17
Benzyl alcohol	2·8	17
N, N-Dimethylaniline	6·2	17
Ethylbenzene	3·0	17
Phenol	3·8	17
Toluene	3·4	17
Acetophenone	1·3	17
Benzaldehyde	1·3	17
Propiophenone	1·2	17
Indol-3-ylacetic acid	6·0†	11
Hippuric acid	3·0†	11
Cytidine	4·8§ 31‡	18
Diphenhydramine HCl	1·4¶	32
Bromodiphenydramine HCl	1·0¶	32
Chlorcyclizine HCl	1·0¶	32
Meclizine HCl	1·3¶	32
Phenindamine tartrate	1·8¶	32
Pyrilamine maleate	1·0¶	32
Methapyrilene HCl	1·2¶	32
Thenyldiamine HCl	2·2¶	32

* Defined as the ratio of the molar phosphorescence intensity in 10% methanol–water–0·75*M* sodium iodide solution (I_p^{NaI}) and 10% methanol–water solution (I_p); other solvents are used as noted.

† In 1*M* aqueous NaI.

§ pH = 10, 0·1*M* NaI–10% methanol–water.

‡ pH = 2·5, 0·1*M* NaI–10% methanol–water.

¶ In ethanolic 0·1*M* NaI.

Table 5. Comparison of minimal detectable amounts* (in ng) in fluorimetry and phosphorimetry for some organic compounds

Compound	Fluorimetry	Phosphorimetry	Ref.
Tyrosine	10^3	0·4	15
2-Methoxy-4-hydroxy-phenylethylamine	40	2·015	
Normetanephrine	10	0·4	15
Metanephrine	10	0·4	15
Homovanillic acid	200	0·8	15
Norepinephrine	0·5	3·0	15
Epinephrine	0·5	4·0	15
Dopa	10^3	2·0	15
Dopamine	10	3·0	15
3,4-Dihydroxy-phenylacetic acid	10^3	4·0	15
3,4-Dihydroxy mandelic acid	10^3	1·8	15
LSD-25	6·5	0·16	16
STP; DOM†	10	0·2	16
N, N-Dimethyl-tryptamine	15	0·3	16
Psilocin	100	0·1	16
Psilocybin	23	0·3	16
Ibogain hydrochloride	7	0·2	16
Adenine	100§	0·4	14

* Minimal detectable amount is defined as the absolute limiting quantity detected by the method, calculated from the limit of detection and taking into account the volume of sample.

† 2,5-Dimethoxy-4-methylamphetamine.

§ Value measured by a spectrophotometric method.

more sensitive method than phosphorimetry, especially when the phosphorescence quantum yield is particularly low.

In Table 5, a comparison is given of the best absolute detection limits for fluorimetry and phosphorimetry. In most cases, that lower absolute quantities can be detected by phosphorimetry than by fluorimetry is partly due to the small volume of sample (20 μl) needed in the phosphorimetric procedure. The analytical curves in phosphorimetry are generally linear over a range of 10^3–10^5 concentration units. As expected from the theoretical equations for optically-inhomogeneous matrices, slopes of the analytical curves are close to unity (between 0·9 and 1·1), at relatively low concentrations, and a decrease of the slope is generally observed in the higher concentration region of $10^{-3}M$, owing to the inner-filter effect.

With the rotating quartz capillary tube, good precision is obtained. A relative standard deviation of 1·5% has been obtained for ten replicate determinations.[12] Generally, in routine triplicate measurements, relative standard deviations of phosphorescence signals are 4% or less.[13–16]

Table 4. Comparison of limits of detection* (in ng/ml) in phosphorimetry and other spectrochemical methods for some organic compounds

Compound	Colorimetry	Fluorimetry	Phosphorimetry	Ref.
Vitamin K_1	$2·5 \times 10^4$	—	10^3	13
Vitamin K_3	$\sim 2 \times 10^3$	~400†	70	13
6-Methyl-mercaptopurine	—	10	0·6	14
LSD-25	50	6·5	8	16
STP; DOM§	—	10	10	16
N,N-Dimethyl-tryptamine	—	15	15	16
Psilocin	—	100	6	16
Psilocybin	—	23	14	16
Ibogain hydro-chloride	—	7	10	16

* Limit of detection is defined as the concentration giving a phosphorescence signal (located on the linear part of the analytical curve) that is twice the background noise. The background signal was subtracted from the observed signal value.

† Value determined by absorption spectrophotometry.

§ 2,5-Dimethoxy-4-methylamphetamine.

PULSED-SOURCE TIME-RESOLVED PHOSPHORIMETRY

Pulsed-source time-resolved phosphorimetry is a useful method for analysing mixtures of fast-decaying phosphors. Some of the fundamental aspects of pulsed-source phosphorimetry were theroretically established by O'Haver and Winefordner,[34,35] and the experimental usefulness of pulsed-source gated detector instrumentation was shown by Winefordner.[20] A more sophisticated pulsed-source phosphorimeter was proposed by Fisher and Winefordner,[21] and recent applications of this technique include the analysis of drugs.[22–24]

Theoretical considerations

In Fig. 3, the sequence of events occurring during one cycle of sample excitation and observation in a pulsed-source gated detector phosphorimeter system[21] is given. After an initial burst of radiant energy from the source, with a duration t_f (see Fig. 3), the phosphoresence intensity climbs to a value I_0 and

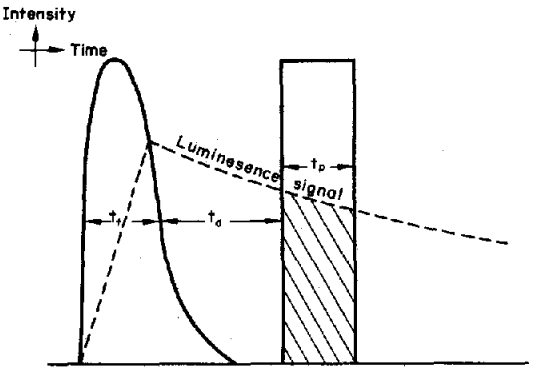

Fig. 3. Schematic diagram of events occurring during one cycle of sample excitation and measurement in a time-resolved pulsed-source phosphorimeter.[21] t_f = half-intensity width of source flash; t_p = "on" time of detector or measurement system; t_d = delay time from end of excitation pulse to beginning of measurement of phosphorescence signal; first solid line = flash intensity temporal distribution; second solid line = detector "on" time; cross-hatched area = measured integrated luminescence signal per source pulse. (Reprinted by permission from *Anal. Chem.*, 1973, **44**, 984. Copyright by the American Chemical Society.)

decays exponentially; the integrated phosphorescence intensity represented by the cross-hatched area is monitored over a time-period t_p, for example with an electronic gate, after a time-delay of t_d. The expression[20,35] for the integrated phosphorescence intensity I (20,35) is given in Table 6; I is directly proportional to f, the source-pulse repetition frequency, in the case of a d.c. read-out system. General expressions for binary and multi-component systems of phosphors, are also given in Table 6.

Three methods, based on the equations in Table 6, may be used to evaluate the analyte concentrations by pulsed-source phosphorimetry.[21]

Table 6. Theoretical expressions for pulsed-source phosphorimetry

Integrated phosphorescence intensity	$I = \dfrac{I_0 f t_f [\exp(-t_d/\tau)][1 - \exp(t_p/\tau)]}{[1 - \exp(-1/f\tau)]}$
Binary system	$I_{tA} = I_{0A}\exp(-t_d/\tau_A)$ $I_{tB} = I_{0B}\exp(-t_d/\tau_B)$ $I_{tT} = I_{tA} + I_{tB}$
Multicomponent system	$I_{tT} = \sum_i I_{ti}\exp(-t_d/\tau_i)$

I = integrated phosphorescence intensity, arbitrary units; I_0 = steady-state integrated intensity, arbitrary units; f = source-pulse repetition frequency, Hz; t_f = flash duration halfwidth, sec; t_d = delay time, sec; t_p = "on" time of detector or read-out system, sec; τ = phosphorescence decay time, sec; I_{tA} and I_{tB} = phosphorescence intensity of molecules A and B, respectively, at a delay time t, arbitrary units; I_{oA} and I_{oB} = phosphorescence intensities of molecules A and B, respectively, at time $t = 0$, arbitrary units; I_{tT} = total phosphorescence intensity of a mixture of i components, at a delay time t, arbitrary units.

(*i*) *Multiple analytical curve method*, in which the dependence of the slopes of the analytical curves on the delay time t_d is used to determine the analytical concentrations in a binary phosphor mixture. This method is most conveniently used for a time-resolved phosphorimeter with a mechanical phosphoroscope.

(*ii*) *Exponential method*; decay times τ_a, τ_b, ... τ_i of the phosphorescent components of the mixture are measured by determining the phosphorescence signal I_{ta}, I_{tb}, ... I_{ti} of each component as a function of the delay time t_d. The principal advantage of this method is that it may be easily applied to systems with more than two components.

(*iii*) *Logarithmic decay time method*; in this method, based on the standard method of determining radioactive isotopic species after nuclear activation, a semi-logarithmic plot of phosphorescence signal *vs.* time is used to determine the analyte concentration in a multi-component phosphorescence system. Calculations are considerably simpler than in the other two methods, but accuracy in the evaluation of the analytical concentration of the phosphor is not as good as the other methods.

Instrumentation

Basic system. The basic diagram of a pulsed-source time-resolved phosphorimeter is given in Fig. 4.

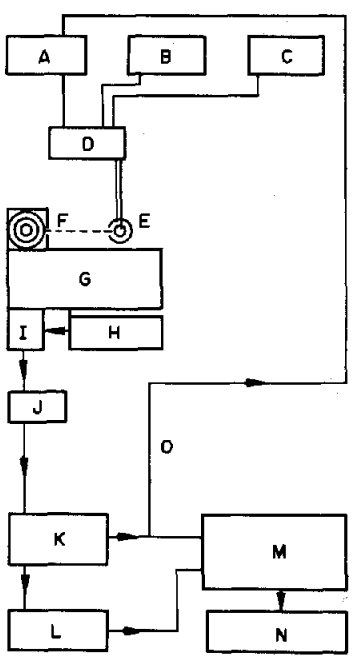

Fig. 4. Block diagram of time-resolution pulsed-source phosphorimeter.[21] A, pulse generator; B, power supply—low voltage; C, power supply—high voltage; D, trigger circuit for source; E, xenon flash-tube source; F, sample-cell compartment; G, emission monochromator; H, photomultiplier power supply; I, photomuliplier; J, variable load resistor; K, oscilloscope; L, preamplifier; M, signal averager; N, potentiometric recorder; O, synchronization for oscilloscope and signal averager. (Reprinted by permission from *Anal. Chem.*, 1973, **44**, 948. Copyright by the American Chemical Society.)

Source. The source used is a short-arc high-pressure xenon flash-tube, pulsed by the trigger module described by Fisher and Winefordner.[21]

Detectors. Read-out devices for pulsed-source systems are somewhat more complicated than the d.c. systems used in commercial phosphorimeters. There are three principal measurement systems:

(*i*) pulsing of the phototube, which is turned off and on at different moments of the cycle; an integrating d.c. measurement system measures the signal during the on-time of the phototube;

(*ii*) phototube operated continuously, with an electronic gate (boxcar integrator) which monitors the phosphorescence signal;

(*iii*) phototube operated continuously, as in the previous method, but with a fast multi-channel read-out device for scanning the entire decay curve.

The main advantages of pulsed-source time-resolved phosphorimeters over conventional phosphorimeters with mechanical modulation are the following:

(*i*) the possibility of achieving higher source peak-intensities (and proportionately less noise) during the measurement period, and thus lower detection limits;

(*ii*) the ability to obtain a greater selectivity for a given short-lived phosphor relative to a long-lived interferent;

(*iii*) the possibility of measuring phosphors with short lifetimes (τ as short as 10 μsec), because of a termination time of several μsec for a flash-tube pulse, compared to 30 μsec for a typical disk chopper and 100 μsec for a typical rotating can;

(*iv*) the improvement of the signal-to-noise ratio and precision (also detection limits) by gating the detector during a predetermined time; and

(*v*) the ability to scan the phosphorescence decay curve easily and to examine the linearity of the log I *vs.* t_d plot, which provides a quick confirmation of the purity of the phosphor standards.

Analytical studies

Phosphorescence lifetimes. A number of organic compounds are structurally and spectrally very similar and are very difficult to differentiate by conventional as well as by other spectrometric methods. However, phosphorescence lifetimes of these compounds are often sufficiently different to allow their temporal resolution: such compounds can be determined by pulsed-source time-resolved phosphorimetry with a precision better than 10%, as shown in the case of arylketones.[23]

Quantitative analysis of mixtures. An important application of pulsed-source phosphorimetry is the quantitative analysis of mixtures of organic compounds which have different decay times, but otherwise very little structural difference, and almost identical absorption, fluorescence,and phosphorence spectra. For these reasons, the analysis of the mixture is practically impossible with a conventional spectrometric technique but very convenient with pulsed-source time-resolved phosphorimetry.

Examples of quantitative determination in binary and ternary mixtures of halogenated biphenyls[22] and drugs[24] are given in Table 7. Relative errors for the composition of binary and ternary mixture are generally within 10%.

However, some mixtures of drugs, such as amphetamine and methamphetamine, or phenobarbital and cocaine, cannot be resolved by pulsed-source phosphorimetry, because of insufficient difference in the phosphorescence lifetimes.[24] As pointed out by O'Donnell *et al.*,[22] the phosphorescence lifetime ratio of any two species should be at least 2 if they are to be resolved in this way.

PHASE-RESOLVED PHOSPHORIMETRY

This new method, recently proposed by Mousa and Winefordner,[25] is based on the phase resolution of the phosphorescence signal from species with different lifetimes. Because of the different phase and amplitude relationships of their luminescence signal, mixtures of structurally similar organic compounds might be quantitatively analysed with this technique.

Table 7. Typical data for the analysis of mixtures by pulsed-source time-resolved phosphorimetry

Mixture	Phosphorescence lifetime, *sec*	Composition of mixture, $\mu g/ml$ Present	Found	Relative error, %	Ref.
4-Chlorobiphenyl	0·570	3·8	3·6	5·0	
4-Bromobiphenyl	0·017	1·1	0·95	4·0	22
4-Iodobiphenyl	$0{\cdot}003_2$	1·4	1·2	14	
2-Chlorobiphenyl	0·170	6·95	7·35	5·4	
4-Chlorobiphenyl	0·570	3·8	3·4	10	22
Codeine	0·039	23	22	4·3	
Morphine	0·020	110	120	9·0	24
Ethylmorphine	0·04	52	42	20	
Morphine	0·02	110	160	45	24
Quinine	1·1	62	58	7·0	
Morphine	0·014†	38	42	10·0	24
Cocaine	0·82†	21	18	14·0	

* Measured in anhydrous ethanol, except otherwise noted.
† Measured in chloroform.

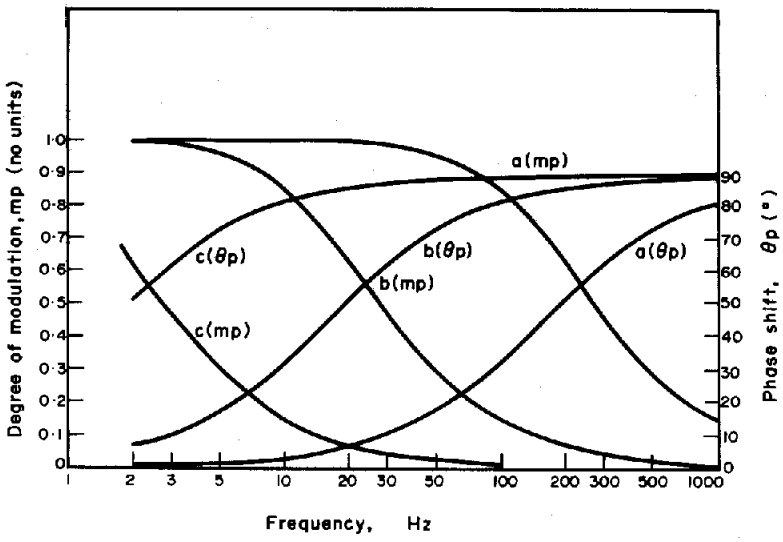

Fig. 5. Semi-logarithmic plots of theoretical variation of degree of modulation, m_p, and phase-shift angle, θ_p, with frequency of modulation, f. (*a*) $\tau_p = 1$ msec; (*b*) $\tau_p = 10$ msec; (*c*) $\tau_p = 100$ msec.

Theoretical considerations

The equations derived by Mousa and Winefordner,[25] describing the phase and frequency characteristics of luminescence, are given in Table 8.

The expression for total luminescence intensity includes a constant intensity-term, and a sinusoidally varying intensity-term, and may be separated into the individual intensities of fluorescence, I_F, and phosphorescence, I_P. A third component, the scattered light intensity, I_S, is assumed to be negligible. If a frequency- and phase-selective detection system is used, only the a.c. terms of the luminescence intensity are observed.

With a proper choice of excitation and emission wavelengths, if strongly phosphorescent compounds are used, the fluorescence term can be neglected, and only the a.c. phosphorescnece term is experimentally important. However, one of the limitations of phase-resolved phosphorimetry is that in many cases this selectivity cannot be achieved, and the a.c. fluorescence term of the theoretical expression in Table 8 must also be considered.

Table 8. Theoretical expressions for phase resolved phosphorimetry

Total luminescence intensity	d.c. term	a.c. term
	$I_L = k_L . I'_0 + m_L . k_L . I''_0 . \cos(\omega t - \theta_L)$	
INDIVIDUAL INTENSITIES		
Fluorescence	$I_F = k_F . I'_0 + m_F . k_F . I''_0 . \cos(\omega t - \theta_F)$	
Phosphorescence	$I_P = k_P . I'_0 + m_P . k_P . I''_0 . \cos(\omega t - \theta_P)$	
FREQUENCY FUNCTIONS of the a.c. term of phosphorescence	Degree of modulation $m_P = (1 + 4\pi^2 f^2 \tau_P^2)^{-1/2}$;	Phase-shift angle $\theta_P = \tan^{-1}(2\pi f \tau_P)$

k_L, k_F and k_P = factors taking into account the quantum efficiency and concentration factors for total luminescence, fluorescence, and phosphorescence respectively; I'_0 and I''_0 = constant-intensity term and sinusoidally-varying intensity term of the exciting-light function $I_o(t)$, respectively; m_L, m_F, and m_P = degree of modulation of total luminescence, fluorescence, and phosphorescence, respectively; θ_L, θ_F, and θ_P = phase-shift angle of total luminescence, fluorescence, and phosphorescence, respectively, degrees; τ_P = phosphorescence lifetime, sec; ω = angular frequency in Hz; f = linear frequency, Hz.

From the expressions in Table 8, the following analytically useful conclusions can be drawn.

(*i*) The phosphorescence parameters, m_P (degrees of modulation), and θ_P (phase-shift angle) are a function of the frequency, f, of modulation of the source, and the lifetime, τ_P, of the phosphorescence. A preliminary study of the variation of these parameters with frequency of the source has to be made for a potential application, in order to choose the optimal analytical conditions for a given species in a mixture. Theoretical curves of $m_P(f)$ and $\theta_P(f)$ are given in Fig. 5.

(*ii*) At a fixed frequency, the phase-shift angle, θ_P, (and the phase-angle difference (θ_P - θ_R) between the analyte and reference signal) is a cosine function of the phosphorescence signal intensity. By adjusting the value of the reference phase angle to a proper value, it is possible to maximize (or minimize) the measured analytical signal of the phosphorescent species of concern.

(*iii*) In the case of a binary mixture, the phase-resolution of the two components can be accomplished either by varying the phase angle of the reference signal (*phase method*), or by varying the frequency of modulation (*frequency method*), to eliminate the signal (not the noise, however) from one of the two phosphorescent components and to maximize the signal of the other phosphor.

Instrumentation

Basic system. The basic system for phase-resolved phosphorimetry is schematically shown in Fig. 6. The basic components are similar to the instrumentation used in phase and modulation fluorometry.

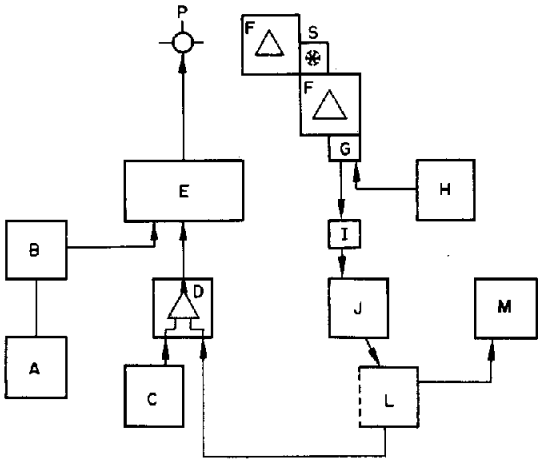

Fig. 6. Block diagram of phase-resolved phosphorimeter.[25] A, power supply; B, source starter circuit; C, power supply; D, operational amplifier and current booster, E, modulation circuit; F, excitation and emission monochromators; G, photomultiplier; H, photomultiplier power supply; I, load resistors for photomultiplier; J, differential amplifier; K, lock-in amplifier; L, potentiometric recorder; M, xenon arc lamp; N, sample composition. (Reprinted by permission from *Anal. Chem.*, 1974, **46**, 1195. Copyright by the American Chemical Society.)

Source. The source of excitation, a 150-W xenon arc lamp, is operated by a special starting and modulation circuit devised to keep the arc operating at a constant intensity level, and to superimpose a sinusoidal variation in source intensity.

Detector. The detector is a conventional photomultiplier tube; the measurement system is a lock-in amplifier which indicates the average a.c. component of the incoming signal.

Analytical studies

Phosphorescence lifetimes. Phosphorescence lifetimes can be determined by phase-resolved phosphorimetry, by using the expressions for the degree of modulation, m_P, or the phase-shift angle, θ_P, (see Table 8), and the experimental curves for variation with the frequency of modulation. Phosphorescence lifetimes calculated by this method are in good agreement with those obtained by time-resolved phosphorimetry, but difficulties of measurement at very low frequencies (<10 Hz) make it very difficult to determine lifetimes longer than about 50 msec.

Qualitative analysis of synthetic mixtures. Severely overlapping emission spectra of phosphors can be resolved by means of either the phase or frequency methods of "phasing out" one of the components of a binary mixture. Even if the excitation and emission spectra of the two components do not completely overlap, phase-resolution may still be very useful, if one component emits a much stronger phosphorescence than the other. If the stronger phosphor is phased out, the spectrum of the weaker phosphor can be more conveniently measured.

Quantitative analysis of binary mixtures. The phase method is also useful for quantitative analysis of binary mixtures of organic compounds. The composition of the mixture is determined from the analytical curves obtained for standard solutions of two compounds of a binary mixture, measured at the phase angle where the phosphorescent signal from one of the compounds is phased out.

Analytical data indicate that relative errors in the concentrations found in synthetic binary mixtures are 10% or less. However, larger errors are observed in two cases:

(*i*) when the concentration of each of the components in the mixture is more than $10^{-5}M$, less accurate results are obtained, probably because of an inner-filter effect;

(*ii*) when the concentration ratio of a strongly phosphorescent species to a weaker phosphorescent species is ≥ 10, a large error is introduced into the determination of the weaker phosphor; this probably results from the inability to phase out the strong signal completely and also the difficulty of detecting the weaker phosphor signal in the presence of the large noise component coming primarily from the species with the stronger signal.

ROOM-TEMPERATURE PHOSPHORESCENCE

The recently observed phenomenon of room-temperature phosphorescence from ionic organic compounds on dry supports[36,37] has just been developed into a new method of phosphorescence analysis by Paynter, Wellons and Winefordner.[26]

A filter-paper cell-system is proposed, and the procedure for drying the sample seems essential for reproducible and sufficiently intense phosphorescence measurements to be obtained.[26]

Although only a few ionic organic compounds have so far been tested by this technique, they are representative of a variety of polynuclear carboxylic or sulphonic acids, phenols, and amines. Preliminary results indicate that relatively low limits of detection, sometimes in the nanogram region, are possible by room-temperature phosphorescence. With necessary improvements, this method should provide a new and sensitive analytical tool, particularly useful for molecules of biological interest.

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A HIGH-PRECISION TITRATION OF 4-AMINOPYRIDINE

A VALUE FOR THE FARADAY

WILLIAM F. KOCH, WILLIAM C. HOYLE and HARVEY DIEHL

Department of Chemistry, Iowa State University, Ames, Iowa 50010, U.S.A.

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Summary—A specimen of 4-aminopyridine purified by repeated sublimation in an atmosphere of nitrogen has been titrated coulometrically in two ways: (1) directly, using the hydrazine-platinum anode, and (2) with perchloric acid, the titration being completed coulometrically and the perchloric acid being standardized coulometrically. The values for the faraday calculated from these titrations are 96,486·40 (1·53) and 96,486·78 (0·57), 1972 NBS coulombs per mole, respectively, the average being 96,486·69 (0·81) and the numbers in the parentheses the standard deviations. The maximum error obtained by combining the estimated maximum errors in the various measurements was 8·4 ppm.

In selecting a base for a high-precision coulometric titration we chose 4-aminopyridine. 4-Aminopyridine can be purified by sublimation, thus ensuring the absence of occluded solvent. The melting point, 159·09°, lies in a convenient range for obtaining a freezing curve for an estimate of the total impurity present. One titratable group is present, $pK_B = 4.63$, sufficiently strong to provide a good end-point. The molecule is made up only of carbon, hydrogen, and nitrogen, elements for which variation in the isotope abundance ratios, natural or as a result of processing, is probably negligible, but elements for which, if necessary, the abundance ratios can be determined without too much difficulty. Thus the titration data may be used for calculation of a value for the Faraday, based directly on carbon-12.

EXPERIMENTAL

Reagents

4-Aminopyridine. Crude 4-aminopyridine (Reilly Tar and Chemical Corporation, Indianapolis, Indiana) was powdered, dried at 105° for 10 hr, and subjected to a preliminary sublimation in a large evaporating dish resting in an electric heating mantle and covered with an inverted glass funnel. During the first 20 hr, the material being held at 100°, a yellow, low-melting substance collected on the funnel; this was removed and discarded. A large, perforated filter paper was placed over the material in the dish, the funnel was replaced, and a coil of lead tubing was wrapped around the outside of the funnel. A stream of cold water was passed through the tubing and the temperature of the material was raised to 125°. Colourless, crystalline sublimate formed above the paper. The sublimate collected during the first 24 hr was discarded; that collected subsequently (during several days) was subjected to further sublimation.

During the initial sublimation a hemispherical shell of sublimed material formed above the crude material in the evaporating dish. This shell consisted of numerous layers of crystalline material, the innermost being light brown, the next very dark brown, and then a series varying progressively from brown through tan to colourless. This material was crystalline in the form of needles parallel to the radius of the hemisphere. Apparently a zone-refining operation was occurring by sublimation. The 4-aminopyridine collected for further purification had passed through this shell. By titration with standard acid this 4-aminopyridine was found to be 100% pure within the limits of normal titrimetric work, that is, to within 1 part in 1000 or so.

The 4-aminopyridine was finally purified by sublimation in an atmosphere of nitrogen in the apparatus shown in Fig. 1. The 4-aminopyridine was placed in the 500-ml round-bottomed flask, the flask embedded in copper shot in an electric heating mantle, the atmosphere in the flask replaced by nitrogen, and flask and material heated to 105°. The neck of the apparatus was maintained at 95° and the elbow at 90° by means of heating tapes; the collecting tube was held at room temperature. The sublimation was carried out at the rate of 1·5–2·0 g/day. The sublimate appeared in successive steps in the neck, elbow, and collecting tube. The material which passed farthest along the collecting tube was rejected as possibly carrying an impurity of slightly higher volatility than 4-aminopyridine. The material in the first 15 cm (from the neck) of the collecting tube was taken for the high-precision titrations; this portion constituted about 90% of the total sublimate in the collecting tube.

No impurity detectable by emission spectrographic examination was present in the 4-aminopyridine, the material being as free in this respect as the best grades of spectrographic carbon.

To measure the total impurity, a freezing curve of this 4-aminopyridine was obtained;[1] although attack by the molten 4-aminopyridine on the gold crucible of the instrument confused the results, it was concluded that the total impurity was less than could be detected by the instrument, that is, less than about 0·001 mole% (10 ppm).

A titration of the 4-aminopyridine with 0·1*M* perchloric acid was carried out in 1·0*M* sodium perchlorate solution, the electrolyte to be used later in the coulometric titrations. Carbon dioxide was removed by passage of nitrogen gas and the solution was maintained at 26·6°. A high-alkalinity glass electrode was used. The pH meter was calibrated with NBS standard buffer [0·025*M* potassium dihydrogen phosphate–0·025*M* disodium hydrogen phosphate, pH

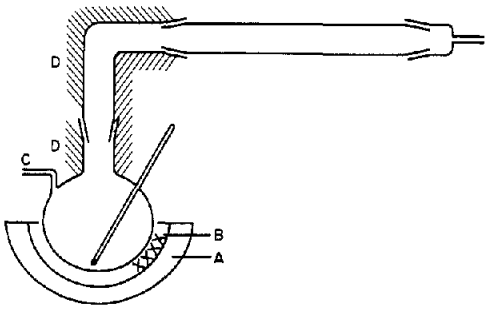

Fig. 1. Sublimation apparatus. A, electric heating mantle; B, copper shot; C, nitrogen inlet; D, electric heating tapes.

6·865 at 25° (Bates[2])] and the range scale was checked against NBS buffers (0·05*M* potassium hydrogen phthalate, pH 4·008 at 25°, and 0·01*M* sodium tetraborate, pH 9·180 at 25°). The pH at the mid-point was taken as pK_A and no correction for activity was made. Found: $pK_B = 4·63$ (26·6°, 1·0*M* sodium perchlorate).

Sodium perchlorate. Vacuum-distilled perchloric acid was heated to boiling, cooled to room temperature with nitrogen bubbling through it to remove chlorine, and diluted to 2·0*M*. The acid was neutralized with carbonate-free sodium hydroxide prepared by filtering 50% sodium hydroxide solution, the pH brought to 5·00, and the solution diluted to 1·0*M*. All dilutions were made with triply-distilled water.

Sodium hydrazinium sulphate solution, 0·25*M*. The commercial hydrazine sulphate, $N_2H_6SO_4$, was found by titration with sodium hydroxide to be 99·9% pure. This material was dissolved in 1·0*M* sodium perchlorate and the pH brought to 4·5 by the addition of carbonate-free sodium hydroxide. The solution was made 0·25*M* in sodium hydrazinium sulphate by dilution with 1·0*M* sodium perchlorate.

Nitrogen. Commercial "prepurified" cylinder nitrogen was passed through a tube containing "Ascarite" and then successively through scrubbers containing: (1) distilled water; (2) vanadium(II) sulphate in 1*M* sulphuric acid over amalgamated zinc; (3) alkaline permanganate (to ensure the absence of hydrogen sulphide which is sometimes generated in the oxygen scrubber); (4) 1·0*M* sodium perchlorate.

Apparatus

Coulometric titration apparatus. A Leeds & Northrup Model Number 7960, as described by Eckfeldt and Shaffer,[3] was used, the specific standard resistance and details of technique used being those described by Knoeck and Diehl.[4] The cell used was essentially that of Eckfeldt and Shaffer as modified by Knoeck and Diehl. A side-arm of short length and large diameter was added to accommodate more conveniently the glass and saturated calomel electrodes, Fig. 2. The ultrafine glass frit used in the construction of the shield tube was replaced by a length of unfired Vycor rod, a use of this material proposed by Durst;[5] two methods of affixing the rod to the glass tube were used [Fig. 3*a* (used in preliminary titrations) and Fig. 3*b* (used in the final titrations)]. In 3*a* the unfired Vycor rod, 25 mm in length, 14 mm in diameter, was sealed inside a glass tube 1·5 mm larger in diameter, with Silicon Seal (General Electric Company). The seal was allowed to cure for a minimum of 2 weeks. In 3*b* the Vycor rod was butted against a glass tube of identical outside diameter and the assembly jacketed with 50 mm of heat-shrinkable Teflon tubing[6] (Chemplast, Inc., Wayne, New Jersey). About 2 mm of the Teflon tubing was left projecting beyond the end of the rod. The assembly was heated in an oven for

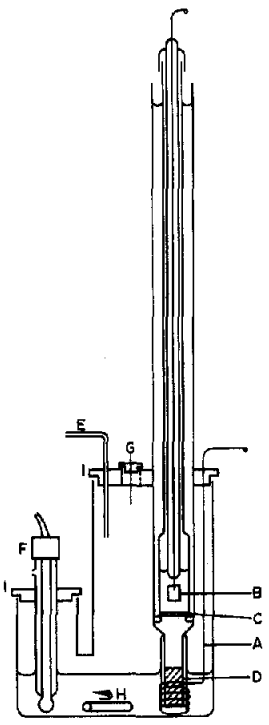

Fig. 2. Coulometric titration cell. A, platinum working electrode; B, platinum counter-electrode; C, glass frit on bottom of inner shield-tube; D, unfired "Vycor" on bottom of intermediate chamber; E, nitrogen inlet; F, combination pH electrode; G, sample inlet; H, magnetic stirring bar. I, "Plexiglass" covers.

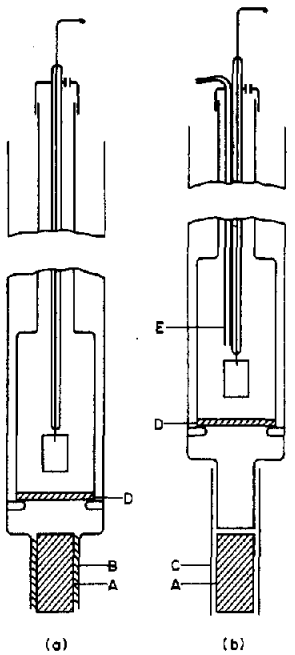

Fig. 3. Shield tube made by using unfired "Vycor": a, seal made with "Silicon Seal"; b, seal made with heat-shrinkable Teflon. A, unfired "Vycor"; B, "Silicon Seal"; C, heat-shrinkable Teflon; D, glass frit; E, siphon tube.

Table 1. Potentials of standard (unsaturated) cells, in 1 July 1972, NBS volts (based on NBS calibration, December 1974)

Date	Cell No. 791896	Cell No. 806020	Difference ($E_{791896}-E_{806020}$) μV
October 1973	1·019244 (24·0°) ($dE/dT = -3·2 \times 10^{-6}$ V/deg)*	1·019212 (24·0°) ($dE/dT = -3·7 \times 10^{-6}$ V/deg)*	32
Interval (5 months)			22–24
March 1974	1·019235 (25·9°) [1·019238 (25·9°)]†	1·019222 (25·9°) [1·019205 (25·9°)]†	13
Interval (2 weeks)			22–24
April 1974	1·019244 (23·2°) [1·019244 (23·2°)]†	1·019225 (23·2°) [1·019212 (23·2°)]†	18–20
October 1974	1·019236 (26·00°)§ [1·019238 (26·00°)]†	1·019209 (26·00°) [1·019205 (26·00°)]†	27

* $E_T = (dE/dT)(T - 24·0°) + E_{24·0°}$.
† Calculated from October 1973 value and temperature coefficient.
§ This value (1·019244 V at 24·00°) was used in the January 1975 recalculation leading to the results in Tables 3 and 4.

Table 2. Resistance of Leeds & Northrup Standard Resistor, Serial Number 1711765

	Resistance, *ohms* at 25·00°	Uncertainty, *ppm*
Leeds & Northrup Company, January 1967*	19·99979	20
C. A. Swenson†, July 1973	19·9996	10
National Bureau of Standards§, October-December 1974	19·999703	0·2

* After having been stored by the manufacturer for 1 yr. Value traceable to the National Bureau of Standards through NBS Test Number 211·01/189516 and 189517, August 1966.
† By comparison with five 10-ohm resistors of similar construction by the Leeds & Northrup Company, using an a.c. potentiometer, Automatic Systems Laboratories, Ltd., Leighton Buzzard, England, Model 103, Serial Number 014. Values of the 10-ohm resistors traceable to the National Bureau of Standards.
§ Calibration made under the same loading (64 mA) as used in the coulometric titrations made in this work.

3 hr at 115°. At higher temperature the Vycor shattered. Both assemblies, 3*a* and 3*b*, were soaked in 1·0*M* sodium perchlorate for 48 hr and conditioned by running electricity through them for 8 hr in a mock coulometric titration. This conditioning was essential to remove the acid remaining within the Vycor from the manufacture. Considerable trouble was experienced with 3*a* cracking, and 3*b* proved better in routine use.

The electrolyte was removed periodically by siphoning through the tube shown in Fig. 3*b*; the level of electrolyte around the counter-electrode was kept just above the top of the electrode, thus ensuring continual flow of electrolyte from the intermediate chamber into the electrode compartment.

Measurement of pH. The pH was measured with a combination electrode and an expanded range pH meter manufactured by Hach Chemical Company, Ames, Iowa, Model No. 8596, Serial No. 4, readable to 0·001 pH unit. The 4*M* potassium chloride solution surrounding the external, silver–silver chloride reference electrode of the combination electrode, was replaced with 4*M* sodium chloride to prevent the precipitation of potassium perchlorate at the porous ceramic junction. The pH meter was calibrated with the NBS buffer 0·025*M* potassium dihydrogen phosphate–0·025*M* disodium hydrogen phosphate, pH 6·865 at 25°, immediately before each titration. The drift of this unit, as indicated by the change in calibration from day to day, was less than 0·02 pH unit per 24 hr.

Measurement of current, potential, time and mass

Electromotive force. Two standard cells were used, both unsaturated Weston Cells manufactured by the Eppley Laboratory, Inc., Newport, R.I., Catalogue Number 100, Serial Numbers 791896 and 806020. The potentials of these

Table 3. Coulometric titration of 4-aminopyridine with acid generated at the hydrazine-platinum anode

Titration No.	Weight of 4-aminopyridine, *g*	Quantity of electricity, *1972 NBS coulombs*	Electrical equivalent per gram *1972 NBS coulombs/g*	Value of the faraday, *1972 NBS coulombs/mole*
1	1·007170	826·0031	1025·1534	96,484·38
2	3·004429	2464·0836	1025·1881	96,487·65
3	3·009784	2468·4327	1025·1703	96,485·97
4	2·004910	1644·3454	1025·1989	96,488·66
5	3·003388	2463·1927	1025·1726	96,486·19
6	3·000431	2460·7518	1025·1658	96,485·55
			Average	96,486·40
			Standard deviation of the individual observations	1·53
			Standard deviation of the mean	0·62

Mol. wt. 4-aminopyridine: 94·11702; purity of 4-aminopyridine: 100%.

Table 4. Titration of 4-aminopyridine with perchloric acid (coulometric end-point) and standardization of perchloric acid coulometrically

Standardization of perchloric acid

Titration No.	Weight of perchloric acid, *g*	Quantity of electricity *1972 NBS coulombs*	Concentration of perchloric acid, *1972 NBS coulombs/g*
1	25·1721	2190·4280	87·01809
2	25·8985	2253·6769	87·01959
3	25·8424	2248·7433	87·01759
4	30·8234	2682·2112	87·01867
5	20·1659	1754·8024	87·01830
6	20·1630	1754·5662	87·01910
		Average	87·01856
		Standard deviation of the individual observation	0·00072
		Standard deviation of the mean	0·00030

Titration of 4-aminopyridine

Headings of columns: A, titration number; B, weight of 4-aminopyridine; C, weight of perchloric acid; D, electricity delivered *via* perchloric acid; E, additional electricity to reach end-point; F, total electricity; G, electrical equivalent per gram; H, value of faraday (*C* = 1972 NBS coulombs).

Mol. wt. 4-Aminopyridine: 94·11702. Purity of 4-aminopyridine: 100%

A Number	B *g*	C *g*	D *C*	E *C*	F *C*	G *C/g*	H *C/mole*
1	2·183418	27·3884	2383·2990	144·8926	2238·4064	1025·1847	96,487·33
2	2·174815	27·4146	2385·5789	156·0075	2229·5714	1025·1773	96,486·63
3	2·155224	27·1490	2362·4667	152·9856	2209·4811	1025·1749	96,486·41
4	2·083729	25·5475	2223·1065	86·9306	2136·1759	1025·1696	96,485·91
5	2·057622	24·8447	2161·9499	52·5151	2109·4348	1025·1810	96,486·98
6	2·102143	25·8854	2252·5101	97·4238	2155·0863	1025·1855	96,487·40
						Average	96,486·78
					Standard deviation of the individual observation		0·57
						Standard deviation of the mean	0·23

cells were determined by Mr. W. A. Rhinehart in the Ames Laboratory of the U.S. Atomic Energy Commission during October 1973, March 1974, April 1974, and again in October 1974, by comparison with a bank of three saturated Weston cells in a constant temperature box, Eppley Model 121, Serial Number 3955. The potential of these three cells is traceable *via* an Eppley certificate dated 1 July, 1969 to a National Bureau of Standards calibration, Test Number 197281, dated 20 February 1969. The potential of these cells was thus based on the value of the NBS volt adopted on 1 January 1969. The potentials of the three cells were redetermined during November 1974 by comparison with the travelling volt standard of the National Bureau of Standards, Enclosure 1900, operating at a nominal temperature of 32·00°; NBS Test Number 211.01/211655 dated 19 December 1974. The procedure followed in this calibration was that prescribed by the NBS. The values obtained for the three cells in set 3955 were on the average 3·01 ppm higher than those of the 1969 calibration. On the assumption that the cells of set 3955 remained unchanged during the period October 1973–October 1974, the potentials of the cells of set 3955 and of the unsaturated cells used in the titration work were recalculated during January 1975 to the NBS values of December 1974; the new values are used in Tables 1, 3 and 4. The calibration of December 1974 places the potentials on the basis of the NBS (U.S. legal) volt, which since 1 July 1972 has been referred to the Josephson junction.[7]

For the comparison of the unsaturated (working) cells 791896 and 806020, cells 791896 and 806020 were placed in an environmental chamber and, in the October 1973 calibration, the temperature was changed successively from 18° to 23°, 28°, 33° and back to 23°, each temperature being steady to better than 0·1°; in the other calibrations measurements were made at a single temperature. After each change, time was allowed for the system to reach thermal equilibrium and comparisons were made until three successive readings at intervals of several hours were essentially identical. The comparison was made by using a differential voltmeter (John Fluke Mfg. Co., Inc., Seattle, Washington, Model 895A) which has an internal Kelvin–Varley voltage divider, as a transfer standard; switching was done with a Leeds & Northrup low thermal switch. The temperature coefficient was obtained from the slope of the straight line obtained from the October data by least-squares treatment.

The coulometric titrations were carried out in a constant temperature room held at 24·0 ± 0·5°. Cells 791896 and 806020 were placed inside a box with polystyrene walls 5 cm thick. The temperature of the cells followed changes in the room temperature very slowly and at no time changed sufficiently to vary the potential by more than 3 μV. Intercomparison of the two cells was made at intervals with the Type K-5 potentiometer used in the titration work.

Cell 791896 proved stable throughout the work (Table 1); cell 806020 underwent changes when moved, but all were below 10 μV. Fortunately, all of the work, that is, the standardization of the perchloric acid, the titration of THAM,[8] and the titration of the 4-aminopyridine, was done with cell 791896.

The sequence of calibrations and titrations was: October 1973 calibrations; perchloric acid standardizations 1, 2 and 3 (Table 4); back-titrations of THAM;[8] standardizations 4 and 5; back-titrations of 4-aminopyridine (Table 4); standardization 6; March 1974 calibration; April 1974 calibration; titrations of 4-aminopyridine, using the hydrazine–platinum anode (Table 3); October 1974 calibration; November 1974 calibrations.

Table 5. Summary of recent values for the Faraday

Method	Faraday Value, *coulombs/mole*[f]	Error, *ppm*[g]	Authors
Silver oxidation[a]	96,486·6 (2·1)[h]	16	Craig, Hoffman, Law and Hamer;[28] see also Hamer[29]
	96,486·70 (0·54)[i, n]	5·5	Craig, Hoffman, Law and Hamer[28] as recalculated by Taylor, Parker and Langenberg[30]
Arsenic trioxide oxidation[b]	96,486·3 (3·1)[j]	32	Marinenko and Taylor[31]
Benzoic acid reduction[c]	96,487·5 (2·1)[k]	25	Marinenko and Taylor[32]
Oxalic acid dihydrate reduction[c]	96,486·2 (1·7)[l]	34	Marinenko and Taylor[32]
4-Aminopyridine oxidation[d] and reduction[e]	96,486·69 (0·81)[m, n]	8·4	This work

[a] Dissolution of silver at the anode.

[b] Titration of arsenite with iodine generated at the anode.

[c] Reduction in the sense of titration with base generated at the cathode.

[d, e] Combination of results by two methods based on 4-aminopyridine. Oxidation in the sense of titration with acid generated at the hydrazine sulphate–platinum anode; reduction in the sense of titration of excess of perchloric acid with base generated at the cathode.

[f] Coulombs on the basis of the NBS as-maintained volt after the change in the value of the volt made 1 January 1969; see reference 30, p. 443, column 1. Pre-1969 values raised 8·4 ppm. None of the numbers appearing in this table is affected by the redefinition in 1972 of the volt, referring it to the Josephson junction.

[g] Error in ppm includes systematic and random errors as cited by authors.

[h] Based on 9 vacuum values by Craig, Hoffman, Law and Hamer as recalculated by Hamer using a new value for the atomic weight of silver. Figure given in parentheses is the standard deviation of the individual result as calculated from the standard deviation of the mean, $\sigma_{\bar{x}} = 0{\cdot}7$, given by the original authors ($\sigma_{\bar{x}} = \sigma/\sqrt{n}$).

[i] Standard deviation obtained by including all 31 values by the original authors.

[j] Standard deviation calculated from results reported, 5 degrees of freedom.

[k] Standard deviation calculated from results reported, 18 degrees of freedom; authors give 25 ppm for "overall limits of error".

[l] Standard deviation of results reported, 10 degrees of freedom; authors give 34 ppm as "overall limits of error".

[m] A weighted average of two sets of titrations. The uncertainty is the combined random plus systematic errors expressed as the standard deviation of the mean and reported in coulombs per mole (in parentheses) and in ppm. The value is given in 1972 NBS coulombs per mole.

[n] An additional figure has been included, following the practice of Taylor, Parker and Langenberg (ref. 30, p. 485, column 2), to avoid errors caused by rounding off.

When purchased in November 1966, the cells had potentials of 1·01936 V (791896) and 1·01930 V (806020) at 23°. The experimentally found drop in potential with aging was predicted by Mr. R. H. Verity of Leeds & Northrup and is not inconsistent with the findings of Hamer in his extensive studies[9] of the potential standards (saturated Weston cells) and other (unsaturated) cells at the National Bureau of Standards. By a detailed review of the calibration work, Mr. Wayne A. Rhinehart placed the uncertainty in the potential of cell 791896 at 4 ppm.

Resistance. The 20-ohm resistor used was manufactured and calibrated by the Leeds & Northrup Company, Catalogue Number 4025-B-S, Serial Number 1711765. The calibrations of this resistor and the uncertainty are given in Table 2. The value 19·999703 ohms at 25·00° was used in calculating the results of the titrations made in this work, Tables 3 and 4 (as recalculated during January 1975).

The temperature coefficient of resistor 1711765 was stated by Leeds & Northrup to be given by

$$R_T = R_{25}[1 + 0{\cdot}000002(T - 25) - 0{\cdot}0000005(T - 25)^2]$$

During the course of the titrations, the resistor was immersed in an oil-bath at 25·0°. A rise in temperature of the resistor of 1·5° occurred owing to the passage of current (about 64 mA). During each titration the temperature of the resistor was measured and the resistance at that temperature used in the calculations.

Potential drop. The potential drop over the 20-ohm resistor, Number 1711765, was measured with a Leeds & Northrup Type K-5 potentiometer, Model 7555-1-B, Serial Number 1713729, calibrated at the Leeds & Northrup standardization laboratory in February 1967 at a room temperature of 25° *via* the set of reference standards mentioned above. During August 1973, calibration of the K-5 potentiometer was checked in accordance with the operating manual. No adjustments were necessary. At the potentials measured, no corrections to the potential readings were required. The certificate accompanying the instrument places the error on the 1·6-V range at less than ±0·001% + 2 μV. This error applies to the difference in the potentials measured in the calibration (cell 791896), 1·019241 V, and that observed at the 63·4-mA current, 1·268 V, *i.e.*, about 0·2498 V; the error is thus 2·5 μV. Since the end correction of +2 μV in effect cancels, the error in the measurement of potential drop was estimated to be less than 3 μV.

Time. An electronic counter, Computer Measurements Co., Model 225CN, Serial Number 74186, was used. It was calibrated by using the standard time signals of Radio Station WWV of the National Bureau of Standards:

Elapsed time, *hr*	13	16	18
Deviation (counter slow), *ppm*	19·3	19·4	19·4

A correction of 19·4 ppm was added to all time intervals recorded.

In preliminary work, the mechanical counter and frequency standard provided as original equipment with the Leeds & Northrup Coulometric Analyser were used. For the calibration of this timing method, see the theses of Hoyle[10] and Koch.[11]

Mass. A set of two-piece rhodium-plated brass weights manufactured by Ainsworth, Inc., Englewood, Colorado, Serial Number 9156, and calibrated at the National Bureau of Standards, NBS Calibration Test Number G-37168, May 1967 was used. The weights in this set are thus "air-weight" weights, the platinum and aluminium fractionals being corrected for buoyancy to apparent weight of brass of density 8·4 g/cm³ in air of density 1·2 g/l. (see the relevant publications of the National Bureau of Standards[12–14] and of Biggs relative to similar practice at the National Physical Laboratory.[15] Weighings were made on an Ainsworth FDJ equal-arm microbalance. All weighings of 4-aminopyridine were made by substitution; the empty boat and the weight of appropriate size were weighed together (tared), the weight was removed, and the 4-aminopyridine added to the boat until the weight was within 0·002 g of the tare, and the weighing completed with the calibrated rider. Boat and 4-aminopyridine together subsequently entered the reaction vessel and electrolyte. Only three weights (1-g, 2-g and rider) were involved in the entire set of weighings.

Weighings were corrected to weight in vacuum, using for the density of 4-aminopyridine 1·2695 g/cm³ (found by the pycnometer method using mineral oil), for the density of the weights 8·40 g/cm³ (the value used by the National Bureau of Standards during the calibration), and for the density of air, a value obtained by measuring the barometric pressure, temperature, and relative humidity prevailing at the time of weighing. For convenience in making the routine determinations of the density of air, a Baxter's globe[16] was constructed, the exterior volume of the globe determined by hydrostatic weighing, and the calibration checked occasionally under different conditions of barometric pressure, temperature and humidity.

The weight-burette containing the perchloric acid was weighed on an Ainsworth single-pan balance, Model 28N, from which the last three figures (down to 0·1 mg) are obtained from an optically projected scale. The burette was weighed and replaced by the calibrated weights to the nearest 0·1 g below its weight, and the last three figures were obtained from the optical scale. The optical scale was checked against the 50 mg and 100 mg weights of the set at loads of 0, 25, and 50 g and found to be independent of the load and true to 0·1 mg. The weight of perchloric acid taken was about 25 g, so the error in the weighing, 0·1 mg, represented a relative error of 4 ppm. In making the correction to weight in vacuum, the density of 1·050 g/cm³, obtained by direct pycnometric measurement, was used.

The weight-burette was a plastic bottle with closure bearing a tip with a very fine bore. This was more convenient than the conventional weight-burette because the sample could be transferred and weighed in a much shorter time and losses due to evaporation minimized. The time of transfer, that is, from initial weighing to final weighing, was less than 3 min. The loss in weight from the tip was less than 0·1 mg in 20 min and thus the loss in weight during the transfer process was estimated to be less than 0·01 mg.

Titration of 4-aminopyridine, using the hydrazine–platinum anode

This series of titrations was carried out in the titration cell described above, using the hydrazine–platinum anode of Hoyle, Koch, and Diehl.[17] The outer chamber of the shield tube was filled with 7·5*M* sodium perchlorate and the inner chamber surrounding the counter-electrode was filled with just sufficient 1·0*M* sodium perchlorate to cover the electrode. In the titration cell, Fig. 2, were placed 100 ml of a solution 0·25*M* in sodium hydrazinium sulphate and 1·0*M* in sodium perchlorate, and a magnetic stirring bar. Purified nitrogen was passed through the solution for 2 hr to remove carbon dioxide and the flow was maintained throughout the titration. A pretitration was then carried out to remove any electroactive species present. The solution was taken forward and backward three times through the equivalence-point region, between pH 3 and 6, by electrolysing with the working electrode alternately anodic and cathodic. During the third anodic electrolysis, the pH was measured as a function of time, at the lower current setting, approximately 6·4 mA. The potential drop across the standard resistor was also recorded.

The weighed sample of 4-aminopyridine was introduced by lowering the weighing boat plus the amine into the electrolyte by a platinum wire. The solution was then electrolysed anodically at about 63·4 mA. The major part of the titration required about 10·5 hr for a 3-g sample. At 30-min intervals the potential across the standard resistor, the temperature of the resistor, and the pH of the solution were recorded. Anolyte was extracted from the inner shield tube and 7·5*M* sodium perchlorate added to the outer chamber of the shield tube to maintain a slow flow of electrolyte into the cathode chamber. When the pH of the main solution reached 5·5, the titration was interrupted and the walls of the titration chamber were rinsed with triply-distilled water. The titration was continued at a current of approximately 6·4 mA delivered in 20-sec increments, the pH, time, and potential drop across the resistor being measured. Between additions sufficient time was allowed for the solution to equilibrate before the pH was recorded.

In each analysis, two equivalence points were determined, that in the pretitration and that in the actual titration. The point of inflection was found by a computer technique[18] that had been found superior to Yan's finite difference method[19] or visual inspection of a graph.

The number of coulombs passed was calculated from

$$C_{\text{Total}} = A + B + C$$

where A is the number of coulombs delivered during the pretitration (current approximately 6·4 mA) from the point of inflection to the beginning of the main phase of the titration, as given by $E_1 t_1/R$ (t = time), B is the number of coulombs delivered during the main phase of the titration (current approximately 63·4 mA), calculated from $E_2 t_2/R$, and C is the number of coulombs delivered during the concluding phase of the titration (current approximately 6·4 mA), calculated from $E_3 t_3/R$. The quantities E_1 and E_3 were the averages of 4–6 readings, E_2 of 15–25 readings. The value of the faraday was calculated from $F = (C_{\text{Total}})(\text{equiv. wt.})/(5/4)(\text{wt. 4-aminopyridine})$.

Titration of 4-aminopyridine, using perchloric acid standardized coulometrically

The outer chamber of the shield tube ("intermediate chamber" of the titration cell) was filled with 7·5*M* sodium perchlorate and the inner chamber surrounding the counter-electrode (anode in this instance) with just sufficient 1·0*M* sodium perchlorate to cover the electrode. In the titration cell, Fig. 2, were placed 80 ml of 1·0*M* sodium perchlorate and a magnetic stirring bar. The pH was brought to 3 by the addition of 1*M* perchloric acid (the same acid as used later). Purified nitrogen was passed through the solution for 2 hr to remove carbon dioxide. The flow of nitrogen was maintained throughout the titration. The electrolyte was then pretitrated to remove any electroactive species present by cathodically generating hydroxide ion in the cell. When the solution reached pH 9, the electrolysis was stopped and the solution was acidified by the addition of 1*M* perchloric acid.

This sequence was repeated three times. During the third electrolysis, the pH was measured as a function of time, at the lower current setting, approximately 6·4 mA. The potential drop across the standard resistor was also recorded. The weighed sample of 4-aminopyridine was introduced by lowering the weighing boat plus the amine

into the electrolyte by a platinum wire. A slight excess of standard perchloric acid was added from the weight burette. The solution was then electrolysed cathodically, at about 63·4 mA. At 5-min intervals, the potential across the standard resistor, the temperature of the resistor and the pH of the solution were recorded. Anolyte was extracted from the inner shield tube and 7·5*M* sodium perchlorate added to the outer chamber of the shield tube to maintain a slow flow of electrolyte into the anode chamber. When the main solution reached pH 3·5 the titration was interrupted and the walls of the titration chamber rinsed with triply-distilled water. The titration was continued at a current of approximately 6·4 mA delivered in 20-sec increments, the pH, time, and potential drop across the resistor being measured. Between additions sufficient time was allowed for the solution to equilibrate before the pH was recorded.

The perchloric acid was standardized in a similar manner. The major part of the titration required about 9 hr; the potential drop over the standard resistor was measured every 30 min during this period.

In each analysis, two equivalence points were determined, that in the pretitration and that in the actual titration. The equivalence points in the pretitrations and the standardization of the perchloric acid were determined by the method of Yan.[19] In the titrations in which 4-aminopyridine was present (actually back-titrations of excess of perchloric acid), the point of inflection was found by the computer method.[18]

The concentration of the standard solution of perchloric acid, expressed in coulombs per gram, was calculated from

$$C_{HClO_4} = (A + B + C)/(\text{wt. solution})$$

where A, B and C have the same meanings as before.

The excess of perchloric acid in the back-titrations, expressed in coulombs, was calculated from

$$C_{\text{Excess HClO}_4} = -A + B + C$$

and the net perchloric acid used, in grams, from

$$C_{\text{Net HClO}_4} = (\text{wt. HClO}_4)(C_{HClO_4}) - (C_{\text{Excess HClO}_4})$$

Finally, the value of the faraday was calculated from

$$F = (C_{\text{Net HClO}_4})(\text{equiv. wt.})/(\text{wt. 4-aminopyridine}).$$

RESULTS AND DISCUSSION

The quantity electrical equivalent per gram has been calculated for each titration and is reported in Tables 3 and 4. One electron being involved per molecule of 4-aminopyridine, it remains simply to multiply the electrical equivalent per gram by the best value of the molecular weight, to obtain the value of the faraday. Using the new hydrazine–platinum anode, five hydrogen ions are generated per four electrons passed; this has been taken into consideration in the calculations.

The values for the faraday obtained by averaging the six titrations by each of the two methods were as follows.

Hydrazine-platinum anode method: F = 96,486·40 1972 NBS coulombs per mole; σ_i = 1·53 (five degrees of freedom); $\sigma_{\bar{x}}$ = 0·62.

Back-titration method (platinum cathode): F = 96,486·78 1972 NBS coulombs per mole; σ_i = 0·57 (five degrees of freedom); $\sigma_{\bar{x}}$ = 0·23

Here σ_i and $\sigma_{\bar{x}}$ are the standard deviations (random errors only) of the individual observation and of the mean, respectively.

We advance for the value of the faraday a weighted average of these values: F = 96,486·69 (0·81) 1972 NBS coulombs per mole, in which the number in parentheses is the uncertainty resulting from combining random and systematic errors and expressed as the standard deviation of the mean. This uncertainty is 8·4 ppm.

The weighted mean $\bar{x}$ and its uncertainty $\sigma_{\bar{x}}$ were calculated by using the method followed by Taylor, Parker and Langenberg [ref. 30, p. 382, equation (10)]:

$$\bar{X} = \frac{\dfrac{\bar{X}_h}{\sigma_h^2} + \dfrac{\bar{X}_b}{\sigma_b^2}}{\dfrac{1}{\sigma_h^2} + \dfrac{1}{\sigma_b^2}}, \qquad \frac{1}{\sigma_{h+b}^2} = \frac{1}{\sigma_h^2} + \frac{1}{\sigma_b^2}$$

in which the subscripts h and b refer, respectively, to the hydrazine–platinum anode and back-titration methods, and the standard deviations of the means, σ_h and σ_b, are the combined random error plus those systematic errors not common to the two methods, all being expressed in ppm. The uncertainties were combined by taking the square root of the sum of the squares (root-sum-square, RSS [ref. 30, p. 383, equation (11)]). Thus

$$\sigma_h = [(\sigma_{x',h})^2 + (\sigma_{ep,h})^2]^{1/2} = [(6{\cdot}40)^2 + (7)^2]^{1/2} = 9{\cdot}48$$

$$\sigma_b = [(\sigma_{x',b})^2 + (\sigma_{ep,b})^2 + (\sigma_{x',stdn})^2]^{1/2}$$
$$= [(2{\cdot}43)^2 + (3)^2 + (3{\cdot}39)^2]^{1/2} = 5{\cdot}14$$

in which the standard deviations of the mean are expressed as ppm (designated by the prime in the subscript), and the subscripts ep and stdn designate end-point and standardization. The end-point errors are the best estimates obtained as described later; for $\sigma'_{\bar{x},stdn}$ see Table 4. Application of these formulae leads to F = 96,486·69 1972 NBS coulombs per mole and σ_{h+b} = 4·52 ppm. To σ_{h+b} was then added, again by the RSS method, the errors common to both methods (in ppm): Weston unsaturated standard cell (4), standard resistor (0·2), time (0·2), potential drop (3), mass (4), purity (3), molecular weight (0·3). The total was 12·7 ppm, or 1·22 coulombs per mole.

The results presented in Tables 3 and 4 are based on a purity of 100% for the 4-aminopyridine; introduction of a lower value for the purity raises the value for the faraday. For the effect of possible impurities in the 4-aminopyridine, see below. The value used for the molecular weight of 4-aminopyridine is based on a recalculation of the atomic weight of nitrogen; see below.

For comparison, values obtained for the faraday since 1960 are tabulated in Table 5.

Estimate of error

In estimating the errors used in the section immediately above, we have attempted to give our best esti-

mate at the one standard deviation (70% confidence) level rather than the maximum possible error. Such estimates, the best guess on the part of the investigator, based on his feel for his subject, are subjective, of course, but the practice has the sanction, and indeed is the general and preferred operating practice, of those engaged in evaluating the fundamental constants; see Taylor, Parker and Langenberg (ref. 30, p. 383) and the discussion in the papers of the 1970 symposium[34] at the National Bureau of Standards, in particular the paper of Thomsen.[35]

The rationale for the assessment of the errors in the standards of electromotive force, resistance, potential drop, time and mass is given in preceding sections under *Experimental*. The larger errors, in the detection of end-point, the measurement and integration of current, and purity, are discussed in the following sections.

Precision in location of end-point. The time of electrolysis in an individual titration is the difference between the points of inflection in plots of pH vs. time during which constant current is flowing, obtained from data at the beginning and the end of the titration. Fifteen or so data points enter into the determination of each point of inflection and it is difficult to assess the cumulative effect of the start–stop errors on the time at the point finally selected for the point of inflection. This error was minimized by reducing the current in the end-point regions to one-tenth that in the main titration. The slope at the point of inflection in the titration using the hydrazine–platinum anode was 0·002 pH/0·0064 coulombs. Judging from this slope and the rate of change of the slope through the point of inflection, we estimate the error in location of the point of inflection to be 0·013 coulombs. This is about the same variation as obtained for any one set of data by using the computer program[18] in conjunction with pH as a function of time and also time as a function of pH. In terms of the current in the main part of the titration, this is 0·013 coulombs in a total of 2560 coulombs, or 5 ppm. The difference between two end-points is involved, so the end-point error is taken as the RSS of the individual errors, or 7 ppm.

Although the slope in the end-point regions in the standardization of perchloric acid was much greater, 0·08 pH/0·0064 coulombs, the data were not amenable to the computer program and the Yan method was used to locate the point of inflection. The uncertainty was estimated at 0·004 coulombs, leading to an error of 1·6 ppm. In the back-titration of excess of perchloric acid in the presence of 4-aminopyridine, the slope was 0·007 pH/0·0064 coulombs and the computer method could be used; the error was estimated to be 2·5 ppm for the point of inflection. The back-titration method involved one each of these end-points and the combined error is thus 3 ppm.

We have identified some five variables affecting the detection of the end-point, control of which must be improved in future work if 1 ppm accuracy is to be achieved. This might be done by using the same end-point (point of inflection) at the beginning and end of the titration, so that the difference between end-point and equivalence point cancels.

Measurement and integration of current. Although the error in the measurement of the potential drop over the standard 20-Ohm resistor with the type K-5 potentiometer was estimated to be 3 ppm, variation in the current supply caused a 5-μV variation on the null-point detector. Slow drifts in the current, corresponding to as much as 400 μV variation in potential drop, occurred over the 8-hr runs; these were caused primarily by variations in the 110-V a.c. mains supply and were less in runs made at night. The potential measurements were made at intervals not exceeding 30 min and the current was obtained by averaging the potential drops recorded. Stepwise integration of current *vs.* time with each reading gave almost identical results. It is assumed that a central value was obtained in the readings of the null-point detector and that the product of current and time has a random error distribution which is included in the general estimate of random error.

Effect of impurities. It is unfortunate that the freezing-point study[1] could give only an upper limit, 10 ppm, for the impurity possibly present in the 4-aminopyridine. At present, organic impurities as this level in organic compounds (metals having been shown to be absent) cannot be identified and determined. If the impurities in the 4-aminopyridine are 2-aminopyridine and 3-aminopyridine, they will be without effect; the equivalent weights are identical and although both isomers are weaker bases than 4-aminopyridine they will be at least 96% in the protonated form at the end-point pH-value used. Even the homologous methylaminopyridine, differing in molecular weight by 14, would be similarly titrated and cause negligible error; thus, 10 ppm of 3-methyl-4-aminopyridine, mol. wt. 108·14411, $pK_B = 4·55$, would affect the results only by 1·2 ppm. The volatility, as reflected in the melting temperature, of the pyridylamines isomeric and homologous to 4-aminopyridine, makes it very unlikely that any of them would be present as an impurity in carefully sublimed 4-aminopyridine. The effect of symmetry of the molecule on melting point is about as dramatic among the pyridylamines as in any class of organic compounds other than the tetra-aryl lead compounds:

Aminopyridine	m.p.	pK_B	Aminopyridine	m.p.	pK_B
4-	159°	4·63	3-	64°	7·97
3-Me-4-	108°	4·55	4-Me-3-	106°	
3-Et-4-	73°	4·51	6-Me-3-	96°	
3-iso-Pr-4-	52°	4·41	2-	56°	7·29
2,6-Di(Me)-4-	192°		3-Me-2-	26°	6·76
3,5-Di(Me)-4-	83°	4·47	4-Me-2-	98°	6·52
2,3,4,5-Tetra(Me)-4-	197°	3·43	6-Me-2-	41°	6·59

Except for the highly symmetrical 2,6-dimethyl and 2,3,5,6-tetramethyl compounds, the low m.p. and the volatility characteristics of all of these aminopyridines would favour their removal early in the process of

subliming 4-aminopyridine. The synthesis of 4-aminopyridine from acetaldehyde (acrolein may be present) and ammonia proceeds through the isolation of 4-methylpyridine from other picolines, the oxidation to pyridine-4-carboxylic acid, conversion into the amide or hydrazide, and degradation to 4-aminopyridine.[20] The quite different properties of the hydrocarbon, carboxylic acid, and amide from those of the aminopyridine make it unlikely that these compounds would be carried through to the final product and thus the likely impurities are the isomeric and homologous compounds. There is no gainsaying, however, that the commercial 4-aminopyridine starting product used in this work was oily and that low melting materials were eliminated in the early stages of the sublimation. This means that great reliance is placed on the efficacy of the sublimation and on the proof of purity afforded by the freezing point analysis, the sensitivity of which is 10 ppm. However, we feel the most probable impurities (if any) are 2-aminopyridine, 3-aminopyridine and the homologous aminomethylpyridines, and place the error at 3 ppm (70% confidence).

Isotopic composition of nitrogen in the 4-aminopyridine. We have been informed[20] that although two routes are followed in the manufacture of 4-aminopyridine at the Reilly Tar and Chemical Corporation, both nitrogen atoms, that of the ring and that of the amino group, are derived from ammonia. Thus, the nitrogen in the 4-aminopyridine used in this work was derived from the nitrogen of the atmosphere of recent geologic time.

The question of the alteration, during the chemical processing and purification, of the ratios of the abundances of the various species of 4-aminopyridine which exist as a result of the existence of isotopes of the three elements making up the compound, is not so easily answered. Probably not more than twenty successive sublimations were made in the purification of the 4-aminopyridine, but the number is uncertain owing to the complexity of what happened in the formation of the layered, hemispherical shell of 4-aminopyridine above the crude mass during the preliminary sublimation. It seems unlikely, however, that the successive steps were anywhere near sufficient in number to disturb the abundance ratios by more than the 10 ppm aimed for in this work.

Atomic weight of nitrogen and the molecular weight of 4-aminopyridine. For calculating the molecular weight of 4-aminopyridine, the following values for the atomic weights were used:

$$C = 12{\cdot}01115 \pm 0{\cdot}00005$$

$$H = 1{\cdot}00797 \pm 0{\cdot}00001$$

$$N = 14{\cdot}00672 \pm 0{\cdot}00001$$

The values for carbon and hydrogen are those given in the 1961 Table of Atomic Weights[21] and were used rather than those of the 1971 Table[22] in which the 1961 numbers have been rounded off for general chemical use. A value for the atomic weight of nitrogen was calculated by using for the abundance ratio $r = {}^{14}N/{}^{15}N = 272 \pm 0{\cdot}3$ and the recent values for the absolute masses of the isotopes of nitrogen, given by Wapstra and Gove:[23]

$${}^{14}N = 14{\cdot}00307440 \pm 0{\cdot}00000013$$

$${}^{15}N = 15{\cdot}0001093 \pm 0{\cdot}0000005$$

These, with the usual formula

$$N = {}^{14}N + ({}^{15}N - {}^{14}N)/(1 + r)$$

yield

$$N = 14{\cdot}006726 \pm 0{\cdot}0000005$$

The value $r = {}^{14}N/{}^{15}N = 272$ is that of Junk and Svec,[24] based on the mass spectrographic analysis of air of different but recent geographical origin. An earlier value by Nier,[25] $^{14}N/^{15}N = 273$, is an unweighted mean of two sets of measurements, made on different instruments; much better precision was obtained on one of the instruments and the average of the measurements on it give a lower value, leading to $^{14}N/^{15}N = 272$, in agreement with Junk and Svec. A more recent work on the abundance of the isotopes of nitrogen by Pilot[26] is devoted to a study of nitrogen from rock and mine gases and appears less relevant to the present work than the Junk and Svec work. The value for the atomic weight of nitrogen reported by De Bievre, Gallet and Debus[27] is based on the unweighted abundance ratios of all three of the works just mentioned and was rejected here in favour of the value calculated above. For the present work, the calculated value was rounded down to

$$N = 14{\cdot}00672 \pm 0{\cdot}0000005$$

giving some weight to the results of the second set of measurements by Nier. Rounding up would cause an error of only 0·2 ppm.

The number following the $\pm$ sign in the values above represents the maximum reported in various studies for the effect resulting from natural variation in isotopic composition. This is specifically stated in the 1961 Report of the International Commission on Atomic Weights.[21] In the De Bievre, Gallet and Debus values the corresponding number given is the standard deviation "as it reflects the variation in isotopic composition of the samples used by the different authors, as well as many differences in the preparation and measurement technique of the sample".

In calculating the molecular weight of 4-aminopyridine these numbers were handled by taking the root mean square of the estimated errors thus:

$5C + 6H + 2N = 94{\cdot}11702$;
sum of squares $= 133 \times 10^{-10}$; root mean square $= 3{\cdot}1 \times 10^{-5}$

The molecular weight of 4-aminopyridine is therefore taken as $94{\cdot}11702 \pm 0{\cdot}00003$. Thus the reported natural variation in the abundance of the isotopes of carbon, hydrogen and nitrogen represents an error

of 0·3 ppm in the m.w. of 4-aminopyridine, which is over an order of magnitude smaller than the error (standard deviation) in the coulometric titrations.

Recent values for the faraday

The currently accepted value for the faraday is based entirely on the silver dissolution experiments of Craig, Hoffman, Law and Hamer[28] as recalculated by Hamer[29] and by Taylor, Parker and Langenberg.[30] Although Taylor, Parker and Langenberg called for further work on the evaluation of the faraday (ref. 30, p. 406, column 1; p. 482, column 2), no account was taken in their review of the three determinations made during 1967 and 1968 by Marinenko and Taylor[31,32] by the coulometric method; surely they deserve consideration. Taylor, Parker and Langenberg made a thorough critique (ref. 30, pp. 403–406) of the Craig, Hoffman, Law and Hamer work. One possible source of error they overlooked is one which would be immediately obvious to an old-fashioned, atomic-weight chemist of the T. W. Richards school, namely that a recovery and transfer of material was involved. During the anodic dissolution of the silver, 2–25% of the silver was sloughed from the anode and was recovered by filtration, drying and weighing. Recovery to ± 10 ppm of the 3-g samples involved means recovery to $\pm 30\ \mu g$. It is difficult to ensure complete recovery from the walls of the vessel without contamination, dry the silver without oxidation, and guarantee the stability of a porous-bottom filtering crucible (of the type used) toward atmospheric moisture. It was to meet this very problem of eliminating the transfer of solids that T. W. Richards devised the titration procedures and the solid-to-solid conversion in gaseous atmospheres that characterized the atomic-weight work at Harvard from 1904 on.[33] The titrimetric method, applied particularly to metal halides, was brought to perfection by the invention of the nephelometer and the nephelometric end-point, and the conversion of solid to solid by heating in a gaseous atmosphere was effected in the so-called "bottling apparatus". The solid-to-solid procedure was used in the several, all important, determinations of the atomic weight of silver that marked the highest point to which the chemical determination of atomic weight was carried. When filtration could not be avoided, complete transfer was proven by chemical recovery of traces of materials left on glass walls; the effectiveness of the filter was checked by repeated filtration of filtrates; constant checks were made on the stability of filters; and of course the removal of water was given paramount attention.

The work described in the present paper has the merits that it is based on a material prepared by sublimation and that no recovery and filtration of a solid is involved. Offsetting this is the necessity of locating an end-point, with its attendant problems. The unique feature of the present work is that it involves the titration of the basic substance, 4-aminopyridine, in two directions, that is, by electrolysis at the anode and then again at the cathode.

Following the recommendations of Taylor, Parker and Langenberg (ref. 30, p. 485), at the conclusion of their long and exhaustive treatment of the fundamental physical constants, we have attempted, within the space limitations imposed by the journal, to provide sufficient information "so that 10 yr hence, the results can be updated in light of any new information or data which may become available." Further details of the work described in the present paper will be found in the theses of William C. Hoyle[10] and William F. Koch.[11] A bound volume of photocopies of the pertinent pages of the laboratory notebooks of W. C. Hoyle and W. F. Koch has been deposited in the Library of the Iowa State University and is catalogued in the University Archives under "Harvey Diehl–Faraday Data".

Acknowledgements—We are deeply indebted to Professor C. A. Swenson of the Department of Physics of Iowa State University and the Ames Laboratory of the United States Atomic Energy Commission for criticism and aid in the calibration and employment of our physical standards of potential, resistance and time. We wish to thank the Hach Chemical Company, Ames, Iowa, for the gift of one of their high-precision, expanded range of pH meters, used throughout this work. A primary-standard grade of 4-aminopyridine is being placed on the market by the Hach Chemical Company.

The calibration of our unsaturated, working cells and the bank of standard saturated cells was carried out personally by Mr. Wayne A. Rhinehart of the Ames Laboratory of the United States Atomic Energy Commission and we wish to express our appreciation of the dedicated and careful work he did.

FURTHER ACKNOWLEDGEMENT AND NOTES ADDED DURING REVISION. THE STATUS OF THE FARADAY CONSTANT

After the manuscripts of this paper and the four supporting papers had been submitted to *Talanta* for publication, they attracted the attention of Dr. Barry N. Taylor, Chief, Electricity Division, Institute for Basic Standards, National Bureau of Standards, Washington, D.C., and co-author of the profound least-squares treatment of the physical constants of 1969 and 1973. Dr. Taylor expressed deep interest in the work and arranged to have our standards of resistance and potential recalibrated at the Bureau under his personal supervision. These calibrations were incorporated into the present paper by recalculations made during January 1975. We are most grateful for Dr. Taylor's generous response.

At the time this manuscript was submitted, the authors were unaware of another least-squares treatment of the fundamental constants, by E. R. Cohen and B. N. Taylor, (*J. Phys. Chem. Ref. Data*, 1973, **2**, 663) bringing the work of Taylor, Parker and Langenberg[30] up to date; the issue carrying this paper did not reach the Iowa State University Library until mid-August 1974. Taking into account more recent measurements (of improved accuracy) of the gyro-

magnetic ratio of the proton and of the magnetic moment of the proton, Cohen and Taylor find the indirect, calculated value of the faraday, 96,484·56(27)(±2·8 ppm) coulombs per mole, to be a more trustworthy value and reject the electrochemical values[28,29,31,32] as being subject to error (see Cohen and Taylor, p. 679 and Table 13.1, pp. 704–705, p. 723, column 2 and Tables 43.1 and 34.2, and p. 725, column 1). The volt and ohm of the National Bureau of Standards and the Bureau International des Poids et Mesures have now been made identical and the designation A_{BI69} is now used for the ampere. The accuracy of the Josephson junction method of establishing the volt has made it possible to follow the progressive changes of the standard saturated cells at the National Bureau of Standards with time, and Cohen and Taylor now correct experimental work to take this drift into consideration. The changes are 1–2 orders of magnitude lower than the error in electrochemical work at the present time.

Further changes in values of the physical constants are impending because of recent work at the National Bureau of Standards leading to a greatly improved value for the Avogadro constant (R. D. Deslattes, A. Henins, H. A. Bowman, R. M. Schoonover, C. L. Carroll, I. L. Barnes, L. A. Machlan, L. J. Moore and W. R. Shields, *Phys. Rev. Lett.*, 1974, **33**, 463). For an insight into the procedures and the current excitement of the physicists in the area of the fundamental constants, see D. N. Langenberg, D. J. Scalapino and B. N. Taylor, *Sci. Am.*, 1966, **214**, No. 5, 30; B. N. Taylor, D. N. Langenberg and W. H. Parker, *ibid.*, 1970, 223, No. 4, 62; B. N. Taylor, *Metrologia*, 1973, **9**, 21.

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DETERMINATION OF LEAD IN CARBONATE ROCKS BY CARBON-FURNACE ATOMIC-ABSORPTION SPECTROMETRY AFTER DISSOLUTION IN NITRIC ACID

W. C. CAMPBELL and J. M. OTTAWAY

Department of Pure and Applied Chemistry, University of Strathclyde, Cathedral Street, Glasgow G1 1XL, Scotland

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Summary—A simple and rapid method for the determination of 1–100 ppm of lead in carbonate rocks is described. Dissolution of the rock samples in 10% v/v nitric acid is shown to give precise and accurate results even though silicates in the samples remain undissolved. A more time-consuming but complete dissolution of the sample with hydrofluoric acid may be used if preferred. The increase in sensitivity and freedom from matrix interference obtained by the use of a carbon-furnace atomizer eliminate the necessity for preconcentration of the lead, saving time and preventing errors from contamination or losses derived from inefficient extraction procedures. The detection limit and precision of the method are 0·4 ppm and 6% (relative standard deviation at the 3-ppm lead level) respectively and accurate results were obtained for the analysis of standard rock samples.

The normal background level of lead in limestones is usually in the range 1–10 ppm and the determination of lead at these levels is becoming increasingly important, especially in geochemical exploration. A rapid and reasonably accurate and precise method for the purpose would be very useful.

Various techniques have been applied to the determination of lead in rocks, but suffer variously from interference effects, lack of sensitivity and long analysis times.[1] Flame atomic absorption lacks sensitivity for the analysis at the required levels and it has been shown by Shaw[2] that calcium, the major cation present in limestones, exhibits a serious depressive effect on the lead atomic-absorption signal from an air–acetylene flame, under all flame and height conditions, if a nitric acid medium is used. The use of a purely chloride medium, with no oxy-acids present, is required to remove this interference. There is an upper limit of approximately 2% w/v to the concentration of total solids in solution for efficient nebulization in flame analysis. Detection limits are therefore of the order of 10–100 ppm, depending on the instrument, and extraction and/or preconcentration techniques must be used to carry out acceptably precise analysis in the range 1–100 ppm.[3] Such procedures will, however, require considerable operator time and will be unsuitable for the analysis of large numbers of rock samples gathered during prospecting.

Atomic-absorption spectrometry using carbon-furnace atomization offers much improved sensitivity over the flame method for the determination of lead.[4–6] If interference from the other cations present, especially calcium, can be controlled or reduced to an acceptable level, then rapid direct analysis of the rocks should be possible after their dissolution. In other methods[5,6] it has been shown that it is necessary to use an oxy-acid as the dissolution agent in order to control the interference effects from the bulk matrix, which are considerably worse in chloride media. It has been suggested[7] that in oxy-acid media, the evaporated salts are converted thermally into metal oxides which are subsequently reduced by the carbon of the carbon-furnace atomizer to produce metal atoms. In chloride media, molecular volatilization may occur from the carbon surface, preventing the formation of atoms.

The determination of lead in standard rocks by means of a tantalum cup system,[8] and in silicate rocks by use of a carbon-furnace system,[9] has recently been reported. However, the methods include a complex and time-consuming dissolution procedure which should be capable of simplification for the analysis of carbonate rocks, since these dissolve readily in mineral acids.

In a preliminary communication we have given a brief outline of the method developed.[1] This paper contains a detailed description of the method and includes an investigation of interference effects and results on the analysis of standard rocks not previously available to us, which help to verify the accuracy of the method.

EXPERIMENTAL

Reagents

All chemicals used were of analytical-reagent grade. Water distilled from quartz was used throughout.

Stock lead solution (100 *ppm lead*). Dissolve 0·160 g of lead nitrate in water, transfer the solution to a 1-litre standard flask and dilute to the mark with water and sufficient nitric acid to make the final solution $10^{-2}M$ in nitric acid.

Solutions for interference studies. Solutions of sodium, potassium, iron(III) and magnesium (all 2000 ppm) were prepared from the nitrates and made 0·01 *M* in nitric acid. A similar solution of aluminium was made by dissolving the powdered metal in nitric acid. Calcium solutions (20,000 ppm) were made by dissolving the carbonate in just sufficient nitric acid or hydrochloric acid.

Apparatus

A Perkin–Elmer H.G.A. 70 carbon-furnace atomizer mounted on a Perkin–Elmer 306 atomic-absorption spectrometer which was equipped with a deuterium-arc background-corrector and coupled to an Electronik 194 strip-chart recorder was used. A Perkin–Elmer Intensitron lead hollow-cathode lamp was used as the radiation source. The design and operation of the carbon-furnace atomizer have been described in detail elsewhere.[4,10] A 50-μl Eppendorf micropipette was used to transfer the samples to the tube. It was found that this volume evaporated to dryness in about 25 sec at programme 2 (100°) and a drying time of 40 sec was therefore selected to ensure that the sample was properly dried. The lead signal was found to increase with applied voltage up to 8 V. Above this voltage both sensitivity and reproducibility tended to decrease. The lead 283·3-nm line was preferred to the 217·0 nm line as it gave rise to a steadier baseline, with an accompanying improvement in detection limit. The background-corrector was used in all the measurements reported.

Procedures

Two different sample dissolution procedures were developed, one for rapidity, the other to ensure that all of the rock sample was brought into solution.

Nitric acid dissolution. Weigh the powdered rock sample and place it in a 100-ml PTFE beaker. (The weight of sample taken depends on the expected lead content: a rough guide is 1 g for 10 ppm, 0·5 g for 10–50 ppm and 0·1 g for 50–100 ppm.) Add 10 ml of concentrated nitric acid and bring to the boil, on a hot-plate. Boil gently for 15 min, then add 10 ml of water and boil for a further 15 min. Transfer the solution to a 100-ml volumetric flask and dilute to the mark with water. Allow the small solid residue to settle to the bottom of the flask.

Hydrofluoric acid dissolution. Weigh the powdered rock sample (weight as above) and place it in a 100-ml PTFE beaker. Add 10 ml of concentrated hydrofluoric acid and place on a steam-bath for 1 hr. Then remove from the steam-bath, add 10 ml of concentrated nitric acid and evaporate to dryness at a low temperature on a hot-plate. Add a further 10 ml of nitric acid and again evaporate slowly to dryness. Finally take up the residue, in 10 ml of nitric acid. Transfer the solution to a 100-ml volumetric flask and dilute to the mark with water.

Preparation of calibration solutions. Dilute 10 ml of the stock lead solution (100 ppm) to 1 litre with water. This solution should be freshly prepared every day. Transfer 2·0, 5·0, 10·0 and 15·0 ml of this solution to 100-ml volumetric flasks. Add 10 ml of concentrated nitric acid to each flask and dilute each solution to the mark with water. The calibration standards will then contain 0·02, 0·05, 0·10 and 0·15 ppm lead respectively in nitric acid.

Determination. The instrument is operated under the following conditions:

Wavelength, *nm*	283·3
Lamp current, *mA*	8
Spectral bandwidth, *nm*	0·7
Drying temperature, °*C*	100
Drying time, *sec*	40
Charring temperature, °*C*	—
Charring time, *sec*	—
Atomization temperature, °*C*	2200
Atomization voltage, *V*	8
Atomization time, *sec*	10
Volume of sample solution, μ*l*	50
Scale expansion	× 3
Argon flow-rate, *l./min* (at 40 psig)	1·5

Inject standards and then samples into the carbon-furnace atomizer and record the atomic-absorption signals during the atomization. At least two injections should be made of each standard and sample solution and an average absorbance taken. Read the sample concentration from a calibration graph. Run a blank test on the whole procedure at the same time as the samples, and then subtract its absorbance from the sample absorbances. The apparent lead concentration of the blank seldom exceeds 0·005 ppm (equivalent to a maximum of 0·5 ppm in a rock sample).

RESULTS AND DISCUSSION

Interferences

The final acid concentration used for both samples and standards was 10% v/v nitric acid (*i.e.*, tenfold dilution of the concentrated acid). For this reason all interference studies were done on a 0·1-ppm solution of lead in 10% v/v nitric acid. It was found to be necessary to match the samples and standards carefully with respect to final acid concentration, as nitric acid itself causes a depressive effect on the lead absorption signal. The magnitude of this depressive effect was found to vary considerably (from 20 to 60%) from day to day, but to be relatively constant over a particular day's work. It would appear to be related to the condition and age of the carbon atomization tube in use. The deuterium-arc background-corrector was used at all times in order to avoid confusion between genuine interference effects and smoke-absorption and/or light-scattering due to the high concentration of solids being injected into the carbon furnace.

The major metallic constituent of limestones is, of course, calcium and its effect on the lead signal is therefore of primary importance. In Fig. 1 the effect of up to 10,000 ppm of calcium on the signal from 0·1 ppm of lead in 10% v/v nitric acid is shown. The maximum depression of the lead signal caused by the calcium is 10% at 100 ppm of calcium and this is reduced to less than 5% at above 1000 ppm of calcium, which is considered negligible for geoprospecting purposes. The effect in 10% hydrochloric acid medium is also shown in Fig. 1. Here the depressive effect is much greater and the lead signal almost disappears at above 1000 ppm of calcium. This is in

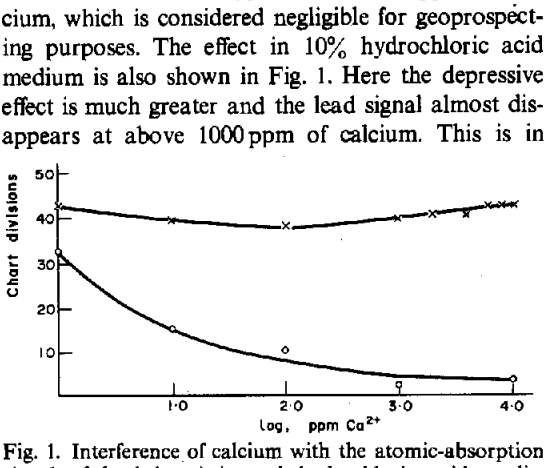

Fig. 1. Interference of calcium with the atomic-absorption signal of lead in nitric and hydrochloric acid media. ×—10% nitric acid solution; ○—10% hydrochloric acid solution.

keeping with our earlier observation that, in contrast to the case with flame atomic absorption, interferences in carbon-furnace atomization in chloride media are in general much larger than those in oxy-acid media.

When halide salts are used in the carbon-furnace atomizer it is likely that some molecular volatilization takes place and that these molecules are not subsequently dissociated into atoms. In the case of lead the absorption signal is smaller in chloride media than in nitrate media and the effect of calcium is possibly to hold more chloride in the solid matrix during the drying stage, thus facilitating the volatilization of lead as the chloride during the atomization stage, leading to further reduction in absorption signal. For this reason nitric acid dissolution of the rock samples is advantageous.

The effect of the presence of hydrochloric and hydrofluoric acids on the lead signal was investigated. It was found that concentrations of hydrofluoric acid greater than 2% v/v caused a depression of the lead signal from a 0·1-ppm lead solution in 10% v/v nitric acid but up to 2000 ppm of chloride had no significant effect. If the hydrofluoric acid dissolution is used, care must be taken to remove all of the hydrofluoric acid, and therefore the double evaporation to dryness was incorporated.

The effects of aluminium, magnesium, iron, sodium and potassium, all of which would be expected to be present to some degree in the rocks being analysed, were also investigated. It was found that up to 500 ppm of iron and magnesium had no effect but the lead signal was depressed by aluminium, sodium and potassium. Table 1 shows the effect in the presence and absence of 10,000 ppm of calcium. Each set of results was obtained on a different day and the baseline signal from 0·1 ppm of lead therefore varied as explained above. The calcium appears to have a releasing effect and allows a much higher concentration of interferent to be tolerated. From Table 1 it would seem that 50 ppm of aluminium, 100 ppm of sodium or 100 ppm of potassium could be tolerated individually, and perhaps together.

Determination of lead in limestone rocks

A random batch of ten powdered limestone rocks obtained from Dr. M. J. Russell of the Department of Applied Geology, Strathclyde University, was analysed by the procedures described. Dissolution of these samples in nitric acid generally leaves a small insoluble residue which is presumably composed of quartz and clays. This rapidly settles to the bottom of the volumetric flasks. The results obtained when the residue is filtered off are similar to those obtained on allowing it to settle. Filtration therefore seemed unnecessary and was omitted. To check whether all of the lead was taken into solution by the nitric acid dissolution, the hydrofluoric acid dissolution, which leaves no residue of quartz and clays, was used and the results compared. As a further check on the accuracy of the procedure we obtained results, for the same rock samples, from a different laboratory using a flame atomic-absorption procedure which involved a complex and time-consuming separation/preconcentration procedure. The results obtained by all three methods[1] were in satisfactory agreement, indicating that the nitric acid dissolution does extract all the lead from the rocks.

Table 1. The effect of aluminium, sodium and potassium on 0·1 ppm of Pb in 10% v/v nitric acid with and without the presence of 10,000 ppm of Ca

Concentration of interferent, *ppm*	Signal from 0·1 ppm Pb, chart divisions, in the presence of					
	Al	Al + Ca	Na	Na + Ca	K	K + Ca
0	53	49	53	50	45	47·5
10	53	48	39	49	33	49
50	47	48	34	50	28	46
100	30	40	30	51	23	44
500	18	31	36	40	36	35

Table 2. Reproducibility tests

	Instrumental reproducibility Sample No. 221 Pb, *ppm*	Overall method reproducibility Sample No. 3R1 Pb, *ppm*	Sample No. 2
	5·20	2·90	97
	5·25	3·20	110
	5·40	3·25	110
	5·40	2·90	107
	4·75	3·05	102
	5·45	3·40	97
	5·30	3·25	96
	5·25	3·40	110
	5·25	3·05	106
	5·50		
Mean	5·28	3·15	104
Standard deviation	0·21	0·19	6·0
Relative std. devn. %	4·0	6·1	5·8
95% Confidence limits	0·47	0·44	13·8
Detection limit (2σ) = 0·4 ppm			

A number of suitable rock standards have been made available to us and the results from the analysis of these standards by the nitric acid procedure are given in Table 3 along with the reported lead contents of the rocks. The results obtained are seen to be in good agreement with the reported values in all cases except for that of the East German standard, KH, where the value obtained appears low.

Both the instrumental reproducibility and the overall reproducibility of the method were investigated. To check for instrumental variations, one rock sample, Code No. 221, was dissolved by the nitric acid procedure and ten 50-μl aliquots of the solution were subjected to carbon-furnace atomization. To check the reproducibility of the complete method nine samples of each of two rocks, 3R1 and 2, were dissolved by the nitric acid procedure and two 50-μl aliquots of each solution were analysed, and the average taken. The results of these tests are shown in Table 2. By far the greatest contribution to the relative standard deviation is seen to come from variations in the instrument itself. The overall precision (relative standard deviation) of about 6% is considered adequate for the analytical requirements discussed earlier.

Table 3. Determination of lead in limestone rock standards by nitric acid procedure

Standard	N.B.S. 1a	N.B.S. 1b	GFS 400	GFS 401	GFS 402	KH
This work, *ppm*	17·2†	2·0 ± 0·4§	2·4 ± 0·4‡	1·1 ± 0·4‡	1·8 ± 0·35‡	5·9 ± 1·1¶
Reported lead content,* *ppm*	15 ± 2	<2	3·3 ± 1·4	<2	1·9 ± 1·0	8

All the rock standards are limestones with the exception of GFS 400 which is a dolostone.

* Results from reference 11 except for KH which is an East German standard from Zentrales Geologisches Institut, Berlin, the reported value for which is the average of eight results.

† Average of three results.

‡ Mean ± one standard deviation on 7 results.

§ Mean ± one standard deviation on 5 results.

¶ Mean ± one standard deviation on 6 results.

The results obtained indicate that the interference effects are small, despite the fact that aluminium, sodium and potassium, which interfere, should be present in these rocks. The bulk matrix elements, namely calcium and perhaps magnesium, would seem to be primarily responsible for this effect. This suggests a method of overcoming interferences in other determinations, *viz.* by the addition of a large concentration of an "inert matrix" element. The aluminium is probably present in the rocks as aluminosilicates and therefore probably has very low solubility in nitric acid, so when the nitric acid procedure is used the aluminium concentration will be lower than that expected from the total aluminium content of the rock.

The nitric acid procedure appears to offer the simple, rapid and accurate method required for the determination of lead in limestones. The hydrofluoric acid procedure offers no apparent advantage and is tedious. Application of this technique to determination of other trace metals in limestones seems feasible but will be critically dependent on the solubility of the elements in nitric acid and on the interference effects and relative volatilities of trace elements and matrix elements in the carbon furnace.

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AUTOMATIC CLASSIFICATION OF CHEMICAL BEHAVIOUR BY SEQUENTIAL HYPOTHESIZATION AND MULTIPARAMETRIC CURVE-FITTING—III

FULLY COMPUTERIZED ELUCIDATION OF POLAROGRAPHIC DATA ON STEPWISE COMPLEX FORMATION

LOUIS MEITES
Department of Chemistry, Clarkson College of Technology, Potsdam, New York 13676, U.S.A.

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Summary—A fully automatic procedure, based on the polarographic technique of DeFord and Hume, is described for deducing the formula of the highest complex formed in the reaction of a metal ion with a ligand and for evaluating the successive overall formation constants. Its results are indistinguishable from those of careful graphical analysis in the traditional fashion.

In 1951 DeFord and Hume[1] devised a polarographic technique for evaluating the maximum co-ordination number and the successive formation constants of the complexes formed by the stepwise addition of a ligand X to a metal ion M. It assumes that the free metal ion is reversibly reduced to the metallic state and that the complexation equilibria are all very rapidly established. It is based on the equation

$$E_{1/2,c} = E_{1/2,s} - \frac{RT}{nF}\ln\frac{I_c}{I_s} - \frac{RT}{nF}\ln(F_0[X]) \quad (1)$$

where $E_{1/2,c}$ is the half-wave potential in a solution containing excess of free ligand at the concentration [X] and I_c is the diffusion current (or diffusion current constant) in that solution; $E_{1/2,s}$ and I_s are the half-wave potential and diffusion current (or diffusion current constant) of the aquo-complex in a non-complexing solution; and R, T, n, and F have their ordinary polarographic significance.

The function $F_0[X]$ is defined by

$$F_0[X] = 1 + \beta_1[X] + \beta_2[X]^2 + \ldots + \beta_j[X]^j \quad (2)$$

in which each β_i is a conditional overall formation constant related to the corresponding thermodynamic constant β_i^0 by an equation of the form

$$\beta_i = \beta_i^0 \frac{\gamma_M \gamma_X^i}{\gamma_{MX_i}}$$

where the γ's denote the appropriate molar activity coefficients, which are assumed to remain constant throughout the measurements. The data have in general been analysed by Leden's graphical extrapolation method.[2] Values of $F_0[X]$ are computed from (1) and plotted against [X], yielding a curve with a slope which approaches β_1 as [X] approaches zero. A new function $F_1[X]$ is then computed from

$$F_1[X] = \frac{F_0[X] - 1}{[X]} = \beta_1 + \beta_2[X] + \cdots + \beta_j[X]^{j-1} \quad (3)$$

and plotted against [X], yielding a curve with an intercept at [X] = 0 which is equal to β_1 and a slope which approaches β_2 as [X] approaches zero. The successive definitions

$$F_i[X] = \frac{F_{i-i}[X] - \beta_{i-1}}{[X]} = (\beta_i + \beta_{i+1}[X] + \cdots + \beta_j[X]^{j-i}) \quad (4)$$

give rise to similar plots until one of F_{j-1} against [X] becomes linear; the next plot, of $F_j[X]$ against [X], is a horizontal straight line. These observations establish the value of the maximum co-ordination number j.

This is a tedious and lengthy procedure and one that requires much judgment and involves many opportunities for graphical error. The present manuscript describes the construction and operation of a least-squares program that accepts the same experimental data and yields values of j and the β_i without requiring human intervention.

This problem, like the one considered in the first paper of this series,[3] is one of linear classification. The simplest possible assumption is of course that $j = 1$; its failure naturally leads to the one that $j = 2$, and so on.

There have been other attempts to computerize the DeFord–Hume procedure. McMasters and Schaap[4] attempted to dissect $F_0[X]$ by linear regression, but had limited success and concluded that the activity coefficients do not remain sufficiently constant over the range of solution compositions required. Momoki, Sato and Ogewa[5] employed elaborately weighted linear regression to show that β_3 for the cadmium–thiocyanate system is either negative (which is impossible) or zero but that β_4 is positive and finite, which is impossible unless β_3 is also positive and finite. Piljac, Grabarić and Filipović[6] proposed a criterion for the rejection of the hypothesis that j has any particular value: it is that any "best" value of a β_i is negative. This criterion is the basis of the procedure described

here, but since the hypothesis $j = 1$ always yields a positive value of β_1 even when j actually exceeds one, it is supplemented by a simple test that is equivalent to automatic deviation-pattern[7–9] recognition.

THEORY

The procedure proposed here is based on non-linear regression, the usefulness of which in the interpretation of physicochemical data has been demonstrated by numerous authors in the last few years.[10]

In applying any least-squares procedure it is necessary to make certain assumptions about the random errors that may be involved in the experimental measurements. The DeFord–Hume technique is somewhat unusual in that it involves two distinct and separately measured dependent variables, which may conveniently be taken as $E_{1/2,c}$ and $(RT/nF)\ln I_c$. The assumptions made were that (1) the values of [X] are free from appreciable errors and (2) the values of $E_{1/2,c} + (RT/nF)\ln I_c$ in any one set of data are drawn from normally distributed populations having identical standard deviations.

Neither of these assumptions seems to require lengthy explanation or defence. Some further discussion of the second does, however, seem justified by the frequency with which authors using the technique have stressed the precisions of their measurements of half-wave potentials while ignoring random errors in their values of I_c. The relative standard deviation of I_c may be estimated from the scatter of the values around a smooth curve. In principle this may yield an overestimate, for the diffusion coefficients of the successive complexes may not be monotonically dependent on i, but the effect will rarely be important. For one set of data, the value of j deduced by the original authors gave rise to a standard deviation from regression that was equal to $\pm 0{\cdot}3$ mV for the quantity $E_{1/2,c} + (RT/nF)\ln I_c$ while the estimated relative standard error of I_c corresponded to a standard deviation of $\pm 0{\cdot}2$ mV for $(RT/nF)\ln I_c$. For another set the corresponding values were $\pm 2{\cdot}2$ and $\pm 1{\cdot}6$ mV. Although it is not surprising that those authors who have taken the greatest care in measuring $E_{1/2,c}$ should also be the ones who have attained the best precision in measuring I_c, it is unexpected that these two independent measures of precision should be as closely related as these examples (among many others) suggest, and astonishing that the uncertainties in I_c should have been thought to be so much less significant than they really are.

On the basis of the assumptions described, equations (1) and (2) may be rewritten in the form

$$E_{1/2,c} - E_{1/2,s} + \frac{RT}{nF}\ln\frac{I_c}{I_s} = -\frac{RT}{nF}\ln(1 + \beta_1[\mathrm{X}] + \beta_2[\mathrm{X}]^2 + \cdots + \beta_j[\mathrm{X}]^j) \quad (5)$$

The symbol Y is used henceforth to denote the quantity defined by the left-hand side of this equation. The computation for any given value of j consists of finding the β_i values that minimize the sum of the squares of the differences between the experimental and computed values of Y. This is easily done by means of a general non-linear regression computer program; the important question is how the value of j is to be chosen. The procedure by which this choice is made is generally analogous to that employed for a closely related problem in an earlier paper:[3] it entails fits to the equations that represent the successive hypotheses that $j = 1,2,...$, and scrutiny of the results thereby obtained. For $j = 1$ and 2 this scrutiny amounts to a search for the characteristic features of a deviation pattern that reflects the systematic errors consequent upon an incorrect choice of j.

Typical curves are shown in Figs. 1 and 2. In Fig. 1 the curves labelled "1" and "2" represent the best one- and two-parameter fits to equation (4) for the data of Hume. DeFord and Cave[11] on the cadmium-(II)-thiocyanate system. They correspond to the hypotheses that $j = 1$ and 2, respectively, and they give rise to the deviation patterns shown in Fig. 2.

A deviation plot resembling curve 1 in Fig. 2 is always obtained when the hypothesis that $j = 1$ is incorrect; if it were correct, as it might be with a multidentate ligand, a random scatter would result instead. On the hypothesis that $j = 2$ a much better fit can be secured, as is shown by Fig. 1, and the deviation pattern obtained when this hypothesis is incorrect has both a more complex shape and a smaller absolute amplitude. In Fig. 2 the curves are normalized by plotting the ratio $\Delta Y/(\mathrm{SD})_Y$ along the ordinate: ΔY is the difference between an experimental value of Y and the corresponding value computed from (4) by use of the best β_i values, and $(\mathrm{SD})_Y$ is the standard error from regression to that equation for the particular value of j under consideration. It is inherent in the nature of the situation that the

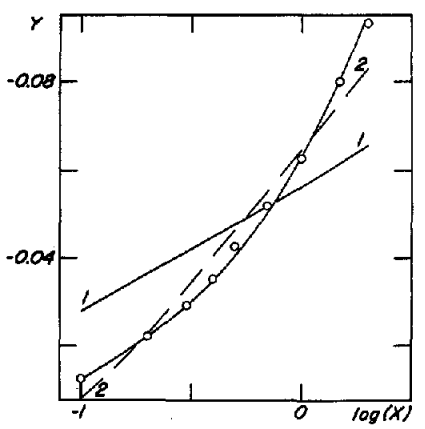

Fig. 1. The open circles and the smooth curve drawn through them represent the data obtained by Hume, DeFord and Cave[11] for the cadmium–thiocyanate system; the curves labelled "1" and "2" represent the best fits obtainable on the hypotheses that $j = 1$ and 2, respectively.

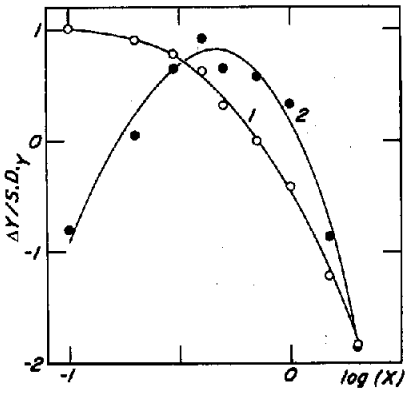

Fig. 2. Normalized deviation patterns derived from Fig. 1.

amplitude of such a normalized plot will differ only slightly among different sets of data.

On completion of each successive fit, the data (which must be arranged in order of increasing [X]) are divided into three groups that are as nearly equal in numbers as possible, and the average value of $\Delta Y/(SD)_Y$ is computed for each group. Two tests are then applied:

(1) if the difference between the average for the points at the lowest values of [X] and that for the points at the highest values exceeds 1·5, the deviation pattern resembles curve 1 in Fig. 2;

(2) If the difference between the average for the points at the intermediate values of [X] and the mean of the averages for the points in the other two groups exceeds 1, the pattern resembles curve 2 in Fig. 2.

In either case the value of j is rejected and the next higher integral value is tested in turn.

The values of $(SD)_Y$ on which these criteria are based involve systematic errors and greatly exceed the standard errors of the experimental measurements. For the data of Figs. 1 and 2, for example, $(SD)_Y$ was 15·1 mV for $j = 1$ and 5·5 mV for $j = 2$; the radii of the open circles in Fig. 1 correspond to an uncertainty of ± 1 mV in Y. On application of these criteria to these data, the hypothesis that $j = 1$ was rejected because the average value of $\Delta Y/(SD)_Y$ was $+0{\cdot}90$ for the three points at the lowest concentrations of thiocyanate and $-1{\cdot}15$ for the three at the highest: these two figures correspond to average errors of $+13{\cdot}5$ and -17 mV in these extremes of the range covered. Similarly, the hypothesis that $j = 2$ was rejected on the ground that the average value of $\Delta Y/(SD)_Y$ was 0·72 for the three points at intermediate concentrations of thiocyanate and $-0{\cdot}41$ for the six others.

For every one of the systems examined in this work it was the first of these criteria that was employed in rejecting the hypothesis that $j = 1$. For almost all it was the second that was employed in rejecting the hypothesis that $j = 2$. There were, however, a few for which the first criterion was again used, and in all such cases the original authors and the program here described agreed on a final assignment of $j \geq 4$.

The deviation-pattern approach would be difficult to pursue beyond this point, for two reasons. One is that increasing j beyond 2 improves the fit so much that the random errors of measurement begin to become appreciable in comparison with $(SD)_Y$, so that a single deviant point might occasionally lead to a mistaken conclusion. The other is that deviation patterns tend to become more complex as the number of parameters increases, as is illustrated by Fig. 2. There are not many sets of data available in the literature that contain enough points to ensure that the features of even a moderately complex deviation pattern would be distinguishable against the random errors of measurement.

Consequently the necessary additional criteria were formulated as follows:

(3) all the β_1 must be positive;

(4) the best value of j is the lowest for which the first three criteria are satisfied, (should independent evidence show that a higher value is correct, the best course is to combine that value with the data in a standard curve-fitting program constrained to yield positive values of all the β_i).

As was noted above, the third criterion was first proposed by Piljac, Grabarić and Filipović,[6] while the fourth is merely Occam's razor in a form appropriate to linear classification problems. It is not, however, trivial. For the data of Figs. 1 and 2, Hume, DeFord and Cave[11] concluded that $j = 4$ and gave $\beta_1 = 11$, $\beta_2 = 56$, $\beta_3 = 6$, and $\beta_4 = 60$. With the fourth criterion as stated, the present program yields $j = 4$, $\beta_1 = 10{\cdot}7_5$, $\beta_2 = 54{\cdot}1$, $\beta_3 = 5{\cdot}0$, $\beta_4 = 59{\cdot}7$, and $(SD)_Y = \pm 0{\cdot}77$ mV. Momoki, Sato and Ogewa[5] obtained similar agreement with the values of Hume, DeFord and Cave. However, there are two other solutions: for one, $j = 5$, $\beta_1 = 12{\cdot}0$, $\beta_2 = 38{\cdot}5$, $\beta_3 = 57{\cdot}2$, $\beta_4 = 2{\cdot}5$, $\beta_5 = 18{\cdot}2$, and $(SD)_Y = \pm 0{\cdot}80$ mV; for the other, $j = 6$, $\beta_1 = 13{\cdot}0$, $\beta_2 = 29{\cdot}2$, $\beta_3 = 76{\cdot}0$, $\beta_4 = 1{\cdot}1$, $\beta_5 = 3{\cdot}7$, $\beta_6 = 5{\cdot}9$, and $(SD)_Y = \pm 0{\cdot}92$ mV. Values of j below 4 or above 6 do not yield fits complying with the first three criteria, but all three of these sets of formation constants meet the graphical requirements of equations (2)–(4), as any internally consistent set must do.

A similar situation arises with the data obtained by Burns and Hume[12] for the lead(II)–acetate system. Their graphical treatment yielded $j = 3$, $\beta_1 = 150$, $\beta_2 = 840$, and $\beta_3 = 3000$; with the fourth criterion the present program yielded $j = 3$, $\beta_1 = 137{\cdot}3$, $\beta_2 = 1026$, $\beta_3 = 2756$, and $(SD)_Y = \pm 1{\cdot}09$ mV; the alternative solution is $j = 4$, $\beta_1 = 118{\cdot}4$, $\beta_2 = 1438$, $\beta_3 = 1495$, $\beta_4 = 696$, and $(SD)_Y = \pm 0{\cdot}98$ mV.

It would be easy to understand the existence of a pair of alternative solutions if they involved formation constants such that the higher value of j was accompanied by indications of the presence of the last complex in proportions too small to have serious effects on the solution for the lower value of j. Certainly the value $j = 4$ for the cadmium–thiocyanate system should not be interpreted to mean that the pentathiocyanato complex cannot exist at all; at most

it would mean that the concentration of this complex was not large enough at any experimental point to be detected by the measurements that were made. Similarly, classifying the acetate ion as monoacidic on the basis of data obtained in a potentiometric titration with dilute acid would not imply that $CH_3COOH_2^+$ cannot exist, but merely that it was not formed at appreciable concentrations under the conditions investigated.

Unfortunately this is not the case. The solution $j = 5$ for the cadmium–thiocyanate data, for example, indicates that the fraction of the total cadmium ion that was present as $Cd(SCN)_5^{3-}$ would exceed 48% in the solution containing the highest concentration of thiocyanate. Whereas the values of β_i for $j = 4$ indicate that $Cd(SCN)_3^-$ is only a minor constituent of the solutions, those for $j = 5$ and 6 indicate that it is the predominating species at thiocyanate concentrations in the vicinity of $1M$. It is suggested that similar ambiguities will be found amoung the data obtained by other techniques for studying stepwise complex formation. It is for this reason that the fourth criterion has been introduced.

Fortunately, most systems exhibit simpler behaviour. For example, the data of Radhakrishnan and Sundaram[13] on the indium(III)–thiocyanate system yield a deviation pattern like curve 1 in Fig. 2 for $j = 1$ and at least one negative formation constant for $j = 2,3,4,5,7$ or 8. Here the fourth criterion is unnecessary because the other three uniquely specify $j = 6$, the value deduced by the original authors. In all of the ambiguous cases that were identified, the inclusion of the fourth criterion gave values of j identical with those chosen by the original authors. The agreement is admittedly arbitrary, for in view of the complexities of the graphical analysis it may fairly be doubted whether all the original authors recognized the existence of alternative solutions and consciously applied a similar criterion in choosing among them. Consequently it is not claimed that the present procedure yields the "correct" value of j, whatever that is in an ambiguous case, but only that it yields the value that would have been obtained by graphical analyses like those in the literature.

Applying these four criteria to the result of each fit in turn results either in the acceptance of some value of j, whereupon in interactive operation the best values of the formation constants are printed out and execution terminates, or in failure to obtain an acceptable result even with $j = 8$, whereupon a notification of that failure is provided and execution stops. It was not judged worth while to provide for testing higher values of j, both because they are wildly improbable and because inordinate amounts of computer time would thus be consumed. None of the systems tested failed to give an acceptable fit for some value of j less than or equal to 6.

COMPUTATIONS

The computations were done with a Digital Equipment Corp. (Maynard, Mass.) PDP8/I minicomputer operated in the manufacturer's EDUSystem 25 BASIC and in a configuration that provided 4096 words of core memory for use in this work, enough for it to have been possible to process many more than 50 data points if so many had been available.

The program incorporates a general multiparametric curve-fitting program, described elsewhere,[14] almost in its entirety. Some of the provisions needed for flexibility in the general program, notably that for constraining the signs of the parameters, were deleted, and the decision-making steps and a subroutine embodying equation (5) were added. Before it is used the program must be provided with the number of data points and their co-ordinates ([X], $E_{1/2,c}$, and I_c). In interactive operation it begins by obtaining values of T, n, $E_{1/2,s}$, and I_s from the user, and combines these to evaluate Y at each experimental point. For each successive value of j hypothesized, the values of $E_{1/2,c}$ at the highest concentration of ligand $[X]_{max}$ $E_{1/2,s}$, and $(RT/nF)\ln[X]^j_{max}$ are combined to obtain a crude initial estimate of β_j on the assumption that only the complex MX_j is formed, and a value equal to the jth root of this initial estimate of β_j is assigned to each of the successive stepwise formation constants. Various intermediate messages appear during execution to show the progress of the calculations and to permit identification of the criteria that lead to the rejections of different hypotheses; the briefest form of the printout is shown in Fig. 3.*

```
RUN

TEMP.,DEG.C=? 25
N=? 2
(E1/2)S=? -0.3743
(I)S=? 1
INTERMEDIATE DIAGNOSTIC PRINTOUT WANTED? 0=NO,1=YES? 0

J= 1 REJECTED (455); S4-S5= 1.822788

J= 2 REJECTED (461); S5-S4= 1.273586

THERE ARE 3 COMPLEXES. THEIR OVERALL FORMATION
 CONSTANTS ARE:
     B( 1 )= 9.84263
     B( 2 )= 8.543259
     B( 3 )= 21.11471

(X),M        Z,EXPTL.      Z,CALC.       DIFF.,E-C     DIFF./STD.DEV.
 .04         -4.288084E-3  -4.187294E-3  -9.291854E-5  -.8464434
 .06         -5.868691E-3  -5.858963E-3  5.896157E-5   .5371579
 .1          -9.108885E-3  -8.973688E-3  -1.351976E-4  -1.152787
 .16         -.01298881    -.01308482    1.048144E-4   .9548914
 .24         -.0176        -.01766098    6.897532E-5   .5555038
 .4          -.02568881    -.02559981    -1.888888E-6  -9.110375E-3
 .6          -.0341        -.03395986    -1.489445E-4  -1.284847
 .8          -.04188881    -.04189797    9.796823E-5   .8924476
 1           -.0473        -.04729227    -7.734634E-6  -.07846488

SUM(DEV.)^2= 7.229119E-8 ,  STD.DEV.= 1.897658E-4

READY
```

Fig. 3. Input and output to the program for the data of Kivalo[17] on the lead–chloride system.

*A briefly annotated hard-copy listing, in BASIC, of the program COUNTX may be obtained by remitting $25.00 to the Computing Laboratory of the Department of Chemistry, Clarkson College of Technology, Potsdam, New York 13676. Hard-copy listings, in BASIC, POLYBASIC, and FORTRAN-IV, of the parent curve-fitting program CFT3, together with a 170-page volume of documentation, explanation, and directions for use, may be obtained at the same time for a total remittance of $45.00.

Table 1. Results obtained. Column 1 of this table identifies the metal ion and the ligand, and the last identifies the literature reference from which the data were taken. In columns 2–8, the first number on each line was obtained from the program described here, along with the standard deviation from regression given in column 9, while the second number (in parentheses) was obtained from the graphical treatment by the original authors

System	j	β_1	β_2	β_3	β_4	β_5	β_6	$(SD)_Y$ m)	Ref.
Cd^{2+}-SCN^-	4(4)	$10{\cdot}7_5$(11)	54·1(56)	5·0(6)	59·7(60)	—	—	0·77	11
-thiourea	6(4)	21·7(24)	43·8(51)	1191(40)	748(3590)	1064(−)	866(−)	0·76	15
In^3 SCN^-	6(6)	43·7(120)	2600(1600)	478(17500)	$4{\cdot}58 \times 10^4$(170000)	9600(65000)	$6{\cdot}20 \times 10^4$(69000)	0·35	13
Pb^2 OAc^-	3(3)	137·3(150)	1026(840)	2756(3000)	—	—	—	0·98	12
	3(3)	143·7(150)	819(900)	3011(3000)	—	—	—	0·68	16
$-Cl^-$	3(3)	9·0(9·1)	8·5(7·4)	21·1(23·4)	—	—	—	0·11	17
$-HCOO^-$	3(3)	12·8(13)	54·8(50)	25·7(30)	—	—	—	0·63	16
-thiourea	5(4)	1·78(4)	0·69(11)	34·5(9·5)	35·0(110)	54·2(—)	—	0·74	15
Zn^{2+}-en	3(3)	$4{\cdot}75 \times 10^{11}$(*)	$2{\cdot}7 \times 10^{13}$($4{\cdot}5 \times 10^{13}$)	$2{\cdot}2_5 \times 10^{14}$($3 \times 10^{14}$)	—	—	—	4·4	18

* Said[18] to be too small to be evaluated graphically.

RESULTS AND DISCUSSION

Data for about 20 systems were taken from the literature. Inspection of these indicated, rather unexpectedly, that many were defective in one way or another. In some cases no information was given about the diffusion currents or diffusion-current constants; in others there was clear evidence that the aquo-complex was not reduced reversibly under the experimental conditions; in many the graphical analysis was obviously erroneous, the most common fault being that $F_j[X]$ increased systematically with [X], so that the value of j was inconsistent with the data; in one the values of [X] and $F_i[X]$ that were plotted by the original authors could not be located in their tabular summary. All such sets of data were rejected, and the remaining ones analysed with the results shown in Table 1.

For most of these systems the result of the automatic classification is identical with that obtained by the original authors and the values of the formation constants agree within the rather wide error range that the nature of the technique entails. In the two cases in which the classifications disagree, inspection of the original data suggested that those at the lowest concentrations of ligand gave rise to values of $F_3[X]$ and $F_4[X]$ so widely deviant that full confidence could not be reposed in these points, which are of special importance in the graphical procedure because the extrapolations rely so heavily on them. The differences between the graphical and least-squares values of the formation constants for the indium(III)–thiocyanate complexes reflect the propagation of experimental errors, which becomes more serious as j increases. Comparing the results for the lead(II)–chloride and zinc(II)–ethylenediamine systems shows that the success of the decision-making steps does not depend on the magnitudes of the random errors involved.

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THE USE OF LONG-CHAIN ALKYLAMINES FOR PRECONCENTRATION OF TRACES OF MOLYBDENUM, TUNGSTEN AND RHENIUM IN THEIR DETERMINATION BY ATOMIC-ABSORPTION SPECTROSCOPY—I

GENERAL STUDIES

C. H. KIM, P. W. ALEXANDER and L. E. SMYTHE

Department of Analytical Chemistry, University of New South Wales, P.O. Box 1, Kensington, N.S.W., Australia 2035

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Summary—Long-chain alkylamines are used for the preconcentration of traces of molybdenum, tungsten and rhenium as thiocyanate complexes, in their determination by atomic-absorption spectroscopy. General studies of factors influencing the extraction show that the thiocyanate complexes can be extracted into chloroform containing a low concentration of Amberlite LA1. Detection limits are 0·02 ppm Mo, 0·75 ppm W and 0·34 ppm Re in the final MIBK solution and are improved by a factor of 5–10 over those obtained by using current extraction methods. Serious interelement effects are eliminated and a range of other cations and anions are shown to have little effect on the absorption.

The atomic-absorption determination of elements that form refractory oxides suffers from low sensitivity and relatively poor detection limits because of the high dissociation energies involved. A high-temperature flame such as nitrous oxide–acetylene[1,2] is required for optimum conditions and even then the sensitivities are only 0·4 ppm for molybdenum, 5·3 ppm for tungsten and 12 ppm for rhenium.[2] Non-flame atomic absorption has been applied only to the determination of molybdenum,[3–6] but serious interference from tungsten was reported.[6]

An improved solvent extraction procedure is now reported, together with a study of extracting agents, detection limits and interference effects for atomic-absorption determination of Mo, W and Re. Solvent extraction is known[7] to be useful in conjunction with the determination of metals by atomic-absorption spectroscopy (AAS). Besides separation and preconcentration of metals, the sensitivity is often enhanced by aspiration with organic solvents, and many investigations have been made on the atomic-absorption characteristics of metals in various organic solvents.[7]

Methyl isobutyl ketone (MIBK) is particularly suitable for atomic-absorption analysis and it has often been used in combination with various chelating agents for extraction and preconcentration.[8–10] Molybdenum has recently been satisfactorily determined[11] by extraction of the thiocyanate complex into MIBK, giving a detection limit of 0·1 ppm in a 1-g sample of geological material, and earlier extraction methods were reviewed.[11]

Few extraction methods, however, have been reported for AAS determination of tungsten[12,13] and rhenium.[14] Rao[13] used Aliquat 336 in di-isobutyl ketone for extraction of tungsten. Biechler and Long[14] separated rhenium from large amounts of molybdenum by extraction in basic solution with 8% Aliquat 336 in chloroform.

In general, liquid ion-exchangers possess many advantages for separation of metals, as discussed in several reports.[15–18] Ure[19] has used solvent extraction of molybdenum with tri-n-octylamine to obtain a detection limit equivalent to 0·2 ppm for 1 g of soil sample. In this paper, therefore, the use of long-chain aliphatic amines is investigated for the extraction and preconcentration of thiocyanate complexes of Mo, W and Re from acid solution, and determination by AAS. The metals are extracted from a large volume of aqueous solution into chloroform/amine solvent and the chloroform is evaporated off. The residue is then redissolved in as much MIBK as required. It is shown that detection limits are improved by reduction of the volume of organic solvent to as little as 1 ml before the aspiration and that interference effects are minimized by the extraction procedure. Comparisons are made with other solvent extraction systems and other organic solvents used for final aspiration into the flame.

EXPERIMENTAL

Reagents

Stock solutions of molybdenum, tungsten and rhenium were prepared at respective concentrations of 10, 250 and 250 ppm from the following reagent grade salts: ammonium molybdate, $(NH_4)_6Mo_7O_{24}.4H_2O$; sodium tungstate, $Na_2WO_4.2H_2O$; potassium perrhenate, $KReO_4$.

Stannous chloride solution (20% w/v) was prepared by warming analytical-grade $SnCl_2.2H_2O$ (40 g) and a small piece of analytical-grade tin metal in 10*M* hydrochloric acid (40 ml) until a clear solution was obtained. After cooling, the solution was diluted to 200 ml with distilled water and a small piece of tin metal placed in the solution.

Potassium thiocyanate solution (20% w/v).

Primene JM-T and Amberlite LA1 were supplied by Rohm and Haas Co. and Alamine 336 and Aliquat 336 by A. C. Hatric Pty. Ltd. Solutions of Amberlite LA1 (0·1–1%) in chloroform were prepared by dilution of a 2% v/v stock solution of the amine in analytical-grade chloroform.

MIBK was redistilled and the fraction boiling at 116–118° was used.

All other reagents and organic solvents used were of analytical grade.

Instrument.

A Techtron AA5 atomic-absorption spectrophotometer was used, equipped with a D1-30 digital indicator. Hollow-cathode lamps were used as light-sources. The following instrumental parameters were used.

Lamp currents, *mA*: Mo, 5; W, 20; Re, 20
Bandwidth, *nm*: Mo, 0·10; W, 0·05; Re, 0·05
Wavelength, *nm*: Mo, 313·3; W, 255·1; Re, 228·7
Burner 50 × 0·5 mm: AB50 (high-temperature)
Light-path height above burner 5 mm
Support gas, nitrous oxide, delivery pressure: 15 psig (*ca.* 6·5 l./min)
Fuel, acetylene, flowmeter reading 6·5–7 (*ca.* 7 l./min)
Flame: 3-cm red-yellow cone, fuel-rich flame during aspiration
Aspiration rate: 2·3 ml/min

Procedure

Less than 10 μg of molybdenum (added as molybdate solution) or 250 μg of rhenium (added as perrhenate solution) was taken in a 100-ml separating funnel containing 50 ml of 2*M* hydrochloric acid. For reduction and thiocyanate-complex formation, 2 ml of 20% potassium thiocyanate solution and 2 ml of 20% stannous chloride solution were then added.

For tungsten, the process was slightly different, because the reduction of tungsten was not quantitative at room temperature and in 2*M* hydrochloric acid. Less than 250 μg of tungsten (added as tungstate solution) was therefore taken in a 50-ml beaker containing 15 ml of 10*M* hydrochloric acid: 2 ml of 20% stannous chloride solution were then added and the beaker was covered with a watch-glass. The solution was boiled for 5 min and then cooled in ice-water. Next, 2 ml of 20% potassium thiocyanate solution were added, the solution was transferred into a 100-ml separating funnel and the beaker was rinsed with 35 ml of distilled water to give 50 ml of a final acid concentration of 3*M* in the funnel.

A 10-ml aliquot of 0·1–1% chloroform solution of Amberlite LA1 was added to the separating funnel, which was then shaken vigorously for 2 min. After separation of the phases, the organic phase was drained into a 25-ml beaker. For a single extraction, the aqueous phase was washed with 5 ml of chloroform by shaking for 30 sec. For a double extraction, a second 10-ml aliquot of the Amberlite solution was added to the separating funnel, and the extraction procedure repeated without the further washing with chloroform. If more than two successive extractions were used, the washing was omitted. The beaker containing the extract was placed on a steam-bath to evaporate off the chloroform. After completion of the evaporation, a few ml of MIBK were added to the viscous brown residue. The beaker was warmed until a homogeneous solution was obtained. The solution was cooled and transferred into a 5- or 10-ml volumetric flask and made up to volume with MIBK. If a smaller volume than 5 ml of MIBK was required because of a smaller quantity of the element, the 25-ml beaker was replaced by a 25-ml weighing bottle and the MIBK was pipetted into the bottle, which was then stoppered.

The absorbance of the MIBK solution was determined, using pure MIBK as a blank, by aspirating into the nebulizer–burner system of the AA5 under the specified conditions. There was no observable difference in the blanks from MIBK and dilute Amberlite LA1–MIBK solutions.

RESULTS

Several experimental factors influencing the efficiency of extraction of Mo, W and Re were investigated in detail. In particular, the use of long-chain alkyl amines for extraction and for rapid preconcentration were studied and compared with extraction with other complexing agents.

Effect of concentration of acidity and other reagents

Figure 1 shows the absorbance values for Mo, W and Re after a single extraction of their thiocyanate complexes with 10 ml of a 1% chloroform solution of Amberlite LA1 from various concentrations of hydrochloric acid. For this test, 1 ml each of 20% potassium thiocyanate and 20% stannous chloride solution were used. The concentration of the 50 ml of hydrochloric acid used in extraction of tungsten was controlled by addition of 10*M* hydrochloric acid and distilled water, after the complexation with thiocyanate in 10 ml of 10*M* hydrochloric acid.

The degree of extraction of tungsten was fairly constant over the entire acid concentration range, but decreased for molybdenum and rhenium at 4*M* and 5*M* acid concentration respectively. The hydrochloric acid concentrations chosen were therefore 2*M* for the extraction of Mo and Re and 3*M* for W. Extraction from solutions of lower acidity is preferable because the extractability of other metals by Amberlite LA1 generally increases with the chloride concentration.[18]

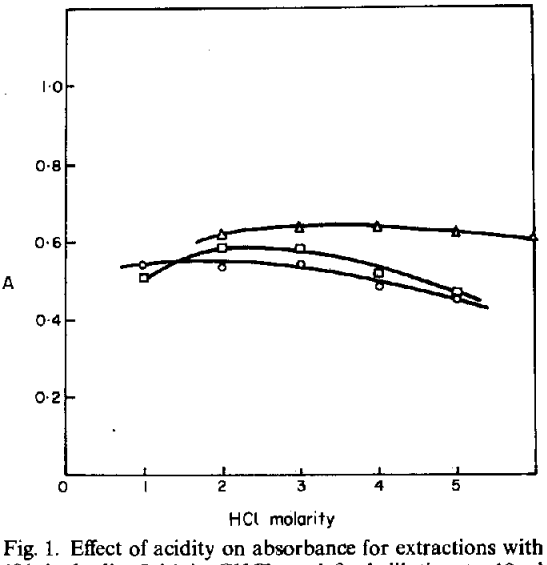

Fig. 1. Effect of acidity on absorbance for extractions with 1% Amberlite LA1 in $CHCl_3$ and final dilution to 10 ml with MIBK. O——O Mo, □——□ Re, △——△ W.

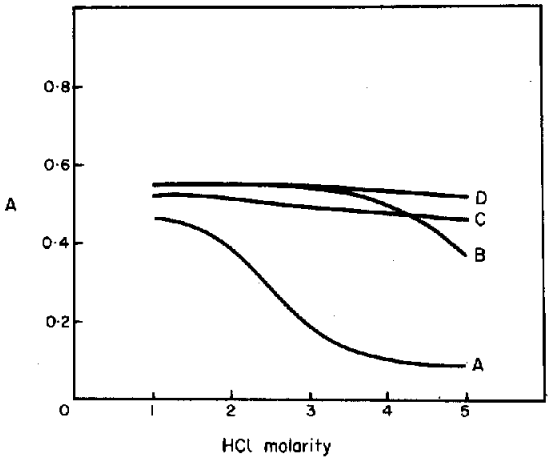

Fig. 2. Comparison of various amines for extraction of Mo (10 μg), with 1% amine in $CHCl_3$ and final dilution to 10 ml with MIBK: A, Primene JM-T; B, Amberlite LA1; C, Alamine 336; D, Aliquat 336.

This could cause possible interference in the determination of Mo, W or Re by the proposed method.

Effects of varying the amount of tin(II) and thiocyanate were studied by adding volumes from 1 to 5 ml of the 20% solution of these reagents to the extraction mixture. There was no marked effect on the extraction of the three elements and for further experiments 2 ml of each reagent were used.

Extraction with various amines

Figures 2, 3 and 4 compare the absorbances, as a function of acid concentration after extraction, obtained when four different types of amine are used. Single extractions were carried out with 10 ml of 1% amine solution in chloroform, with the following amines: Primene JM-T, Amberlite LA1, Alamine 336 and Aliquat 336. These are respectively primary, secondary, tertiary and quaternary long-chain aliphatic amines.

The results show that the effect of the amines on the degree of extraction at high acid concentrations

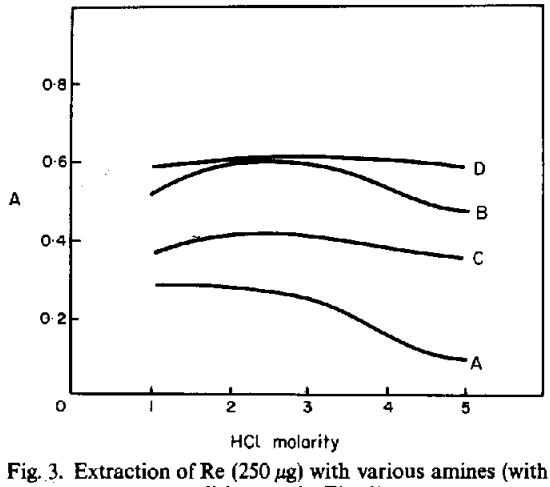

Fig. 3. Extraction of Re (250 μg) with various amines (with conditions as in Fig. 2).

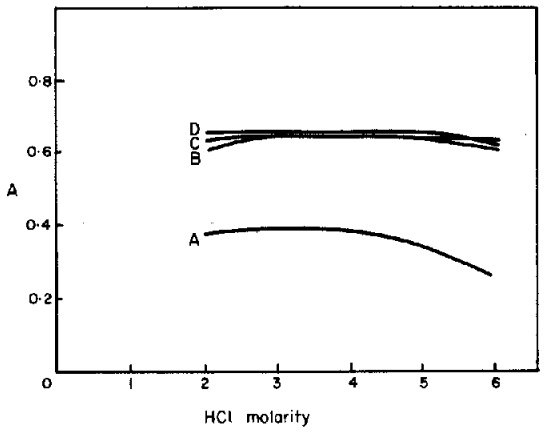

Fig. 4. Extraction of W (250 μg) with various amines (with conditions as in Fig. 2).

decreased in the order quaternary > tertiary > secondary > primary except for extraction of Re. Amberlite LA1 was chosen for subsequent work with 2*M* hydrochloric acid, but it was concluded that Aliquat 336 or Alamine 336 could be used to replace Amberlite LA1 in the proposed extraction method if required, and would be particularly useful at high acid concentrations.

Effect of concentration of Amberlite LA1 in chloroform

The extractive capacity of liquid ion-exchangers for anions increases directly with increasing concentration of the exchanger in the organic phase. The degree of the extraction at constant concentration also depends to some extent on the diluent used. It is essential in the present method to keep the concentration of Amberlite LA1 as low as possible, because the amount used finally goes into the MIBK solution. Chloroform and carbon tetrachloride are very suitable as solvents because, being heavier than water, they facilitate successive extractions from aqueous solution, and the low boiling points allow rapid evaporation.

Figure 5 shows the effect of varying the concentration of Amberlite LA1 in chloroform, on single extractions. Maximum recoveries were obtained with concentrations above 1·5% and a similar result was obtained with carbon tetrachloride as the solvent. For the quantitative extraction of 10 μg of Mo, 250 μg of W or 250 μg of Re, 1% solution of Amberlite LA1 in chloroform (10 ml) was employed and two successive extractions were carried out in order to use small quantities of Amberlite LA1. Chloroform was preferred as the diluent because it evaporates faster than carbon tatrachloride does.

Table 1 shows the effects of various concentrations of Amberlite LA1 dissolved in MIBK on the absorbance of the Mo–thiocyanate–MIBK solution. Significant negative deviations were observed with increasing concentration of Amberlite LA1, probably due to a reduction in nebulization efficiency caused by the highly viscous Amberlite LA1. The concentration of

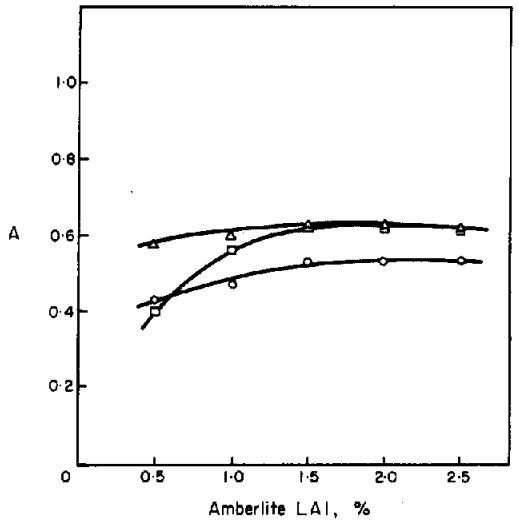

Fig. 5. Effect of concentration of Amberlite LA1 in $CHCl_3$ on the extraction of Mo, W and Re (with conditions as given in Fig. 1).

the amine should therefore be kept as low as possible, consistent with retaining efficient extraction.

Recovery tests

Extractions with variation in quantity of Mo, W or Re over a 10-fold range were used to test for quantitative recovery of each element, as shown in Table 2. Three successive extractions with 7 ml of 0·1–0·2% solution of Amberlite in chloroform were used for the lowest concentrations. Double extractions with 10 ml of solvent were used for the other concentrations chosen, and from 1 to 10 ml of MIBK was used to redissolve the residues, as shown in Table 2. The absorbance values obtained indicate quantitative extraction of the elements over the range reported.

Calibration curves and standards

The calibration curves obtained after double extraction with 2% Amberlite LA1 in chloroform were linear for a range of 1–10 μg of Mo and 25–250 μg of Re or W in a final volume of 10 ml of MIBK (0·1–1 ppm Mo and 2·5–250 ppm Re or W). A detection limit of 0·02 ppm for Mo, 0·75 ppm for W and 0·34 ppm for Re was obtained, representing an improvement of between 5- and 10-fold over previous methods.[2,11,19] By use of a 1-ml final volume, the concentration factor from the original sample to the final test solution can be improved 10-fold.

Calibration curves can also be constructed by diluting a concentrated solution of Mo(W or Re)–SCN–Amberlite LA1–MIBK. It is also useful to note that the extracts of standard solutions (1 ppm Mo, 25 ppm W or Re), stored in glass bottles, remained stable for over one month.

Table 1. Effect of concentration of Amberlite LA1 on atomic absorption of 1 ppm Mo–SCN–MIBK solution

% Amberlite in MIBK	0	1	2	4	6	8	10
Absorbance	0·50	0·50	0·50	0·50	0·50	0·49	0·47
Rel. error, %	0	0	0	0	0	−2·0	−6·0

Interference studies

Cations known to have comparatively high extraction coefficients with Amberlite LA1[17] and a number of anions were tested for interference. The results are given in Table 3. Large amounts of tungsten did not interfere with molybdenum because the tungsten was not reduced in 2*M* hydrochloric acid at room temperature. Also, large amounts of molybdenum had little effect on tungsten, presumably because molybdenum was reduced in hot concentrated hydrochloric acid to too low an oxidation state to complex with thiocyanate. However, large amounts of molybdenum severely depressed the rhenium absorbance.

In general, only the molybdenum extraction was almost free from interferences. Copper(II), when present, was reduced and precipitated as CuSCN, which caused difficulties in separation of the organic phase. Zinc, lead, bismuth and nitrate interfered with the tungsten extraction, and bismuth also interfered with rhenium.

Table 2. Recovery tests after extraction and final dilution with MIBK

Element	Taken, μg	MIBK, ml	No. of detns.	Mean absorbance	Range	Relative std. devn., %
Mo	1	1	5	0·51	0·05	4·2
	1	2	5	0·27	0·01	1·6
	5	10	2	0·27	—	—
	10	10	2	0·54	—	—
Re	25	1	5	0·55	0·11	8·6
	25	2	5	0·28	0·04	6·2
	125	10	2	0·30	—	—
	250	10	2	0·62	—	—
W	25	1	5	0·58	0·08	5·9
	25	2	5	0·29	0·04	5·8
	125	10	2	0·31	—	—
	250	10	2	0·61	—	—

Table 3. Effect of foreign elements

Element (salt used)	Amount added, μg	Absorbance Mo	W	Re
No addition		0·26[a]	0·38[a]	0·37[a]
W (Na_2WO_4)	50	0·26	—	—
	250	0·24	—	—
	500	0·23	—	—
	1500	—	—	0·39
	7500	—	—	0·39
	15000	—	—	0·37
Re ($KReO_4$)	5	0·26	—	—
	10	0·24	—	—
	150	—	0·33	—
Mo [$(NH_4)_6Mo_7O_{24}$]	1500	—	0·38	0·36
	7500	—	0·37	0·07
	15000	—	0·33	0·02
No addition	—	0·52[b]	0·62[b]	0·62[b]
Fe [$FeNH_4(SO_4)_2$]	5000	0·52	0·62	0·61
	10000	0·52	0·62	0·62
Mn ($MnCl_2$)	5000	0·52	0·62	0·62
	10000	0·52	0·62	0·62
Cu ($CuCl_2$)	5000	0·52	0·58	0·62
	10000	0·52	0·46	0·70
Zn ($ZnCl_2$)	5000	0·52	0·60	0·62
	10000	0·53	0·41	0·64
Pb [$Pb(NO_3)_2$]	5000	0·52	0·55	0·64
	15000	0·53	0·60	0·63
Bi ($BiCl_3$)	5000	0·52	0·40	0·65
	15000	0·52	0·39	0·67
NO_3^- ($NaNO_3$)	0·5*	0·52	0·43	0·63
	1·0*	0·53	0·38	0·62
SO_4^{2-} (Na_2SO_4)	0·5*	0·52	0·62	0·62
	1·0*	0·52	0·62	0·62
ClO_4^- ($NaClO_4$)	0·5*	0·52	0·62	0·61
	1·0*	0·52	0·62	0·61

[a] Mo: 5 μg, W: 150 μg, Re: 150 μg.
[b] Mo: 10 μg, W: 250 μg, Re: 250 μg.
* mmole.
Double extractions with 10 ml of 1% Amberlite LA1 in chloroform.

Absorbances in various organic solvents

Various organic solvents miscible and immiscible with water were tested and the relative absorbances compared, as shown in Table 4. After the extraction and evaporation of the extracts, the residue was dissolved in the organic solvents given in Table 4 instead of in MIBK, and the absorbance value was measured, against a blank of the solvent concerned. Because each organic solvent had different background absorbance, it was necessary to adjust the flow-rate of the acetylene at a constant pressure of nitrous oxide to obtain a consistent flame with a 3-cm red cone when aspirating each solvent.

Acetone and ethyl acetate showed a similar enhancement of absorbance relative to MIBK. The background absorption of MIBK was lower than for any other solvent and MIBK was therefore superior for absorbance measurement. However, these data indicate that a wide variety of organic solvents can be used if necessary in the final dissolution step before aspiration.

Table 4. Comparisons of absorbance in various solvents

Organic solvent	Absorbance* Mo	Re	W
Methyl alcohol	0·32	0·30	0·32
Ethyl alcohol	0·23	0·28	0·28
Acetone	0·55	0·60	0·57
Methyl isobutyl ketone	0·52	0·61	0·60
Ethyl acetate	0·54	0·40	0·43
Butyl acetate	0·38	0·34	0·51
Di-isobutyl ketone	0·19	0·33	0·28
Methyl n-amyl ketone	0·29	0·44	0·41

* 10 μg of Mo, 250 μg of Re, 250 μg of W in final volume of 10 ml of each organic solvent.

Table 5. Results of recovery of Mo with some chelating agents

No.	Mo taken, μg	Absorbance	Reagent
1	5	0·24	Ammonium pyrrolidinecarbodithioate
2	5	0·24	
3	10	0·48	
4	10	0·48	
1	5	0·24	8-Hydroxyquinoline
2	5	0·25	
3	10	0·48	
4	10	0·48	

Extraction with other chelating agents

Aqueous solutions containing 5 or 10 μg of molybdenum in 50 ml at pH 2 were extracted with 10 ml of 0·5% ammonium pyrrolidinecarbodithioate or 8-hydroxyquinoline solution. The extract was evaporated to dryness, dissolved in 10 ml of MIBK and the absorbance measured.

Table 5 shows the results obtained for extraction of molybdenum. They were comparable in sensitivity to those from the Amberlite LA1 extraction. However, these extraction systems suffer from the need for critical pH-control and from the possibility of co-extraction of potentially interfering metals.

DISCUSSION

The method developed here gives a single extraction system applicable to the determination of all three elements, Mo, W and Re, giving detection limits of 0·02, 0·75 and 0·34 ppm respectively (which are lower than any previously reported), and eliminates potential interferences from diverse ions by use of solvent extraction. The earlier work by Rao[13] on extraction of tungsten with Aliquat 336 and by Biechler and Long[14] on rhenium extraction cannot be used for concentrations less than 500 ppm. For molybdenum, the method of Kim *et al.*[11] is not useful below 1 ppm.

In addition, by extraction of W, Re and Mo it has been possible to overcome mutual interferences between these elements in AAS with the nitrous oxide–acetylene flame, in contrast to the interference of tungsten in flameless methods.[6] The only serious interference was by molybdenum with rhenium, as shown in Table 3, where a 50-fold excess of Mo caused a marked depression in the Re absorbance.

The proposed method has been shown to be versatile in several other respects: (*a*) the volume of extracting solvent used is unimportant, (*b*) there is a wide choice of organic solvents for aspiration, and (*c*) a

small final volume of organic solvent for aspiration into the flame can be used and precision retained, allowing low detection limits to be achieved for Mo, W and Re. In addition, there is a wide choice of extracting agents, Amberlite LA1 can be replaced by other amines such as Alamine 336 or Aliquat 336, and other chelate extraction systems can also be employed, though with some disadvantages.

Because of the high sensitivity and lack of interferences, the method is expected to be useful in the determination of Mo, W and Re in ores, soils, waters and biological materials. Future reports will deal with applications to determination of sub-ppm levels of Mo in soils and sediments by solvent extraction of molybdenum thiocyanate and atomic absorption, and to the determination of trace tungsten in soils and geological materials by solvent extraction of the tungsten thiocyanate complex with Alamine 336.

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EXTRACTIVE CONCENTRATION OF PLATINUM-GROUP ELEMENTS AND THEIR DETERMINATION BY ATOMIC-ABSORPTION SPECTROPHOTOMETRY

A. A. VASILYEVA, I. G. YUDELEVICH, L. M. GINDIN, T. V. LANBINA, R. S. SHULMAN, I. L. KOTLAREVSKY and V. N. ANDRIEVSKY

Institute of Inorganic Chemistry, Siberian Division of the Academy of Sciences, Novosibirsk, U.S.S.R.

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Summary—The extraction of Pt, Pd, Ir, Rh, Ru, Ag, Au, Co, Cu, Ni and Fe with n-octylaniline has been investigated. Noble metals are extracted 10^3–10^4 times better than Cu, Ni, Co and Fe. A method of determination of Pt, Pd, Ir, Rh and Ru is proposed. They are first separated from Cu, Ni, Co and Fe by means of extraction (and then determined, in either the aqueous or organic phase, by atomic-absorption spectrophotometry. The atomic absorption of platinum metals (with the exception of Pd) is affected by other elements of the platinum group and by non-noble metals. $La(NO_3)_3$ and $Nd(NO_3)_3$ lower the limit of detection for Pt, Rh, Ir and Ru and inhibit the effect of Co, Cu, Ni, Fe, Bi, Zn, Na, *etc.* on their determination. Lanthanum and neodymium chlorides and sulphates produce a similar effect but only on the determination of Pt and Rh. The coefficient of variation of the determination, in both phases, is within 2–6·8%.

The advantages of extraction over other techniques for the concentration of platinum metals are well known.[1–3] Many reagents have been proposed as the extractants,[4,5] but a considerable number of these will only extract one or two metals of the group, mostly palladium and platinum. Pt, Pd, Ir, Rh and Ru usually occur together, and thus it is of practical importance to have methods for the selective extraction of the whole group.

For this purpose, we have employed n-octylaniline $C_8H_{17}.C_6H_4.NH_2$. Extraction of platinum metals with aromatic amines has been studied by Gindin *et al.*[6] Aniline and toluidine extract these elements well from hydrochloric acid media. However, these substances are readily soluble in water, whereas their hydrochlorides are not readily soluble in organic diluents; these properties limit the application of aniline and toluidine as extractants. These limitations do not apply to n-octylaniline. We have also studied the extent to which the platinum group metals interfere with each other when they are determined by atomic-absorption spectrophotometry.

EXPERIMENTAL

Reagents

Solutions of metal ions. $H_2PtCl_6.6H_2O$, $PdCl_2$, $RhCl_3.4H_2O$, K_2IrCl_6, K_3IrCl_6, $K_2Ru(H_2O)Cl_5$, and cupric, nickel, cobalt and sodium chlorides were used as standard compounds; they were dissolved in hydrochloric acid of appropriate concentration. Rhodium chloride was first treated with 11*M* hydrochloric acid.

Extractant solution. A 2*M* solution of octylaniline in toluene was shaken three times with equal volumes of 3*M* hydrochloric acid for 3 min each time.

Metal complexes. Concentrated solutions of Cu, Ni and Fe in octylaniline were prepared by shaking extractant solution with 1*M* solutions of Cu(II), Ni(II) and Fe(III) in 3*M* hydrochloric acid. Lanthanum(III) was extracted with tributylphosphate from 20% solutions of $La(NO_3)_3$ in 1*M* nitric acid. The extraction was performed three times, each time with a fresh solution of the element. Concentrations of Cu, Ni, Fe and La in the organic phases were calculated from the difference of the concentrations of the elements in the aqueous phase before and after extraction.

Apparatus

Atomic-absorption spectrometer. A Perkin-Elmer model 4A was used. The flames were air–acetylene and nitrous oxide–acetylene. The analytical lines were: Pt—2659 Å, Pd—3404 Å, Rh—3435 Å, Ir—2640 Å, and Ru—3499 Å.

The solutions were introduced into the flame under the following conditions. For aqueous solution and the air–acetylene flame, the flow-rates (l./min) were: air—8; additional air—10·3; acetylene—2·2 (for Pt, Pd and Rh) and 3·3 (for Ir and Ru); for organic solutions the flow-rates were: air—12·7; additional air—11·9; acetylene—2·2. For the nitrous oxide–acetylene flame, the flow-rates (l./min) were: nitrous oxide—13·5; air—7·5 (for aqueous solutions) and 5·2 (for organic solutions).

RESULTS AND DISCUSSION

Extraction of platinum and other metals with octylaniline hydrochloride

The effect of a number of factors on the extraction of Pt, Pd, Ir, Rh, Ru, Cu, Ni, Co, Zn, Fe, Ag(I) and Au(III) with 2*M* octylaniline is shown in Tables 1–3.

The distribution coefficients of platinum metals, and also of Ag and Au, are much greater than those of Cu, Co, Ni and Fe. Because of this it is possible, first to separate the group Pt, Pd, Ir, Rh, Ru, Ag and Au, and secondly to extract these metals irrespective of their oxidation state, which is a considerable advantage over other extractants. The extractability

Table 1. The distribution coefficients of some metal ions (15 min equilibration)

C_{HCl}, M	Distribution coefficients						
	Ni(II)	Co(II)	Cu(II)	Fe(III)	Zn(II)	Ag(I)	Au(III)
	Concentration of HCl—1M						
0·01	0·0097	0·017	0·017	0·025		421*	869
1·0	0·021	0·020	0·13		1·4		
	Concentration of HCl—3M						
0·01						93	198
0·1					6·4	269*	
1·0	0·026	0·034	0·18	0·24	2·4		

* Extraction of $AgNO_3$ from nitric acid solution.

of Rh and Ru increases with increasing concentration of hydrochloric acid, and consequently all the extractions reported below were performed with the 3M acid. The extractability of platinum metals remains high in the presence of high concentrations of Cu and Ni, and also when the ratio, λ, of the aqueous and organic phase volumes is increased up to 5 (Table 3).

Although the distribution coefficients of Cu, Co, Ni and Fe are very small, an appreciable concentration in the aqueous phase leads to extraction of a considerable amount into the octylaniline phase. For this reason, we studied the conditions for scrubbing of Cu, Ni and other metals. Cu, Co, Ni and Fe are re-extracted quantitatively with 1–3M hydrochloric acid. The platinum metals remain in the octylaniline phase.

From this evidence it was concluded that n-octylaniline may be employed to separate the platinum metals group from Cu, Co, Ni, Fe and other metals. We investigated the following extractive concentration procedure. The platinum metals are extracted from 3M hydrochloric acid with three portions of octylaniline solution ($\lambda = 2$, extraction time 15 min). The combined organic phases are scrubbed twice with equal volumes of 3M hydrochloric acid (5 min shaking) to remove Cu, Co, Ni and Fe. In order to avoid loss of Pd and Rh to the wash-solution, the latter is extracted once with octylaniline solution ($\lambda = 2$), and all the organic phases are combined.

To check this procedure, Rh was extracted from solutions containing Cu and Ni. It is seen from Table 4 that Rh is extracted quantitatively, and concentrated to a considerable extent. Similar results were obtained when Pt, Pd, Ir, Rh and Ru were extracted from a solution which contained 15 g of Cu. The ratio of copper to platinum metals was 4000:1 in the starting solution, and 20:1 in the extract.

Table 3. Effect of the ratio (λ) of aqueous and organic phase volumes on the extractability of platinum metals in the presence of Cu and Ni*

λ	Extracted in one stage, %					Concentration of metal, M	
	Pt	Pd	Rh	Ir	Ru		
1	99·8	98·2	98·9	99·7	93·4	Pt, Pd, Ir	3×10^{-3}
5	99·9	91·7	99·0	99·7	94·4	Rh	7×10^{-3}
						Ru	3×10^{-4}
10	99·9	91·4	93·5	98·7	73·3	Cu, Ni	$5{\cdot}5 \times 10^{-2}$
1	99·9	85·4	100	96·2	—	Pt, Pd, Ir	3×10^{-4}
5	98·0	88·0	—		100	Rh	7×10^{-4}
						Ru	3×10^{-5}
10	93·1	—	95	98·4	79·9	Cu, Ni	5×10^{-1}

* Platinum metals in the organic phase were determined by the spectral method.[6]

Table 4. Concentration of Rh from Cu and Ni solutions

Rhodium		Me/Rh ratio			
		In the starting solution		In the extract	
Taken, μg	Found, μg	Nickel	Copper	Nickel	Copper
10·5	11·5	45×10^3:1		5:1	
155	148	$1{\cdot}2 \times 10^3$:1		0·4:1	
25	23		40×10^3:1		4·5:1
248	226		640:1		0·3:1

This procedure may be applied to the analysis of various materials. The platinum metals in the concentrate may be determined by any suitable method. We employed atomic-absorption spectrophotometry to determine the metals both in the aqueous and in the octylaniline phase.

Atomic-absorption spectrophotometry of platinum metals

We first compared the detection limits of Pt, Pd, Rh, Ir and Ru in aqueous (2M hydrochloric acid) and organic (octylaniline) solutions, because use of an organic extract often results in increased sensitivity. For example, we found[7] that using the extract of Pt, Pd, Ir(IV) and Ru(IV) in tetraoctylammonium bromide lowers the detection limit by a factor of 2–10. Similar results have been obtained by other workers.[8,9]

Platinum metal solutions were prepared in 2M hydrochloric acid, and in octylaniline by extraction of their chloro-complexes from 3M hydrochloric acid ($\lambda = 1$, single extraction with 2M octylaniline). The distribution coefficients were high enough for the concentrations of the metals in the organic phase to be assumed to be the same as those in the aqueous solution subjected to extraction.

Table 2. The distribution coefficients of platinum metals ($C_{me} = 0{\cdot}01M$; 15 min equilibration)

C_{HCl}, M	Distribution coefficients								
	Pt(IV)	Pt(II)	Ir(III)	Ir(IV)	Rh(III)	Pd(II)	Ru(III)	Ru(IV)	$RuNOCl_5^{2-}$
1	300	300	>100	70	6·1	300	1·0	—	—
3	337	41	106	70	20	37	>160	>160	>160

Table 5. Comparison of the detection limits of platinum metals, $\mu g/ml$

Element	Flame: Air–acetylene* 2M HCl	Air–acetylene* Octylaniline	N_2O–acetylene† 2M HCl	N_2O–acetylene† Octylaniline
Pt	1·25	0·51	3·75	1·28
Pd	0·16	0·04	1·12	0·15
Rh	0·07	0·02	0·24	0·05
Ir	5·00	31·50	10·65	10·55
Ru	1·65	3·00	1·80	0·62

* Length of the absorbing layer 10 cm; height of measurement in the flame, Pt 5 mm (both types of solution); Pd, Ir, Rh, Ru 10 mm (aqueous solution; 7 mm for the extracts).

† Length of the absorbing layer 5 cm; height of measurement in the flame, Pt 8 mm; Pd, Ir, Rh and Ru 24 mm (with both types of solution).

Evaluation of the detection limits by the 4σ criterion (Table 5) shows that with the extracts the sensitivity is improved by a factor of 2–4 for Pt, Pd and Rh (in both flames) and for Ru (in the nitrous oxide–acetylene flame). However, for the air–acetylene flame the sensitivity for Ir and Ru is improved when the aqueous solution is used. This behaviour determined the choice of the solvent for the atomic-absorption measurements. The differing effect of octylaniline may be due to the formation of compounds of different stability, owing to the creation of reducing conditions within the flame, *etc.* To find the reasons for the effect of organic solutions on the atomic absorption of platinum metals we studied earlier[10] the absorption and temperature profiles for aqueous and organic solutions, and also their physical properties. It was found that use of organic solutions results in (*i*) increase in the efficiency of introduction of the substance into the flame, and a considerable decrease in the size of the aerosol droplets; (*ii*) an upward shift and increase of the volume of the zone of maximum absorption; (*iii*) increase in the temperature of the flame (by about 100°). All this results in more efficient feed to the flame and evaporation.

Studies of the effect of other elements on the atomic absorption of Pt, Pd, Ir, Rh and Ru

A series of solutions was made, with constant content of a given element, and with increasing content of another. The absorbance was measured by the procedure above. The following results were obtained: the absorption for Pd in either solvent does not change in the presence of platinum metals or of the non-platinum metals studied (in both flames), but that for Pt, Rh, Ir and Ru in either solvent changes in the presence of all the elements studied. The changes are similar for all four metals; Fig. 1 shows the effect for Rh.

To suppress this effect in the aqueous solution, previously used additives[11] such as $CuSO_4$, $CuCl_2$, $NaHSO_4$, $CuSO_4 + Na_2SO_4$, $CuSO_4 + CdSO_4$, $LaCl_3$, $La(NO_3)_3$, $La_2(SO_4)_3$, were investigated. Also, we employed for the first time neodymium compounds: $NdCl_3$, $Nd(NO_3)_3$, $Nd_2(SO_4)_3$. To choose

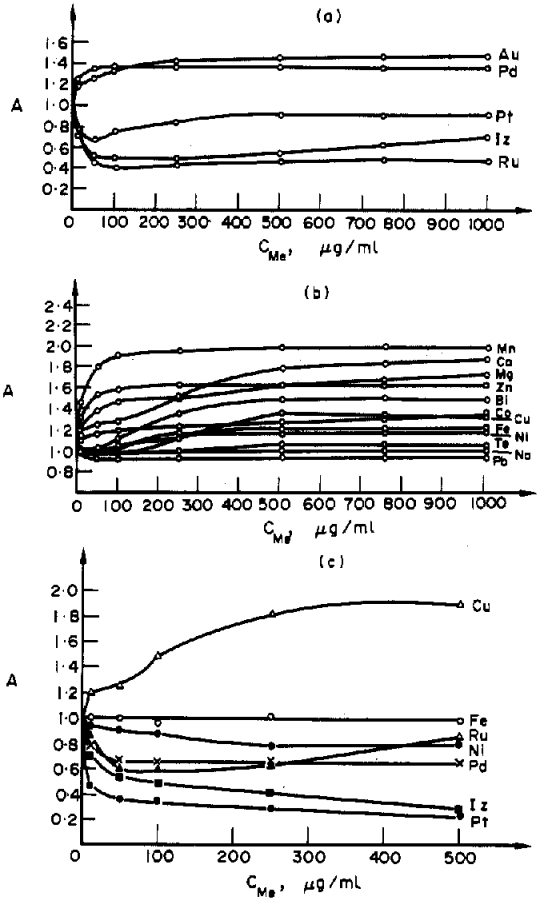

Fig. 1. Effect of various elements on the atomic absorption of rhodium in 2*M* HCl (*a*,*b*) and in octylaniline (*c*).

the proper radiation buffer we looked for an increase in the absorbance and for simultaneous suppression of the effect of other elements. Of the compounds studied, only lanthanum and neodymium nitrates appeared to be suitable. Increase in the concentrations of La and Nd does not affect the determination of Rh, Ir and Ru very much, but produces a considerable effect on the Pt determination. For this reason we used 1% lanthanum and neodymium solutions in all the following experiments. The effect of $La(NO_3)_3$ on the position of the calibration curves for Rh in the presence and absence of other elements is shown in Fig. 2: it is seen that the absorbance of Rh increases in the presence of lanthanum nitrate, and it becomes possible to determine it in the presence of elements which produce considerable effects in the absence of lanthanum nitrate (Fig. 1). The calibration curves for Pt, Ru and Ir change in a similar manner.

All the other compounds studied produce effects which are different for different platinum metals. For example, whereas lanthanum and neodymium chlorides are proper additives for Pt and Rh, cupric, lanthanum and neodymium sulphates and nitrates are better for Ru and Ir.

Finally, it was found that: (*i*) under identical conditions, the absorbance of Ir(IV) is greater than that

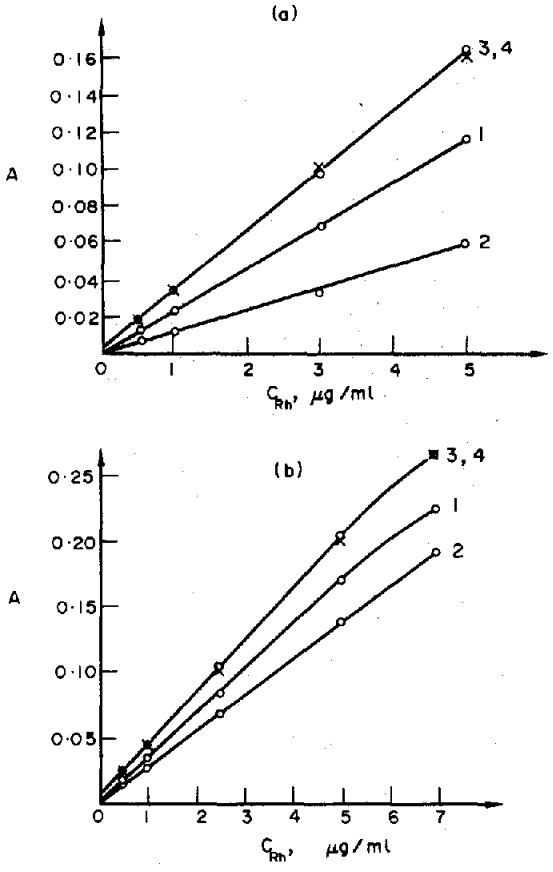

Fig. 2. Effect of $La(NO_3)_3$ on the position of the calibration curves for rhodium in 2*M* HCl (*a*) and in octylaniline (*b*). 1—Rh; 2—Rh + Pt, Pd, Ir, Ru, Cu, Ni, Fe, JEetc. (ΣMe); 3—Rh + $La(NO_3)_3$; 4—Rh + ΣMe + $La(NO_3)_3$.

of Ir(III), and that of $[RuCl_6]^{2-}$ and $[RuCl_6]^{3-}$ is 3–5 times greater than that of $[RuNOCl_5]^{2-}$, (*ii*) the absorbance of rhodium and iridium solutions decreases with time, this effect being most pronounced at concentrations of 1 ppm of Rh and 20 ppm of Ir.

By using the two-nebulizer method and isomolar series, we confirmed the conclusions of Pitts *et al.*[12] concerning the effect of other elements on platinum-metal determination. To suppress the effect of other elements on the determination of Pt, Rh, Ir and Ru in the octylaniline phase, we attempted to use lanthanum nitrate both as a solution in ethanol and as a TBP extract. Addition of the ethanolic solution resulted in precipitation of the lanthanum salt. The TBP extract produced a homogeneous solution when added to octylaniline solution, and for this reason it was chosen for further experiments. Addition of lanthanum nitrate to rhodium–octylaniline solution sprayed into the air–acetylene flame results in an effect similar to that observed with the aqueous solution (Fig. 2). Similar results were obtained with Pt and Ru. Determination of iridium in the presence of Pt, Pd, Ru, Rh, Cu, Ni and Fe is only possible by using the nitrous oxide–acetylene flame, because lanthanum does not suppress the effect of other elements in the air–acetylene flame.

Hence, the studies described resulted in choice of the conditions for the atomic-absorption determination of platinum metals in aqueous solution and in octylaniline–toluene mixture. These conditions are the basis of the following analytical procedures.

Procedures

Determination of platinum metals in aqueous solution. The extract, obtained by the procedure described above, is eva-

Table 6. Results of the analysis of some products

Product	Element determined	Method of analysis: Atomic absorption, From aqueous solution	Atomic absorption, From organic solution	Spectral[6]	Photometric
Nickel powder	Pt, %	0·026	0·028	0·021	0·028
	Pd, %	0·070	0·067	0·066	0·071
	Rh, %	$2·00 \times 10^{-3}$	$2·4 \times 10^{-3}$	$2·03 \times 10^{-3}$	$1·95 \times 10^{-3}$
	Ru, %	$3·1 \times 10^{-4}$		$2·8 \times 10^{-4}$	5×10^{-4}
Copper–nickel solution	Pt, *g/l.*	1·07	1·1	0·95	0·81
	Pd, *g/l.*	3·17	3·35	3·09	3·36
	Rh, *g/l.*	0·11	0·12	0·11	0·08
	Ru, *g/l.*	0·021	—	0·024	0·025
	Ir, *g/l.*	0·012	—	0·014	0·008
Copper slime	Pt, %	1·65	1·75	1·63	1·82
	Pd, %	4·48	4·50	4·85	4·51
	Rh, %	0·12	0·12	0·13	0·12
	Ir, %			0·021	0·021
Anode nickel	Pt, %	0·031			0·032
	Pd, %	0·081			0·085
	Rh, %	0·0019			0·0015
Nickel slime	Pt, %		0·48	0·47	0·46
	Pd, %		1·8	1·29	1·4
	Rh, %		0·06	0·085	0·084

porated in a corundum crucible to remove the solvent and some of the extractant, and the residue is ignited at 650°. The residue is fused with sodium peroxide, and the resulting glass is dissolved in 6*M* hydrochloric acid. The solution is filtered, the filtrate evaporated and the residue dissolved in 2*M* hydrochloric acid. To determine Pt, Rh, Ir and Ru, enough lanthanum or neodymium nitrate is added to give a 1% concentration of the metal. The same concentrations of La or Nd are used in the standard solutions of the platinum metals. The atomic absorption is measured in the air–acetylene flame. To determine only Pt and Rh, lanthanum chloride is used as the radiation buffer. The content of Pd is found with standard solutions containing no additive. The coefficient of variation is 4–6·8%.

Atomic-absorption determination of platinum metals in the octylaniline phase. To determine Pt, Pd, Ir, Rh and Ru directly in the octylaniline phase, enough La–TBP solution is added to give a 1% La concentration, and the atomic absorption is measured: that of Pd, Pt, Rh and Ru in the air–acetylene flame, that of Ir in the nitrous oxide–acetylene flame. The radiation buffer is also added to the standard solutions. For Pd, standard solutions containing no buffer may also be used. The coefficient of variation is 2–6·8%.

Because of the variation in sensitivity with conditions (Table 5) it is convenient to determine some elements in the extract, and others in the aqueous phase.

The method proposed has been tested on a number of materials. The results shown in Table 6 demonstrate that the extractive concentration techniques combined with the atomic-absorption method may be successfully applied to analysis of materials widely different in their content of Pt, Pd, Ir, Rh and Ru.

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DETERMINATION OF CARBON DIOXIDE IN COAL AND MINERALS

A. C. KNOTT and C. B. BELCHER

The Broken Hill Proprietary Co. Ltd., Central Research Laboratories, Shortland, N.S.W. 2307, Australia

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Summary—A simple and rapid semi-micro gravimetric procedure for the determination of carbon dioxide (0·005–60%) in coal, rocks and minerals is described. Particular advantages include small sample weights (0·25–1·0 g), high precision (relative standard deviation 0·01%) and improved speed of analyses (20 min). The apparatus is designed as a simple vertical layout to minimize bench space requirements and utilizes commercially available components to reduce the number of joints and rubber tubing connections. The low swept volume (165 ml) gives good sensitivity and reduced analysis time, and the scavenging train ensures removal of water, halogens and gaseous sulphur compounds.

Carbon dioxide determinations are required for corrections of volatile matter, carbon and oxygen determinations on organic coal matter;[1] evaluation of carbonate minerals such as limestone and magnesite; assessment of the carbonation of iron ore sinters and burnt lime; summations of total analyses.

The determination of carbon dioxide has been established for many decades but recent literature is sparse despite the importance of the analysis. Meyrowitz[2] described a gravimetric micro-procedure for minerals when limited sample weights are available; a special feature was the use of nitrogen carrier gas. However, most recent papers have been concerned with the analysis of coal, using gravimetric,[1,3,4] manometric[5] and titrimetric[1,6] methods, together with a comparison of the three techniques.[7] Criticisms of the validity of the manometric procedure for certain Australian bituminous coals have been made,[8,9] because low results were obtained, owing to adsorption of released carbon dioxide on the sample, and on silica gel in the guard tube; this standard method[1] has since been withdrawn.

The micro-procedure described by Meyrowitz[2] is not suitable for routine analyses, and particularly for high carbonate materials, because a very small sample weight (20 mg) would be necessary. The titrimetric procedures are elegant and sensitive, but the preparation, storage and standardization of the potassium methoxide titrant present difficulties in routine analysis, and safety aspects of the absorbent and titrant cannot be overlooked.[10] All of the recommended gravimetric procedures[1,3,4] stipulate a large sample weight (5 g) and an unduly long analysis time of 70–95 min.

The work described in this paper covers the development of a simple and rapid semi-micro gravimetric procedure applicable to coal, coal mineral-matter,[11,12] rocks and minerals. The particular objectives sought were the use of an inert carrier-gas, a non-liquid purification train, relatively small sample weights (1 g of coals, 0·25 g of limestone), wide applicability (0·005–60%), high precision (relative standard deviation 0·01%) and accuracy, and much improved speed of analysis (20 min).

EXPERIMENTAL

Reagents

Magnesium perchlorate, anhydrous, G. F. Smith, Cat. 55, 0·8–2 mm.

Soda asbestos, Merck Cat. 1564, 1·5–3·0 mm, and Cat. 1567, 0·75–1·5 mm (absorption capacity for CO_2, 50% minimum).

Schütze catalyst,[13] 0·25–0·5 mm.

Activated manganese dioxide, 0·7–1·4 mm.

Tetrabase (4,4′-tetramethyldiaminodiphenylmethane) granulated on pumice, 0·5–2·0 mm.

Apparatus

Analytical balance, 0·01 mg sensitivity.

U-tubes, fully sealable, borosilicate glass, clear joints, flame-polished tubulures, internal diameter 13·5 mm, packed weight 65–75 g.

Purification tube, nominally 25 mm o.d., length 400 mm, packed as shown in Fig. 1.

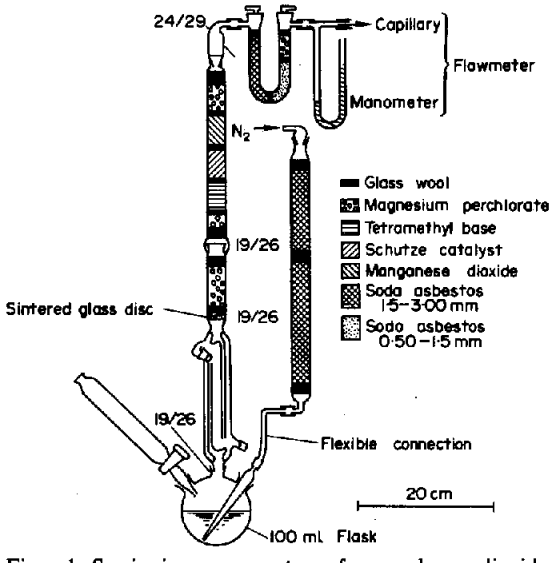

Fig. 1. Semi-micro apparatus for carbon dioxide determination.

Apparatus components (Fig. 1) are commercially available ground-joint glassware.

Procedure

Standardization. Pass nitrogen at 200 ml/min for 10 min through the U-tube to bring it to equilibrium, and weigh immediately. Weigh into a dry reaction flask, 60·0 or 300·0 mg of anhydrous sodium carbonate (dried at 105°) as appropriate for the expected range of carbon dioxide in the samples. Add 40 ml of distilled water free from carbon dioxide, connect to the apparatus and pass nitrogen at 200 ml/min for 5 min to remove atmospheric carbon dioxide from the train. Reduce the nitrogen flow to 50 ml/min, connect the weighed U-tube, slowly add 20 ml of hydrochloric acid (1 + 1), adjust the nitrogen flow to 200 ml/min and raise the reaction flask to boiling point in 5 min, using a micro bunsen burner. Boil gently for 10 min, remove the U-tube, and weigh it immediately. The carbon dioxide recovery should be within the ranges 24·8–25·0 and 124·3–124·9 mg respectively for sodium carbonate weights of 60·0 and 300·0 mg.

Assays. Samples are ground to pass a 62-μm screen and air-equilibrated. A maximum sample weight of 1 g is used and smaller weights are used as required to limit the yield of weighed carbon dioxide to ≯125 mg. Concurrent moisture determinations[14] are carried out as required. Various materials are analysed by the standardization procedure with the following modifications. *Coal*—add 3 drops of 50% v/v detergent solution, 30 ml of carbon dioxide-free water, close the flask with a stopper and shake it vigorously for 5 min before connecting it to the apparatus. *Carbonate minerals*—use 250 mg of sample. *Sulphide minerals*—add only 20 ml of water initially, heat to boiling in 5 min, slowly add 20 ml of 60% w/v ferric chloride solution, return to the boil and slowly add 20 ml of hydrochloric acid (1 + 1). *Manganese dioxide*—use phosphoric acid (1 + 1) instead of hydrochloric acid.

Calculation

$$\%\ CO_2\ (\text{dry basis}) = \frac{CO_2\ \text{absorbed (mg)} \times 100}{\text{Sample weight (mg)}} \times \frac{100}{100 - H_2O}$$

where H_2O is the water lost (%) at 105°.

RESULTS AND DISCUSSION

The apparatus was designed as a vertical layout to minimize bench space requirements and to enable three trains to be fixed to one portable board. The apparatus components were chosen from commercially available or simply modified items, to minimize the number of ground-glass joints and restrict rubber tubing connections in the analysis train. The low swept volume (165 ml) of the apparatus gives lower flow-rates and blanks, together with reduced analysis time. A feature of the apparatus is the use of swivel clamps which enable rapid changing of the flasks without altering the alignment of the main apparatus. Borosilicate glass U-tubes are stronger than soda-glass and can be used in humidity-controlled (50–60% RH), air-conditioned laboratories without difficulties from static electricity effects, even when a semi-micro balance is used. Immediate weighing is possible when a controlled environment is used, because the U-tubes are far removed from the micro bunsen burner and the relationship between the masses of the U-tube and the absorbed carbon dioxide is such that the temperature rise from the exothermic reaction is not significant. The use of fully sealable U-tubes in conjunction with a 0·01-mg sensitivity balance enables consistently low blanks and good reproducibility to be obtained; a 0·1 mg sensitivity balance is adequate for many applications.

The scavenging train contains magnesium perchlorate for removal of residual water vapour passing through the condenser; tetrabase for the self-indicating removal of halogens[15,16] released from samples, particularly those containing quantities of manganese dioxide, and for preventing the back-bleed of iodine; Schütze catalyst for the oxidation of residual hydrogen sulphide;[17] manganese dioxide for adsorption of sulphur oxides and to remove any iodine. The bottom drying section of the scavenging train is changed readily, and is used to extend the life of the main upper scavenging train by removing water vapour passing through the condenser. Meyrowitz[2] used sulphuric acid–potassium dichromate solution for removal of H_2S and traces of hydrocarbons, and copper sulphate on pumice to remove chlorine, residual hydrochloric acid and H_2S not absorbed by the H_2SO_4–$K_2Cr_2O_7$. Liquid purification trains are regarded as less preferable by the present authors because the carrier gas sweeps vapour from the liquid to the adjacent purification units, the swept volume of the purification train is unnecessarily increased and the number of apparatus joints is increased. Further, Meyrowitz acknowledges that the use of sulphuric acid in the train adjacent to magnesium perchlorates constitutes an explosion hazard. The addition of ferric chloride to sulphide-containing samples significantly reduces the evolution of H_2S, by the reduction of Fe^{3+} to Fe^{2+},[18] although more frequent replacement of the Schütze catalyst and manganese dioxide may be required. Stronger oxidants are not recommended because of the danger of conversion of organic compounds such as humic acid into spurious carbon dioxide.[19]

The initial surge of carbon dioxide evolved can cause a problem in the gravimetric determination of carbon dioxide when using soda-asbestos as absorbent. Total exhaustion of the immediate front section of the absorbent vessel can cause cohesion of the particles and result in blockage. The use of soda-asbestos (1·5–3·0 mm) in the front section of the absorbent vessel, followed by fine soda-asbestos (0·75–1·5 mm) was found to eliminate blocking and ensure full utilization of the absorbent and total recovery of carbon dioxide.

The preferred acid [hydrochloric acid (1 + 1)] was found to give erroneously high results when applied to manganese dioxide materials; the evolved chlorine quickly saturates the purification train and is absorbed subsequently on the soda-asbestos and is reported as carbon dioxide. The incorporation of tetrabase in the purification train permits the analysis of a range of materials which may contain moderate amounts of manganese dioxide, but phosphoric acid

Table 1. Carbon dioxide recovery from 301·00 and 60·20 mg of Na_2CO_3, with HCl and H_3PO_4

Acid	HCl (1 + 1)		H_3PO_4 (1 + 1)	
CO_2 taken *mg*	124·98	25·00	124·98	25·00
Mean CO_2 found, *mg*	125·02	25·03	124·95	25·09
Relative standard deviation, $n = 6$,	0·0014	0·0016	0·0005	0·009

dissolution is better suited to samples rich in manganese dioxide.[20] The British standard method for coal[1] states that phosphoric acid is not effective for materials containing siderite ($FeCO_3$) and investigation showed that complete recovery of carbon dioxide from siderite requires prolonged dissolution time in phosphoric acid (60 min) or use of an additional hydrochloric acid attack. For a natural siderite sample (34·5% CO_2), the recovery when using phosphoric acid was only 26·4% CO_2; the residual carbon dioxide was released by decanting the phosphoric acid and continuing the analysis with hydrochloric acid.

The optimum carrier-gas flow-rate consistent with complete recovery of the carbon dioxide evolved was investigated. A flow-rate of 200 ml/min was found to give good recoveries in the preferred analysis time cycle and a 50% variation in this flow could be tolerated without an adverse effect on the analyses.

There is a lack of suitably standardized commercially available materials for validation of carbon dioxide analyses, particularly in regard to solid fuels, and iron and manganese dioxide ores. Consequently it was necessary to establish recovery and reproducibility values by using sodium carbonate, a limestone standard and a standardized coal sample. Results obtained (Tables 1 and 2) show that excellent recoveries and reproducibility can be achieved.

Table 2. Carbon dioxide content of standard samples

Acid Material Sample	HCl Coal BHP SC114	H_3PO_4 Coal BHP SC114	HCl Limestone NBS1a
Certified CO_2 value, %	0·555	0·555	33·53
Mean CO_2 found, %	0·554	0·556	33·42
Relative standard deviation, ($n = 6$),	0·0119	0·0081	0·0007

The apparatus and method developed have been shown to be simple, sensitive and rapid, and with minor modifications are applicable to a wide range of materials.

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SHORT COMMUNICATIONS

TITRIMETRIC STUDY OF THE REACTION OF CHLORAMINE-T WITH AMMONIA

V. J. JENNINGS and A. DODSON

Lanchester Polytechnic, Priory Street, Coventry CV1 5FB, U.K.

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There have been a number of references to the reaction of chloramine-T (CAT) with ammonia. Engfelt[1] claimed that there was little reaction in aqueous medium at room temperature. Later, however, it was reported that when excess of CAT was mixed with ammonia at a solution pH of less than 4, there was a brisk evolution of nitrogen and a stinging smell of chloramine was observed, while the proposed reaction was thought to be similar to that of hypochlorite:[2,3]

$$3NaOCl + 2NH_3 = N_2 + 3NaCl + 3H_2O \qquad (1)$$

It was found that more CAT was being consumed by the reaction than required by the equation above, assuming that 1 mole of CAT is equivalent to 1 mole of hypochlorite. The precise excess consumed depended on the time of standing, up to a period of 24 hr. Dietzel *et al.*[4] suggested that this was due to further oxidation of the normal final reduction product of CAT, *p*-toluenesulphonamide to *p*-benzoic acid sulphonamide.

More recently it has been reported[5] that the oxidation of ammonia with CAT occurs rapidly in neutral medium and sluggishly in acid medium (0·1*M* hydrochloric acid). At pH 10 and above there was no oxidation. Agterdenbos[6] has reported that ammonia seriously interferes in the determination of nitrite by oxidation with CAT in 0·5*M* acetic acid medium. Though the claim that CAT behaves as a hypochlorite solution is well disproven,[7,8] there are many reports of oxidations with CAT in alkaline media and we have chosen to examine the reaction of excess of CAT with ammonia in the presence and absence of bromide.

A priori, it was assumed that for titrations of CAT and ammonia at room temperature there were three possible and significant variables: (1) the excess of CAT used, measured as a molar concentration ratio of CAT to ammonia; (2) the time for which the excess of CAT was allowed to react with the ammonia, and (3) the pH of the medium for the reaction.

EXPERIMENTAL

Reagents

Chemicals used were of analytical-reagent grade. The solutions prepared were 0·1*M* sodium thiosulphate, 0·05*M* CAT and 0·015*M* ammonium sulphate. The sodium thiosulphate solution was standardized against 0·1*M* iodine prepared from a commercially available concentrate and the CAT solution was standardized against the thiosulphate solution.[7] One sample of "AnalaR" ammonium sulphate used was standardized acidimetrically[9] and found to be above the 99·6% minimum assay guaranteed and solutions of this reagent were therefore usually prepared by weight standardization.

Procedure

A 50-ml portion of 0·05*M* CAT (2·5 mmole) was added from a grade-A burette to a 250-ml glass-stoppered bottle. To this solution was added the required quantity of buffer and, if appropriate, 1 g of potassium bromide (8·4 mmole). The required volume of ammonium sulphate solution from 10 to 50 ml (0·15–0·75 mmole) was added from a burette. The bottle was stoppered, well shaken and kept in the dark for the required reaction time from 1 to 60 min. Then 10 ml of 2*M* sulphuric acid (20 mmole) were added, followed by 1 g of potassium iodide (6·0 mmole). The iodine liberated was titrated with 0·1*M* sodium thiosulphate, with starch as indicator. The following buffers were used; the measured pH values for the buffers are given in brackets:

(*a*) 10 ml of 2*M* sulphuric acid, 20 mmole (0·8)
(*b*) 1·02 g of potassium hydrogen phthalate, 5 mmole (4·9)
(*c*) 0·36 g of disodium hydrogen phosphate, 2·5 mmole, plus 0·34 g of potassium dihydrogen phosphate, 2·5 mmole (6·6)
(*d*) 1·0 g of sodium bicarbonate, 1·2 mmole (7·7)
(*e*) 0·4 g of disodium tetraborate, 1 mmole (9·04)
(*f*) 0·2 g of sodium hydroxide, 5 mmole (12·1).

The equation for quantitative oxidation of ammonia to nitrogen is:

$$3CH_3C_6H_4SO_2NCl^- + (Br^-) + 2NH_3 \rightarrow$$
$$3CH_3C_6H_4SO_2NH_2 + N_2 + 3Cl^- + (Br^-)$$

The molar ratio is calculated from number of moles of CAT added, divided by twice the number of moles of ammonium sulphate added. The number of moles of CAT is calculated from the volume of CAT added to the stoppered flask. For a mole ratio of 1·5 exactly enough CAT is present as is required to oxidize all the ammonia present to nitrogen. Some of the results obtained are given in Tables 1–4.

RESULTS

Table 1 shows that in the presence of bromide the oxidation to nitrogen in bicarbonate medium is complete but non-quantitative. More CAT is consumed than the reaction above requires. There was little further change in the degree of reaction, when reaction times of up to 60 min were used. Table 3 shows the 0·5% relative standard deviation attained for a set of nine titrations. It was often noted

Table 1. Effect of time of reaction on degree of reaction of CAT with ammonium chloride

(*a*) In presence of 1 g of potassium bromide, and 1 g of sodium bicarbonate, mole reaction ratio $CAT:NH_3$ = 3·24:1

Time, *min*	1	2	3	5	10	20
Reaction, %	87·1	95·0	98·4	100·3	101·9	104·3

(*b*) In presence of 1 g of sodium bicarbonate, mole reaction ratio $CAT:NH_3$ = 3·24:1

Time, *min*	10	20	30	40	50
Reaction, %	(6·3)	(8·8)	12·3	15·5	14·0

Table 2. Effect of mole ratio on degree of reaction

(*a*) In presence of 1 g of potassium bromide and 1 g of sodium bicarbonate, time of reaction 20 min							
Mole ratio ($CAT:NH_3$)	1·65	1·88	2·37	3·29	4·11	5·48	8·22
Reaction, %	(80·3)	(85·8)	97·2	103·2	106·0	109·2	(115·0)
(*b*) In presence of 1 g of sodium bicarbonate, time of reaction 30 min							
Mole ratio	2·03	2·70	3·24	4·05	5·39	8·09	
Reaction, %	(10·1)	(7·0)	(9·0)	(14·4)	19·1	20·9	

Table 3. Precision of titration in presence of 1 g of potassium bromide and 1 g of sodium bicarbonate, time of reaction 20 min, mole ratio 3·54

Reaction, %	103·1	103·7	103·5	104·0	103·7	102·5	104·0	103·6	103·6

Mean 103·6%, relative standard deviation 0·5%

that while pairs of titration results could show close agreement, attempts to repeat such results with different solutions showed deviations of up to 1%, the deviations being the larger, the further the degree of reaction was from 100%; such results are bracketed in the tables.

Table 1 also shows that in the absence of bromide there is only a slight oxidation of ammonia by CAT. Table 2 shows that increase in mole ratio increases the degree of reaction both in the presence and absence of bromide.

Table 4 shows the effect of pH on the reaction. In the presence of bromide there is very incomplete reaction at pH 9·2 and practically no reaction in dilute sodium hydroxide solution. There appears to be an increased over-consumption of titrant at pH 4 and again a very incomplete (and poorly reproducible) reaction in dilute sulphuric acid medium. In the absence of bromide at pH 4·8 there was a very marked over-consumption of CAT, a fairly complete reaction at pH 6·8 and otherwise little or no reaction.

Some additional experiments were conducted with addition of 0·17 g (1 mmole) of solid recrystallized *p*-toluenesulphonamide in titrations carried out in bicarbonate buffer and in the presence of bromide. There was no marked change in the degree of reaction, but the *p*-toluenesulphonamide did not dissolve completely. The result suggests that the reduction product of CAT (*p*-toluenesulphonamide) was not being further oxidized under these conditions.

DISCUSSION

In an attempt to understand both the causes of over-consumption of CAT and lack of reproducibility, some gas-liquid chromatography experiments were carried out, with a Pye series 104 chromatograph. It was thought that one cause of the over-consumption could be the formation of oxidation products other than nitrogen gas. Nitrogen forms compounds having all oxidation states from −3 (NH_3) to +5 (HNO_3). There are two intermediates between ammonia and nitrogen (−3 and 0), namely hydrazine (−2) and hydroxylamine (−1). It is claimed[10] that any oxidizing agent which will oxidize ammonium ion to hydroxylamine will be powerful enough to oxidize it to nitric acid. However, hydroxylamine is unstable and the following reaction is possible:

$$4\,NH_3OH^+ = N_2O + 2NH_4^+ + 3H_2O + 2H^+$$

The latter reaction is favoured by alkali and it has been suggested that the reaction between hypochlorite and ammonia will give oxides of nitrogen.[11] The head-space analysis method[12,13] was used. Gas samples (20 ml) were taken by syringe from a 250-ml flask that contained the reaction mixture (CAT/ammonium sulphate in bicarbonate media) and was sealed with a "Subaseal" rubber seal (R. W. Jennings Ltd.). The gas samples were then injected into the gas-liquid chromatograph.

It proved difficult to achieve a reproducible reaction. Gaseous products other than nitrogen were formed, but not consistently. One unidentified component, which also occurred in the reaction of ammonium sulphate and sodium hypochlorite, increased in concentration with time of standing.

The possibilities ammonia, nitrogen, nitrous oxide, nitrogen dioxide, carbon dioxide, carbon monoxide and chlorine were excluded, since none of these gave the same retention time as the unknown component. It is likely that the unknown component is a chloramine.

In the absence of bromide, possible volatile products of the reaction are chloramine and dichloramine. Chapin[14,15] claimed that in the reaction of chlorine with ammonia, the nature of the product depended on the pH of the medium. Below pH 3, nitrogen trichloride was formed, at pH 3–5 dichloramine, and above pH 8 monochloramine.

Polarographic analysis showed that an electroactive component was formed slowly in a solution that was $10^{-3}M$ in CAT, 0·05*M* in ammonia, 0·05*M* in ammonium chloride and 0·5*M* in potassium sulphate. The reduction wave had an $E_{\frac{1}{4}}$ of −0·34 V *vs.* SCE, while the $E_{\frac{1}{4}}$ for CAT in this medium was about 0 V *vs.* SCE. (The latter value is not in agreement with some early work,[16] where the $E_{\frac{1}{4}}$ for CAT was given as −0·13 V *vs.* SCE; however, there are more recent references to the polarographic behaviour of CAT.[17,18]) The wave with an $E_{\frac{1}{4}}$ of −0·34 V was found only in the presence of ammonia and after allowing at least 10 min for reaction to occur. The wave-height increased with time up to about 2 hr and then slowly decreased. This showed that even when the ammonia is in excess, relative to CAT, a reaction product that is not nitrogen is found.

While the formation and loss of a volatile reaction product explains the apparent lack of repeatability in the reaction of CAT with ammonia, it does not explain the over-consumption of CAT. If chloramine is formed and escapes into the gas phase, then one expects an underconsumption of CAT, *i.e.*, less than 100% reaction. This is because one mole of CAT oxidizes 1 mole of ammonia to chloramine, whereas 1·5 moles of CAT are required to oxidize one mole of ammonia to nitrogen. On the other hand, if the chloramine remains in the solution, then it will be oxidized to

Table 4. Effect of pH on degree of reaction of CAT with ammonium chloride

(*a*) In presence of 1 g of potassium bromide, mole ratio 3·11:1, time of reaction 30 min					
pH	0·8	4·8	6·6	9·0	12·1
Reaction, %	(47·4)	106·4	101·8	(42·4)	(1·4)
(*b*) Mole ratio 3·11:1, time of reaction 30 min.					
pH	0·8	4·8	6·8	9·2	12·1
Reaction, %	(5·1)	(133·0)	(95·9)	(0·5)	(0·3)

nitrogen by the iodine formed on adding iodide ions to the excess of CAT before the titration with thiosulphate. It is therefore necessary to postulate that overconsumption of CAT is due to the formation of dichloramine, some of which volatilizes.

$$2CH_3C_6H_4SO_2NCl^- + 2H^+ + NH_3 = 2CH_3C_6H_4SO_2NH_2 + NHCl_2$$

Such a postulate would account for the large overconsumption of CAT at pH 4. In this pH region the chloramine-T anion disproportionates into dichloramine-T and *p*-toluenesulphonamide.[7,8] However, the formation of dichloramine from the CAT–ammonia reaction is probably not the complete story. It has been observed[19] that solutions of CAT alone, buffered with acetate in this pH region, show a loss in titre of 2% after a period of 1 hr. Rao *et al.*[20] have suggested that in the formation of dichloramine-T in the disproportionation reaction

$$2CH_3C_6H_4SO_2NCl^- + 2H^+ = CH_3C_6H_4SO_2NH_2 + CH_3C_6H_4SO_2NCl_2$$

free-radical side-reactions can produce a dimer with the structure $(CH_3C_6H_4SO_2NCl-)_2$. The reaction of CAT with ammonia in the presence of bromide shows that bromide promotes the reaction and one may suppose that the CAT initially reacts with bromide to form the analogous bromo-anion, which would react in a similar manner, forming bromamine and dibromamine.

CONCLUSIONS

The reaction between CAT and ammonia does not take place unless the pH is less than about 8. The presence of bromide increases the rate of reaction and extends the pH range up to about 9. There are no conditions under which the reaction results in a quantitative formation of nitrogen. There are some species formed during the reaction which are believed to be chloramines (or bromamines when bromide ions are present).

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Summary—A titrimetric study of the reaction between chloramine-T (CAT) and ammonia is described. The effects of the presence of bromide, the ratio of CAT to ammonia concentrations, the time for reaction and the pH of the reaction media are all significant in the quantitativeness of the reaction that occurs.

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IODOMETRIC MICRODETERMINATION OF HYDRAZINES BY AMPLIFICATION REACTIONS

Y. A. GAWARGIOUS and AMIR BESADA
Microanalytical Research Laboratory, National Research Centre, Dokki, Cairo, Egypt (A.R.E.)

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Hydrazine salts are familiar in many industrial fields, *e.g.*, they are used as antioxidants, photographic developers, preservatives, welding fluxes, oxygen scavengers and propellents. The mode of utilization of the hydrazines is governed by the oxidation route they take.

Many methods have been proposed for the determination of hydrazine compounds. Most are oxidimetric, applying various finishing methods, *e.g.*, titrimetry,[1–5] potentiometry,[6–8] colorimetry,[9] coulometry,[10] amperometry,[11] conductometry.[12] and gasometry.[13–18] Whereas some of

nitrogen by the iodine formed on adding iodide ions to the excess of CAT before the titration with thiosulphate. It is therefore necessary to postulate that overconsumption of CAT is due to the formation of dichloramine, some of which volatilizes.

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Summary—A titrimetric study of the reaction between chloramine-T (CAT) and ammonia is described. The effects of the presence of bromide, the ratio of CAT to ammonia concentrations, the time for reaction and the pH of the reaction media are all significant in the quantitativeness of the reaction that occurs.

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IODOMETRIC MICRODETERMINATION OF HYDRAZINES BY AMPLIFICATION REACTIONS

Y. A. GAWARGIOUS and AMIR BESADA
Microanalytical Research Laboratory, National Research Centre, Dokki, Cairo, Egypt (A.R.E.)

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Hydrazine salts are familiar in many industrial fields, *e.g.*, they are used as antioxidants, photographic developers, preservatives, welding fluxes, oxygen scavengers and propellents. The mode of utilization of the hydrazines is governed by the oxidation route they take.

Many methods have been proposed for the determination of hydrazine compounds. Most are oxidimetric, applying various finishing methods, *e.g.*, titrimetry,[1–5] potentiometry,[6–8] colorimetry,[9] coulometry,[10] amperometry,[11] conductometry.[12] and gasometry.[13–18] Whereas some of

these methods require special equipment, others demand carefully controlled conditions, particularly with the gasometric methods where the oxidation reactions involved do not always lead to quantitative formation of elemental nitrogen. Side-reactions can occur during oxidation with some inorganic oxidants and may give rise to gaseous products other than nitrogen, *e.g.*, ammonia and/or hydrazoic acid.[19]

In the present investigation two new iodometric methods are described for the determination of micro amounts of hydrazine salts. Both are simple, rapid, and highly sensitive, since 6- and 3-fold amplification reactions are involved.

EXPERIMENTAL

Reagents

All reagents used were of analytical grade and doubly distilled water was always used.

Hydrazine compounds. Aqueous solutions of concentrations 0·05, 0·1, and 1·0 g/l. were used.

Iodine solution. Prepared weekly by dissolving *ca.* 0·3 g of pure iodine in 250 ml of pure dry chloroform, and stored in an amber bottle.

Sodium thiosulphate solution, 0·01 and 0·005N. Standardized against potassium iodate solutions of similar normality.

Potassium periodate solution. Prepared by dissolving 1 g of reagent (previously crystallized from hot water) in *ca.* 600 ml of water.

Buffer solution, pH 3. Made from 40 ml of 0·2*M* sodium acetate and *ca.* 110 ml of glacial acetic acid.

Solutions of sodium acetate (2*M*), potassium bicarbonate (5 and 0·5%) ammonium molybdate (25%), potassium iodide (10%, prepared daily), formic acid (1:1), and bromine (saturated) were also prepared.

Iodine procedure

Transfer a portion of sample solution, containing 0·1–1·0 mg of the hydrazine salt, to a 100-ml separating funnel and dilute to *ca.* 10 ml with water. Add the bicarbonate and iodine solutions (0·5 and 1·0 ml respectively for each 0·1 mg of hydrazine salt). Dilute the non-aqueous layer to *ca.* 10 ml with chloroform, shake the mixture for 2 min, leave it for 1 min, and separate the organic layer. Remove the last traces of iodine from the aqueous layer by extraction with three 10-ml portions of chloroform. Transfer the aqueous phase quantitatively to a 250-ml conical flask, add 3 ml of 2*M* sodium acetate and 10 ml of bromine water, and stir for 3 min with a magnetic stirrer. Destroy the excess of bromine by dropwise addition of formic acid, add 5 ml of buffer and 5 ml of 10% iodide solution, and titrate the liberated iodine with 0·01*N* thiosulphate, using starch as indicator.

1 ml of 0·01*N* thiosulphate ≡ $54{\cdot}2_2$ μg of hydrazine sulphate or $43{\cdot}7_4$ μg of hydrazine dihydrochloride.

Periodate procedure

Dilute an aliquot of sample solution, containing 0·05–1·0 mg of the hydrazine salt, in a 100-ml conical flask to *ca.* 5 ml with water and adjust the pH of the solution to *ca.* 8 by addition of 2·5 ml of 0·5% bicarbonate solution. Add 2 ml of the periodate solution for the oxidation of 0·05–0·2 mg of hydrazine, for 0·5–1·0 mg use 10 ml. Stir the reaction mixture with a magnetic stirrer for 15 min, at room temperature, to allow for complete oxidation. Add

Table 1. The iodometric determination of hydrazines

Compound	Iodine method			Periodate method		
	Weight, μg			Weight, μg		
	Taken	Found	Recovery, %	Taken	Found	Recovery, %
Hydrazine sulphate		99·0	99·0		49·7	99·4
	100	98·1	98·1	50	49·6	99·2
		98·5	98·5		50·1	100·2
		196·4	98·2		99·1	99·1
	200	197·0	98·5	100	99·2	99·2
		196·7	98·4		100·1	100·1
		492·6	98·5		198·6	99·3
	500	493·1	98·6	200	199·0	99·5
		495·8	99·2		198·7	99·4
		691·3	98·8		497·3	99·5
	700	690·6	98·6	500	498·1	99·6
		693·7	99·1		500·2	100·0
		982·9	98·3		998·4	99·8
	1000	989·5	98·9	1000	995·4	99·5
		981·0	98·1		994·3	99·4
Hydrazine dihydrochloride		98·6	98·6		49·5	99·0
	100	98·7	98·7	50	49·8	99·6
		98·3	98·3		49·6	99·2
		198·0	99·0		99·3	99·3
	200	197·6	98·8	100	99·0	99·0
		197·3	98·7		99·7	99·7
		493·7	98·7		198·1	99·1
	500	496·2	99·2	200	199·0	99·5
		490·4	98·1		197·9	99·0
		690·2	98·6		496·4	99·3
	700	692·3	98·9	500	495·3	99·1
		690·0	98·6		498·0	99·6
		987·6	98·8		996·1	99·6
	1000	990·1	99·0	1000	993·2	99·3
		983·3	98·3		990·0	99·0

5 ml of acetate buffer, 5 ml of molybdate solution, and 5 ml of iodide solution and then titrate and liberated iodine with 0·005*N* thiosulphate in the usual manner.
1 ml of 0·005*N* thiosulphate ≡ 54·2$_2$ μg of hydrazine sulphate or 43·7$_4$ μg of hydrazine dihydrochloride.

RESULTS AND DISCUSSION

The iodine method

The conventional method for assay of hydrazine compounds is the iodometric[1] method which involves oxidation with excess of aqueous iodine solution and back-titration with thiosulphate.

$$NH_2NH_2 + 2I_2 \rightarrow N_2 + 4H^+ + 4I^- \qquad (1)$$

This method has hitherto been applied for macro scale assay only, yet is still the most popular procedure despite the many other methods[6–12] available. This motivated us to search for new methods for the determination of micro amounts of hydrazine compounds with use, whenever possible, of the iodine–starch end-point. An obvious approach was the application of amplification reactions.

As clear from equation (1) for four iodine atoms, consumed in oxidation of one molecule of hydrazine, are quantitatively reduced to four iodide ions which can then be dealt with by the Leipert amplification procedure,[20] after extraction of the iodine with chloroform.

In this way, one mole of hydrazine is equivalent to 24 iodine atoms, instead of the 4 in the normal reaction, so the amplification is 6-fold.

Preliminary studies confirmed that the amount of bicarbonate added must be carefully controlled[1] to avoid the decomposition of hydrazine. For 1 mg of sample, 5 ml of 5% bicarbonate gave the optimum concentration. For lower amounts of hydrazine, proportionately smaller amounts of bicarbonate were used. The second factor is the amount of iodine, of which a 2·5–3-fold excess was found essential for rapid and quantitative oxidation. Higher excesses of iodine should be avoided in order to decrease the number of extractions necessary, since these increase the risk of mechanical loss of aqueous phase which causes low results. Any iodine left in suspension in the aqueous phase would cause high results, and so must be removed by washing the aqueous phase with chloroform.

The working procedure finally developed was applied successfully to the analysis of 0·1–1·0 mg amounts of hydrazine compounds. Sample weights outside this range gave rise, unfortunately, to insufficiently accurate results. For sample weights lower than 100 μg, the inconsistent errors (*ca.* ± 5%) obtained may be attributed to mechanical losses in the extraction, separation and transfer processes, and/or the partial decomposition of hydrazine in these more dilute solutions. On the other hand, for sample weights higher than 1 mg, low (by *ca.* 4%) recoveries were generally found and these are most probably due to volatilization of some of the iodine produced in the amplification reaction.

Table 1 shows the recoveries obtained for hydrazine sulphate and dihydrochloride. They range between 98·1 and 99·2%. The overall average recovery is 98·6%.

The periodate method

The periodate method recently used for the determination of α-amino-alcohols,[21] was adapted to determination of hydrazine.

Hydrazine undergoes periodate[22] oxidation according to

$$2IO_4^- + N_2H_4 \rightarrow 2IO_3^- + N_2 + 2H_2O \qquad (2)$$

This reaction has, so far, been applied to the potentiometric[22] titration of periodate with hydrazine as reductant. An excess of periodate could be used to oxidize hydrazine at pH 7·5–9·0, followed by iodometric titration of the unreacted periodate. However, a more sensitive approach is to determine the iodate produced, the excess of periodate being masked with molybdate,[23] and this affords the basis of the second method developed, which involves reaction with periodate, in bicarbonate medium at pH 8, masking of the excess of reagent with molybdate at pH 3, followed by determination of the liberated iodate by the iodate–iodide reaction, giving a 3-fold amplification relative to reaction (1).

The reaction proceeds smoothly and quantitatively within 15 min at room temperature, and gives an average recovery of 99·4% for hydrazine sulphate and dihydrochloride (Table 1).

Both methods are satisfactory, since both involve amplification and keep the iodometric finish. Although the amplification of the periodate oxidation is only half that of the iodine oxidation the former method is simpler and more rapid and accurate, and thus to be preferred to the latter, which involves several extractions.

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Summary—Two new, simple, rapid, and accurate iodometric amplification methods are described for the micro and submicro determination of hydrazine. The first depends on oxidation with a chloroform solution of iodine and removal of its excess, oxidation of the resulting iodide with bromine, and iodometric titration of the liberated iodate. The second method is based on oxidation with periodate at pH 8, masking of the excess of periodate with molybdate at pH 3, and iodometric titration of the iodate. The order of amplification involved in the two methods is 6- and 3-fold, respectively. Micro amounts of hydrazine sulphate and dihydrochloride were determined satisfactorily by both methods, the average recoveries being 98·6 and 99·4%.

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SPECTROPHOTOMETRIC DETERMINATION OF TUNGSTEN WITH THIOCYANATE

V. YATIRAJAM and SUDERSHAN DHAMIJA
Department of Chemistry, Kurukshetra University, Kurukshetra 132119, Haryana, India

(*Received* 21 *August* 1974. *Revised* 30 *December* 1974. *Accepted* 28 *January* 1975)

Most spectrophotometric methods[1a] for tungsten are based on its complexes with organic reagents having hydroxy groups, are only moderately sensitive and are subject to interference from several elements, including molybdenum, vanadium, chromium, iron, nickel and cobalt. The dithiol method uses a very high acidity, is moderately sensitive with a short Beer's-law range, suffers interference from molybdenum and other alloying elements and is also time-consuming.

The most commonly used tungsten(V)–thiocyanate method[2] is much more sensitive, and free from interference from iron and from an equal amount of molybdenum, though not from other coloured ions. Stannous chloride is used as the reductant in highly acid medium and extraction with organic solvents is avoided to keep down interferences. Titanous chloride[3] has also been proposed as reductant, but with no decisive advantage.

In the following method, mercury metal is used for reduction of W(VI) to W(V) in the presence of thiocyanate, followed by extraction of the yellow tungsten(V)–thiocyanate complex with a tertiary amine, offering many advantages.

EXPERIMENTAL

Reagents

Tungsten solutions. Stock solutions (mg/ml level) were prepared by dissolving sodium tungstate and standardized by the oxine method.[4] Working solutions were made by suitable dilution.

Tribenzylamine solution (TBA), 2% w/v in distilled chloroform.

Potassium thiocyanate solution, 5*M*.

Mercury. Purified with nitric acid.[5]

Procedure

A solution containing not more than 600 μg of tungsten was placed in a 100-ml separating funnel, and adjusted to be 0·2*M* in potassium thiocyanate and 4*M* in hydrochloric acid in a total volume of 25 ml. Then 2 ml of mercury were added and the funnel was shaken vigorously for 1 min. The yellow thiocyanate complex formed was extracted by shaking for 1 min with 20 ml of TBA solution. The mercury was run off and the solvent layer was transferred to a 25-ml volumetric flask and made up to volume with TBA solution. The absorbance of the solution at 410 nm was measured in a 1-cm cell.

Modification for vanadium and titanium. When vanadium and/or titanium were present, the yellow solvent layer was transferred to another separating funnel and scrubbed with 20 ml of 7*M* hydrochloric acid for 1 min. The organic phase was transferred to a 25-ml flask and the absorbance measured as before.

Modification for iron. With up to 100 mg of iron present, the reduction step was extended to 3 min of shaking.

High-speed steel. The sample (0·1 g) was dissolved in 10 ml of perchloric acid (1 + 1), with heating. Concentrated nitric acid was added dropwise till all carbides had dissolved. Concentrated hydrochloric acid (1 ml) was then added and the solution evaporated to a paste which was taken up in 50 ml of water containing 5 ml of concentrated hydrochloric acid and 2 g of tartaric acid. The solution was made up to 100 ml in a standard flask and 1 or 2 ml were used for determination of tungsten.

Ferrotungsten. The sample (0·1 g) was carefully fused with sodium peroxide (2 g) in a nickel crucible.[1b] The cold melt was transferred with hot water to a beaker. The nickel crucible was rinsed with 13·0 ml of hydrochloric acid (1 + 1). The rinsings and tartaric acid (2 g) were added to the beaker and boiled. Any black particles were filtered off. The filter paper was dried and ignited and the residue was dissolved in concentrated nitric acid (1 ml) with heating. The nitric acid was expelled by three successive evaporations each with 1 ml of concentrated hydrochloric acid, until a paste was left. The latter was dissolved in 20 ml of water containing 2 ml of concentrated hydrochloric acid and 1 g of tartaric acid. The solution was added to the main solution, which was finally accurately made up to 250 ml. Aliquots of 1 ml were taken for determination of tungsten.

RESULTS AND DISCUSSION

The use of stannous chloride for reduction of W(VI) to W(V) requires very high acid and chloride concentrations to avoid formation of tungsten blue and needs a 20-min waiting period. Tungsten concentrations > 15 μg/ml cause turbidity.[2] Titanous chloride can be used in media of moderate acidity with praetically no advantage other than some improvement in the Beer's-law range. The colour of the excess of titanous chloride requires compensation in the blank.[3] In both cases, extraction increases the interference from other elements. Mercury reduces tungsten to the quinquevalent state in the presence of thiocyanate and

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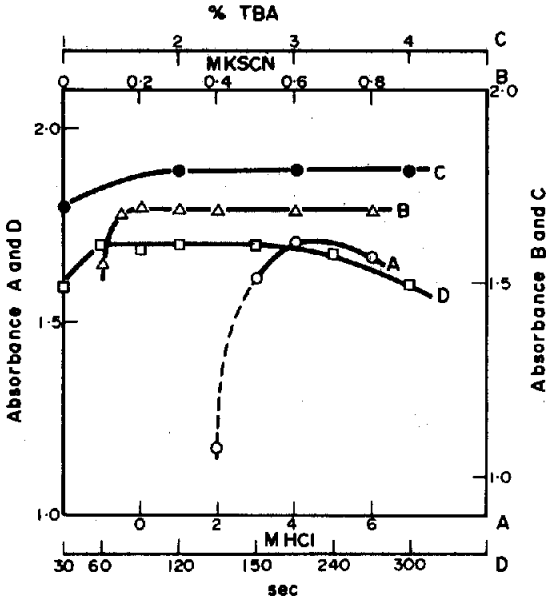

Fig. 1. Dependence of W(V)–thiocyanate complex formation on various parameters. (Curves and scales indicated by the same letters). Tungsten concentration 24 μg/ml. A—[HCl], B—[KSCN], C—[amine], D—time of shaking.

acid very rapidly and no waiting time is required. As the reductant is not present in solution, the absorbance of the complex in aqueous solution decreases with time, but very slowly.

The influence of various parameters on the absorbance of tungsten(V) thiocyanate is shown in Fig. 1. The reduction starts at an acidity of 2*M* hydrochloric acid and increases to a maximum at 4*M*., then decreases very slightly above 5*M* (curve *A*). The colour extracted at up to 3*M* acidity is unstable (shown by dotted line). Reduction increases with concentration of potassium thiocyanate up to

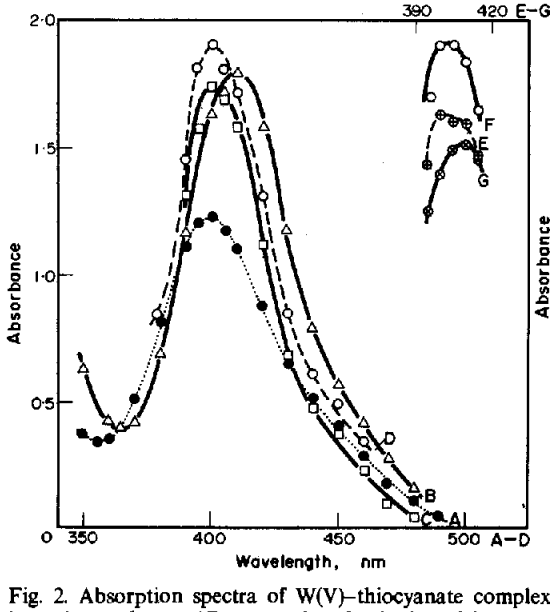

Fig. 2. Absorption spectra of W(V)–thiocyanate complex in various solvents. (Curves and scales indicated by same letters). Tungsten concentration = 24 μg/ml. A—aqueous phase, B—2% w/v TBA, C—tetraphenylarsonium chloride, D—1% v/v n-hexylamine, E—1% v/v tri-n-butylamine, F—1% v/v tri-iso-octylamine, G—1% v/v tri-n-octylamine.

Table 1. Influence of anions on absorbance of tungsten extract (W 600 μg/25 ml)

Salt	Amount*	Absorbance
None	—	1·79
Disodium salt of EDTA	1·0	1·79
Sodium chloride	2·0†	1·79
Sodium sulphate	2·0†	1·78
Sodium acetate	3·0	1·75
Tartaric acid	2·0	1·75
Trisodium phosphate	2·0†	1·65
Potassium citrate	3·0	1·64
Sodium oxalate	2·0	1·25

* g/25 ml of aqueous solution, added after forming the complex.

† added before forming the complex.

0·2*M*, remaining nearly constant thereafter (curve *B*). Extraction increases with the concentration of TBA up to 2% and is found to remain constant up to 4% (curve *C*). It also increases with the length of the reduction step, remains constant for 1–3 min shaking-time, but decreases on longer shaking (curve *D*).

Only oxygenated solvents[6–8] have been proposed for the extraction of the tungsten(V)–thiocyanate complex. In the present system, the complex can be extracted into isoamyl alcohol or methyl isobutyl ketone but is not stable, probably owing to the absence of reductant in the solvent phase. However, we have found that tertiary amines (Fig. 2) also extract the complex, which is stable in them even though the reductant is not extracted. The complex has λ_{max} at 400 nm in aqueous solution and also in tri-n-butyl, n-hexyl and iso-octyl amines, and at 410 nm in TBA and n-octylamine. The colour in tri-n-butylamine is unstable, but stable in the other amines for 2 hr and probably longer. The absorbance increases with the number of carbon atoms (up to six) in the amine and then remains constant. The branched-chain amines give higher absorbances than the unbranched ones. The absorbance in TBA is about 50% higher than that in aqueous solution, slightly better than that in tetraphenylarsonium chloride and 5%

Table 2. Extraction of other elements under conditions of the method

Element	Concn. in aqueous phase, μg/ml	Absorbance*	Absorbance†
None	—	−0·004	—
Sb(III)	400	0·000	—
Co(II)	400	0·002	—
Ni(II)	400	0·002	—
Ce(IV)	400	0·004	—
Al(III)	400	−0·001	—
Pb(II)	400	−0·002	—
Pd(II)	240	−0·002	—
Mn(II)	400	−0·004	—
U(VI)	400	−0·005	—
Fe(III)	400	−0·006	—
Sn(II)	400	−0·008	—
Bi(III)	400	−0·012	0·002
Cr(III)	400	−0·017	0·012
Zr(IV)	400	−0·025	0·007
Ti(IV)	400	0·068	0·002
V(V)	400	0·072	0·002
Pt(IV)	200	0·057	—
Mo(VI)	40	0·055	—

* Measured against 2% TBA in $CHCl_3$.

† After a single scrub with 7*M* HCl.

Table 3. Analysis of synthetic samples by the proposed method

Sample composition*	W added, μg	W found, μg
Fe(3400),Ni(350),Cr(1000),Mn(25)	200	199
Fe(7600)	400	402
Fe(3420),Co(2100),Cr(180)	300	301
Fe(1500),Cr(120),V(6)	360	358
Fe(95),Mn(72),Sn(9),Bi(1·7)	500	498

* These samples are analogous to Midvale HR, tungsten steel, K.S. Magnet steel, high-speed steel, and Spanish wolframite respectively. Figures in brackets are the number of μg of the element present in the aliquot analysed.

less than in the most efficiently extracting amines. Therefore, TBA is chosen as it is also much cheaper and easily recoverable.[9] About 99·5% of the tungsten is removed in a single extraction.

Beer's law is obeyed up to 24 μg of tungsten per ml in the final solution.

Effect of diverse ions

Large amounts of chloride, sulphate, EDTA, tartrate and acetate do not decrease the absorbance, or do so only very slightly (Table 1). Phosphate, citrate and oxalate in large amounts decrease the absorbance in that order. Nitrate should not be present. Fluoride even in small amounts suppresses the extraction.

Uranium, titanium, vanadium, chromium, iron, cobalt, nickel, manganese, aluminium, lead, tin, bismuth, palladium and antimony do not interfere in the method, if any necessary modifications are made, such as scrubbing with 7*M* hydrochloric acid, or compensation in the blank (Table 2). Platinum and molybdenum can be tolerated in amounts equal to that of tungsten, with errors of up to 0·4 and 2% respectively, but in larger amounts should be separated. Copper, in concentrations of more than a few μg/ml, is precipitated, but the interference can be avoided by filtration of the solvent layer. When arsenic is present, the mercury does not collect neatly together, and the solvent phase requires filtration.

Applications

With better sensitivity and wider Beer's-law range than the existing thiocyanate methods, the present method takes less than 8 min for a single determination. With suitable cells and standard curves the method can be used for determination of a wide range of tungsten concentrations with an error of around 0·5% and good reproducibility. The usefulness and wide applicability of the method is shown by satisfactory analysis of several synthetic samples (Table 3) analogous to industrial products. Analysis of BCS 241/1 high-speed steel (19·61% W) gave 19·5 and 19·5%W, and analysis of two ferrotungsten samples gave 75·0 and 75·3% for 75·2%W, and 73·4 and 73·5% for 73·3%W.

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Summary—The yellow W(V) thiocyanate complex is formed by shaking sodium tungstate solution in 0·2–0·8*M* potassium thiocyanate and 4–5*M* hydrochloric acid, with mercury. It is extracted with 2% tribenzylamine solution in chloroform and measured at 410 nm. U, Ti, V, Cr, Fe, Co, Ni, Mn, Al, Pb, Sn, Bi, Pd, Sb and Cu do not interfere. Pt and Mo in amount equal to that of tungsten give errors of up to 0·4 and 2% respectively. The sensitivity is 0·013 μg/ml and Beer's law is obeyed up to 24 μg/ml.

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SEPARATION OF LEAD SULPHATE FROM BARIUM SULPHATE IN THEIR DETERMINATION IN GLASS

B. C. SINHA and S. K. ROY

Analytical Chemistry Laboratory, Central Glass & Ceramic Research Institute, Calcutta-32, India

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Lead and barium are often present together in various ratios in certain silicate materials such as optical glass and low-melting glass frits. The conventional gravimetric methods for determination of lead and barium are based on the decomposition of the sample with hydrofluoric and sulphuric acids and precipitation of the sulphates. Lead is then separated from the mixed sulphates as the soluble lead acetate complex[1] (log $K = 2{\cdot}7$) by extraction with ammonium acetate solution. The literature reveals a confusing picture of the accuracy of the gravimetric method. Allen and Zies[2] stated (no experimental results were furnished) that barium sulphate was slightly soluble in ammonium acetate solution. This statement has been referred to in standard books.[3,4] However, Alldredge and Scott[5] did not find any solubility of barium sulphate in ammonium acetate solution even when the ratio of Ba:Pb was 100:1. On the contrary, they found that the recovery of lead was only 95%. Mellor[3] and Lundell[4] stated that quantitative dissolution of lead sulphate in ammonium acetate was hardly possible when basic iron sulphate and barium sulphate were present. Scott[6] observed that tin and antimony also prevented the dissolution of lead sulphate in ammonium acetate solution. The formation of a mixed sulphate $(Ba,Pb)SO_4$, which is insoluble in ammonium acetate solution, was also reported.[7]

The present investigation was therefore undertaken with a veiw to studying critically the separation of lead sulphate from barium sulphate with ammonium acetate and also with EDTA, in order to work out an accurate method for gravimetric determination of lead and barium, particularly in glass.

EXPERIMENTAL

Reagents

All reagents are of analytical reagent quality:

Hydrofluoric acid, 40%. Sulphuric acid, 50% v/v. Absolute alcohol. Ammonium acetate solution, 50% w/v. Gelatine solution, 0·5% w/v, freshly prepared. Buffer solution (sodium acetate–acetic acid), pH 4·3. Lead nitrate solution (1 ml ≡ 2·75 mg of PbO). Barium chloride solution (1 ml ≡ 2·0 mg of BaO). EDTA (disodium salt) solution, 0·05 *M*. Tartaric acid–oxalic acid solution, each 2·5% w/v.

Procedure for separation and estimation of BaO and PbO after precipitation as sulphate

To solutions containing barium chloride (10–60 mg of BaO) and lead nitrate (11–88 mg of PbO), 15–20 ml of sulphuric acid (1 + 1) were added. The solution was heated on a sand-bath till fuming and then cooled and diluted to 50–60 ml.

Absolute alcohol (40–50 ml) was added to the solution and the precipitate was left standing overnight. The precipitate was filtered off on Whatman No. 44 paper or equivalent, and after thorough washing with dilute sulphuric acid (1 + 9) and then with 50% aqueous alcohol, was transferred into the original beaker. Then 5 ml of gelatine solution, 20 ml of buffer solution (pH 4·3) and 20 ml of EDTA (0·05*M*) were added and the beaker was heated on a hot-plate for 1 hr with occasional stirring. The remaining precipitate was then allowed to settle.

The precipitate of barium sulphate was filtered off on Whatman No. 44 or equivalent paper and washed several times with warm water. The paper and precipitate were ignited in the usual way in a platinum crucible and then treated with sulphuric acid to deal with reduction products. The amount of BaO was calculated by multiplying the weight of product by 0·657.

To the filtrate, 10 ml of sulphuric acid (1 + 1) were added and the solution was evaporated to about 50 ml. It was then cooled, 50 ml of absolute alcohol were added and the precipitate was allowed to settle. The precipitate was filtered off on a weighed porosity-4 sintered-glass crucible dried at 120°, washed with alcohol, and weighed again after drying at 120° for 1 hr. The amount of PbO was calculated by multiplying the weight of product by 0·736.

A correction was made for the reagent blank.

RESULTS AND DISCUSSION

Quantitative and selective dissolution of lead sulphate by ammonium acetate (100 ml of 50% w/v solution) from the combined precipitate of lead and barium sulphates was critically studied by precipitating the sulphates from solutions having various molar ratios of the two metals, and then determining barium and lead in the residue and filtrate respectively by the procedure given. The results presented graphically in Fig. 1 show that the amounts of barium sulphate found are always higher while those for lead sulphate are equivalently lower than the actual amounts taken. The positive error for barium sulphate first increases with increase of the molar concentration ratio of barium to lead present in the solution, reaching its highest value at a molar ratio of 0·42, then with further increase in the concentration ratio it decreases again and at or above a ratio of 4·2, the results for both sulphates are almost correct. Therefore, the classical gravimetric method for determination of barium and lead as sulphate after extraction of the latter with ammonium acetate is not expected to give satisfactory results below a 4·2 mole-ratio of barium to lead. The reason for retention of lead sulphate by barium sulphate during extraction with ammonium acetate is not very clearly known. A literature survey reveals the possible formation of either a double sulphate of barium and lead[7] or a solid solution of the two sulphates[8] which is insoluble in ammonium acetate. The formation of a solid solution is the more probable because both the sulphates form isomorphous crystals and the ionic radii of lead (1·32 Å) and barium (1·43 Å) are very similar. Figure 1 shows the maximum formation of solid solution as occurring with precipitation from a solution containing barium and lead in a mole-ratio of 0·42. However, at or above 4·2 mole-ratio, formation of such a solid solution was not observed.

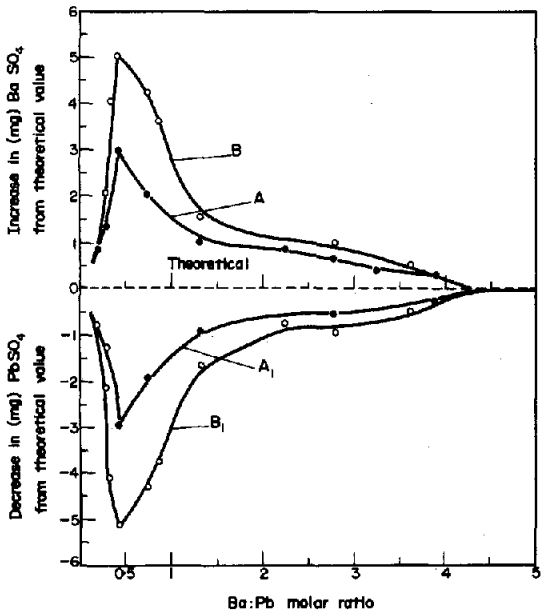

Fig. 1. Extraction of lead sulphate with ammonium acetate from a combined sulphate precipitate of lead and barium of different molar concentration ratios. Curves A, B and A_1, B_1 show the deviations of the amounts of $BaSO_4$ and $PbSO_4$ from their respective theoretical values.

An attempt to extract lead sulphate selectively with EDTA from the mixed sulphate precipitate obtained from different mole-ratios of barium and lead was found to be quantitative at pH around 4·3, probably because EDTA forms a much stronger complex with lead (log K = 18·3) than ammonium acetate does (log K = 2·7) while it does not form any complex with barium in acid solution. Again, lead can be quantitatively precipitated as sulphate from its EDTA complex simply by increasing the acid strength with sulphuric acid because of protonation of the EDTA. However, for accurate work the acid concentration should be 5% and alcohol should also be added in order to minimize the solubility of lead sulphate. The creeping of barium sulphate during filtration is reduced by adding gelatine solution.

The observations of the present study have been utilized to work out a method for quantitative separation of barium sulphate from lead sulphate and then determination of both gravimetrically as sulphate. The results shown in Table 1 were obtained by following the recommended procedure and compare favourably with the actual amounts of barium and lead taken over a wide range of concentration ratios. Cations such as tin and antimony which interfere with the classical gravimetric method by co-precipitating with the mixed sulphates can be dealt with by complexing with oxalic and tartaric acids respectively before the dilution in the procedure. Magnesium and calcium also have no significant effect on the method.

The procedure has been successfully applied to the gravimetric estimation of barium and lead in glass and enamels after decomposing the samples with hydrofluoric and sulphuric acids as follows. A 0·5–1·0 g sample was decomposed with 15–20 ml of sulphuric acid (1 + 1) and 10 ml of hydrofluoric acid in a platinum dish. The solution was heated on a sand-bath to fumes of sulphur trioxide. The hydrofluoric acid treatment was repeated with 5 ml of the acid. The dish was cooled and the contents were transferred into a 250-ml beaker with 50–60 ml of tartaric–oxalic acid solution (5%) and digested on a hot-plate. After cooling, determinations were made according to the second paragraph of the recommended procedure.

Table 1. Separation and estimation of BaO and PbO after precipitation as sulphate

BaO taken, *mg*	PbO taken, *mg*	BaO found,* *mg*	PbO found,* *mg*
10·0	11·0	10·13	10·95
20·0	11·0	20·08	10·99
20·0	66·0	20·13	66·20
20·0	88·0	20·10	88·20
40·0	22·0	40·08	22·08
40·0	44·0	40·08	44·20
40·0	66·0	40·10	66·10

* Mean of three determinations.
Standard deviation for BaO = ±0·0577 mg.
Standard deviation for PbO = ±0·0410 mg.

Table 2. Determination of BaO and PbO in glass

Type of sample	BaO, %	Mean, %	PbO, %	Mean, %
Synthetic solution	19·94		20·18	
BaO 20%	20·24	20·06	20·20	20·09
PbO 20%	20·00		19·90	
Lead-barium	16·78		17·37	
crown glass	16·74	16·77	17·38	
BF 584/469	16·80		17·40	17·38
Lead-barium	1·50		17·42	
glass	1·40	1·45	17·40	17·41
NBS 89	1·46		17·41	

NBS-89 (certified values)—BaO 1·40%, PbO 17·50%.

The results presented in Table 2 compare favourably with the certified values. Other constituents of these materials do not have any interfering effect.

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IODOMETRIC DETERMINATION OF PEROXYDIPHOSPHATE IN THE PRESENCE OF COPPER(II) OR IRON(II) AS CATALYST

SURINDER KAPOOR, P. D. SHARMA and Y. K. GUPTA
Department of Chemistry, University of Rajasthan, Jaipur, India

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A literature survey reveals that not much is reported about the chemistry of peroxydiphosphate and much less about its determination.

The minimum oxidation potential of peroxydiphosphate is 2·07 V, which is a little higher than that (2·01 V) of peroxydisulphate, but peroxydiphosphate is kinetically inhibited as an oxidant. Its indirect cerimetric estimation has been reported by Edwards *et al.*,[1] who also mentioned its determination by gravimetric estimation of total phosphorus. However, since phosphate is always present as impurity[2] in peroxydiphosphate, the total phosphate method does not give a correct determination. Spectrophotometric determination in the ultraviolet region has also been reported by Edwards *et al.*[3] A slow reaction between iodide and peroxydiphosphate has been reported by Indelli and Bonora.[4] This work led us to investigate the conditions for iodometric determination, employing suitable catalysts.

EXPERIMENTAL

Materials

Potassium peroxydiphosphate was a gift sample from FMC Corporation, U.S.A. Other chemicals were analytical-reagent grade. The solution of peroxydiphosphate was prepared by direct weighing and dissolution in water. It does not deteriorate on standing and was standardized cerimetrically.[1] Copper(I) was used in the form of cuprous iodide.

Procedure

A 5–10 ml portion of peroxydiphosphate solution of suitable concentration in 0·1–1·0 *M* perchloric, sulphuric or hydrochloric acid was taken in a 250-ml Erlenmeyer flask. 10–15 ml of 20% potassium iodide solution and enough copper(II) sulphate or iron(II) sulphate to give a concentration of $2–8 \times 10^{-4}$ *M* were added, and the liberated iodine was titrated with a standard solution of sodium thiosulphate. A blank value with the Cu(II) or Fe(II) was also determined and subtracted from the titration values. Representative results are shown in Table 1. Similar results were obtained throughout the acidity range quoted.

RESULTS AND DISCUSSION

The results are within ±1% of the cerimetric assay, and are similar with perchloric, sulphuric and hydrochloric acids, but somewhat lower with acetic acid. The minimum concentration of the catalyst [copper(II) sulphate or iron(II) sulphate] should be 2×10^{-4} *M* otherwise the liberation of iodine is not instantaneous. Nickel(II), cobalt (II), manganese(II), silver(I) and phosphate were without effect.

Phosphorus present as phosphate in the sample of peroxydiphosphate was determined gravimetrically[5] as well as colorimetrically[6] and was found to be 6·25%. Total phosphorus as phosphate in the sample was determined by converting the peroxydiphosphate into phosphate by boiling it with concentrated nitric acid and was found to be equivalent to 97·3% purity. However, the oxidizing capacity (iodometric or cerimetric assay) is only 91%. Another sample of peroxydiphosphate from FMC corporation gave the following results:

Iodometric or cerimetric assay 92·7%. Phosphorus impurity as phosphate 4·7%. Total phosphorus as phosphate equivalent to 97·4% purity.

It is obvious that in both the samples the sum of the phosphorus equivalent of the iodometric or cerimetric assay and the phosphate impurity is nearly equal to the total phosphorus content. Although the oxidizing capacities of the two samples may vary for preparative reasons, impurities other than phosphate are also present in both the samples.

The catalytic activity of copper(II) appears to be due to the production of CuI and the operation of the cycle

$$Cu(II) + I^- \rightarrow \tfrac{1}{2}I_2 + Cu(I) \qquad (1)$$

$$P_2O_8^{4-} + 2Cu(I) \rightarrow 2PO_4^{3-} + 2Cu(II) \qquad (2)$$

Oxidation of iodide by copper(II) is well known,[7] but that of copper(I) by peroxydiphosphate is not known. However, visual observations with cuprous iodide and its catalytic activity in iodometric determination show that copper(I) is readily oxidized by peroxydiphosphate. This also

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Table 1.

$P_2O_8^{4-}$ taken, 10^{-3} *M*	Cerimetric assay, 10^{-3} *M*	Acid and concn., *M*	Catalyst	Catalyst concn., 10^{-4} *M*	Iodometric assay, 10^{-3} *M*
2	1·83	0·2 $HClO_4$	$CuSO_4$	4	1·82
4	3·66	0·2 $HClO_4$	$CuSO_4$	4	3·64
6	5·50	0·2 $HClO_4$	$CuSO_4$	4	5·46
8	7·32	0·2 $HClO_4$	$CuSO_4$	4	7·28
10	9·10	0·2 $HClO_4$	$CuSO_4$	4	9·10
15	13·6	0·2 $HClO_4$	$CuSO_4$	4	13·3
20	18·3	0·2 $HClO_4$	$CuSO_4$	4	18·0
2	1·82	0·2 HCl	$CuSO_4$	4	1·83
10	9·1	0·2 HCl	$CuSO_4$	4	9·15
15	13·6	0·2 HCl	$CuSO_4$	4	13·5
4	3·66	0·2 CH_3COOH	$CuSO_4$	4	3·60
6	5·50	0·2 CH_3COOH	$CuSO_4$	4	5·38
2	1·82	0·2 H_2SO_4	$CuSO_4$	4	1·82
10	9·15	0·2 H_2SO_4	$CuSO_4$	4	9·15
10	9·10	0·2 H_2SO_4	$CuSO_4$	4	9·10
10	9·10	0·2 H_2SO_4	$CuSO_4$	5	9·10
10	9·10	0·2 H_2SO_4	$CuSO_4$	8	9·15
10	9·10	0·2 H_2SO_4	$FeSO_4$	2	9·10
10	9·10	0·2 H_2SO_4	$FeSO_4$	4	9·15
10	9·10	0·2 H_2SO_4	$FeSO_4$	6	9·15
10	9·10	0·2 H_2SO_4	$FeSO_4$	8	9·10
10	9·10	0·2 H_2SO_4	Cu_2I_2	ppte	9·10
10	9·10	0·2 H_2SO_4	Cu_2I_2	ppte	9·05
10	9·10	0·2 H_2SO_4	$Fe_2(SO_4)_3$	2	9·05
10	9·10	0·2 H_2SO_4	$Fe_2(SO_4)_3$	8	9·10

appears to be likely because the oxidation of copper(I) by peroxydisulphate is very fast.[8]

Catalysis by iron(II) appears to work through the cycle

$$P_2O_8^{4-} + 2Fe(II) \rightarrow 2PO_4^{3-} + 2Fe(III) \quad (3)$$

$$2Fe(III) + 2I^- \rightarrow 2Fe(II) + I_2 \quad (4)$$

Oxidation of iron(II) by peroxydiphosphate is the basis of the cerimetric determination, although the oxidation of ferroin (the indicator) is not rapid. Reduction of Fe(III) by iodide is reported by Hershey and Bray[9] and many other workers.

Acknowledgement—We are indebted to the FMC Corporation, New York, for a generous gift of two samples of potassium peroxydiphosphate.

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Summary—Peroxydiphosphate can be determined iodometrically in the presence of a large excess of potassium iodide with copper(II) or iron(II) as catalyst through the operation of the Cu(II)/Cu(I) or Fe(II)/Fe(III) cycle. The method is applicable in $HClO_4$, H_2SO_4, HCl and CH_3COOH acid media in the range 0·1–1·0 *M* studied. Nickel, manganese(II), cobalt(II), silver, chloride and phosphate are without effect.

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NITRON AS A TITRANT IN POTENTIOMETRIC DETERMINATION OF NITRATE

ADAM HULANICKI and MAGDALENA MAJ
Institute of Fundamental Problems in Chemistry, The University, Warsaw, Poland

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The number of reagents which precipitate nitrates quantitatively is limited to a few organic, or organometallic cations. Among them some benzylammonium ions[1,2] have been mentioned, as well as diphenylthallium(III)[3,4] and dicyclohexylthallium[5] ions. The nitrates of the last two cations have solubility products of approx. 10^{-7} and 10^{-10}, respectively. The development of an ion-selective membrane electrode sensitive to nitrate ions has stimulated the development of new analytical procedures based on titration of 0·01–0·1*M* nitrate with diphenylthallium(III) sulphate.[6]

These precipitants are not commercially available, and their synthesis is rather difficult. Therefore we have explored the well-known precipitation reaction with nitron (3,5,6-triphenyl-2,3,5,6-tetra-azobicyclo[2,1,1]-hex-1-ene), which is used for gravimetric determination of nitrate.[7,8] In this study some analytically useful properties of this reagent have been investigated and a potentiometric method for nitrate titration with the nitrate-sensitive membrane electrode[9] has been developed.

EXPERIMENTAL

Reagents

Nitron, 25% solution in 5% acetic acid.
Hydroxylammonium sulphate, 1*M* solution, analytical-grade reagent.
Silver sulphate, analytical-grade reagent.
Phosphoric acid 25%.
Sulphuric acid (1 + 1).
Potassium nitrate.

Procedure

A 10-ml sample containing 6·2–62 mg of nitrate (0·01–0·1*M*) is acidified with sulphuric acid (1 + 1) to pH 2–3. The titrant is added in 0·05-ml increments and the potential recorded by using the nitrate ion-selective electrode,[9] with a saturated calomel electrode as the reference electrode. The end-point is found graphically from a potential–volume plot or by the Gran method. The titrant is standardized with a solution of potassium nitrate.

If nitrite (which interferes in equivalent or larger amounts) is present, 13 ml of 1*M* hydroxylammonium sulphate solution are added to the sample. After 1 min, 1 drop of 25% phosphoric acid is added, and when evolution of gases has ceased (up to 10 min) the sample is diluted and analysed as above.

RESULTS AND DISCUSSION

Determination of dissociation constant of nitron

Nitron is slightly soluble in water, its highest concentration being about $10^{-4}M$; however, organic solvents and also dilute acids increase its solubility. Zwitter-ions are formed,[10] stimulating protonation to give a cation stabilized through possible mesomeric forms. The structure suggests strong basicity of the nitron molecule and indicates a small affinity towards the second proton. Because of lack of data in the literature we have evaluated the dissociation constant spectrophotometrically.

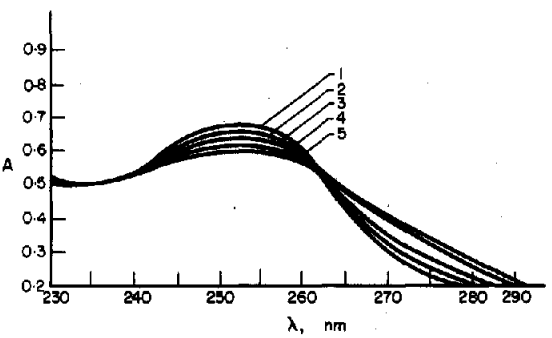

Fig. 1. Absorption specta of $7 \times 10^{-5}M$ nitron solutions in ammonia buffers of pH 9·13 (curve 1), 9·76 (curve 2), 10·54 (curve 3), 10·97 (curve 4) and 11·30 (curve 5).

Of the two absorption maxima at 200 and 250 nm the latter was used in this study, because of smaller interferences. At this wavelength the absorbance changes from 0·680 at pH 9·50 to 0·615 at pH 11 for $7 \times 10^{-5}M$ solution, allowing the use of ammonia buffers (Fig. 1) in this pH range, for determination of pK_a.

The absorbances taken for calculation were extrapolated to zero time because of the instability of nitron, especially in its basic form (Fig. 2). For the pH range 9·76–10·97 the mean pK_a value is 10·34 ± 0·02.

Attempts to confirm this value by using potentiometry failed because of the small solubility of nitron in water. However, the pH of $10^{-4}M$ aqueous solutions of nitron

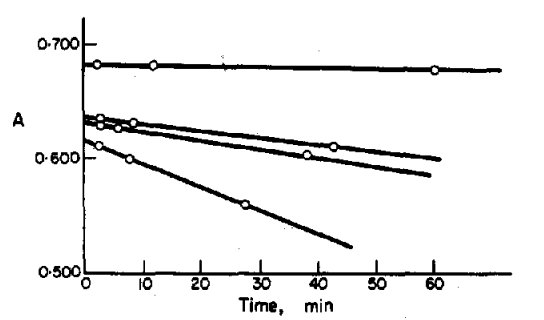

Fig. 2. Absorbance changes of the basic form of nitron with time at various pH values, indicating extrapolation to zero time.

nitrate is close to 6·4, giving $pK_a \sim 9{\cdot}5$. This discrepancy was obviously caused by the presence of carbonates in the potentiometric measurements, but nevertheless indicates that the spectrophotometric determination gives at least a proper order of magnitude.

The solubility of nitron nitrate

Some discrepancy exists in the previously published values for the solubility of nitron nitrate. Welcher[11] mentioned the value 9·9 mg/100 ml ($2{\cdot}6 \times 10^{-4}M$), which seems to be low. A more reasonable value is given by Winkler[12]—37·1 mg/100 ml at 20° ($9{\cdot}9 \times 10^{-4}M$), attained within 24 hr equilibration. This value increases (53·1 mg/100 ml) if the solution is heated first.

In our measurements the nitron nitrate, precipitated and washed with distilled water, was dissolved at no more than 40° and cooled to 20°. The concentration of nitrate ions was measured by using the nitrate membrane electrode and was found to be $1{\cdot}3 \times 10^{-3}M$, which may be assumed to be the solubility of the precipitate. After 10 days' storage of this solution at 3° in darkness the measured concentration decreased to $1{\cdot}0 \times 10^{-3}M$, and after 15 days to $8 \times 10^{-4}M$. This may suggest formation of a less soluble product in the course of decomposition of the nitron. However, for analytical interpretation the first value seems to be the most useful, corresponding to the solubility product $K_{so} = 1{\cdot}7 \times 10^{-6}$.

Choice of conditions for potentiometric titrations

In order to find the best conditions for titration of nitrates, various concentrations were titrated with solutions of nitron in 5% acetic acid that were approximately 10 times more concentrated than the sample. The titration curves are shown in Fig. 3. The increase of concentration is disadvantageous because the amount of precipitate makes proper mixing difficult; at the same time the precipitate tends to adsorb on the electrode, introducing the possibility of an error.

Decreasing the concentration below 0·01*M* is also disadvantageous. The rate of formation of the precipitate is small so the initial part of the curve is greatly disturbed because some excess of the titrant must be present before the precipitation starts (curve D, Fig. 3). When the titration curves were calculated, with neglect of the activity coefficients, they appeared to have a larger end-point break than the experimental curves. However, when the titration was performed at constant ionic strength (0·05*M* potassium sulphate) and the activity coefficients were calculated, very good agreement was found. From the titration curve after the end-point the solubility product of nitron nitrate was calculated as $1{\cdot}78 \pm 0{\cdot}03 \times 10^{-6}$, in fair agreement with the value reported above.

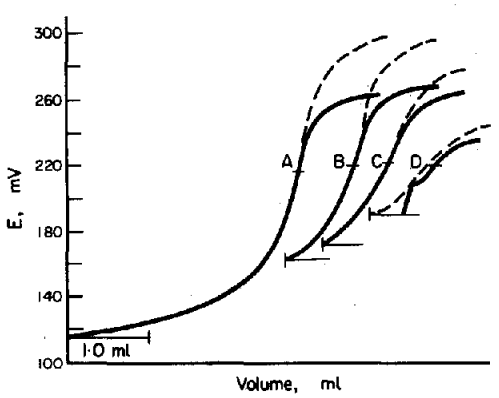

Fig. 3. Titration curves of 0·1*M* NO_3^- (curve A), 0·02*M* NO_3^- (curve B), 0·01*M* NO_3^- (curve C) and 0·005*M* NO_3^- (curve D). The corresponding dashed lines were calculated from the solubility product without taking into account the activity coefficients. The concentrations of titrant were 0·33*M*, 0·22*M*, 0·11*M* and 0·055*M*, respectively.

Table 1. Effect of nitrite and chloride on titration of 0·1000 mmole of nitrate with nitron

Nitrite, *mmole*	Nitrate found, *mmole*	Error, %	Chloride, *mmole*	Nitrate found, *mmole*	Error, %
0	0·1005	+0·5	0	0·1004	+0·4
0·010	0·0919	−2·1	0·050	0·1009	+0·9
0·050	0·0994	+0·6	0·10	0·1014	+1·4
0·10	0·1082	+8·2	0·20	0·1023	+2·3
0·20	0·1155	+15·5	0·50	0·0995	−0·5
0·50	0·1915	+91·5	1·00	0·1030	+3·0
0·70*	0·0975	−2·5			

* After decomposition of nitrite.

The effect of anions on the titration results

The other anions present in the sample may interfere in the determination in several ways. Some may precipitate with nitron and simultaneously influence (or not) the potential of the indicator electrode. Others may only effect the electrode potential. Of the first group the interference of nitrite was studied, and of the second group that of chloride, because both may often accompany nitrate in various samples.

When the sample contained nitrite in amounts smaller than that of nitrate no interference was observed. However, starting from equivalent amounts of nitrite the error increased gradually. In such cases nitrite should be decomposed with hydroxylammonium sulphate (Table 1).

For chloride the selectivity coefficient of the nitrate electrode is $K_{NO_3,Cl} = 6 \times 10^{-3}$ and the titrant does not precipitate this anion. Up to 10-fold excess of chloride does not increase the error of the determination significantly (Table 1). When larger amounts are present the flattening of the titration curve makes it necessary to add silver sulphate to precipitate silver chloride, which need not be filtered off.[9]

Determination of nitrate nitrogen in fertilizers

Nitrogen fertilizers contain approx. 12–14% nitrogen, the majority of it being in the form of nitrate. A sample of flower fertilizer "Flora" was taken for analysis. The total amount of nitrogen was determined by reduction with Devarda's alloy followed by distillation and titration of ammonia. The concentration of ammonia nitrogen was determined similarly but without preliminary reduction. The presence of nitrite in the sample was not confirmed, but the nitrate nitrogen was determined by the full procedure. The results are given in Table 2, where the error of determination is the difference between the total amount of nitrogen determined and the sum of the ammonia and nitrate nitrogen. The magnitude of this error is reasonable, indicating that the method is well suited to this purpose. In general application of the method the relatively high

Table 2. Determination of nitrate nitrogen in flower fertilizer

Total nitrogen, %	Ammonia nitrogen, %	Nitrate nitrogen, %	Sum of ammonia and nitrate nitrogen, %	Error of determination, % rel.
12·52	2·85	9·30	12·15	−3·0
12·74	2·85	10·21	13·06	+2·5
12·33	2·88	9·71	12·59	+2·1
12·36	2·81	9·51	12·32	−0·3

cost of nitron may be a hindrance. However it can fairly simply be recovered from the titrated samples.[13]

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A NEW TYPE OF LABILE PALLADIAZO–Pd(II) SANDWICH(?) COMPOUND FORMED IN NON-COMPLEXING AQUEOUS MEDIA

J. A. PÉREZ-BUSTAMANTE

Departamento de Química Analítica, Facultad de Ciencias y C.S.I.C., Universidad Complutense, Ciudad Universitaria, Madrid-3, Spain

(*Received* 9 *October* 1974. *Accepted* 14 *February* 1975)

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The most congruent results are shown in Fig. 1. They were obtained when the concentration of the ligand blank C_L was $2C_M$, which corresponds to the formation of an ML_2 complex in the test solution ($C_L = 4C_M$).

Three isosbestic points located at 370, 490 and 625 nm are clearly exhibited, and are obtained within 5 hr. This may indicate the existence of a chemical equilibrium involving two different complex species (one forming whilst the other is decomposing). The maximum absorbance is obtained within 6–10 min of mixing. This agrees with earlier findings.[4, 5]

Another interesting feature of Fig. 1 is the existence of two different series of spectra.

(*a*) Within the first 20 min two absorption maxima appear at 525 and 660 nm (spectra 1–4). This type of spectrum is commonplace for arsenazo III complexes, (–AsO_3H_2 groups *ortho* to the –N=N–), but hitherto, despite years of research, no spectrum of this type has been recorded for the palladiazo complexes (–AsO_3H_2 groups *para* to the –N=N–). This suggests the formation of a substantially new type of complex. The kinetic lability of the new complex is also remarkable. Doubtless reaction mechanisms and steric factors quite different from those usually investigated are responsible. Phenomena of this kind involving the appearance of "anomalous" spectral forms have been observed earlier by the author with palladiazo,[8] and others have reported similar phenomena in connection with different bis(azophenyl) derivatives of cbromotropic acid, first in non-aqueous media[9–11,15] more recently in phosphoric acid solutions.[16] Perishich-Yanich *et al.* have also investigated the phenomena.[12]

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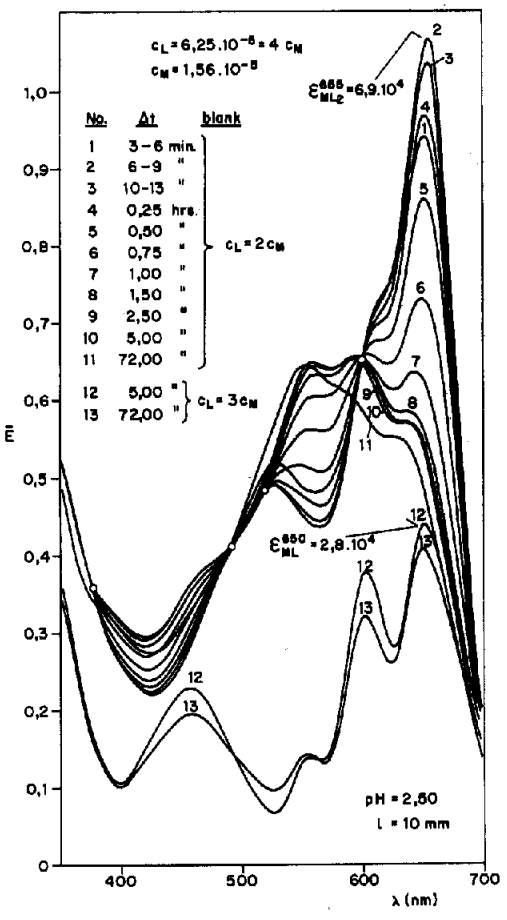


Fig. 1. Kinetic and spectral features of the palladiazo–Pd (II) system. 1–4: ML_2 complex; 4–8: mixed ML_2, ML and free ligand complex spectrum; 12–13: ML pure complex.

hyperchromic-bathochromic effect on the secondary absorption band (λ_{max} = 525 nm). This combined effect is associated with a hypochromic–hypsochromic effect on the main absorption band (spectra 5–10). The process stabilizes asymptotically during 1–2 days (spectra 8–11). These kinetic phenomena are related to the occurrence of an irreversible equilibrium[4,5] such as

$$ML_n \rightarrow ML_{n-1} + L$$

(any attempts to reform the ML_2 complex through addition of a large ligand excess, after kinetic stabilization of the system, have proved completely unsuccessful). Consequently, the recorded spectrum is the sum of the spectra of ML_n, ML_{n-1} and ligand released during the decomposition of ML_n (spectra 8–11).

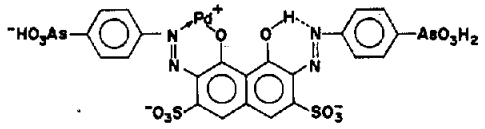
Attempts to resolve the final mixed spectrum by "filtering" with varying amounts of free ligand used as a reference blank have resulted in a "pure" spectrum of the new stable species corresponding to an ML type, since congruent results were obtained when the spectrum of the stabilized mixed complex solution was recorded against a blank for which $C_L = 3C_M$ (spectra 12 and 13).

These facts justify the correction of an earlier hypothesis[4,5] which assumes the initial formation of an ML_3 complex which decomposes to a stable ML_2 complex. The present findings point clearly to the initial formation of an ML_2 complex (λ_{max} = 525 and 660 nm) which decomposes to a stable ML complex (λ_{max} = 600 and 650 nm).

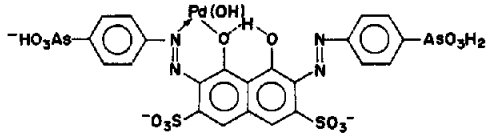
The molar absorptivity of the ML_2 complex is about 7×10^4 l. mole^{-1}.cm^{-1}, one of the highest values so far reported for any Pd(II)–metallochromic reagent and comparing very well with similar high absorptivities reported by Savvin *et al.*[13] for certain bis(azophenyl) derivatives of chromotropic acid. On the other hand, the maximum absorptivity (at 650 nm) exhibited by the stable ML-type Pd(II)–palladiazo complex is only about $2{\cdot}8 \times 10^4$ l. mole^{-1}.cm^{-1}.

From a practical analytical viewpoint, the ML_2 complex allows a much more sensitive determination of Pd(II) although an important drawback of the method lies in its critical kinetic characteristics, which make it mandatory to work under strictly controlled conditions.[4,5] The ML-type complex is stable but the sensitivity is poorer by a factor of about three.

The ML complex could be ascribed either structure I or II (depending on the pH, since this type of complex has been shown to form over practically the entire pH range).



(I)



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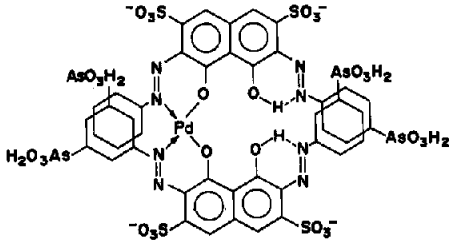

(III)

We consider it highly probable that the ML_2-type complex is a "sandwich-type" complex compound of structure III. It has been argued that the complexes formed with reagents related to palladiazo are of the sandwich type, because of steric effects.[14] There appears to be a correlation between "anomalous" spectral forms exhibited occasionally by this type of reagent and the possibility of formation of "sandwich" complexes of high molar absorptivity.

It is possible that the characteristic kinetic instability shown by the ML_2 complex derives from the presence of the bulky *p*-AsO_3H_2 groups which may be too voluminous to allow for the formation of a stable "sandwich" aggregate complex.

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ESTIMATION OF GLUTATHIONE WITH CHLORAMINE-T AND DICHLORAMINE-T

D. S. MAHADEVAPPA and N. M. MADE GOWDA

Department of Postgraduate Studies and Research in Chemistry, University of Mysore, Manasagangotri, Mysore-570006, India

(*Received* 9 *October* 1974. *Accepted* 23 *February* 1975)

The mechanism of oxidation of thiols has been extensively investigated by a number of workers.[1] The thiol group in thioglycollic acid[2] and cysteine[3] is generally oxidized to the corresponding disulphide, although instances of oxidation beyond the disulphide stage are known.[2–4] Kinetic investigations of the oxidation of thiols as a rule require rapid analytical techniques. Glutathione (GSH) is a tripeptide (glutamylcysteinylglycine) and its importance in mammal systems is believed to be related to its functions in oxidative metabolism and detoxication. Several analytical reagents have been employed for assaying this compound by direct titration, by spectrophotometry and amperometry[5,6] and an excellent review of the subject is given by Jocelyn.[7] The iodometric method developed by Woodward and Fry[8] is generally acclaimed as quite suitable for estimating this polypeptide. In the present investigations we have examined the behaviour of chloramine-T (CAT) and dichloramine-T (DCT) towards glutathione. It was found that the thiol is oxidized by these reagents. A direct titration of GSH with CAT or DCT at room temperature with a visual or potentiometric end-point was practicable as the oxidation of the —SH group to the disulphide was found to be quite rapid. A back-titration procedure using excess of the oxidants, with oxidation taking place beyond the disulphide stage, was found to be satisfactory only in the case of CAT.

EXPERIMENTAL

Triply distilled water was used in preparing aqueous solutions. Reduced glutathione was used; analysis by Mason's method[9] showed the purity as 98%—assay by Woodward and Fry's method[8] gave 100·5% purity (std. devn. 0·13%). The purity was taken as 100%. Paper chromatography showed the compound was homogeneous. An aqueous solution (~2 mg/ml) was prepared in deareated water. Other solutions of glutathione were prepared by dissolving the solid in appropriate buffers and solvents. CAT was purified by the method of Morris *et al.*[10] Approximately 0·1 and 0·01*N* solutions were prepared and standardized by the iodometric method. DCT was prepared and purified by the method of Jacob and Nair.[11] An approximately 0·01*N* solution in glacial acetic acid was prepared and standardized by the iodometric method. Compounds of accepted grades of purity were used in preparing other solutions. Standard buffer systems[12] were employed. Potentiometric titrations were done with a Pt indicator electrode and a calomel reference electrode.

Direct titration

Visual end-point. To the aqueous glutathione solution add about 2 ml of starch–KI solution (20% potassium iodide, 5% starch) and enough 2*N* sulphuric acid to make the overall acid concentration approximately 0·04*N*.

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Direct titration

Visual end-point. To the aqueous glutathione solution add about 2 ml of starch–KI solution (20% potassium iodide, 5% starch) and enough 2*N* sulphuric acid to make the overall acid concentration approximately 0·04*N*.

Titrate with CAT to the appearance of a permanent pale blue colour.

A similar procedure can be used with DCT as titrant, but without the addition of 2*N* sulphuric acid.

Potentiometric end-point. The oxidation potential of the thiol–disulphide system[13] is only −0·24 V, and a potentiometric titration between aqueous glutathione and CAT solutions was found to be suitable. A potential break of about 70 mV was recorded for a 0·1-ml addition of titrant near the end-point.

With DCT, the potential break was not sharp with aqueous GSH solutions or in buffer media of pH 1–3 and addition of perchloric acid or potassium bromide did not improve the results.[14] However, the titration in buffer of pH 4 was satisfactory and a potential break of about 50 mV was found for a 0·1-ml addition of DCT near the end-point.

Back-titration

Preliminary studies. In preliminary experiments with CAT, known amounts of glutathione solution (~0·04 mmole) prepared in the appropriate buffer or solvent were added to a known and excessive volume of CAT solution (~1·25 mmole) in an iodine flask at room temperature. The reaction mixture was set aside for various intervals of time, with occasional shaking. Then the excess of CAT was determined by back-titration.

A typical set of results for the extent of oxidation of glutathione in 30 min by an excess of CAT is given in Table 1. Oxidation of the thiol is erratic in presence of hydrochloric acid and non-stoichiometric at pH 3 and 4, but there is a reproducible 10-electron oxidation of GSH in sodium acetate–acetic acid buffer of pH 5·0, and the stoichiometry again changes at higher pH.

Recommended procedure. Prepare a solution containing glutathione (~2 mg/ml) in pH 5·0 buffer. Add an aliquot to 25 ml of 0·1*N* CAT in an iodine flask, shake the mixture occasionally, and after 30 min add 10 ml of 2*N* sulphuric acid and 10 ml of 20% potassium iodide solution and titrate the liberated iodine with standard thiosulphate solution. Repeat without addition of the glutathione. The amount (x mg) of glutathione in the sample solution is given by $x = 30{\cdot}73\,y(V_1 - V_2)$ where y is the normality of the thiosulphate, V_1 the blank titration and V_2 the test sample titration.

Table 1. Extent of oxidation of glutathione in different buffer and solvent media with excess of chloramine-T

Medium	mmole CAT used / mmole GSH taken
1*N* HCl	4·46
0·1*N* HCl	5·31
pH 1*	5·35
pH 2*	4·85
pH 3†	5·60
pH 4§	5·60
pH 4·5§	5·55
pH 4·9§	5·01
pH 5§	5·01
pH 5·1§	5·01
pH 5·5§	4·63
pH 6§	4·06
pH 7‡	3·85
pH 8‡	3·71
0·1*N* NaOH	3·46

GSH taken = 0·0326 mmole; CAT taken = 1·24 mmole; time = 30 min.

* HCl–KCl buffer.

† Potassium biphthalate–HCl buffer.

§ Sodium acetate–acetic acid buffer.

‡ Borax–boric acid buffer.

Table 2. Estimation of glutathione with CAT, DCT and iodine by direct titration, with a visual end-point*

	Titrant CAT		Titrant DCT		Titrant iodine	
Thiol taken, *mg*	Thiol found, *mg*	Recovery, %	Thiol found, *mg*	Recovery, %	Thiol found, *mg*	Recovery, %
6·38	6·35	99·5	6·35	99·5	6·17	96·7
10·59	10·55	99·6	10·59	100·0	10·36	97·8
14·83	14·87	100·2	14·74	99·4	14·43	97·3
16·94	17·03	100·5	17·04	100·6	16·65	98·3
21·18	21·22	100·2	21·29	100·5	20·74	97·9
25·42	25·42	100·0	25·47	100·2	24·68	97·1
31·77	31·78	100·0	31·77	100·0	30·96	97·5
36·13	36·21	100·2	36·08	99·9	35·54	98·4
42·50	42·45	99·9	42·51	100·0	41·21	97·0
46·75	46·63	99·7	46·76	100·0	45·90	98·1
53·13	52·76	99·3	53·13	100·0	52·07	98·0

* Calculations based on consumption of 1 equivalent of oxidant per mole of GSH.

The back-titration procedure with DCT is not satisfactory, as the reaction is very sluggish and only a 7–8-electron oxidation is obtained even in 1 hr reaction time.

RESULTS AND DISCUSSION

Some typical results of direct titration of GSH with CAT and DCT with a visual end-point are shown in Table 2 and the results of potentiometric titration are given in Table 3. Table 2 also contains results for titration of GSH with 0·01*N* iodine[9] at temperatures below 25°. The present method seems superior to the iodometric method. Furthermore, CAT and DCT are comparatively more stable in solution and the titrations can be done at room temperature.

The direct oxidation of glutathione under the conditions stated involves a 1-electron change which can be represented as follows:

$$2\,GSH + RNClNa \rightarrow GSSG + RNH_2 + NaCl$$

$$4\,GSH + RNCl_2 \rightarrow 2GSSG + RNH_2 + 2HCl$$

where R = p-$CH_3C_6H_4SO_2$

The presence of the disulphide (GSSG) in the reaction products was detected by paper chromatography (R_F = 0·088), with phenol saturated with water as solvent and ninhydrin spray reagent.[15]

Cysteine, methionine and thiourea interfere in the determination, but glutamic acid, leucine, glutamine, serine, glycine, threonine, alanine, valine, proline, arginine, histidine, glucose and urea (~0·05 mmole) do not.

Results for the back-titration method are shown in Table 4. The most probable hydrolytic cleavage of the GSH molecule produces the three amino-acids, glutamic acid, cysteine and glycine, of which only cysteine can react with

Table 3. Estimation of glutathione with CAT and DCT, with a potentiometric end-point

Titrant CAT		Titrant DCT	
Thiol taken, *mg*	Thiol found, *mg*	Thiol taken, *mg*	Thiol found, *mg*
6·35	6·31	6·88	6·91
10·59	10·60	11·65	11·73
16·94	16·91	18·64	18·68
21·18	21·19	23·30	23·35
25·42	25·49	27·96	28·02
31·77	31·55	29·80	29·86
36·00	35·84	34·95	34·93
42·36	42·36	45·84	46·07

Table 4. Estimation of glutathione with excess of CAT by the back-titration procedure

Thiol taken, *mg*	Thiol found, *mg*	Thiol taken, *mg*	Thiol found, *mg*
8·21	8·17	28·46	28·45
11·72	11·65	33·48	33·45
16·42	16·48	36·83	36·93
20·09	20·13	39·65	39·65
24·63	24·67	46·10	46·01

CAT. However, the 10-electron change observed suggests that the oxidation of GSH can be represented as

$$G'.CH_2SH + 5RNClNa + 5H_2O \rightarrow G'CHO + 5RNH_2 + 5NaCl + H_2SO_4$$

where G' = HOOC.CH(NH_2).CH_2.CH_2.CONH—CH(—HOOC.CH_2.HNOC)

Paper chromatography was used to identify the reaction products. Benzyl alcohol saturated with water was used as solvent for detecting the sulphonamide (R_F = 0·091) and 0·5% vanillin in 1% hydrochloric acid in ethanol was the spray reagent. Attempts were made to detect the aldehydic peptide G'CHO with the amino-acid developing solvent and spray reagent.[15] A single spot corresponding to R_F = 0·39 was observed, which shows the absence of the expected hydrolytic cleavage of the two peptide bonds. It could perhaps be taken as evidence for the presence of G'CHO in the reaction products. Similar behaviour has been noted in the oxidation of cysteine[3] with excess of CAT.

Oxidations involving more than a 10-electron change (*cf.* Table 1) could also involve chlorination of the α-methylene group, as observed in the case of thiols.[4]

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2-METHOXYETHANOL AS A SOLVENT FOR CONDUCTOMETRIC ACID–BASE TITRATIONS

GARY A. SCHWARTZ* and BARBARA J. BARKER

Department of Chemistry, Hope College, Holland, Michigan 49423, U.S.A.

(*Received* 13 *November* 1974. *Accepted* 23 *February* 1975)

Although alcohols have frequently been used as non-aqueous media for the determination of acids and bases,[1] there have been few reports of the use of methoxyethanol (methyl cellosolve) as an analytical solvent. Cellosolves often serve as media for organic reactions since they are excellent solvents for a wide range of organic compounds.

One of the most frequently employed methods of acid–base analysis is potentiometric titration; however, the cellosolves are somewhat limited as media for such analyses because they display a relatively narrow potential range. Experimental potentiometric end-points in methoxyethanol are often not well defined.[2] These limitations can be overcome through conductometric titrations which are often used successfully for the analysis of relatively weak acid–base systems. Since there have been no reported

* National Science Foundation Undergraduate Research Participant, Summer 1974.

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* National Science Foundation Undergraduate Research Participant, Summer 1974.

studies of conductometric titrations in the cellosolves and since these relatively inexpensive solvents continue to be used widely as media for chemical reactions, the present conductance analysis of a variety of organic acids in methoxyethanol was undertaken.

EXPERIMENTAL

Reagents

"Distilled-in-glass" 2-methoxyethanol was obtained from Burdick and Jackson Chemical Co. (Muskegon, MI.) Benzoic, phthalic, and salicylic acids and *p*-phenylphenol were recrystallized from aqueous acetone. Adipic acid was recrystallized from water, and barbital from aqueous acetone. Picric, *p*-chlorobenzoic and *p*-hydroxybenzoic acids and 1,3-diphenylguanidine (DPG) were recrystallized from acetone–water, acetone–ether, water, and toluene, respectively. All acids and the diphenylguanidine were ground finely and dried before use.

Apparatus

Titrations were performed at room temperature (approximately 25°) in Sargent model S-29870 conductance cells. The electrodes were adjusted to obtain a cell constant of approximately 0·15 cm^{-1}. Resistances were measured at 1000 Hz on an RC-18 Industrial Instruments conductivity bridge. The titrant was dispensed from a 10-ml burette graduated in 0·05-ml divisions. For some titrations a stream of nitrogen was used as a protective atmosphere. During the titrations the solutions were agitated with a magnetic stirrer.

A Sargent S-84805 thermostatic bath assembly filled with light mineral oil and maintained at a constant temperature of 25·00 ± 0·02° was used in the determination of the equivalent conductances of several acids and of DPG. The conductance cell used for these measurements has been described previously.[3] By the method of Lind, Zwolenik and Fuoss,[4] the cell constant 0·1865 ± 0·0002 cm^{-1} was obtained with aqueous potassium chloride solutions ranging in concentration from 2·5 to 5·0 × $10^{-3}M$.

Procedure

For the titrations an accurately weighed sample of acid (approximately 0·1 g) was transferred to the conductance cell and dissolved in 50·0 ml of methoxyethanol of specific conductance 3–8 × 10^{-7} ohm^{-1} cm^{-1}. After each addition of titrant (0·10M diphenylguanidine), the solution was stirred well and several resistance readings were obtained. The resistance values were verified after reagitation of the solution.

For equivalent conductance measurements, 10·0 ml of an approximately 0·001M stock solution were placed in the conductance cell containing 50·0 ml of solvent. Concentrations were varied by adding successive 10·0-ml portions of pure solvent to the cell. The solution was thoroughly mixed after each addition of solvent. Series resistances for these dilute solutions were calculated from measured parallel resistances.

RESULTS AND DISCUSSION

Organic acids of various types—monoprotic and diprotic carboxylic acids and phenols—were titrated in methoxyethanol. Diphenylguanidine was chosen as the titrant since it is a conveniently recrystallized, stable, standard material which is quite soluble in non-aqueous media. As expected, and as the curvature in the Λ *vs.* $C^{1/2}$ plot (Fig. 1) reveals, diphenylguanidine and the acids are weak electrolytes in methoxyethanol.

As Fig. 2 indicates, the titrations of monoprotic acids in methoxyethanol gave very distinct end-points. The conductance curves have been displaced both horizontally and vertically in order that typical results for all acids investigated may be presented clearly and concisely. Volume corrections were applied to all conductance data from which Figs. 2 and 3 were prepared. Even for *p*-phenylphenol the difference in slope before and after the end-point was sufficient for obtaining an excellent result. The results for duplicate titrations of the acids in methoxyethanol are presented in Table 1.

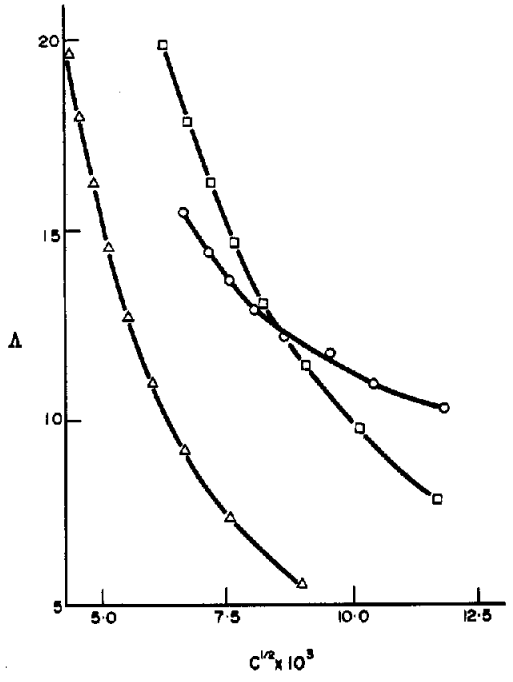

Fig. 1. Λ *vs.* $C^{1/2}$ plots of organic compounds in methoxyethanol. △—*p*-Phenylphenol; ○—*p*-hydroxybenzoic acid; □—1,3-diphenylguanidine.

During some analyses, nitrogen was used as a protective atmosphere over the titration solutions; however, the conductance results were the same as when no nitrogen was used. Although benzoic acid could not be determined successfully by conductometric methods in pyridine, methanol or dimethylformamide media,[5] satisfactory analyses could be performed in t-butyl alcohol[6] as well as in methoxyethanol.

The analysis of several diprotic acids was of interest in order to determine whether multiple end-points could be

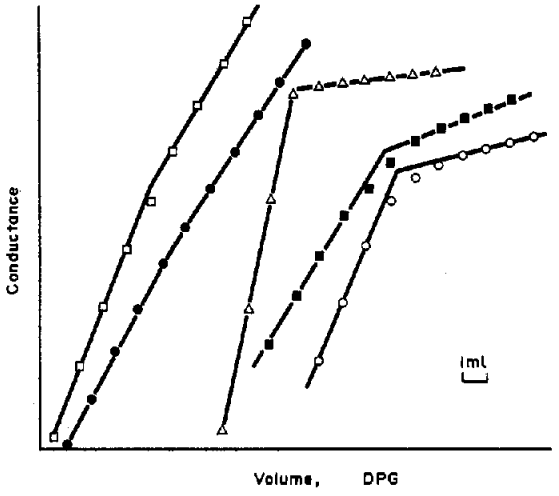

Fig. 2. Conductometric titration curves of organic acids in methoxyethanol. □—Barbital; ●—*p*-phenylphenol; △—picric acid; ■—benzoic acid; ○—*p*-chlorobenzoic acid.

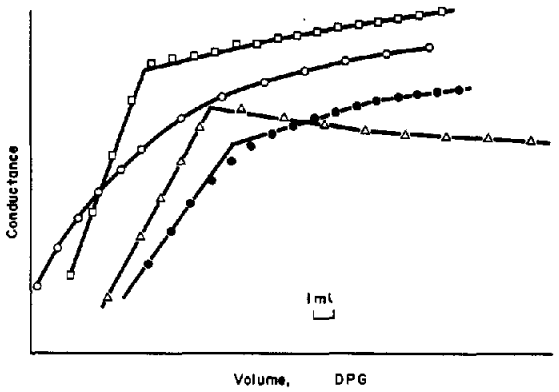

Fig. 3. Conductometric titration curves of organic acids in methoxyethanol. □—Salicylic acid; ○—*p*-hydroxybenzoic acid; △—phthalic acid; ●—adipic acid.

detected in methoxyethanol. Although, as Fig. 3 reveals, "N-shaped" and "chair-shaped" titration curves[7] were not obtained, the results for phthalic and adipic acids generally were quite good in methoxyethanol. The second equivalence point for phthalic acid, however, is more distinct in t-butyl alcohol medium[6] than in methoxyethanol. Although two distinct end-points could be determined for salicylic acid in methoxyethanol, results calculated from these graphical end-points were low. In previous conductometric titrations of salicylic acid in tetramethylguanidine,[8] fairly distinct end-points were obtained but the results were high. Unlike the conductance titrations of *p*-hydroxybenzoic acid in t-butyl alcohol with tetrabutylammonium hydroxide[6] or in dimethylformamide with potassium methoxide,[5] no precipitate formed during the titration of this acid in methyl cellosolve. However, as Fig. 3 indicates, no end-points could be determined conductometrically for *p*-hydroxybenzoic acid in methoxyethanol. The diprotic acids which contain two —COOH groups could be successfully titrated conductometrically in methoxyethanol, but the acids containing one —COOH group and one —OH group could not be determined by this method. The precision of the results is comparable to that generally obtained from titration of organic acids in non-aqueous solvents.[8]

Oxalic acid, which is structurally similar to adipic acid, was also titrated in methoxyethanol. In contrast to titrations in other solvents,[5,6] "N-shaped" conductance curves were not obtained. As in the titration of oxalic acid in dimethylformamide with tetramethylammonium hydroxide,[5] precipitation began after the first equivalence point in methoxyethanol. The conductance then dropped until the second equivalence point was reached, after which it remained almost constant. No satisfactory results could be obtained from the titration plots.

Table 1. Conductometric titrations of organic acids in methoxyethanol

Sample	Taken for analysis, *mmole*	Error in results, %
Benzoic acid	0·9807	+1·1
	0·9856	+1·1
p-Chlorobenzoic acid	0·7051	0
	0·7415	0
Picric acid	0·4678	−2·9
	0·6267	0
p-Phenylphenol	0·8847	+0·5
	0·7067	+1·0
Barbital	0·6971	−1·7
	0·6319	−3·1
Phthalic acid	0·7710	+0·4* −0·4†
	0·7030	−1·5* +3·9†
Adipic acid	0·9415	0* +0·6†
	0·8813	−0·1* −0·8†

* From first equivalence point.
† From second equivalence point.

In this investigation 2-methoxyethanol has been shown to be a useful solvent for conductometric titrations of a wide variety of acidic compounds. The conductometric analysis of monoprotic acid mixtures would be of interest in future studies.

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Summary—Conductometric titrations of a series of organic acids in 2-methoxyethanol were performed with 1,3-diphenylguanidine (DPG) as titrant. For benzoic, *p*-chlorobenzoic and picric acids, phenylphenol and barbital, excellent recoveries were obtained from well-defined conductance *vs.* volume plots. Results for the dicarboxylic phthalic and adipic acids were also good. However, the titration curves for the difunctional salicylic and *p*-hydroxybenzoic acids were not clearly defined. The results are discussed and compared with conductometric titrations of acids in other non-aqueous solvents. Several determinations of electrolyte conductance as a function of concentration revealed that, as expected, the selected substances are weak electrolytes in methoxyethanol.

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SPECTROPHOTOMETRIC DETERMINATION OF SILICON IN FERROPHOSPHORUS

K. A. BROOKING and C. B. BELCHER

The Broken Hill Proprietary Co. Ltd., Central Research Laboratories, Shortland, N.S.W., 2307, Australia

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Summary—A method is described for the spectrophotometric determination of 0–4% silicon in ferrophosphorus, following fusion with sodium peroxide in a zirconium crucible. Silicomolybdic acid is formed with sodium molybdate. The acidity is increased to 2*N* and the solution stood for 10 min to destroy phosphomolybdic and arsenomolybdic acids. The silicomolybdic acid is reduced with ascorbic acid and the absorbance measured at 810 nm. The colour is stable, and a standard deviation of 0·006% was achieved for 0·7% silicon. Results obtained for three samples with alternative procedures are compared.

Phosphorus in minor amounts has a significantly deleterious influence on the properties of steel and a low concentration ($\neq$0·05%) is usually specified. However, higher additions (0·05–0·30%) of phosphorus are used to achieve significant hardening effects[1] with steel and to increase the fluidity of iron.[1] The silicon content of ferrophosphorus is controlled in order to prevent a contrary influence to that of phosphorus on these properties.

A long-established technique[2] for the determination of silicon in ferrophosphorus uses dissolution in nitric acid and dehydration by fuming with perchloric acid; however, alkali metal salts and phosphorus pentoxide adsorbed on the crude silica can volatilize along with the hydrofluosilicic acid in the final steps of the determination. The present authors earlier adapted an ISO steel method for the gravimetric determination of total silicon,[3] using dissolution with hydrochloric–nitric acid mixture and an increased volume of perchloric acid to avoid adsorption of salts on the crude silica; satisfactory results were obtained. However, gravimetric methods are tedious and not suitable for samples containing tungsten, tantalum, niobium, zirconium, titanium or molybdenum. Yelinek *et al.*[4] determined silicon in ferrophosphorus by X-ray fluorescence; the sample was fused at 1100° with La_2O_3 and $Li_2B_4O_7$ in the ratio 1:1:8 (sample:La_2O_3:$Li_2B_4O_7$). The fused bead was ground together with an inert binder, pressed into a pellet and backed with cellulose; a range of 0–10% Si (standard deviation 0·10%) was covered, but the overall accuracy was strongly dependent upon the method of sample preparation.

Accordingly a spectrophotometric determination was sought and developed. The determination of silicon by formation of the yellow silicomolybdic acid and reduction to the blue species is well established.[5,6] Phosphorus and arsenic respectively form phosphomolybdic and arsenomolybdic acids, and if not destroyed interfere by reduction to the blue species; destruction is achieved normally through the use of selective masking agents such as oxalic acid,[6] increase in the acidity after formation of silicomolybdic acid[6,7] or selective extractants such as ethyl acetate.[8] However, these variants are not designed to cope with such massive concentrations of phosphorus as encountered in the determination of silicon in ferrophosphorus, where P:Si ratios of 100:1 are not abnormal.

EXPERIMENTAL

Solutions and reagents

Silicon standard solution. Fuse 1·0696 g of pure silicon dioxide, (previously ignited at 1000°) with 8 g of sodium carbonate in a platinum crucible at 1050° for 30 min, extract with water and filter before dilution to 500 ml; 1 ml contains 1·000 mg of silicon. Dilute an aliquot with water to give a 10-μg/ml solution.

Other reagents. Sodium peroxide, dry and powdered; pure iron powder; potassium dihydrogen phosphate; boric acid; concentrated hydrochloric acid; 25% w/v manganese sulphate solution; 3·6% w/v potassium permanganate solution; 0·3% w/v hydrogen peroxide solution; 0·6*N* sulphuric acid; sodium molybdate; oxalic acid; ascorbic acid.

Recommended procedure

Weigh 100 mg of ferrophosphorus (76 μm particle size) into a 45-ml zirconium crucible containing 1·00 g of sodium peroxide and 20 mg of boric acid. Also prepare a blank for the calibration series by using 60 mg of iron sponge and 110 mg of potassium dihydrogen phosphate; this approximates to 60% Fe, 25% P and can be varied for differing alloy compositions. Stir carefully with a clean platinum wire to mix the sample and sodium peroxide. Cover with a layer of sodium peroxide (0·50 g), fuse for 10 min at 550°, quench the crucible, and when cool extract the melt with $\neq$20 ml of water. cool, add 5·0 ml of concentrated hydrochloric acid, stir with a plastic rod to ensure dissolution of soluble hydroxides and phosphates, and add 1 drop of 25% w/v manganese sulphate solution. Filter to remove insoluble zirconium phosphate. Extract the residual contents of the crucible with 13 ml of hydrochloric acid (1 + 4), scrubbing and boiling to recover soluble material, and wash into the filter with water. Wash the filter paper, destroy excess of peroxide by dropwise additions of 3·6% w/v potassium permanganate solution until

a pink colour is produced, stand for 1 min, and just decolorize with 0·3% w/v hydrogen peroxide. Dilute to volume in a 100-ml graduated flask.

Transfer two aliquots (0–1% Si, 10 ml; 0·5–2% Si, 5 ml; 1–4% Si, 2·5 ml) to 50-ml graduated flasks, and add respectively 0, 3·5 or 5·0 ml of 0·6*N* sulphuric acid. Prepare a calibration series by adding appropriate volumes of 10-μg/ml silicon solution to aliquots of the blank solution.

At 15–25°, using polypropylene pipettes, and mixing after each reagent addition, treat as follows.

Assays. Add 10 ml of 5·0% w/v sodium molybdate–0·75% v/v sulphuric acid solution, swirling during the addition. Allow to stand for 20 ± 1 min. Add 7·5 ml of 25% v/v sulphuric acid, swirl and let stand for 10 ± 1 min. Add 5 ml of 5% w/v oxalic acid solution, and 5 ml of 2% w/v ascorbic acid solution.

Blanks. Add 7·5 ml of 25% v/v sulphuric acid, 5 ml of 5% w/v oxalic acid solution, 10 ml of 5·0% w/v sodium molybdate–0·75% v/v sulphuric acid solution and 5 ml of 2% w/v ascorbic acid solution.

Immediately dilute assays and blanks to volume and let stand for 30 min. The colour is stable. Measure the absorbance at 810 nm, using 10-mm cells.

RESULTS AND DISCUSSION

Sodium peroxide[9] in conjunction with a zirconium crucible is a powerful flux and oxidant which decomposes most materials. The determination of silicon as reduced silicomolybdic acid after sodium peroxide fusion is well established.[5,6] An Australian Standard[6] for the determination of silicon in iron and steel uses the reduced silicomolybdic acid procedure which yields a stable colour free from interferences; the use of ascorbic acid is a significant factor in achieving colour stability, and the potential interference of phosphorus and arsenic is controlled through the use of oxalic acid and by increased acidity after the formation of silicomolybdic acid. Boric acid is used in the fusion to prevent attack on the glassware by any fluoride present. The small amount of granular zirconium phosphate formed by reaction between zirconium extracted from the crucible and phosphate ions can be simply removed by filtration.

The Mo/Si ratio of 975/1 (w/w) at the maximum silicon concentration allowed by the Standard[6] was a compromise aimed at avoiding the formation of non-specific molybdenum blue, but providing sufficient molybdate to obtain conformance to Beer's law and achieve stable colour development within a suitable elapsed time. Greenfield's procedure[7] for silicon in phosphate rock used an Mo/Si ratio of 1620/1 at the maximum silicon concentration of 5%, and the method was applied in the presence of 30% P (ratio P/Si of 6/1). Increased standing time (10 min) and acidity (2·5*N*), after formation of silicomolybdic acid allowed more complete destruction of phosphomolybdic acid. However, the colour was not stable and the method was only applicable in the presence of small amounts of iron oxide.

The relevant literature may be summarized as follows. Phosphomolybdic acid[10] starts to decompose at a sulphuric acid concentration of 1·1*N*, and completely decomposes at 3*N*, and Jean[11] states that a final acidity of 2*N* sulphuric acid is optimal; silicomolybdic acid, after formation in the range 1×10^{-4}–$1 \times 10^{-1}N$ sulphuric acid, can be reduced to the blue species in the range 1×10^{-4}–4*N* sulphuric acid.[11,12] Oxalic acid forms a complex ($MoO_3.C_2O_4H_2$) with molydate, which is more stable than the heteropoly acids but is formed very much more rapidly from phosphomolybdic and arsenomolybdic acids than from silicomolybdic acid, which is kinetically stabilized.[13]

The present requirement was for a procedure which would yield similar precision and accuracy to corresponding methods for the spectrophotometric determination of silicon in steel and which could cope with a P/Si ratio of ≮40/1 at the maximum silicon concentration. Since iron also reacts with molybdate ions, it was considered that a modern Standard method[6] which was applicable to steel would provide the best starting point for developing a method for silicon in ferrophosphorus, wherein the concentrations could be expected to vary as follows: iron 60–80%, phosphorus 20–40% and silicon 0·1–4%. Obviously increased molybdate concentration would be required to ensure complete formation of silicomolybdic acid, because of increased molybdate consumption by phosphate ions. Consequently an increased acid addition with extra standing time[7] would be required to overcome the increased buffer action of molybdate and to destroy phosphomolybdic acid.

Initial studies were confined to three silicon levels in the lowest silicon range (0–1%) where P/Si could rise to 40/1 at 1% silicon. Matrix experiments indicated that potentially suitable conditions for quantitative determinations[6] could be defined with a twofold increase in molybdate concentration and 1·5-fold increase in sulphuric acid concentration, and the use of at least a 5-min standing time with sulphuric acid. Lower molybdate concentrations gave incomplete development of the silicomolybdic acid, whereas significantly higher concentrations caused the development of non-specific molybdenum blue species. With respect to increasing sulphuric acid concentrations, increased standing time was more effective than acidity increases; excessive increase in sulphuric acid concentration caused deviations from Beer's law.

When optimum conditions had been chosen, a series of investigations was carried out at 20° to determine the extent to which calibration standards must be matched to the assays. Test solutions with varying Fe, P and Si concentrations and stood for various times at increased acidity after formation of silicomolybdic acid, were evaluated for consistency of absorbance. The results are presented in Table 1 and show that the amount of phosphomolybdic acid reduced to molybdenum blue decreases significantly even with only 5 min standing at increased acidity. A more stable and reliable result is obtained after 10 min standing and no significant benefits are obtained from further standing. The procedure outlined can accommodate up to 40% phosphorus for the range 0–1·0% silicon. Results of a similar set of tests at 15° showed no significant deviation from those obtained at 20°.

Table 1. The effect of variation in significant parameters on absorbance of reduced silicomolybdic acid at 20°

Standing time with $2N$ H_2SO_4, *min*	P, %	Fe, %	Si, % Si, *μg/ml*	Absorbance (810 *nm*, 10-*mm* cell) 0 0	0 5 1	1 0 2
10	20	20		0·046	0 831	1·592
10	20	40		0 038	0·821	1 584
10	20	60		0 040	0·818	1·578
10	0	40		0 058	0 830	1 592
10	20	40		0·038	0·821	1 584
10	40	40		0·036	0 818	1·577
0	25	60		0 169	0 967	1 754
5	25	60		0·024	0 807	1 584
10	25	60		0·032	0 812	1 590
15	25	60		0·031	0·805	1·593

Table 2. Comparative silicon results achieved with ferrophosphorus samples

Sample	Si, % Lab. 1	Lab. 2	Lab. 3
AIS 1	0·545	0·537	0·550 (0·006)
AIS 2	3·13	n.d.	3·136 (0·002)
NBS 90a	n.d.	n.d.	0·688 (0·006)

Laboratory 1—Na_2CO_3/Na_2O_2 fusion, $HClO_4$ dehydration, SiO_2 volatilization, gravimetric determination.

Laboratory 2—HCl/HNO_3 solution, $HClO_4$ dehydration, SiO_2 volatilization, gravimetric determination.

Laboratory 3—Recommended procedure; the means and standard deviation (in parentheses) refer to 6 results.

AIS—Australian Iron and Steel Limited.

n.d.—not determined.

The results show no major interference effects from the varying iron or phosphorus concentrations; precise results can be obtained by matching calibration standards and assays to within 20% absolute.

A standard ferrophosphorus sample with a certified silicon result is not available. The US Bureau of Standards ferrophosphorus NBS 90a was analysed together with two ferrophosphorus samples (Australian Iron and Steel Ltd.) having high and low silicon contents. A comparison of results between three laboratories using the recommended procedure and gravimetric techniques is outlined in Table 2.

The results show that reproducibility and accuracy are satisfactory, thereby confirming the validity of the proposed procedure.

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METAL ION INTERACTIONS OF PICOLINE-2-ALDEHYDE THIOSEMICARBAZONE

D. J. LEGGETT and W. A. E. MCBRYDE

Department of Chemistry, University of Waterloo, Waterloo, Ontario, Canada N2L 3G1

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Summary—The reactions of picoline-2-aldehyde thiosemicarbazone (PATS) with silver, mercury, iron(II) and cobalt have been investigated in various environments. The compositions of the complexes have been investigated by continuous variation and molar ratio methods. Stability constants have been evaluated by means of SCOGS and a new program SQUAD. The formation constants, measured at 25° and 0·10*M* ionic strength were as follows: Ag(PATS), $\log \beta_{101} = 13{\cdot}40$; HgH(PATS), $\log \beta_{1110} = 23{\cdot}6$; $HgH_2(PATS)_2$, $\log \beta_{1220} = 42{\cdot}1$; $HgH_2(PATS)(EDTA)$, $\log \beta_{1211} = 44{\cdot}0$; $FeH_3(PATS)_3$, $\log \beta_{133} = 44{\cdot}9$; $FeH_2(PATS)_3$, $\log \beta_{123} = 41{\cdot}7$; $FeH(PATS)_3$, $\log \beta_{113} = 38{\cdot}4$; $Fe(PATS)_3$, $\log \beta_{103} = 34{\cdot}2$. A tentative value for a cobalt complex is also suggested. A computer program, suitable for calculation of optimum conditions for a chemical analysis is also introduced and its use is illustrated for the silver–PATS–EDTA system.

Reagents for the determination of metal ions must be both selective and sensitive. The first condition implies that the complex between the reagent and the metal of interest must be appreciably more stable than any other complexes containing the reagent and interfering metal ions. Frequently this condition is only partially fulfilled and in these instances the interfering ions must be excluded from reaction with the reagent. This is normally achieved by employing a masking reagent or by the physical removal of the metal ion by precipitation or extraction techniques.

The choice of a suitable masking reagent is governed by its ability to complex with only the interfering cations whilst forming no (or weak) complexes with the cation of interest. Perrin[1] and Ringbom[2] give calculation procedures, aided by suitable approximations, for evaluation of a particular masking reagent in a given environment. We have adapted a computer program SPECON based on COMICS[3] requiring only a knowledge of the relevant stability constants and solution composition, and capable of producing profiles for the pH-dependence of all species in solution. This enables the choice of working pH, ideal masking reagent concentration, maximum limits of interference, *etc.*, to be made quickly, as well as providing detailed knowledge of the composition of the solution as a function of pH*. Alternatively the correct masking reagent may be empirically sought but this is a time-consuming process. This latter approach was employed by one of us (D.J.L.) during the evaluation of picoline-2-aldehyde thiosemicarbazone (PATS) as an analytical reagent for silver.[4] At that time it was shown that whilst EDTA was a suitable masking reagent, four out of 21 cations tested showed some interference. Other workers have reported the use of PATS as an analytical reagent for iron(III),[5] nickel and copper(II).[6]

This publication deals in detail with reactions of PATS and silver (in an excess of EDTA) and also those with mercury(II), iron(II) and cobalt, and the determination of relevant stability constants.

The spectrophotometric and potentiometric determination of the pK_a's of PATS in various ionic media has been previously reported.[7] We also illustrate the use of SPECON in evaluating the effective working range of a reagent in a given environment.

EXPERIMENTAL

Apparatus and reagents

Only Class A volumetric glassware was used, and all transfer pipettes were calibrated. All relevant details of reagents and apparatus have been previously reported.[7]

Procedures

Silver–PATS–EDTA system. The stoichiometry of the reactions was studied spectrophotometrically by continuous-variations and molar-ratio measurements at pH 5·49 in an acetic acid–sodium acetate buffer of ionic strength 0·1*M*. Stock solutions ($1{\cdot}00 \times 10^{-3}M$) of silver and PATS were prepared and diluted appropriately. The spectrally measured solutions all contained a hundredfold excess of EDTA. These conditions were employed to duplicate those of the analytical procedure[4] as closely as possible.

The stability constants were determined spectrophotometrically. First the method of proportional absorbances[8] was used to give values of the stability constants for the major species. Five sets of solutions were prepared, each set consisting of two pairs of solutions such that the total silver and PATS concentrations of one were double those of the other. The pH in each set was fixed by means of acetate buffers to cover the pH range 5·36–7·41.

A second evaluation of the stability constants was performed in the following manner. Ten solutions were prepared with various concentration ratios $C_{Ag}:C_{PATS}$ and

* The listing and implementation details of this and other programs alluded to in the text are available from the authors upon request.

covering the C_{Ag} range from $1{\cdot}0 \times 10^{-5}M$ to $4{\cdot}0 \times 10^{-5}M$. All solutions contained a hundredfold excess of EDTA, and were prepared in a potassium nitrate background contrived to maintain the ionic strength at $0{\cdot}100M$. The absorbances were measured over the range 260–390 nm, and the results digitized at 5·0 nm intervals and then processed by the computer program SQUAD,[9] to find best-fit values of molar absorptivities and stability constants of all postulated species formed in solution. All such programs require a reasonably good estimate of the constant(s) sought, and in this case such an estimate was forthcoming from the method of proportional absorbances. Other input required for SQUAD includes values of relevant pK_a's and stability constants together with any known molar absorptivities. For this study the pK_a and ϵ values of PATS had been determined spectrophotometrically,[7] and the published pK_a values[10] for EDTA were used. The equilibrium constants for the reaction between silver and EDTA were redetermined as part of this investigation and found to be in agreement with Wikberg's values.[10]

Mercury (II)–PATS–EDTA system. The stoichiometry of these complexes was determined by continuous-variation and molar-ratio methods. The particulars of these are outlined in Table 2. In all experiments the ionic strength was maintained at $0{\cdot}10M$, and the pH controlled by a hexamine–sodium perchlorate–perchloric acid buffer.

Stability constants for the indicated complexes were determined spectrophotometrically, the data being processed by SQUAD. The solutions prepared for spectral measurement included all combinations of the following concentrations:

C_{Hg}	C_{PATS}	C_{EDTA}	
2·00	1·93	2·06	$\times 10^{-5}M$
4·00	3·86	4·12	

Iron (II)–PATS–ascorbic acid and cobalt–PATS systems. To prevent oxidation of iron(II) to iron(III) by PATS, Pino *et al.*[5] have suggested the inclusion of ascorbic acid in the solutions. The kinetics of the iron(II)–PATS reaction in the presence and absence of ascorbic acid were studied in the following manner. The absorbance of a solution containing iron(II) and PATS was determined as a function of time until no further change was observed. This was repeated for a solution containing ascorbic acid. The data were plotted in the conventional first and second order modes. This investigation, together with continuous-variation and molar-ratio studies, was performed in solutions of ionic strength $0{\cdot}1M$ and maintained at pH 5·86 with an α-picoline buffer.

These latter two techniques, when used to investigate the stoichiometry of the cobalt–PATS reaction, were performed at two different pH's. Sodium acetate–acetic acid and potassium nitrate–nitric acid gave pH 5·53 and pH 2·57 respectively, $0{\cdot}1M$ ionic strength being maintained for all studies.

Stability constants for each system were evaluated potentiometrically and spectrophotometrically. The programs SCOGS[11] and SQUAD were used to process the data, obtained from suitable solutions of ionic strength $0{\cdot}1M$ (potassium chloride).

Proportional absorbances—an extension

The method of determining equilibrium constants from spectrophotometric data and associated with the term proportional absorbances was developed by Buděšínský.[8] It involves evaluation of a quantity designated X_{mn} from experimental observations of pairs of solutions. This quantity in turn leads to a value of a functionally related quantity y that allows calculation of the conditional stability constant K_{mn} by means of equation (1):

$$\log K_{mn} = n\log(m/n) - \log y + (1 - m - n)\log C_M \quad (1)$$

Buděšínský provided tables of corresponding values of X_{mn} and log y, and graphical representations of the functions of $y(z_{mn})$ and $y(z^*_{mn})$. However, the tabulated values (X_{mn}, log y) can only lead to approximate values of log y. A direct equation linking these parameters was sought.

A quantity k is defined, such that

$$K = (a.X_{mn})^{1-m-n} \quad (2)$$

where a is the ratio of the concentrations of a reactant in the pairs of solutions.

Recalling the relevant equations from reference 8, we have

$$X_{mn} = Z_{mn}/Z^*_{mn} \quad (3)$$

$$Z^{-1}_{mn}.(1 - m\,Z_{mn})^{m+n} = a^{1-m-n}.Z^{*-1}_{nn}.(1 - mZ^*_{mn})^{m+n} = y \quad (4)$$

where Z and Z^* are the ratios of maximum concentration of complex to concentration of a reactant in the pairs of solutions. Substituting equation (2) into equation (4), and then eliminating Z^*_{mn} from the resultant expression and equation (3), we get

$$Z_{mn} = (X_{mn}.k^{1/(m+n)} - 1)/m(k^{1/(m+n)} - 1) \quad (5)$$

and thus Z_{mn} is now expressed in terms of determined quantities. If the logarithm of equation (4) is taken, log y can be evaluated from X_{mn} by utilizing (4) and (5):

$$\log y = (m + n).\log(1 - mZ_{mn}) - \log Z_{mn}$$

RESULTS AND DISCUSSION

Silver–PATS–EDTA system

Since preliminary experiments had disclosed some instability among the solutions of (Ag + PATS) prepared for continuous-variation analysis, all solutions eventually prepared for spectral measurement contained an excess of EDTA. The occurrence of a single maximum in the excess absorbance in the continuous-variation measurements and of a single change in slope in the molar-ratio experiments indicated the formation of a single complex species $Ag_mH_jL_n$ (L = PATS) with $m/n = 1$. Because of solubility problems, evaluation of its stability constant had to be performed spectrophotometrically.

By definition, the equilibrium constant found by the method of proportional absorbances is a conditional constant K_{11} and requires conversion into the true stability constant β_{1j1} as follows:

$$K_{11}.\alpha_{Ag}.\alpha_L = \beta_{1j1}.[H]^j$$

where

$$\alpha_{Ag} = (C_{Ag} - [AgH_jL])/[Ag]$$
$$= ([AgY] + [AgHY] + [Ag])/[Ag]$$
$$= 1 + [Y](\beta^1_{101} + \beta^1_{111}.[H])$$

β^1 refering to Ag–EDTA species (Y ≡ EDTA). Provided $C_Y \gg C_{Ag}$, $[Y] = C_Y/\alpha_Y$, where

$$\alpha_Y = \sum_{q=0}^{Q} \beta^0_q[H]^q,$$

with β^0_q = qth cumulative proton association constant for Y.

$$\alpha_L = \sum_{r=0}^{R} \beta^0_r[H]^r$$

has the same significance for L.

These α quantities can all be evaluated for the conditions and overall concentrations occurring in any chosen solution. Values of log K_{mn} + log α_{Ag} + log α_L were calculated, and proved to be constant over the range of pH in which measurements were made. This implies that $j = 0$, and the value of log β_{101} is thus determined. The results are shown in Table 1. Proportional absorbances also allow the possibility $m = n = 2$ to be tested. These integers were substituted into equation (5) but gave widely varying final values for log β_{2j2}, thus suggesting that $m = n = 1$.

This value for log β_{101} (the initial guess), together with other invariant parameters previously specified, was used with SQUAD to obtain a refined value of log β_{101} that best corresponded to the spectral data. Convergence and satisfactory refinement were rapidly achieved.

When $Ag_2(PATS)_2$, AgH(PATS) or Ag(EDTA)(PATS) were tried as alternative or additional species, indications of non-convergence were noted, *viz.*, negative molar absorptivities for a complex, or attempted location of the pit in negative regions of space. It should be noted that these species had already been shown to be unlikely, by the method of proportional absorbances, but this procedure is only applicable to one major species and could be misleading if experimental conditions are not conducive to this requirement. One combination of species that did give convergence and values of stability constants was Ag(PATS) + AgH(PATS). However, this possibility was discounted for two reasons. First, the values for log β_{101} were about 5 logarithmic units different from the initial guess, and the value of (log β_{101} − log β_{111}) indicated that protonation occurred at pH < 1. Such a process was not compatible with the experimental data, which covered the range pH 5·2–6·2. Secondly, if the spectral data for any one of the ten solutions were removed, the resulting values of log β_{111} were several logarithmic units different. But if the same procedure was adopted for the original, successful model of Ag(PATS) alone, the resultant changes in log β_{101} were less than 0·03. Consequently the evidence for the protonated species was considered unconvincing.

The final value for log β_{101} for the silver–PATS system in the presence of EDTA is 13·40 ± 0·05 [standard deviation in absorbance (SDAB) = 0·008]. This value compares satisfactorily with that determined by the method of proportional absorbances, given that two different background electrolytes were used. The spectrum of Ag(PATS) is shown in Fig. 1, while Fig. 2 indicates the goodness of fit for five of the ten spectra, comparing observed data and those calculated from the refined constant and calculated molar absorptivity.

Table 1. Stability constants for Ag–PATS–EDTA by proportional absorbances

pH	log K_{11}	log $\alpha_{Ag(Y)}$	log $\alpha_{H(PATS)}$	log β_{101}
5.25_7	6.43_4	1.12_3	5.77_5	13.33
5.50_4	6.36_6	1.32_6	5.52_1	13.21
5.78_0	6.50_7	1.53_4	5.24_3	13.28
6.03_6	6.50_6	1.70_4	4.98_4	13.19
6.23_8	6.70_3	1.81_9	4.72_2	13.30
		Average log β_{101} = 13·27 ± 0·15		

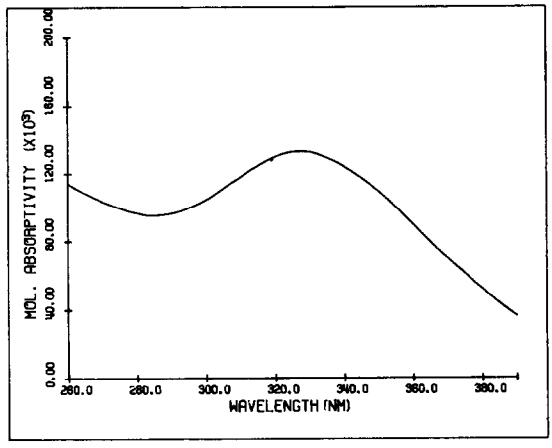

Fig. 1. Computed spectrum of Ag(PATS).

Mercury(II)–PATS–EDTA system

Interpretation of the results summarized in Table 3 proved difficult. Horizontal shifts of the position of maxima in the excess absorbance must signify the presence of more than one major species. Only in a few favourable instances, where supplementary information about the chemical system has been utilized, has it proved possible to interpret continuous-variation observations in terms of more than one principal species formed.[12] For this present system such information was not available; however, some inferences could be drawn from the data.

The observations in Table 2 admit the possibility that two complexes of the type HgH_j(PATS) and $HgH_k(PATS)_2$ are formed, as well as a mixed complex HgH_i (PATS)(EDTA). Further spectrophotometric measurements were therefore made at specific stoichiometric ratios of C_{Hg}:C_{PATS}:C_{EDTA}, and are summarized in Table 3.

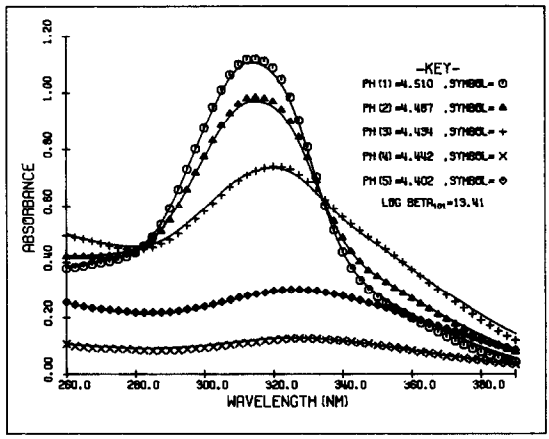

Fig. 2. Experimental (symbols) and computed (solid line) spectra at various acidities.

Table 2. Summary of conditions and observations of (*A*) continuous-variation and (*B*) molar-ratio methods for mercury–PATS–EDTA

A	*Continuous variation*		
Component A	Component B	Other variables	Observation‡ (Ratio Hg:PATS)
Mercury(II)*	PATS	No EDTA pH = 2·27	1:2 at 360 nm; tendency for 1:1 at < 330 nm
Mercury(II)*	PATS	100-fold excess of EDTA pH = 2·18	Strongly indicative of 1:1 only from 310 to 370 nm
Mercury(II) + PATS†	EDTA	pH = 2·20	Strongly indicative of 1:1 only from 310 to 370 nm
Mercury(II) + EDTA§	PATS	pH = 2·18	Indicative of 1:2 at 360 and 370 nm; similarly for 1:1 at < 330 nm
B	*Molar ratio*¶		
$4{\cdot}0 \times 10^{-5}M$ PATS + $4{\cdot}0 \times 10^{-5}M$ EDTA	Mercury(II)	pH = 1·90	Severe slope changes at $C_{Hg}:C_{PATS}:C_{EDTA}$ = 1:1:1 and 2:1:1 at < 330 nm
$2{\cdot}0 \times 10^{-5}M$ EDTA + $2 \times 10^{-5}M$ Hg(II)	PATS	pH = 1·96	Moderate slope changes at 1:1:1 and 1:2:1; only changes for 1:1:1 at < 330 nm
$4 \times 10^{-5}M$ PATS + $2 \times 10^{-5}M$ Hg(II)	EDTA	pH = 1·96	Barely discernible deviation from linearity at 1:2:1; no observable plateau at < 1:2:20
$2{\cdot}0 \times 10^{-5}M$ Hg(II)	PATS	pH = 1·94	Slope changes at 1:1 only at < 320 nm and 1:2 only at < 360 nm

* $C_{Hg} + C_{PATS} = 8{\cdot}40 \times 10^{-5}M$; † $C_{Hg} + C_{PATS} = 8{\cdot}60 \times 10^{-5}M$, $C_{EDTA} = 4{\cdot}30 \times 10^{-5}M$.
§ $C_{Hg} + C_{EDTA} = 8{\cdot}40 \times 10^{-5}M$, $C_{PATS} = 4{\cdot}20 \times 10^{-5}M$; ‡ unless otherwise noted, both methods gave inconclusive curves for measurements at 330–355 nm.
¶ Component A was held at constant concentration and that of B systematically increased.

From all the evidence it is inferred that the order of stability of the presumed complexes is

$$HgH_k(PATS)_2 > HgH_i(PATS)(EDTA) > HgH_j(PATS) \sim HgH(EDTA)$$

That $HgH_k(PATS)_2$ is the most stable complex seems reasonable in view of the observations in group 1, Table 3, and the third experiment in Table 2*B*. The difference in spectrum between (Hg + PATS) alone and in the presence of a 100-fold excess of EDTA

Table 3. Observations on stoichiometrically related mixtures of mercury(II)/PATS/EDTA

Group	Composition Hg	PATS	EDTA	Spectral details λ_{max}, nm	A_{max}	Observation and tentative comment
1	1	2	0	326	0·870	Within exp. error—identical spectra.
	1	2	1	327	0·864	Stability of $HgH_k(PATS)_2$ > Hg–EDTA
	1	2	2	326	0·865	complexes. No effect of EDTA on $C_{Hg}:C_{PATS}$ = 1:2
2	1	1	1	327	0·490	Possibly HgH(PATS)(EDTA)
	1	1	2	327	0·508	since Hg–EDTA complexes do not absorb
	2	1	2	327	0·495	in this region
3	1	1	0	322	0·373	Spectra of HgH(PATS)
	2	1	1	322	0·341	Possibly spectra of $HgH_j(PATS)(EDTA)$ + $HgH_j(PATS)$
4	1	1	0	322	0·373	Indicates spectral perturbation due to
	1	1	1	327	0·490	presence of EDTA at this $C_{Hg}:C_{PATS}$ ratio.
5	2	2	0	320	0·608	As previous grouping
	2	2	1	326	0·830	
6	0	1	0	347	0·480	Reference spectra for comparison of
	0	2	0	347	0·955	complex spectra with those of PATS only
	1	1	1	327	0·490	
	2	2	2	327	0·975	

* 1 implies a nominal concentration of $2 \times 10^{-5}M$; 2 implies $4 \times 10^{-5}M$.

tends to confirm the position of HgH_j(PATS) in the order above. The spectral differences observed in group 3, Table 3, must indicate the presence of a third complex. Stoichiometrically then, two solutions for group 3 are (Hg + PATS) and (Hg + PATS + Hg + EDTA); however, since Hg(EDTA) complexes do not absorb in this region, the noted differences in absorbance are presumably due to the presence of a mixed complex. This postulate is reinforced by the third experiment in Table 2*A*.

There proved to be no easily applicable method for a graphical determination of the relevant stability constants. Certainly the proportional absorbances method is invalid for complexes more stable than HgH(EDTA). Instead, an attempt was made to arrive at plausible values for β_{1j10}, β_{1k20}, and β_{1l11}, which would result in finite concentrations of all these species at pH ~ 2. This required that a choice be made for the integers *i*, *j* and *k*. These were put at 1, 2 and 2 respectively on the basis that at this pH PATS would be in the form H_2L^+, and that complex formation would displace only one proton. The protonated mercury–EDTA complex also predominates at this low pH. Such crude estimated values of the stability constants were then arrived at by trial and error with the aid of SPECON; these were log $\beta_{1110} = 23{\cdot}5$, log $\beta_{1220} = 43$, log $\beta_{1211} = 45$.

Spectrophotometric data corresponding to the solutions listed in Table 3 were used for the PITMAP evaluation. The trial-and-error values of the stability constants were put in to start the cycle of refinement. The invariant constants used were those for PATS determined previously, and literature values for EDTA[13] and mercury–EDTA complexes.[14] Since a complex buffer solution was employed, there was some uncertainty about the conversion of pH measurements into hydrogen-ion concentrations; accordingly the equilibrium constants in this case contain 10^{-pH} as the hydrogen-ion function, and are thus Brønsted constants. However, a simply relationship exists between these and true concentration quotients, β^*, *viz.*

$$\log \beta^*_{1110} = \log \beta_{1110} + \log \Gamma_H$$

$$\log \beta^*_{1220} = \log \beta_{1220} + 2 \log \Gamma_H$$

$$\log \beta^*_{1211} = \log \beta_{1211} + 2 \log \Gamma_H$$

where Γ_H is the experimentally determined[15,16] ratio $10^{-pH}/(H)$ in the hexamine buffer (*ca.* 0·8).

The values of the stability constants determined by SQUAD from the data for eight solutions are

$$\log \beta_{1110} = 23{\cdot}59 \pm 0{\cdot}29 \sim 23{\cdot}6$$

$$\log \beta_{1220} = 42{\cdot}09 \pm 0{\cdot}33 \sim 42{\cdot}1$$

$$\log \beta_{1211} = 43{\cdot}99 \pm 0{\cdot}25 \sim 44{\cdot}0$$

The standard deviations in these constants, though undesirably high, appear to be the almost inevitable consequence of attempting to evaluate equilibrium constants of stable species. In such cases, indirectly fixing the concentration of free metal or free ligand, whichever reactant is not in stoichiometric excess, is difficult both chemically and mathematically.

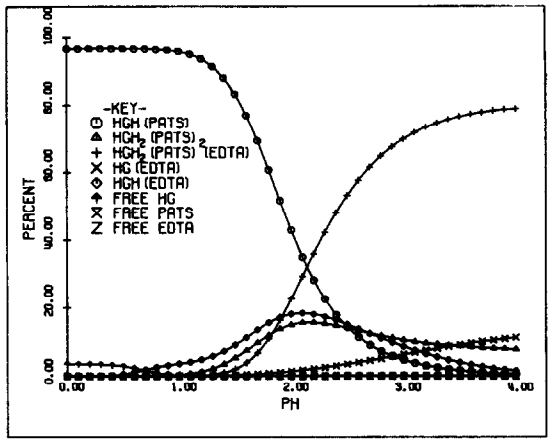

Fig. 3. Species distribution of Hg/PATS/EDTA system. Proton complexes of PATS and EDTA have been omitted for clarity.

The distribution diagram, Fig. 3, indicates that $HgH_2(PATS)_2$ is a minor constituent, but when the data were submitted to PITMAP without this included, typical symptoms of non-convergence rapidly became apparent. The individual spectra of the three postulated species are shown in Fig. 4. The "goodness of fit" between measured and calculated spectra is depicted in Fig. 5; this is probably the most significant criterion for a good or bad description of the experimental observations.

Iron(II)–PATS–ascorbic acid system

Simple kinetic studies on the iron(II)–PATS system confirmed that the presence of ascorbic acid was necessary to maintain the oxidation state of the iron in the PATS complex as +2. The initial purple colour formed on mixing solutions of iron(II) and PATS in the absence of ascorbic acid changed to yellow after about 2 hr and after 4 hr the spectrum of the solution was identical with that obtained by mixing the same concentration of iron(III) with PATS. In the presence

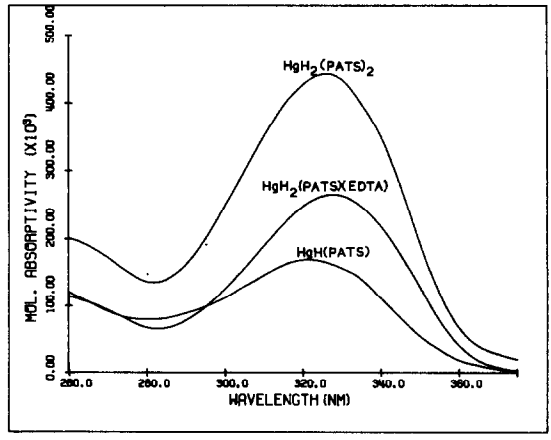

Fig. 4. Computed spectra of HgH(PATS), $HgH_2(PATS)_2$ and HgH_2(PATS)(EDTA).

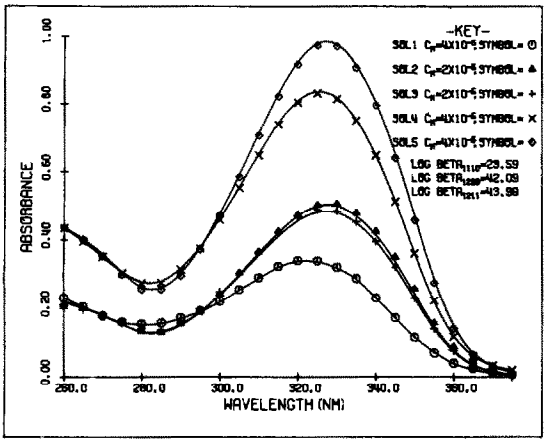

Fig. 5. Experimental (symbols) and computed (solid line) spectra at pH 1·90. Solutions 1, 2 and 3, C_{PATS} = 1·93 × $10^{-5}M$; 4 and 5, C_{PATS} = 3·86 × $10^{-5}M$. Solutions 1, 3 and 4, C_{EDTA} = 2·06 × $10^{-5}M$; 2 and 5, C_{EDTA} = 4·12 × $10^{-5}M$.

of L-ascorbic acid the spectrum of the initial iron(II) complex was stabilized.

The ratio of oxidation of the latter in the absence of ascorbic acid was measured by plotting log $(A_t - A_\infty)$ against time: A_t is the absorbance at time t, A_∞ a steady value after a sufficiently long time. The reaction was thus found to be first order with respect to iron(II) with a rate constant $k_1 = 8{\cdot}34 \times 10^{-4}$ sec^{-1} ($t_{\frac{1}{2}}$ = 832 sec). This conversion was very slow under anaerobic conditions.

Before the study of the reaction of iron(II) and PATS in the presence of ascorbic acid a number of spectral measurements in the ultraviolet were made, of which representative values are shown in Table 4, which appear to indicate no evidence of interaction between ascorbic acid and either of the other substances. The possibility of such interactions was also investigated potentiometrically. The pK_a values of ascorbic acid were determined in 0·1M potassium chloride; solutions containing iron(II) and ascorbic acid were similarly titrated up to pH 4·4 and the observed data processed by the computer program SCOGS. No refinement was possible for any proposed set of iron(II)–ascorbate complexes. However,

Table 5. Ascorbic acid pK_a values

log β_{011}	σ_{011}	log β_{021} ("pK_{a_1}")	σ_{021}	Reference	Medium
11·40$_5$	0·002	15·47 (4·03 ± 0·001)	0·003	This work	0·10M KCl
11·34		(4·04)		17	0·10M KNO_3
11·09		(4·08)		18	2M NaCl
11·14	0·10	(4·08 ± 0·02)		18	2M NaCl

when this set of data was used to calculate pK_a for ascorbic acid (that is, by assuming no iron present) the values generated by SCOGS were within 0·01 of those previously determined. This was construed to indicate that no significant part of the ascorbic acid had reacted with the metal ion.

Since the completion of this work, Williams[19] has reported the existence of a 1:1 complex between iron(II) and ascorbic acid (log β_{101} = 7·09). Calculation of equilibrium constants from this value together with those determined for iron(II) and PATS show that the formation of iron(II) ascorbate is totally suppressed in the presence of the highly stable iron(II)–PATS complexes.

Although reaction between ascorbic acid and PATS seemed unlikely, a check was made by titrating solutions of the two compounds together. The pH-titre data were processed by SCOGS to seek best values of pK_a for each compound. The actual values were:

PATS log β_{011} = 10·89 ± 0·005;
log β_{021} = 14·57 ± 0·006
(*cf.* 10·87; 14·55)[7]

H_2Asc log β_{011} = 11·42 ± 0·008;
log β_{021} = 15·47 ± 0·010
(*cf.* Table 5).

It is obvious that any interaction between the two compounds would have invalidated the mass balances on which these calculations depend, and made such a confirmation of the individual acidity constants impossible.

The stoichiometry of the principal species formed when iron(II) and PATS react was investigated by continuous-variation and molar-ratio methods at pH 5·86. Both techniques gave clear indications of a com-

Table 4. Iron(II)/H_2Asc system: a spectrophotometric study

Soln. No.	Concentration of HCl, $10^{-4}M$	Concentration of Fe(II), $10^{-5}M$	*pH*	Absorbance 350 *nm*	320 *nm*	260 *nm*	245 *nm*
1	20·0	—	2·72	0·018	0·018	0·490	0·857
2	20·0	4·0	2·72	0·018	0·018	0·497	0·861
3	10·0	—	3·00	0·019	0·017	0·772	0·863
4	10·0	4·0	3·00	0·017	0·017	0·770	0·860
5	5·0	—	3·31	0·020	0·018	0·914	0·801
6	5·0	4·0	3·31	0·020	0·016	0·913	0·801
7	—	—	4·40	0·025	0·024	1·025	0·747
8	—	4·0	4·40	0·025	0·024	1·025	0·752
9*	20·0	—	2·72	0·910	0·610	0·855	1·249
10*	—	—	4·40	0·245	1·015	1·323	0·993

Note: All solutions are 1·00 × $10^{-4}M$ in ascorbic acid and 0·10M in potassium chloride.
* Solutions 9 and 10 are 4·008 × $10^{-5}M$ in PATS.

Table 6. Stability constants of iron(II)/PATS/H_2Asc system derived from individual titrations in 0·100M potassium chloride background*†

Run No.	log β_{133}	σ_{133}	log β_{123}	σ_{123}	log β_{113}	σ_{113}	log β_{103}	σ_{103}
1*	$44\,81_4$	0·015	$42\cdot21_6$	0·017	$38\cdot91_6$	0·032	$34\,58_6$	0·171
	$44\,52_6$	0·009	$41\cdot39_8$	0·015	$37\cdot59_4$	0·031	—	—
2*	$45\cdot56_8$	0·044	$41\,47_8$	0·067	$37\cdot87_0$	0·122	$32\,51_3$	1·120
	$44\cdot56_0$	0·010	$41\cdot48_2$	0·010	$37\,81_7$	0·010	—	—
3*	$44\cdot41_6$	0·071	$41\,37_6$	0·033	$37\cdot24_2$	0·068	$33\,37_4$	0·053
	$44\cdot65_9$	0·071	$41\,22_5$	0·071	$37\cdot49_6$	0·065	—	—
4*	$44\cdot67_4$	0·459	$41\,94_4$	0·201	$38\cdot02_5$	0·445	$34\,20_5$	0·217
	$44\,51_7$	0·025	$41\cdot37_1$	0·027	$38\cdot00_1$	0·051	—	—
5	$44\,53_8$	0·017	$40\cdot88_9$	0·062	$37\cdot35_8$	0·053	—	—
6	$45\,53_4$	0·028	$42\cdot10_7$	0·043	$38\,89_1$	0·038	—	—
7	$45\cdot22_1$	0·021	$41\,63_0$	0·066	$38\,44_8$	0·037	—	—
8	$45\,28_0$	0·027	$41\,79_6$	0·052	$38\cdot54_4$	0·040	—	—

* For runs 1–4 the result of both model systems tested are shown.

† The following concentration ranges were used: C_{Fe} = 1·12–20·0 × $10^{-4}M$; C_{PATS} = 7·17–21·3 × $10^{-4}M$; $C_{H_2Asc} = 4C_{Fe}$.

plex $FeH_j(PATS)_3$. The linearity of the plots (not shown) suggested a very stable complex. Further information concerning composition and stability of the complex(es) was sought from pH-titrations. The results could be accommodated with reasonable precision as shown in Table 6, by the formulation $FeH_j(PATS)_3$ with j = 1–3 or possibly j = 0–3. Owing to the limited solubility, titrations could not be carried to pH > 4·0, and since the indicated value of β_{103} corresponds, at pH 3·8, to the occurrence of $Fe(PATS)_3$ as a minor species, its existence is not adequately demonstrated. In any event, the data in Table 6 show that with a single exception (run 3) the experimental titration results are better fitted by assuming 1–3 protons bound in the complex. In a second series of experiments solutions of these complexes were prepared at different pH's and their absorption spectra measured in the visible region and the data were subjected to analysis by SQUAD. Refinement of the data, based on several combinations of protonated species, led to a choice between three possible models, summarized in Table 7.

As we have noted earlier (mercury–PATS–EDTA) the evaluation of very high stability constants is a difficult task. It is rendered more difficult when protenated complexes form, and in this system the situation is further burdened by the ascorbic acid equilibria. Thus

$$C_H - [H] + [OH] = [HL] + 2[H_2L] + [HAsc] + 2[H_2Asc] + [FeHL_3] + 2[FeH_2L_3] + 3[FeH_3L_3] \quad (6)$$

where L stands for PATS. Any uncertainty in the measurement of [H], for instance, will be accompanied by uncertainties in estimating all of the concentrations on the right-hand side of this equation. As this is a necessary step in seeking values of β for the three metal complexes, it is not surprising that estimates of these constants are associated with an appreciable uncertainty. This is apparent from the results in Table 6. This difficulty can be illustrated

Table 7. Stability constants of iron(II)–PATS complexes determined spectrophotometrically

Model	log β_{1j3}	σ_{1j3}	$\sigma_{Absorbance}$
FeH_3L_3*	$45\cdot16_9$	0·016	0·017
FeL_3	$33\cdot90_7$	0·042	
FeH_3L_3	$44\cdot99_7$	0·036	
FeH_2L_3	$41\cdot71_4$	0·065	0·015
FeL_3	$33\cdot63_6$	0·093	
FeH_3L_3	$45\cdot05_3$	0·027	
FeH_2L_3	$41\cdot56_9$	0·035	0·018
$FeHL_3$	$37\cdot40_5$	0·038	

The model FeH_3L_3, FeH_2L_3, $FeHL_3$ and FeL_3 would not refine.

* L = PATS

in another way. An uncertainty of ± 0·005 in Γ_H, corresponding to an uncertainty of ± 0·006 in pH at pH 3·0, leads to profound changes in the values of the stability constants of these metal complexes when the constants are derived from a pH-titration. The following are "best" values for the indicated constants, computed from the data of a particular titration with the value of Γ_H alone being altered.

Γ = 0·868		Γ = 0·858
45·20 ± 0·025	log β_{133}	45·35 ± 0·029
41·75 ± 0·047	log β_{123}	41·84 ± 0·058
38·46 ± 0·039	log β_{113}	38·63 ± 0·042

Even when the utmost precautions are taken with replicate titrations the variation among the derived stability constants is quite large. On this account we did not combine the data from all titrations, and reprocess with SCOGS, as is normal practice, to find mean values of the constants. Instead we have merely calculated the numerical averages of the constants from each titration, and these are: log β_{133} = 44·9; log β_{123} = 41·7; log β_{113} = 38·4; log β_{103} = 34·2 (tentative).

The iron(II)–PATS system, evaluated by spectrophotometry, definitely indicates the presence of a set of protonated species, $FeH_j(PATS)_3$; however values of j again cannot be assigned with certainty. In general, when confronted with conflicting evidence of this nature it is felt that potentiometric results are often more reliable than spectrophotometric.

All least-squares methods are based on the minimization of

$$R = \sum_i (f_{obs} - f_{calc})^2 W_i$$

where f_{obs} and f_{calc} are the observed and calculated quantities for the ith point and W_i is a suitable weighting factor.

The program SCOGS equates the observed titre with f_{obs}, and f_{calc} is obtained from an equation closely related to equation (6), *i.e.*, the stability constants are the only unknown parameters. However, SQUAD derives the calculated absorbance values from Beer's law, *i.e.*, k molar absorbtivities, in addition to the stability constants, are unknown parameters. It therefore seems reasonable to infer that more than one set of

molar absorptivities and stability constants could describe the experimental observations. In practice this situation is not often encountered, since spectrophotometric evaluations produce more data than potentiometry.

The three sets of constants obtained spectrophotometrically (Table 7) exemplify this occasional lack of uniqueness. By analogy with polyprotic acids the third model is more acceptable than the other two. It is significant that this model does not necessarily give the best mathematical description of the system (smallest σ_{DATA}).

Cano Pavon *et al.* have investigated the iron(II) system[5] under the same conditions. We agree with their evaluations of the stoichiometry of the complex $Fe(PATS)_3$, but not with the value quoted for the stability constant. Their calculation methods are only applicable to weak complexes and even if this was the situation, their value would be suspect owing to inherent assumptions concerning their accuracy of measurement. The value reported, $6{\cdot}9 \times 10^{-17}$ for the reaction

$$Fe(PATS)_3 \rightleftharpoons Fe(II) + 3\,PATS$$

cannot be considered as typical of a weak complex and we feel that this determination is therefore of doubtful significance.

Cobalt(II)–PATS system

Both continuous-variation and molar-ratio studies indicated a single complex, $CoH_j(PATS)_2$ existing in the range pH 2·0–5·5. The linearity of these plots suggested that this complex was very stable.

The results obtained from SCOGS and SQUAD reflected, for both techniques, a poor fit to the supplied data, irrespective of model chosen. Potentiometric data indicated the presence of only one protonated complex $CoH_3(PATS)_2$($\log \beta_{132} = 32{\cdot}7$) while spectrophotometric data favoured $CoH_4(PATS)_2$ ($\log \beta_{142} = 36{\cdot}9$). The problems associated with very stable complexes and assessment of the degree of protonation of such complexes are believed to be the principal causes for the uncertainty in the description of this sytem.

It is possible that $CoH_3(PATS)_2$ represents an "average" description of the complexes $CoH_2(PATS)_2 + CoH_4(PATS)_2$ but this model resulted in non-convergence for the potentiometric data. If deprotonation does not cause a change in the chromophore than the spectrophotometric data could only lead to indications of one complex.

The effectiveness of EDTA as a masking reagent

The analytical procedure has been shown to be effective in the range $0{\cdot}0–4{\cdot}0 \times 10^{-5}M$ silver, with use of $8{\cdot}0 \times 10^{-5}M$ PATS in the presence of a 100-fold excess of EDTA (with respect to silver). The extent of interference of the three metal ions was investigated by calculating the degree conversion of silver into Ag(PATS) in the presence of increasing quantities of each metal ion. The results of the calculations, taken at several concentrations of interfering ion are collected in Table 8. They indicate that cobalt and iron(II) do not affect the determination of silver provided the limiting pH's are heeded. However, mercury would cause severe interference. This is to be expected from the high stability of $HgH_2(PATS)_2$ and $HgH_2(PATS)(EDTA)$.

Table 8. Calculated optimum pH ranges for the determination of silver with various degrees of interference

Metal ion	Concentration,* $10^{-4}M$	*pH* range† (for 98% recovery of Ag)
	1·0	4·50–7·0
	3·0	5·63–7·0
Mercury(II)	5·0	5·87–7·0
	7·0	6·13–7·0
	10·0	6·13–7·0
Cobalt(II)	1·0–10·0	3·50–7·50
Iron(II)	1·0–10·0	3·50–7·50

* All solutions are $1{\cdot}0 \times 10^{-4}M$ silver, $2{\cdot}0 \times 10^{-4}M$ PATS, $5{\cdot}0 \times 10^{-3}M$ EDTA.

† The calculations were stopped at pH = 7·0.

CONCLUSION

The systems of complex equilibria reported here are less tractable by either potentiometric or spectrophotometric procedures than the majority of systems hitherto examined. Much of the difficulty with the iron(II) system is due to the problem of correctly assigning the proton balance among the several complexes, the ligand, and the added ascorbic acid. For the cobalt(II) system all evidence points to a remarkably strong complex, or perhaps more than one. Evaluation of formation constants of strong complexes has always been plagued by difficulties in fixing concentrations of the uncomplexed metal or ligand, and evidence presented here suggests a further difficulty due to the complex being non-labile. Hence the equilibrium constants reported are the best values that could be determined by the methods tried, but should be regarded as tentative for the present.

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APPENDIX

Definitions

1. The overall stability constant defines the reaction between free components of the complex to give a particular complex. For instance β_{1211} defines the reaction

$$M + 2H + L + L' \rightleftharpoons MH_2LL'$$

where

$$\beta_{1211} = \frac{[MH_2LL']}{[M][H]^2[L][L']}$$

To avoid the confusion inherent in the meaning of pK_{a1}, pK_{a2}, the overall stability constant notation has been used

to describe the process

$$nH + L \rightleftharpoons H_nL \text{ (charges omitted for clarity)}$$

$$\beta_{0n1} = \frac{[H_nL]}{[H]^n[L]}$$

Hence log β_{011} has the same numerical value as pK_{a2} and log β_{021} is the sum of pK_{a1} and pK_{a2}. This symbolism has been used in the text where specific numbers are quoted. However, the synonym "pK'_as" has been used to denote the collection of log β's related to a particular ligand.

This practice of using overall association constants unifies pK'_as and complex stability constants as well as simplifying the algorithms used in computer programs.

2. Throughout the text, pH is used to denote the pH-meter reading and not the concentration, or activity of hydrogen ions in solution; these latter two quantities are defined as p[H] and pa_H respectively.

List of implicit symbols used in the text and some definitions:

C_M = Analytical concentration of metal ion M (mole/l.)

C_L = Analytical concentration of ligand L (mole/l.)

[x] = Concentration of species x in solution (mole/l.)

β_{pjqr} = Overall stability constant of the complex $M_pH_jL_qL'_r$ formed from one metal and two ligands. Where no confusion arises, $r = 0$ is not included in the subscript when there is not a second ligand.

pK_a = The collection of pK values related to a particular ligand.

Γ_H = pH/[H] determined experimentally.

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PREDICTION OF CONDITIONS FOR USE OF SPECTROPHOTOMETRIC REAGENTS: *p*-DIMETHYLAMINOBENZILIDENERHODANINE AS A SPECTROPHOTOMETRIC REAGENT FOR SILVER AND PALLADIUM

RAHILA BORISSOVA, MARIA KOEVA and ELENA TOPALOVA

Department of Analytical Chemistry, Higher Institute of Chemical Technology, Sofia-56, Bulgaria

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Summary—A method for theoretical estimation of the detection limits of spectrophotometric reagents is reported. The concentration limits of Beer's law when *p*-dimethylaminobenzilidenerhodanine is used for determination of silver and palladium are defined on the basis of the stability constants. Conditions for determination of 2–10 μg of Ag per 25 ml and 1–5 μg of Pd per 25 ml with standard deviation 0·03 μg per 25 ml are proposed.

It is our experience that calibration curves given in the literature cannot always be reproduced. We suppose that this is due to fortuitous choice of conditions which give a linear plot but may also suffer interference from a number of sources. In the present paper we attempt to propose a theoretical estimation of the limits of use of a spectrophotometric reagent, with reference to *p*-dimethylaminobenzilidenerhodanine (DMABR) as a reagent for silver and palladium.

To tell whether a colour reaction can be used for spectrophotometric determination it is necessary to define the conditions under which the determined substance is bound in a single species having a sufficiently high molar absorptivity. Usually this is the highest complex because a large excess of reagent is used so that any absorption by the reagent is virtually constant. If the metal ion (M) forms several complexes with 1,2,...*n* ligands (L) this means that the following condition must be valid:

$$\beta_n[\mathrm{L}]^n \gg 1 + \sum_{i=1}^{n-1} \beta_i[\mathrm{L}]^i \qquad (1)$$

where $\beta_1, \beta_2, \ldots \beta_n$ are the successive overall stability constants. If the ligands take place in protolytic equilibria, then

$$[\mathrm{L}] = \frac{C_\mathrm{L}}{\alpha_{\mathrm{L(H)}}} \qquad (2)$$

where C_L is the total concentration of the reagent, and

$$\alpha_{\mathrm{L(H)}} = 1 + \sum_{i=1}^{n} \beta_i^{\mathrm{H}}[\mathrm{H}^+]^i \qquad (3)$$

the β_i^{H} being the stability constants of the protonated ligand species.

Equation (1) then becomes:

$$\beta_n\left(\frac{C_\mathrm{L}}{\alpha_{\mathrm{L(H)}}}\right)^n \gg 1 + \sum_{i=1}^{n-1} \beta_i\left(\frac{C_\mathrm{L}}{\alpha_{\mathrm{L(H)}}}\right)^i \qquad (4)$$

Equations (1) and (4) make it possible to estimate the conditions for use of the ligand in a spectrophotometric determination. Thus, if (4) holds only at a high pH-value, at which the metal ion is partially hydrolysed in spite of the formation of ML_n, the determination must be carried out in more acidic medium, but leads to poor sensitivity (incomplete formation of ML_n) and bad reproducibility, because small changes in pH can lead to large changes in the degree of formation of ML_n. Further, in a pH-region where $\alpha_{\mathrm{L(H)}}$ depends very much on the pH, small differences in pH between the samples can lead to large errors if some of the ligand species absorb at the wavelength used for measurement.

As seen from (2), the equilibrium concentration of the ligand depends on the total reagent concentration as well as on the pH. Low solubility of the reagent or complex can make a colour reaction unsuitable for analytical purposes, even if the complex is highly stable with a high molar absorptivity and it is possible to use a relatively acidic medium.

To apply these considerations to DMABR, we investigated its protolytic equilibria and its reactions with silver and palladium in 20% v/v aqueous ethanol, which we had found to give clear, not colloidal, solutions.

DMABR was first proposed as an analytical reagent by Feigl.[1] In weakly acidic medium it gives red or red-violet precipitates with Ag(I), Au(III), Pd(II), Cu(I), Hg(I), Hg(II) and Pt(IV).[2–5] It is widely used for separation and spectrophotometric determination of Ag[6–21] and Pd.[20–25] It is also used as a reagent for Au,[20,26] Hg[27] and Pt,[28] for indirect determination of Cl^- and CN^-,[29,30] as an acid–base indicator in acetic acid medium,[31] and in selective resins.[32]

DMABR and its complexes have low solubility in water, which is why factors such as method of mixing,

quantity of reagent and use of protective colloids strongly influence the results. Each author proposes a different set of conditions and this is not caused by differences in the quality of the reagent. We have established that there is no difference in the measured absorbance for complexes formed from DMABR produced by different manufacturers, or recrystallized from ethanol or acetone.

EXPERIMENTAL

Reagents

DMABR solutions, $1{\cdot}25 \times 10^{-4}$ and $6{\cdot}25 \times 10^{-4}M$. Prepared by dissolving the reagent in ethanol, butyl acetate, isoamyl acetate or benzene. The solutions are stable for months.

Silver nitrate solution, $1{\cdot}00 \times 10^{-3}M$. Prepared daily in doubly distilled water.

Palladium(II) solution, $2{\cdot}84 \times 10^{-3}M$. Prepared by dissolving $PdCl_2$ in $1M$ hydrochloric acid, and standardized gravimetrically with dimethylglyoxime.

Buffers, $1M$. HCl/NaCl; $HClO_4/NaClO_4$; sodium acetate at pH 3–6·5; $NaOH/NaClO_4$; NaOH/NaCl.

All reagents used were "*pro analysi*" grade. Only doubly distilled water was used.

Spectrophotometers

A universal VSU-1 (for measuring absorbance at a fixed wavelength); Perkin–Elmer UV-VIS (for absorption spectra); Perkin-Elmer 458 (for infrared spectra).

RESULTS AND DISCUSSION

Protolytic equilibria of DMABR

The acid–base properties of DMABR have been studied before, but not completely. Navrátil and Kotas[33] determined by the extraction method in perchlorate medium, at pH > 4, only the second dissociation constant, $pK_2 = 8{\cdot}20$. They said nothing about the ampholytic nature of the reagent, to be expected by analogy with *p*-diethylaminobenzilidene-

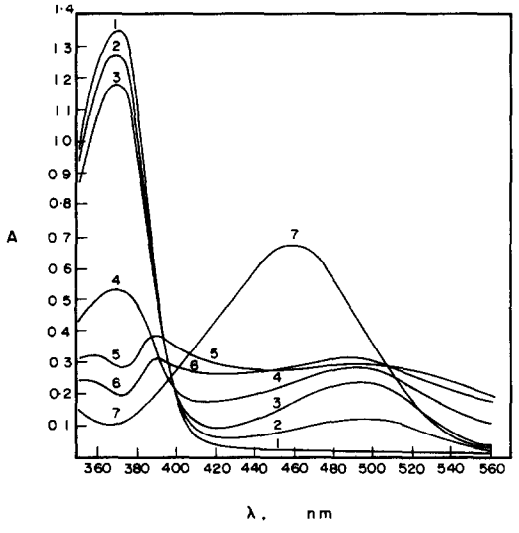


Fig. 1. Absorption spectra; $C_{Rh} = 5{\cdot}0 \times 10^{-6}M$, 4-cm cell, pH: **1**, 0·46; **2**, 1·05; **3**, 1·38; **4**, 1·70; **5**, 2·15; **6**, 2·55; **7**, 8–13.

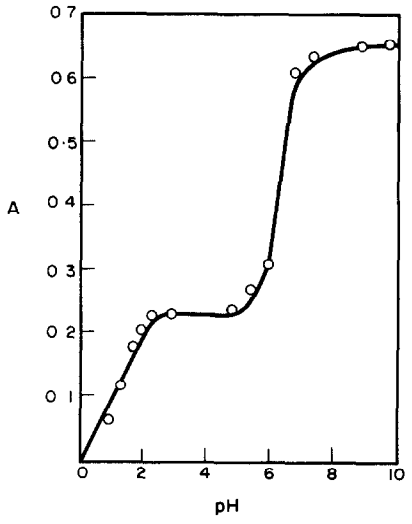


Fig. 2. Absorbance as a function of pH; $C_{Rh} = 1{\cdot}00 \times 10^{-5}M$; 2-cm cell; 460 nm.

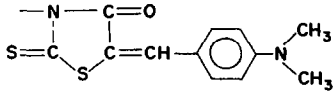
rhodanine,[34] the solubility of DMABR in strong acid medium and the change of the colour from very pale yellow (in strong acidic medium) through pink to yellow in alkaline medium.[35]

From the absorption spectra of DMABR at various pH-values (Fig. 1), the dependence of the absorbance at fixed wavelength on pH (Fig. 2) and the decrease of the distribution ratios (D_{Rh}) in alkaline and acidic media (Fig. 3) it is evident that three species are present, depending on the pH. The equilibria may be written as follows:

$$\text{at pH} > 5{\cdot}5 \qquad R^- + H^+ \overset{\beta_1^H}{\rightleftarrows} RH \qquad (5)$$

$$\text{at pH} < 2{\cdot}0 \qquad RH + H^+ \overset{K_2^H}{\rightleftarrows} RH_2^+ \qquad (6)$$

where R^- is



Equilibrium (6) is valid because the equation

$$\log \frac{[RH_2^+]}{[RH]} = \log K_2^H - pH \qquad (7)$$

gives a straight line with slope of unity.

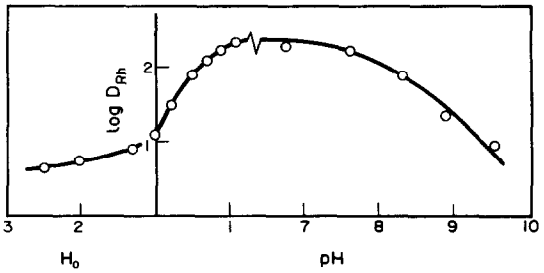


Fig. 3. Distribution ratio as a function of pH or H_0; $C_{Rh} = 1{\cdot}25 \times 10^{-4}M$; HC 10_4/NaC10_4/butyl acetate.

Table 1. Stability constants of protonated DMABR, $\mu = 0.1$

Medium	$\log \beta_1^H$	$\log K_2^H$	$\log \beta_2^H$
20% v/v ethanol	6·67 ± 0·08	1·44 ± 0·09	8·11 ± 0·17
water	8·06 ± 0·14	1·45 ± 0·14	9·51 ± 0·28

The stability constants of protonated DMABR species were calculated from spectrophotometric data for 20% v/v ethanol medium and from extraction data for aqueous media. We used six systems, varying the organic solvent (butyl acetate, isoamyl acetate, benzene) and the acid (hydrochloric or perchloric). The value for $[H^+]$ at pH < 0 was calculated from the Hammett function.[36] We established experimentally that measured pH values were the same in aqueous and 20% v/v ethanol media. Statistical treatments were made of 15 results, at the 95% confidence limits. The values obtained are shown in Table 1.

Determination of silver(I) with DMABR

From Neumayer's data shown in Table 107 in Sandell's book[2] the apparent molar absorptivity of the Ag–DMABR complex at 595 nm decreases from $4{\cdot}10 \times 10^4$ l.mole^{-1}.cm^{-1} for 0·05 μg/ml to $2{\cdot}32 \times 10^4$ for 1·00 μg/ml. The results have good reproducibility and the solutions are stable for 20–30 min. Evidently, the calibration curve is only apparently a straight line. This fact cannot be explained in terms of physical causes alone.

Silver(I) forms two mononuclear complexes with DMABR, with composition AgR and AgR_2^-.[14,25,33] The reported stability constants are given in Table 2.

Our results[25] were calculated (after spectrophotometric study of the system) from 18–22 values, at the 95% confidence limits, by use of the conditional constants defined as follows, and the β_1^H and β_2^H values given in Table 1 (20% ethanol):

$$Ag^+ + RH \overset{\beta'_1}{\rightleftharpoons} AgR + H^+ \quad (8)$$

$$AgR + RH \overset{K_2}{\rightleftharpoons} AgR_2^- + H^+ \quad (9)$$

$$\beta'_2 = \beta'_1 . K'_2 \quad (10)$$

In the paper by Castagna and Chaveau[11] the dissociation constants of AgR_2^- in ammoniacal medium were determined spectrophotometrically ($pK_1 = 4{\cdot}3$ and $pK_2 = 6{\cdot}8$). The values given in Table 2 were calculated by us, taking into account the formation of silver–ammonia complexes. Navratil and Kotas[33] worked with perchlorate medium, using extraction data at pH > 3.

Our studies were made on a more acidic medium, *i.e.*, under the real conditions for the spectrophotometric determination, where DMABR is present as RH or RH_2^+. There is good agreement between the results for β_2. This is one confirmation of the values for β_1^H and β_2^H of DMABR in 20% v/v ethanol. The value of K_2 is similar to that obtained by Navratil and Kotas but there is a difference for β_1. We therefore determined the distribution ratio of Ag(I) at pH < 1 in the system $HClO_4(NaClO_4)$–DMABR–butyl acetate:

Table 2. Stability constants of AgR and AgR_2

Conditions	$\log \beta_1$	$\log K_2$	$\log \beta_2$	Ref.
0·3*M* NH_3 + 0·55*M* $(NH_4)_2SO_4$, pH = 9·3; 1·5% gelatine	13·81	4·30	18·11	14
$HClO_4$ + $NaClO_4$; pH > 3; $\mu = 0{\cdot}1$	9·15	8·41	17·56	33
$HClO_4$ + $NaClO_4$; pH < 3, $\mu = 0{\cdot}1$; 20% v/v ethanol	9·97 ± 0·02	8·29 ± 0·12	18·26 ± 0·14	25

$$D_{Ag} = \frac{P_{AgR} \cdot \beta_1 [R^-]}{1 + \beta_1 [R^-]} \quad (11)$$

where

$$P_{AgR} = \frac{[AgR]_0}{[AgR]}$$

$$[R^-] = C_{Rh} . \alpha_{Rh}^{-1} =$$

$$C_{Rh}\{1 + (P_{RH} + 1)\beta_1^H[H^+] + \beta_2^H[H^+]^2\}^{-1}$$

C_{Rh} = total concentration of DMABR; $P_{RH} = [RH]_0/[RH]$,

β_1^H, β_2^H = stability constants of protonated DMABR (water) from Table 1. The DMABR was determined spectrophotometrically in alkaline medium and the silver with dithizone.[37]

From (11) we found $\log P_{AgR} = 2{\cdot}46$; Navrátil and Kotas gave the value 2·61. This agreement between the values confirms the further stability constants for DMABR in water (Table 1).

From the values of β_1 and β_2 for the Ag–DMABR complexes we calculated the degree of formation of AgR, AgR_2^- and free Ag(I) as a function of pH for different total concentration of DMABR (Fig. 4):

$$\alpha_{Ag}^{-1} = [Ag^+] C_{Ag}^{-1} = (1 + \beta_1[R^-] + \beta_2[R^-]^2)^{-1} \quad (12)$$

$$\alpha_{AgR}^{-1} = [AgR] C_{Ag}^{-1} = \beta_1[R^-](1 + \beta_1[R^-] + \beta_2[R^-]^2)^{-1} \quad (13)$$

$$\alpha_{AgR_2}^{-1} = [AgR_2^-] C_{Ag}^{-1} = \beta_2[R^{-2}]^2(1 + \beta_1[R^-] + \beta_2[R^-]^2)^{-1} \quad (14)$$

In the pH-region 1–2 (at pH > 2 the solubility of the reagent decreases) the predominant species is

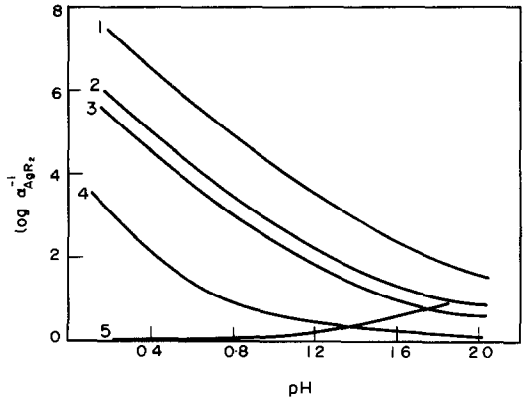


Fig. 4. Log α^{-1} as a function of pH; **1**, **2** and **3**, α_{AgR_2}; C_{Rh} is respectively $1{\cdot}00 \times 10^{-5}M$, (1), $5{\cdot}00 \times 10^{-5}M$ (2), $1{\cdot}00 \times 10^{-4}M$ (3). **4**, α_{AgR}; $C_{Rh} = 5{\cdot}00 \times 10^{-5}M$. **5**, α_{Ag}; $C_{Rh} = 5{\cdot}00 \times 10^{-5}M$.

AgR. The condition (4) for $C_{Rh} = 5 \times 10^{-5}M$ becomes:

$$1{\cdot}82 \times 10^{18} \frac{2{\cdot}5 \times 10^{-9}}{\alpha^2_{R(H)}} \gg 1 + 9{\cdot}33 \times 10^{9} \frac{5{\cdot}0 \times 10^{-5}}{\alpha_{R(H)}} \qquad (15)$$

from which follows $\alpha_{R(H)} \sim 9{\cdot}5 \times 10^2$. This is possible at pH ~ 3·6, a condition unrealizable in practice because of the low solubility of DMABR at this acidity. Therefore, for analytical purposes the complex AgR must be used. This is not ideal, because there is an excess of DMABR and not more than 80% of the silver can be bound as AgR. However, α_{AgR} changes very little when pH > 1·2 and the solubility of the reagent is increased in more acidic medium. At pH = 1·3 the solution is clear when $C_{Rh} \leq 2 \times 10^{-5}M$. Therefore, the highest silver concentration on the calibration curve must be $2 \times 10^{-6}M$. Determination in alkaline (ammonia) medium could not give any better results, because although the solubility of the reagent increases, that of the complexes does not.

When DMABR is used as a spectrophotometric reagent for silver, two factors require the pH-value to be kept strictly constant.

1. It is not possible to use the conditions necessary for only one light-absorbing species (except the reagent) to be formed. In the pH-region 0–2, AgR and AgR_2^- are formed in variable degree, and have very different absorptivities. Part of the silver is not bound (curve 5 in Fig. 4).

2. The absorbance of the blank solution changes sharply with pH, as a result of the change of the ratio between $[RH_2^+]$ and [RH], which also have very different absorptivities.

In our opinion, DMABR is a reagent suitable for spectrophotometric determination of low concentrations of silver (0·08–0·40 μg/ml) if a long path-length cuvette is used. In spite of the lower sensitivity, it is better to work at $\lambda \geq 580$ nm, where the absorbance of the reagent is negligible.

Procedure. Place the sample solution, containing 2–10 μg of silver, in a 25-ml volumetric flask. Add 5·00 ml of 0·25*M* nitric acid, dilute to 15–20 ml, add 5·00 ml of $1 \times 10^{-4}M$ DMABR in ethanol and mix. Dilute to the mark with doubly distilled water, mix, and measure the absorbance within 15–30 min at 580 nm against water in a 5-cm cell. The standard deviation is 0·03 μg/25 ml.

Determination of palladium(II) with DMABR

Pantani[20] and Ayres and Narang[23] have shown that Pd(II) forms only a mononuclear complex, with two DMABR ligands. No values were given for the stability constants.

Our studies have been carried out on hydrochloric acid medium. The ultraviolet absorption spectra of a continuous-variations series of solutions at pH = 0·80 and overall concentration $4{\cdot}00 \times 10^{-6}M$ has two isosbestic points (Fig. 5). When the concentration is increased to $1{\cdot}00 \times 10^{-5}M$ and the pH to 1·10 the picture changes (Fig. 6). It is evident that the number of absorbing species depends on the pH and on the concentrations of Pd(II) and DMABR. We have studied this system spectrophotometrically and established[25] that three mononuclear complexes are formed: PdR^+, PdR_2 and $Pd(Rh)_4$. The first complex exists when $C_{Pd} > C_{Rh}$ and pH ≤ 0·80. The formation of PdR_2 involves the release of two hydrogen ions:

$$PdCl_4^{2-} + 2RH \rightleftharpoons PdR_2 + 2H^+ + 4Cl^- \qquad (16)$$

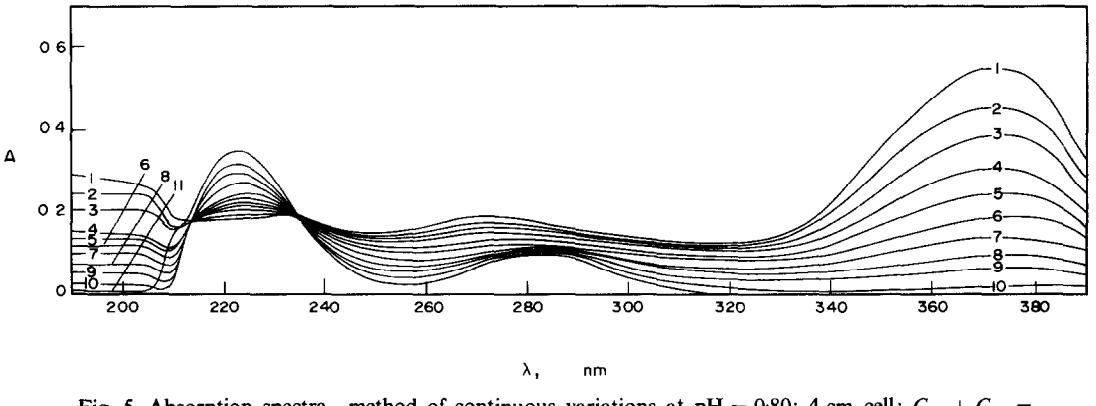


Fig. 5. Absorption spectra—method of continuous variations at pH = 0·80; 4-cm cell; $C_{Pd} + C_{Rh} = 4{\cdot}00 \times 10^{-6}M$; from **1** to **11** C_{Pd} is respectively 0·0; $4{\cdot}00 \times 10^{-7}M$; $8{\cdot}00 \times 10^{-7}M$; ... $4{\cdot}00 \times 10^{-6}M$.

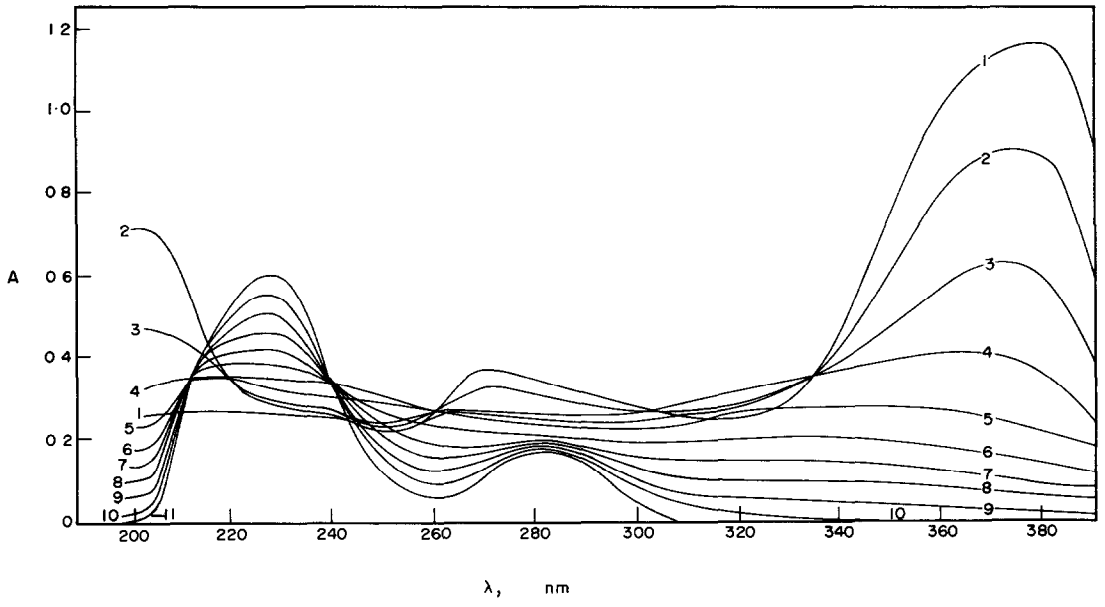


Fig. 6. Absorption spectra—method of continuous variations at pH = 1·10; 4-cm cell; $C_{Pd} + C_{Rh} = 1{\cdot}00 \times 10^{-5}M$; from **1** to **11** C_{Pd} is respectively 0·0; $1{\cdot}00 \times 10^{-6}M$; $2{\cdot}00 \times 10^{-6}M$; ... $1{\cdot}00 \times 10^{-5}M$.

It is the predominating species when pH > 1, $C_{Pd} \leq 1{\cdot}8 \times 10^{-6}M$ and $C_{Rh} \leq 5{\cdot}0 \times 10^{-5}M$. At higher concentrations of Pd(II) and DMABR, $Pd(Rh)_4$ is formed; in that case the solutions are opalescent and after some time give a deposit. The measured absorpance is reproducible to only about 5–7%, but the absorbtivity decreases when the concentration of Pd(II) increases from 2×10^{-6} to $1{\cdot}4 \times 10^{-5}M$ and remains constant only within the range $1{\cdot}4$–$2{\cdot}4 \times 10^{-5}M$. We suppose that in $Pd(Rh)_4$ two DMABR dimers are bound to one Pd(II)-ion, because the complex is not charged and the band at 3420 cm^{-1} in the infrared spectrum of the reagent (Fig. 7), due to the associated amino-groups,[38] remains in the spectrum of the complex with palladium(II) but disappears in that of silver(I). This band is very sharp in the spectra of rhodanine complexes

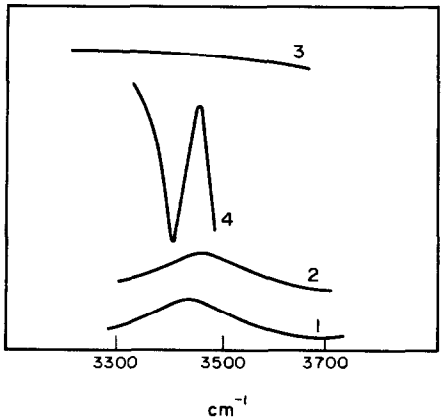


Fig. 7. Infrared spectra (nujol); **1**, DMABR; **2**, Pd(II)–DMABR; **3**, Ag(I)–DMABR; **4**, Cu(I)–DMABR.

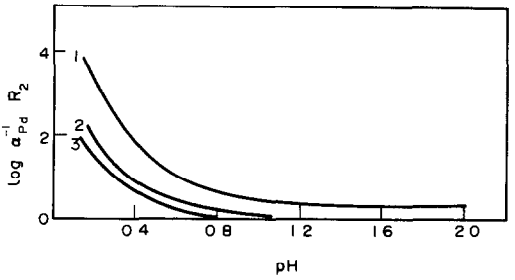


Fig. 8. Log $\alpha^{-1}_{PdR_2}$ as a function of pH; C_{Rh}: **1**, $1{\cdot}00 \times 10^{-5}M$; **2**, $5{\cdot}00 \times 10^{-5}M$; **3**, $1{\cdot}00 \times 10^{-4}M$.

of Cu(I), the polymeric structure of which was discussed by Moers *et al.*[39,40] We suppose that this polymerization, rather than impurities, caused the variable results for the isolated solid species, described by Ayres and Narang.[23]

For the spectrophotometric determination of Pd(II) the conditions for obtaining clear solutions are of interest. Therefore, we investigated the equilibria concerned in the formation of the first two complexes, for which the molar absorptivities at 515 nm are $(1{\cdot}85 \pm 0{\cdot}06) \times 10^4$ and $(4{\cdot}88 \pm 0{\cdot}05) \times 10^4$ l. $mole^{-1}.cm^{-1}$ respectively (10 values, 95% confidence limits). We determined the apparent formation constants in the presence of 0·25*M* chloride: $\log \beta_1' = 3{\cdot}20 \pm 0{\cdot}01$ and $\log \beta_2' = 7{\cdot}77 \pm 0{\cdot}38$ (15 results, 95% confidence limits). From the literature data for the stability of the chloro-complexes of Pd(II)[41–43] and our data for the stability constants of DMABR (Table 1) we calculated the stability constants of the palladium(II)–DMABR complexes: $\log \beta_1 = 22{\cdot}05$, $\log \beta_2 = 37{\cdot}10$.

For analytical purposes the complex PdR_2 is suitable. Figure 8 shows the degree of its formation as

a function of pH and the concentration of DMABR, calculated from:

$$\alpha_{PdR_2} = [PdR_2].C_{Pd}^{-1} =$$
$$\beta_2[R^-]^2(\beta_4^{Cl}[Cl^-]^4 + \beta_1[R^-] + \beta_2[R^-]^2)^{-1} \quad (17)$$

where

$$\beta_4^{Cl} = \frac{[PdCl_4^{2-}]}{[Pd^{2+}][Cl^-]^4}$$

In this case the condition (4) becomes

$$\beta_2\left(\frac{C_{Rh}}{\alpha_{R(H)}}\right)^2 \gg \beta_4^{Cl}[Cl^-]^4 + \beta_1\frac{C_{Rh}}{\alpha_{R(H)}} \quad (18)$$

At $C_{Rh} = 5 \times 10^{-5}M$ and $[Cl^-] = 0{\cdot}1M$, (18) holds when $\alpha_{R(H)} > 10^7$. This is possible at pH > 0·6.

In nitric acid medium the determination can be carried out at pH about 0·5. The method is convenient for low concentration of palladium(II) if a long path-length cell is used.

Procedure. In a 25-ml volumetric flask place 5·00 ml of 0·5*M* hydrochloric or nitric acid and a solution containing 1–5 μg of palladium(II). Dilute with doubly distilled water to about 15–20 ml and add 5·00 ml of $2{\cdot}5 \times 10^{-4}M$ DMABR in ethanol, mix, dilute to the mark with doubly distilled water, mix, and measure the absorbance in a 5-cm cell within 10–60 min, at 515 nm against a reagent blank. The standard deviation for 1–5 μg/25 ml is 0·03 μg/25 ml.

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SPECTROPHOTOMETRIC DETERMINATION OF GOLD(III) WITH *p*-DIMETHYLAMINOBENZILIDENERHODANINE IN HYDROCHLORIC ACID–ETHANOL MEDIUM

RAHILA BORISSOVA

Department of Analytical Chemistry, Higher Institute of Chemical Technology, Sofia-56, Bulgaria

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Summary—The reaction between gold(III) and *p*-dimethylaminobenzilidenerhodanine in hydrochloric acid medium containing 20% v/v ethanol has been studied spectrophotometrically. It has been established that the process is very complicated: gold(III) is reduced to gold(I) which reacts with unchanged reagent. The value of the equilibrium constant is 2·56 ± 0·45. Conditions are proposed for the determination of 2–8 μg of gold in 25 ml, with a standard deviation of 0·04 μg/25 ml.

p-Dimethylaminobenzilidenerhodanine (DMABR) is one of the widely used spectrophotometric reagents for gold(III),[1–10] but the literature on the mechanism of the process is very scanty. Sandell established that at pH = 0·9 Au(III) reacts with a little more than a 1:1 molar ratio of DMABR and considers that this is due to the reduction of Au(III) to Au(I), which then reacts with unchanged reagent.[11] According to Cotton and Woolf, the gold remains as Au(III) in the 1:1 complex.[12] Pantani[13] found the composition $Au(Rh)_2$ in 20% v/v dioxan medium. No stability constants have been published.

In the present paper we discuss our spectrophotometric study of the reaction of gold(III) with DMABR in hydrochloric acid medium, and its analytical application. The studies were done with 20% v/v ethanol media, the conditions for obtaining non-saturated solutions.[14–16]

EXPERIMENTAL

Reagents

Gold(III) solution, 5·06 × 10^{-3}*M*. Prepared by dissolving the pure metal in *aqua regia* and evaporating to dryness with concentrated hydrochloric acid (repeated thrice). The concentration was determined electrogravimetrically.[17]

DMABR solution, 1·25 × 10^{-4}*M in ethanol.*

The reagents used were "*pro analysi*" grade, and all water was doubly distilled. All investigations were carried out at 18 ± 2° and constant ionic strength of 0·2, maintained by addition of the required amount of sodium chloride.

RESULTS AND DISCUSSION

The time needed to achieve equilibrium in the system Au(III)–HCl–DMABR depends on the pH-value: 45 min (pH = 0·75), 25 min (pH = 0·92), 15 min (pH = 1·22) and 5 min (pH = 1·52–2·00). The time for which the measured absorbance remains constant also depends on the pH-value: 55–60 min (pH = 0·75–1·22), 15–25 min (pH = 1·52) and 5 min (pH = 2·00).

The absorption spectra of solutions containing gold(III) and reagent in different proportions and at different pH-values are shown in Figs. 1–4. At pH = 0·75 the curves are analogous to those in Figs. 3 and 4. There is only one change in the absorption spectra of the reagent when gold(III) is added—the disappearance of the maximum at 370 nm, accompanied by appearance of the wide band at about 500 nm, or increase in the absorbance in this region, depending on pH. Therefore, only one complex is formed.

In our case the total concentration of gold(III) is about 10^{-6}*M* and that of chloride 0·1*M*. Obviously, the gold is present as the stable $AuCl_4^-$ (log β_4 = 21·4).[18] The reaction can be written as follows:

$$a\mathrm{AuCl_4^-} + n\mathrm{Rh} \rightleftharpoons \mathrm{Au}_a(\mathrm{Rh})_n\mathrm{Cl}_{4-p} + p\mathrm{Cl^-} + m\mathrm{H^+} \quad (1)$$

The apparent molar absorptivity remains constant when the concentration of gold(III) is varied from 1 × 10^{-6} to 5 × 10^{-5}*M*. This means that there are no polynuclear species, so $a = 1$. Analysis of the isolated complex showed the absence of chloride, so $p = 4$.

Continuous-variations (Fig. 5) and mole-ratio (Fig. 6) methods were used for the determination of n.[19,20] The Job curves have a maximum corresponding to a 1:1 complex, but the plot is not symmetric. The mole-ratio method gives a stoichiometric coefficient for DMABR of more than unity, increasing with pH from 1·3 (pH = 0·75) to 2·0 (pH = 2·0). The value of n for a given pH-value does not depend on the concentration of the components (Figs. 7 and 8). We think that this is not due to the formation of the second complex, because that would cause changes in the absorption spectra. We recorded the spectra for 72 combinations of the concentrations of gold(III)

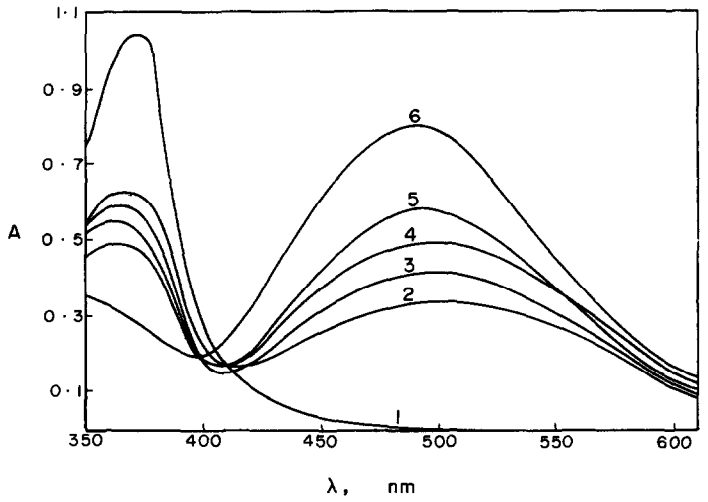


Fig. 1. Absorption spectra, $C_{Au} = 5{\cdot}0 \times 10^{-6}M$, $C_{Rh} = 1{\cdot}0 \times 10^{-5}M$, $b = 4$ cm, **1**, pH = 0·46; **2**, pH = 0·75; **3**, pH = 1·05; **4**, pH = 1·38; **5**, pH = 1·95; **6**, pH = 2·55.

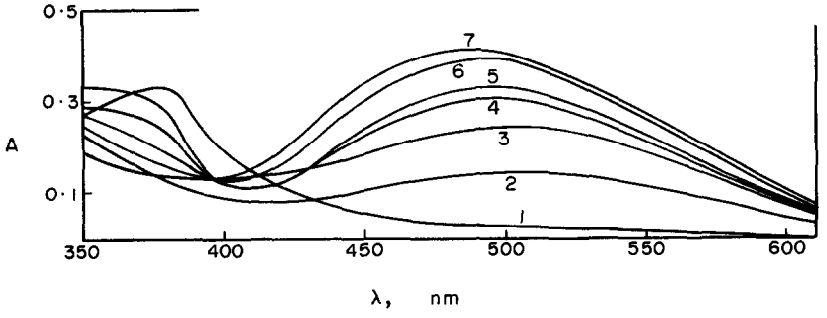


Fig. 2. Absorption spectra, $C_{Au} = 1{\cdot}0 \times 10^{-5}M$, $C_{Rh} = 5{\cdot}0 \times 10^{-6}M$, $b = 4$ cm, **1**, pH = 0·46; **2**, pH = 0·75; **3**, pH = 1·05; **4**, pH = 1·38; **5**, pH = 1·70; **6**, pH = 1·95; **7**, pH = 3·05.

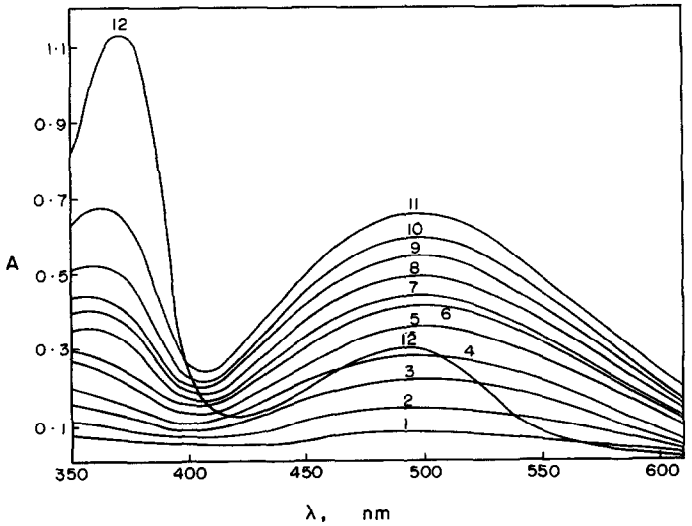


Fig. 3. Absorption spectra, pH = 1·45, $b = 4$ cm, $C_{Au} = 5{\cdot}0 \times 10^{-6}M$, **1**, $C_{Rh} = 1{\cdot}0 \times 10^{-6}M$; **2**, $C_{Rh} = 2{\cdot}0 \times 10^{-6}M$; **3**, $C_{Rh} = 3{\cdot}0 \times 10^{-6}M$; **4**, $C_{Rh} = 4{\cdot}0 \times 10^{-6}M$; **5**, $C_{Rh} = 5{\cdot}0 \times 10^{-6}M$; **6**, $C_{Rh} = 6{\cdot}0 \times 10^{-6}M$; **7**, $C_{Rh} = 7{\cdot}0 \times 10^{-6}M$; **8**, $C_{Rh} = 8{\cdot}0 \times 10^{-6}M$; **9**, $C_{Rh} = 9{\cdot}0 \times 10^{-6}M$; **10**, $C_{Rh} = 1{\cdot}0 \times 10^{-5}M$; **11**, $C_{Rh} = 1{\cdot}2 \times 10^{-5}M$; **12**, $C_{Rh} = 1{\cdot}0 \times 10^{-5}M$, $C_{Au} = 0$.

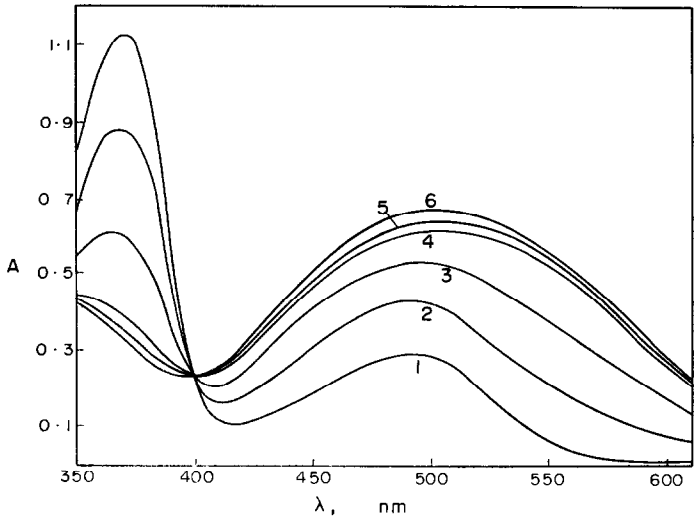


Fig. 4. Absorption spectra, pH = 1·45, b = 4 cm, $C_{Rh} = 1{\cdot}0 \times 10^{-5}M$. **1.** $C_{Au} = 0$; **2.** $C_{Au} = 2{\cdot}0 \times 10^{-6}M$; **3.** $C_{Au} = 4{\cdot}0 \times 10^{-6}M$; **4.** $C_{Au} = 6{\cdot}0 \times 10^{-6}M$; **5.** $C_{Au} = 8 \times 10^{-6}M$; **6.** $C_{Au} = 1{\cdot}0 \times 10^{-5}$–$3{\cdot}0 \times 10^{-5}M$.

and DMABR (some are shown in Figs. 1–4) but the only change was that already stated. It is probable that some side-reaction takes place.

We think that the interaction between gold(III) and DMABR is a complex process including the reduction of Au(III) to Au(I), which then forms the complex with unchanged reagent. This assumption is based on the following facts.

1. The spectra of the complex in the visible or infrared region are the same in the presence or absence of hydrazine sulphate. Therefore, it is just gold(I) that forms the complex.

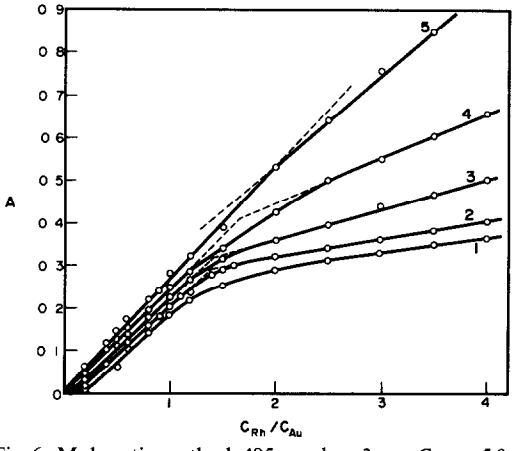


Fig. 6. Mole-ratio method, 495 nm, b = 3 cm, $C_{Au} = 5{\cdot}0 \times 10^{-6}M$. **1.** pH = 0·75; **2.** pH = 0·92; **3.** pH = 1·22; **4.** pH = 1·52; **5.** pH = 2·00.

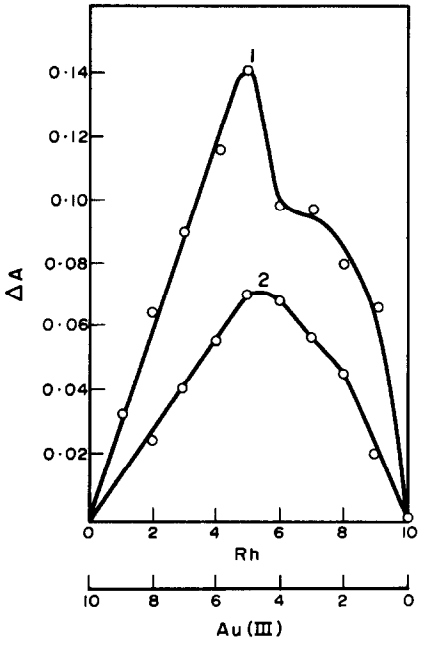


Fig. 5. Method of continuous variations, $C_{Au} + C_{Rh} = 2{\cdot}5 \times 10^{-6}M$. **1.** pH = 0·60, 370 nm; **2.** pH = 1·45, 500 nm.

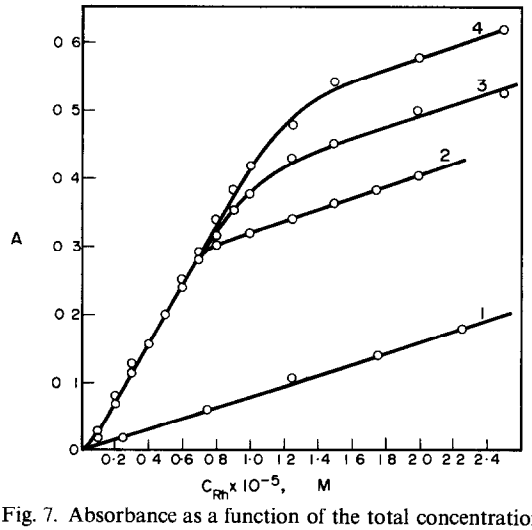


Fig. 7. Absorbance as a function of the total concentration of DMABR, 495 nm, b = 3 cm, pH = 0·92. **1.** $C_{Au} = 0$; **2.** $C_{Au} = 5{\cdot}0 \times 10^{-6}M$; **3.** $C_{Au} = 7{\cdot}0 \times 10^{-6}M$; **4.** $C_{Au} = 9{\cdot}0 \times 10^{-6}M$.

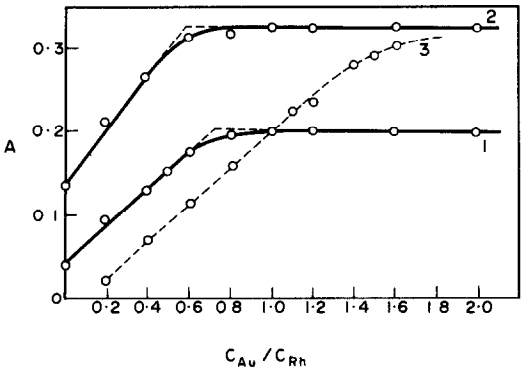


Fig. 8. Mole-ratio method. **1.** pH = 0·92, 495 nm, b = 3 cm, $C_{Rh} = 5{\cdot}0 \times 10^{-6}M$ = const. **2.** pH = 1·45, 500 nm, b = 2 cm, $C_{Rh} = 1{\cdot}0 \times 10^{-5}M$ = const. **3.** pH = 0·92, 495 nm, b = 3 cm, $C_{Au} = 5{\cdot}0 \times 10^{-6}M$ = const.

2. Comparison of the infrared spectra of the complexes of DMABR with different metals (where there is no possibility of redox processes) shows that the changes in the spectrum of the reagent are similar (Table 1). This shows that the gold complex is formed with unchanged reagent.

3. At pH < 0·5, even with a large excess of gold(III) in relation to DMABR, there is no visible complex-formation (red-violet colour). The absorbance at 500 nm (maximum of the complex) does not change, but that at 370 nm (maximum of the reagent) decreases (Fig. 9). Confirmation of the reduction of gold (III) by DMABR comes from calibration curves for the reagent in the presence and absence of gold(III). When a constant concentration of gold(III) is added, the slope of the line for absorbance *vs.* C_{Rh} decreases and the line does not pass through the origin. We extracted with ether the product of this interaction and took its infrared spectrum after eliminating the ether (the residue was yellow, but DMABR is red). Comparison with the infrared spectrum of DMABR showed that the $\nu_{C=O}$ band for the oxidized reagent (we shall denote this by Rh*) is strongly increased in intensity and is split into peaks at 1720 and 1735 cm^{-1}. Moers and Steggerda investigated the reaction of rhodanine and its three alkyl derivatives with Cu(I) and Cu(II). They considered that Cu(II) oxidized part of the rhodanine.[21]

4. As will be shown (Fig. 11), besides the complex and the free reagent there is another absorbing species, the absorbance of which depends on pH. Therefore, this could not be a second complex, because

Table 1. Main bands in the region 200–4000 cm^{-1} for DMABR and its complexes with silver(I), palladium(II) and gold(III); (nujol)

	ν_{N-H}	$\nu_{C=O}$ I amide	$\delta_{NH} + \nu_{C-N}$ II amide	thioamide	ν_{M-S}
Rh	3420	1675	1535	670	—
AgR	—	1670	1505	—	405
$PdR_2(Rh)_2$	3440	1685	1520	—	405
AuR	—	1685	1525	—	410

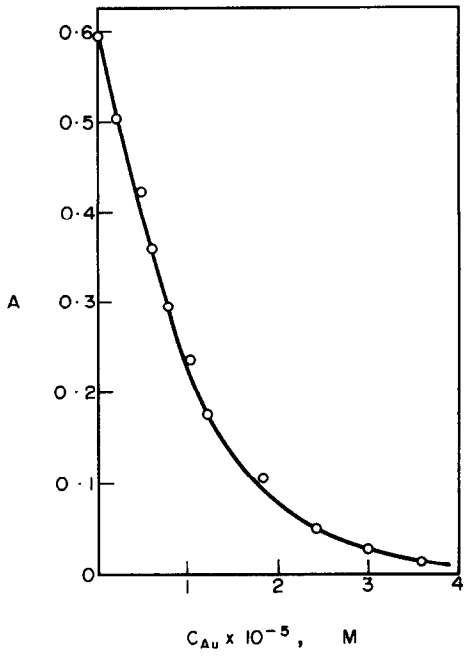


Fig. 9. Absorbance as a function of C_{Au}, pH = 0·30, b = 3 cm, 370 nm, $C_{Rh} = 6{\cdot}0 \times 10^{-6}M$.

the complex would have definite spectral characteristics which would not depend on pH, and there would be two isosbestic points on each of Figs. 1–4.

5. The simultaneous occurrence of the two processes can explain the shape of curve 1 in Fig. 6: at lower pH and concentration of DMABR the complex formation is of low degree, and the absorbance of Rh* is negligible at pH = 0·75.

When determining the molar absorptivity by varying the concentration of DMABR or gold(III) we obtained consistent results if we assumed that when the gold concentration was kept constant and $> C_{Rh_{(max)}}$ the concentration of product was equal to half the concentration of DMABR, and when the reagent concentration was kept constant and $> 2C_{Au_{(max)}}$ the concentration of product was equal to the concentration of gold.

Therefore, the following equation can be written:

$$AuCl_4^- + 2Rh \overset{K}{\rightleftharpoons} AuR + Rh^* + mH^+ + 4Cl^- \quad (2)$$

At pH 2 this reaction is accomplished only to some degree which depends on the value of pH (Fig. 10). The curve correlating the absorbance and pH is similar. It is evident that for every pH-value the corresponding stoichoimetric coefficient n must be given:

$$AuCl_4^- + nRh \overset{K'}{\rightleftharpoons} \frac{n}{2}AuRh + \frac{2-n}{2}AuCl_2^- + \frac{n}{2}Rh^* + mH^+ + (2+n)Cl^- \quad (3)$$

The value of n was determined by the molar-ratio method (Fig. 6) at 6 wavelengths (471, 483, 495, 507 and 539 nm). For pH 0·75, 0·92, 1·22, 1·52 and 2·00

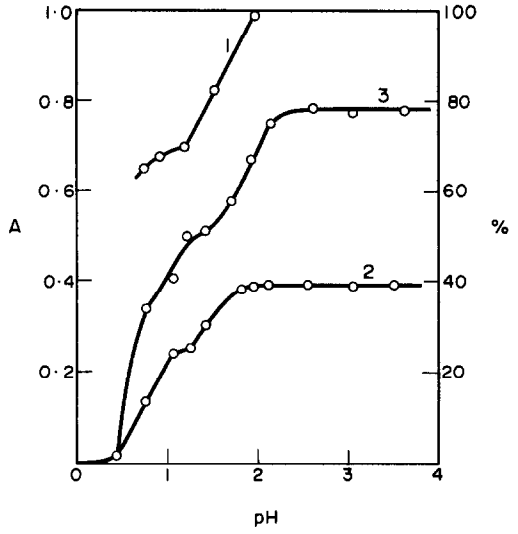


Fig. 10. The degree of interaction between Au(III) and DMABR as a function of pH—curve **1.** Absorbance as a function of pH, 500 nm, $b = 4$ cm, $C_{Au} = 1{\cdot}0 \times 10^{-5}M$. $C_{Rh} = 5{\cdot}0 \times 10^{-6}M$—curve **2.** Absorbance as a function of pH, 500 nm, $b = 4$ cm, $C_{Au} = 5{\cdot}0 \times 10^{-6}M$, $C_{Rh} = 1{\cdot}0 \times 10^{-5}$—curve **3.**

the values obtained for n were 1·30, 1·36, 1·40, 1·66 and 2·00 respectively.

The number of protons released and the value of K were determined from the parameters of the straight line:

$$\log K' = \log K + m\text{pH} \tag{4}$$

where

$$K' = \frac{[\text{AuR}]^{[(n)/2]}[\text{AuCl}_2^-]^{[(2-n)/2]}[\text{Rh*}]^{[(n)/2]}[\text{Cl}^-]^{(2+n)}}{[\text{AuCl}_4^-][\text{Rh}]^n} \tag{5}$$

The concentration of the components taking part in the equilibrium (3) can be expressed as a function of [AuR] and the following equation obtained:

$$K' = \frac{\left(\frac{2-n}{n}\right)^{[(2-n)/2]}[\text{AuR}]^{[(2+n)/2]}[\text{Cl}^-]^{(2+n)}}{\left(C_{Au} - \frac{2}{n}[\text{AuR}]\right)(C_{Rh} - 2[\text{AuR}])^n} \tag{6}$$

where

$$[\text{AuR}] = \frac{A - b\epsilon_2 C_{Rh}}{b(\epsilon_1 - 2\epsilon_2 + \epsilon_3)} \tag{7}$$

C_{Au} and C_{Rh} are the total concentrations of gold and DMABR, ϵ_1, ϵ_2, ϵ_3 are the molar absorptivities of AuR, Rh and Rh* respectively, and b is the cuvette path-length.

The values of ϵ_1 and ϵ_3 were determined on the basis of the following considerations: when $C_{Rh} > nC_{Au}$, $[\text{Rh}] = C_{Rh} - nC_{Au}$ and therefore, for every pH-value the absorbance of the free reagent (A_{Rh}) can be calculated:

$$A_{Rh} = b\epsilon_2[\text{Rh}] = b\epsilon_2(C_{Rh} - nC_{Au}) \tag{8}$$

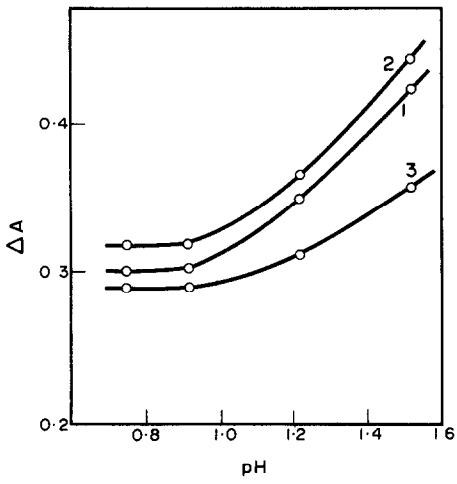


Fig. 11. ΔA as a function of pH, $b = 3$ cm, $C_{Au} = 5{\cdot}0 \times 10^{-6}M$. **1.** 471 nm; **2.** 495 nm; **3.** 539 nm.

If the complex (AuR) and the free reagent are the only light-absorbing species (at $\lambda > 450$ nm, $AuCl_4^-$ and $AuCl_2^-$ do not absorb), the difference

$$\Delta A = A - A_{Rh} \tag{9}$$

must have a constant value, when $C_{Rh} > nC_{Au}$, in spite of increase in the concentration of DMABR and the change in pH. As can be seen from Fig. 11 ΔA remains constant when pH < 0·9 (for a given value of pH, ΔA does not depend on C_{Rh}, and the curves are plotted from the average of three values), and at pH > 0·9 it increases. This can be explained by the presence of the third absorbing component (Rh*), the concentration of which does not change when the concentration of DMABR is more than nC_{Au}, but the absorbance of which depends on the pH. From the horizontal part of the curves ϵ_1 and ϵ_3 can be determined, by means of the equation

$$\epsilon_3 = \frac{2\Delta A}{nbC_{Au}} - \epsilon_1 \tag{10}$$

The value of log K' is a linear function of pH, and Table 2 shows the values obtained from it for the equilibrium constant K, since $K = K'[\text{H}^+]^2$. The slope of the plot of log K' *vs.* pH gives $m = 2$, and the intercept on the ordinate at pH = 0 gives log $K \sim 0{\cdot}4$.

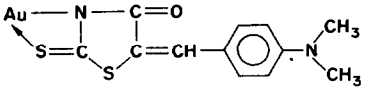
The values calculated for K are equal at different pH-values and this confirms the correctness of the mechanism accepted for the reaction between gold (III) and DMABR in hydrochloric acid medium. When pH > 2 it can be written as

$$\text{AuCl}_4^- + 2\text{Rh} \rightleftharpoons \text{AuR} + \text{Rh*} + 2\text{H}^+ + 4\text{Cl}^- \tag{11}$$

Table 2. Values of the equilibrium constant K for different values of pH; (10 results, 95% confidence limits)

pH	0·75	0·92	1·22	1·52	Mean
K	2·47 ± 0·47	2·54 ± 0·10	2·54 ± 0·55	2·79 ± 0·50	2·59 ± 0·45
log K	0·39 ± 0·09	0·40 ± 0·02	0·40 ± 0·09	0·45 ± 0·08	0·41 ± 0·08

The data shown in Table 1 give the possibility of drawing some conclusions about the bonding sites of Au(I) with DMABR. $\nu_{C=O}$ is shifted by only 10 cm^{-1} when AuR is formed. This means that it is very unlikely that the CO-group takes part in the complex formation. The band at 670 cm^{-1}, connected with the vibration of the N–H and C=S bonds[21–24] disappears in the spectrum of AuR, but an intensive new band at 410 cm^{-1} appears, which is due to the Au–S bond. This lets us assume that the NH-group takes part in the complexation. The hydrogen atom is displaced by the cation (the band at 3420 cm^{-1} disappears) and there is also co-ordination at the sulphur atom. Perhaps it is because of just this that the II-amide band (1535 cm^{-1}) shifts by 10 cm^{-1}. On the other hand, in the spectrum of the reagent there is no band in the interval 2550–2600 cm^{-1}, which shows that DMABR is in the thioketo form. Therefore, the following scheme may be given:



Analytical application

The apparent molar absorptivity increases with pH, but the solubility of DMABR decreases and the reproducibility becomes worse. We think that the most suitable acidity is about 0·12*N* (the conditions given by Sandell[11]). The following factors impose the necessity of working with a variation in pH-values of not more than 0·05.

1. The addition of the absorbance of Rh*, which depends on pH, to that of AuR and DMABR.

2. The sharp change in the absorbance of the blank solution with shift of pH.

3. The complicated complex-formation and redox processes take place to a degree depending on the pH.

Even a trace of oxidizing species must be absent. Because of the low solubility of the reagent and of the reaction products, Beer's law is valid over a very narrow range of concentrations of gold(III). Evidently, DMABR is a reagent suitable for spectrophotometric determination of low concentrations of gold.

Procedure. Evaporate the solution containing 2–8 μg of gold to a moist residue, on a water-bath. Moisten the residue with exactly 6 drops of concentrated hydrochloric acid and one drop of hydrogen peroxide. Heat for 3 min on the water-bath (all the samples in the series together), add 2·500 ml of 1*M* hydrochloric acid and heat for 5 min. Transfer the solution with doubly-distilled water to a 25-ml volumetric flask, add 5·00 ml of $1 \times 10^{-4}M$ DMABR in ethanol, dilute to the mark with doubly-distilled water and mix. Measure the absorbance, after 25 min, in a 5-cm cell, at 500 nm against a reagent blank. The standard deviation for 2–8 μg of gold in 25 ml is 0·04 μg/25 ml.

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ELEKTROPHORETISCHE UND POLAROGRAPHISCHE UNTERSUCHUNGEN DER ZUSAMMENSETZUNG UND STABILITÄT VON Cd- UND In-ACETATKOMPLEXEN

VILIM VAJGAND und TEREZIJA SURÁNYI-MIHAJLOVIĆ

Lehrstuhl für Analytische Chemie, Chemisches Institut der Universität in Belgrad, Jugoslawien

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Zusammenfassung—Eine allgemeine Gleichung für die mittlere elektrophoretische Beweglichkeit, wenn das Zentralion gleichzeitig in verschiedenen Gleichgewichte teilnimmt, wird gegeben. Zwei Methoden für die Berechnung der Stabilitätskonstanten aus den experimentell erhaltenen Beweglichkeit: (*a*) die Methode der Kurvenüberlappung bei Verwendung der Gleichung für die mittlere Ladung, und (*b*) die Methode der explizite Lösung der Gleichung der mittleren Beweglichkeit, wurden beschrieben. Die erwähnte Methoden wurden zur Bestimmung der Zusammensetzung und Stabilität der Cadmiumacetat- und Indiumacetatkomplexe aus der mittleren elektrophoretischer Beweglichkeit angewandt und die erhaltene Werte wurden mit den polarographisch bestimmten Werten verglichen. Elektrophoretisch fanden wir bei der Ionenstärke $\mu = 0{,}1$ ($NaClO_4$), bei 0° und pH-Bereich 2,8–4,7 zwei Cadmiumacetatkomplexe, $CdCH_3COO^+$ und $Cd(CH_3COO)_2$ mit Stabilitätskonstanten $\log \beta_1 = 1{,}41$ und $\log \beta_2 = 1{,}96$. Bei den gleichen Bedingungen wurden vier Indiumacetatkomplexe gefunden: $InCH_3COO^{2+}$, $In(CH_3COO)_2^+$, $In(CH_3COO)_3$ und $In(CH_3COO)_4^-$ mit $\log \beta_1 = 3{,}53$, $\log \beta_2 = 5{,}90$, $\log \beta_3 = 7{,}90$ und $\log \beta_4 = 9{,}12$. Bei gleichen Bedingungen wurden polarographisch für die Cd-Acetatkomplexe die Werte $\log \beta_1 = 1{,}49$ und $\log \beta_2 = 2{,}42$, für die In-Acetatkomplexe die Werte $\log \beta_1 = 3{,}53$, $\log \beta_2 = 5{,}95$, $\log \beta_3 = 7{,}95$ $\log \beta_4 = 9{,}04$ und für $In(CH_3COO)_5^{2-}$ $\log \beta_5 = 11{,}15$ erhalten.

Die Papierelektrophorese ist bereits öfter zur Entscheidung des Problems, ob zwischen Kation und Anion Komplexbildung stattfindet, herangezogen worden. Durch Bindung des negativen Liganden zum zentralen Ion verändert sich die Kationladung und dadurch auch die elektrophoretische Beweglichkeit.[1,2] In welchem Maße sich diese Beweglichkeit in Funktion von der Konzentration des Liganden ändert, hängt von der Art des gebildeten Komplexes und auch von der Stabilität der entstandenen Komplexe ab.[3–5] Wenn die Art der Komplexe bekannt ist, oder vorausgesetzt werden kann, welche Komplexe bei den gegebenen Bedingungen entstehen können, dann ist es möglich, aus Veränderung der elektrophoretischen Beweglichkeit des Kations, in Funktion von der Konzentration des Liganden, die Stabilitätskonstanten zu berechnen.[6–8]

Die polarographische Methode von DeFord und Hume[9] kann auch herangezogen werden, um Stabilitätskonstanten zu bestimmen, wenn die Komplexionen reversibel reduzierbar sind. Ziel dieser Arbeit war es, die zwei Systeme Cadmium–Acetat und Indium–Acetat zu untersuchen und die Ergebnisse dieser zwei Verfahren zu vergleichen.

PAPIERELEKTROPHORESE

Wenn in der Lösung ein Gemisch von mehr oder weniger dissoziierter Ionen der gleichen Substanz, z.B. ein Gemisch der Komplexen MeA, MeA_2, MeA_3,...MeA_q vorhanden ist*, dann wandert nicht jede Ionenart für sich unter dem Einfluß des elektrischen Feldes zur entsprechenden Elektrode, sondern, da an jeder Stelle der Wegstrecke, in jeden Augenblick, zwischen allen Ionenarten der entsprechenden Substanz Gleichgewicht herrscht, verhält sich das Gemisch wie ein Ganzes mit der Ladung $\bar{z}$. Alberty und King[10] haben folgenden Ausdruck für die mittlere Komplexbeweglichkeit, $\bar{u}$, als die Summe der einzelnen Produkte aus den Beweglichkeiten u_q, und der Molfraktionen α_q der einzelnen Komplexarten, erhalten:

$$\bar{u} = \Sigma u_q \cdot \alpha_q \tag{1}$$

Wenn die Ionenfraktionen der Komplexionen durch die Stabilitätskonstanten β_q ausgedrückt werden, ergibt sich für $\bar{u}$

$$\bar{u} = \frac{\Sigma u_q \cdot \beta_q \cdot C_A^q}{\Sigma \beta_q \cdot C_A^q} \tag{2}$$

Diese Gleichungen hat Jokl,[8] durch Einführung der ersten Hydrolysestufe des Metallions etwas erweitert, und sie kann noch erweitert werden, wenn man alle Gleichgewichte berücksichtigt, in denen das Kation teilnimmt. In solchen Fällen ist die mittlere Beweglichkeit der Komplexe eine Funktion aller entstandener Verbindungen, und die Kurve der Funktion $\bar{u} = f([A])$ für verschiedene Konzentrationen des Metallions fallen nicht zusammen.[11] Nur wenn es nicht zur Hydrolyse des Metallions kommt, und keine hydroxo- oder polynukleare Komplexe gebildet werden, gilt die Gleichung (2), aus der man erkennen

* Zwecks Vereinfachung sind die Ladungen weggelassen.

kann, daß $\bar{u}$ nur eine Funktion der Ligandkonzentration ist und von der Konzentration des Metallions und dem pH-Wert nicht abhängt. Die weiteren Erläuterungen beziehen sich nur auf diesen einfachsten Fall.

Die elektrophoretische Stabilitätskonstantenbestimmung wird meistens durch die Anwendung der Gleichung (2)—für die Beweglichkeitskurve—die in expliziter Form folgendermasse gegeben wird, durchgeführt:

$$\bar{u} = \frac{u_0 + u_1 \cdot \beta_1 \cdot C_A + u_2 \cdot \beta_2 \cdot C_A^2 + \ldots + u_q \cdot \beta_q \cdot C_A^q}{1 + \beta_1 \cdot C_A + \beta_2 \cdot C_A^2 + \ldots + \beta_q \cdot C_A^q} \tag{3}$$

Bei sukzessiver Bildung einer größeren Zahl von Komplexen deren Stabilitäte sich wenig unterscheiden, ist die Berechnung der Stabilitätskonstanten aus der Gleichung (3) sehr umständlich, da die Gleichung ($2Q$-1) Unbekannte enthält, wobei Q die Koordinationszahl des höchsten Komplexes, der bei gegebenen Bedingungen entsteht, bedeutet. Die Zahl der Unbekannten vermindert sich um eins, wenn die Messungen bei solchen Bedingungen durchgeführt werden können, bei denen die Konzentration des freien Liganden annähernd gleich der Gesamtkonzentration des Liganden ist. Damit diese Bedingung erfüllt sei, muß $C_A \gg C_{Me}$ und die Lösung in Bezug auf den Liganden gepuffert sein. Die Werte für u_q und β_q können durch die explizite Lösung der Gleichung (3) erhalten werden, d.h. durch Ablesung von $2q$ Paare der Werte von der Kurve $\bar{u} = f(C_A)$, wodurch man ein System von $2q$ Gleichungen erhält, ebenso wie bei der Berechnung der Stabilitätskonstante aus der mittleren Koordinationszahl.[12,13] Die einzelne Konstanten sind in jenen Ligandenkonzentrationsintervalle zu suchen wo diese Komplexe vorherrschen. Zu diesen Zweck können wir die Orientationswerte von u_q und u_{q-1} mit Hilfe folgender Gleichung erhalten:[14]

$$u_q = z\left(\frac{14{,}7}{\sqrt{M}} - 0{,}29\right) \tag{4}$$

und für die β_q Werte können die $\bar{u}$ *vs.* C_A Paare in den Intervallen $\bar{u} = u_q - u_{q+1}$ abgelesen werden. In der Gleichung (4) bedeutet u_q die Beweglichkeit, z die Ladung, M das Molgewicht des Komplexes MeA_q.

Die Beweglichkeit des Komplexes ist eine Funktion der Ladung,[1,15,16] und bei Komplexen bei welchen die Größe des Ligandes sich nicht viel von der Größe des Wassermoleküls unterscheidet, wird die Beweglichkeit durch die durch Einbau des neuen Liganden an Stelle von Wasser hervorgerufene Volumänderung nicht verändert.[17] Die mittlere Ladung der Komplexenreihe, die das Zentralion Me^{n+} mit den Anionen A^{m-} bildet, erhält man durch den Ausdruck:

$$\bar{z} = \frac{n + (n-m)\cdot\beta_1 \cdot C_A + (n-2m)\cdot\beta_2 \cdot C_A^2 + \ldots + (n-qm)\cdot\beta_q \cdot C_A^q}{1 + \beta_1 \cdot C_A + \beta_2 \cdot C_A^2 + \ldots + \beta_q \cdot C_A^q} \tag{5}$$

Beim Vergleich der Gleichung (5) mit (3) sieht man, daß die zwei Gleichungen nur in den Koeffizienten von dem Produkte der Stabilitätskonstanten und der Ligandenkonzentration im Zähler verschieden sind. Die zwei gegebenen Gleichungen stellen zwei unter sich parallele Kurven dar, darum können wir die Stabilitätskonstanten aus der mittleren Ladung des Komplexes berechnen. Für die Berechnung der Konstanten kann die "curve fitting" Methode angewendet werden,[18–20] wobei jene Stabilitätskonstantenwerte zu ermitteln sind die, die Kurve 5 mit der experimentell bestimmten Kurve 3 parallel machen.

EXPERIMENTELLER TEIL

Bei den elektrophoretischen Untersuchungen benützten wir das Gerät für Hochspannungspapierelektrophorese (Elektrophoreser, Dr Virus KG, Meckenheim, Bonn, Modell HE 10100).[21] Die Elektrophoresestreifen wurden zwischen zwei Glasplatten gestellt, wobei die Platten mit thermostatierter Kühllösung (aus den Thermostaten "Ultra Kryomata TK 30D, Wobser KG Messgeräte-Werk Lauda") gekühlt wurden. Um das Einsaugen von Kühllösung an den Streifenenden zu vermeiden, hatten wir in die Wanne mit dem Labyrinthensystem noch heissen, 0,3% Agar-Agar enthaltenden Elektrolyt eingegossen. Kontakt zwischen den Streifen mit Elektrolyt erhält man durch Aufstellen der Wanne auf die Enden der Streifen, die mit Zellophanmembranen umgehüllt sind.[22] Der Boden der Wanne ist aus Sinterglass G-4.

Für die Elektrophorese benützten wir Papierstreifen 2 × 60 cm Whatman No. 1. Auf jeden Streifen hatten wir einen Tropfen in die Mitte des Streifen, quer zu Streifenlänge, als eine Zone (Linie) aufgetragen. Auf die Streifen hatten wir 0,01 ml 0,01M $In(ClO_4)_3$, oder 0,005 ml 0,01M $Cd(ClO_4)_2$* aufgetragen. Indium wurde mittels 8-Oxychinolin,[23,24] Cadmium durch die Radioaktivität identifiziert. Um elektroosmotische- und Strömungseffekte an den Papierstreifen zu verfolgen, benützten wir Wasserstoffperoxyd.[25] Die Beweglichkeit des Komplexes drückten wir als einen Relativwert in Bezug auf $(C_2H_5)_4NOH$ aus.[26] Die Feuchtigkeit des Papiers regulierten wir durch pressen der Streifen zwischen zwei Gummiwalzen von bestimmten Abstand. Auf chromatographischen Wege prüften wir ob die untersuchten Ionen an den Papierstreifen adsorbiert wurden.[27]

Die Elektrophorese wurde mit Lösungen von verschiedenem Natriumacetatgehalt ausgeführt. Alle Lösungen waren 0,1M in Essigsäure, um die Lösungen in Bezug auf Acetationen zu puffern. Um die Gesamtacetatkonzentration in Lösung zu berechnen, wurde für die Dissociationskonstante der Essigsäure der Wert $2{,}17 \cdot 10^{-5}$ genommen. Zu diesen Werte kamen wir durch Umrechnung des für 0° ($\mu = 0$)[28] gegebenen Wertes auf die Ionenstärke 0,1. Die Ionenstärke wurde durch Zugabe von Natriumperchlorat auf 0,1 eingestellt. Die Elektrophorese wurde bei 0 ± 0,05° durchgeführt; der Spannungsabfall betrug 44 V/cm; Elektrophoresedauer 45 Minuten.

Durch die "curve fitting" Methode hatten wir die Stabilitätskonstanten der Cadmiumacetatkomplexe bestimmt. Die beste Überlappung der Kurve 3 wurde mit Kurve 5 erhalten, wenn $q = 2$ gesetzt war; die Stabilitätskonstanten betrugen $\log \beta_1 = 1{,}40$ und $\log \beta_2 = 1{,}95$. In Abb. 1 sind die Werte der mittleren Ladung der Cadmiumacetatkomplexen und der Ionenfraktionen der Ionen, errechnet aus den beiden gegebenen Stabilitätskonstanten in Bezug auf die Konzentration des Acetates, dargestellt. Auf dem gleichen Bilde sind auch die Werte der relativen Beweglichkeiten der Cadmiumacetatkomplexe gegeben.

Durch explizite Lösung der Gleichung (3) hatten wir zuerst aus den erhaltenen Werten im Intervalle $6{,}3 \cdot 10^{-3}$

* Aus radioaktiven CdO hergestellt.

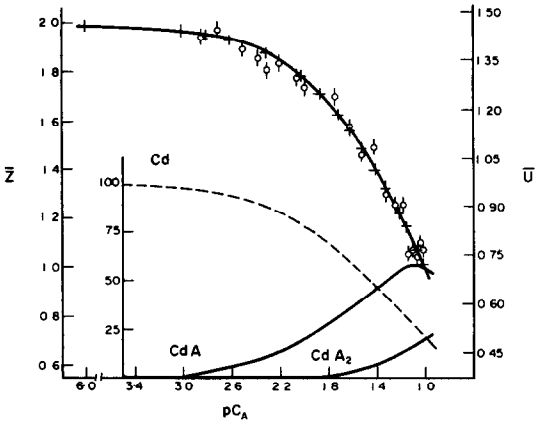

Abb. 1. Mittlere Beweglichkeit, mittlere Ladung und Ionenfraktionen der Cd-Acetatkomplexe bei 0°C und μ = 0,1, wenn $CdCH_3COO^+$ ($\beta_1 = 25$) und $Cd(CH_3COO)_2$ ($\beta_2 = 90$) gebildet werden. + mittlere Ladung; Φ mittlere elektrophoretische Beweglichkeit mit den durchschnittlichen Fehler.

bis $2{,}6 \cdot 10^{-2} M$ die Werte für β_1 und u_1 errechnet, wobei die Bildung des zweiten Komplexes nicht in Betracht genommen wurde. Dann hatten wir bei $C_A > 7{,}10^{-2} M$ den Wert von β_2 ermittelt. Es wurden folgende Werte erhalten: $\log \beta_1 = 1{,}43$; $\log \beta_2 = 1{,}96$ und $u_1 = 0{,}71 \pm 0{,}06$.

Durch Berechnung der mittleren Ladung von Indiumacetatkomplexen durch Anwendung der Gleichung (5) und Vergleichen der Kurve $\bar{z} = f(C_A, \beta_q)$ mit der experimentell erhaltenen Kurve $\bar{u} = f(C_A)$ wurde die beste Überlappung bei $q = 4$ gefunden und für die entsprechenden Stabilitätskonstanten wurden folgende Werte gefunden: $\log \beta_1 = 3{,}52$; $\log \beta_2 = 5{,}93$; $\log \beta_3 = 7{,}91$ und $\log \beta_4 = 9{,}00$. In Abb. 2 sind die Werte der mittleren Ladung und Ionenfraktionen der Indiumacetatkomplexe, aus den erwähnten Stabilitätskonstanten berechnet, in Funktion der Acetatkonzentration dargestellt. In der gleichen Abbildung sind auch die Werte der relativen elektrophoretischen Beweglichkeiten mit den mittleren Abweichung von jeden Punkte dargestellt. Durch explizite Lösung der Gleichung (3) hatten wir folgende Werte für die Stabilitätskonstanten der Indiumacetatkomplexe erhalten: $\log \beta_1 = 3{,}54$; $\log \beta_2 = 5{,}86$; $\log \beta_3 = 7{,}89$; $\log \beta_4 = 9{,}23$. Die Beweglichkeiten der Indiumionen in Abwesenheit von Acetaten u_0 konnten wir wegen Hydrolyse des In^{3+}-Ions nicht messen, darum ermittelten wir u_0 durch Extrapolation der Kurve $\bar{u} = f(C_A)$ auf $C_A = 0$. Für die Beweglichkeit der Komplexe erhielten wir $u_1 = 0{,}542 \pm 0{,}002$; $u_2 = 0{,}20 \pm 0{,}04$; $u_3 = 0$ und $u_4 = -0{,}08 \pm 0{,}09$.

POLAROGRAPHIE

Über die polarographische Untersuchungen von Cadmiumacetatkomplexen haben wir sehr wenige Angaben in der Literatur gefunden[29,30]. Von den In-(III)-Ionen wurden polarographisch meistens die Komplexe mit den Halogeniden[31,32] untersucht. Cozzi und Vivarelli[32] studierten den Einfluß von Acetatkonzentration auf das Halbstufenpotential der In-(III)-Ionen und aus der Verschiebung des Halbstufenpotentials berechneten sie den Wert der Stabilitätskonstante des Indiumtriacetatkomplexes. Die Bildung anderer Komplexe hatten sie nicht registriert.

EXPERIMENTELLER TEIL

Die Messungen wurden am Polarograph "Radiometer Po 4" durchgeführt. Als polarographische Zelle wurde ein Glasrohr mit Glassinter G-4 in der Nähe des Gefäßbodens benutzt. Das Glasrohr ist in ein Erlenmeyerkolben gesteckt, der mit Ableitungen an der Seiten versehen ist. Im Erlenmeyerkolben befand sich eine gesättigte Natriumchloridlösung. Kontakt mit der gesättigter Kalomelelektrode wurde durch ein U-Rohr, mit gesättigten Natriumchlorid in 3%-igem Agar-Agar, erreicht. Das gleiche Gel ist

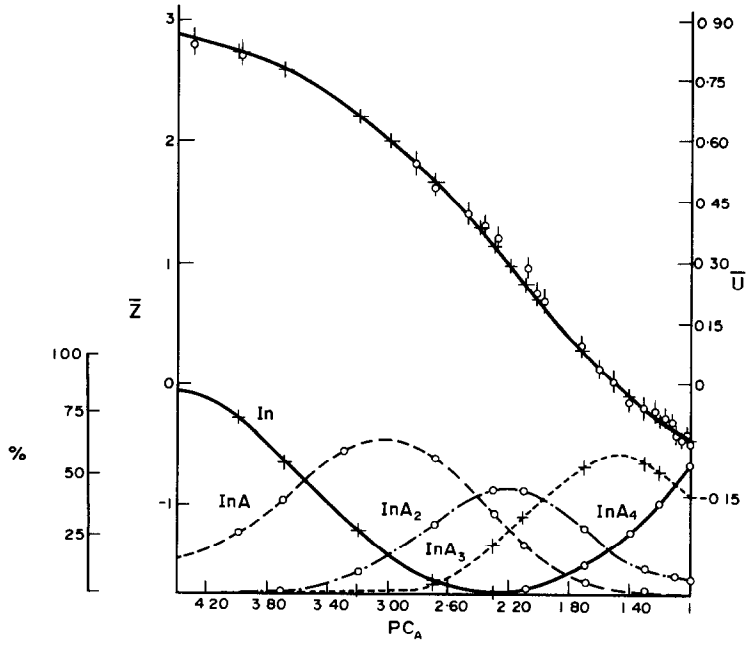

Abb. 2. Mittlere Beweglichkeit, mittlere Ladung und Ionenfraktionen der In-Acetatkomplexe bei 0°C und μ = 0,1 ($NaClO_4$), wenn vier Komplexe gebildet werden mit Stabilitätskonstanten $\beta_1 = 3{,}3 \cdot 10^3$, $\beta_2 = 8{,}6 \cdot 10^5$, $\beta_3 = 8{,}2 \cdot 10^7$ und $\beta_4 = 1 \cdot 10^9$. + mittlere Ladung; Φ mittlere elektrophoretische Beweglichkeit mit den durchschnittlichen Fehler.

auch in die Sintermasse der polarographischen Zelle eingesaugt worden. Erlenmeyerkolben sammt mit der polarographischen Zelle und Kalomelelektrode waren in einem Thermostaten aufgestellt. Die Temperatur betrug $0 \pm 0{,}05°$. Die Kältelösung wurde mit den Ultrakriomaten TK 30 D erzeugt. Um eine Ausscheidung von Kaliumperchlorat zu vermeiden, war die Kalomelelektrode mit Natriumchlorid gesättigt.

Das Potential der Elektrode wurde derweise kontrolliert daß man das Halbwellenpotential des Tl(I)-Ions, in 1*M* Kaliumnitratlösung maß und mit dem in der Literatur befindlichen Wert verglich. Wir fanden 0,509 V, was in guter Übereinstimmung mit 0,508 V steht, den Wert, der mit der Kalomelelektrode, welche mit gesättigten Natriumchlorid gefüllt war, erhalten wurde.[33]

Der Potentiometer des Polarographs wurde mittels eines Westonelementes nach der Poggendorff-Methode und durch Aufnahme der Strom-Spannungs-Kurven geeicht. Der Widerstand der polarographischen Zelle wurde durch Anwendung einer Platinhilfselektrode konduktometrisch gemessen und war um 2200 Ohm in der Lösung der Ionenstärke 0,1. Mit der Änderung des Acetatgehaltes zeigte der Zellenwiderstand keinen wesentlichen Änderung.

Das Halbwellenpotential wurde bei der Methode von DeFord und Hume[9] bis auf $\pm 0{,}1$ mV genau in jedem Experiment gemessen und die Reproduzierbarkeit bei wiederholten Experimenten betrug $\pm 0{,}3$ mV.

Eine 0,01*M* Cadmiumperchloratlösung wurde durch Lösen von CdO in einem kleinen Überschuß von 70%-iger Perchlorsäure vorbereitet und gravimetrisch nach Winkler[34] durch Wägen des Niederschlags von $CdNH_4PO_4 \cdot H_2O$ standardisiert. Die 0,01*M* Indiumperchloratlösung wurde durch Lösen von elementaren Indium (99,9999% rein) in 70%-iger Perchlorsäure unter Erwärmen vorbereitet. Die Lösung wurde bis zu sirupänlicher Konsistenz eingedampft und nach Verdünnen wurde Natriumhydroxid zugegeben um den pH-Wert auf ungefähr 3 zu bringen. Die Lösung wurde gravimetrisch durch Wägen des Hydroxydniederschlags in der Form von In_2O_3 bestimmt. Die 1,2*M* Natriumacetatlösung wurde durch Neutralisation von Essigsäure mit karbonatfreier Natriumhydroxyd-Standardlösung bis zum pH 9,5 vorbereitet, wobei die pH-Werte mittels eines pH-Meters kontrolliert wurden. Die Konzentration der Lösung wurde aus der Menge des zugegebenen Hydroxyds berechnet. Die 2*M* Natriumperchlorat-Standardlösung wurde in gleicher Weise vorbereitet: die Titration der Perchlorsäure wurde bis zum pH-Wert 7 durchgeführt. Eine 4*M* karbonatfreie Natriumhydroxyd-Lösung wurde nach Sørensen vorbereitet und in Polyäthylenflaschen unter Stickstoffatmosphäre aufbewahrt. Die Standardisation der Lösung wurde mit Kaliumbiphthalat durchgeführt. Eine 4*M* Lösung der Essigsäure wurde potentiometrisch mit Natriumhydroxyd standardisiert. Alle verwendete Chemikalien waren von *p.a.* Reinheit.

Zwecks Untersuchungen der Cadmium- und Indium-Acetatkomplexe hatten wir die Bestimmung des Halbwellenpotentials beider Kationen in verschiedenen Acetathaltigen Lösungen vorgenommen. Die Ionenstärke der Lösungen betrug 0,1. Alle Lösungen der Acetationen wurden so vorbereitet daß bestimmte Volumen der standarden 1,2*M* Natriumacetat mit soviel 4*M* Essigsäure vermischt wurden daß sie 0,1*M* in Bezug auf Essigsäuregehalt waren. Die Säure wurde zugegeben um Hydrolyse des Kations zu vermeiden. Die Ionenstärke wurde durch Zugabe von 2*M* Natriumperchlorat eingestellt.

Für die polarographische Messungen wurden 24,70 ml der Grundlösung und 0,30 ml 0,01*M* $Cd(ClO_4)_2$, bzw. $In(ClO_4)_3$ vermengt. Sauerstoff wurde mittels Stickstoff aus der Lösung verdrängt. Um die Reversibilität der Reduktion zu prüfen, ermittelten wir die Anzahl der Elektronen n durch folgende Gleichung:

$$\log \frac{i}{i - i_d} = \frac{n}{0{,}4343\,RT} \cdot F(E_{1/2} - E) \qquad (6)$$

wo i der in μA gemessener Strom auf dem Potential E entspricht. Für Cd erhielten wir den Wert 1,96, und für In(III) Werte um 2,75. Auch bei der Untersuchung der Neigung der Wellen, die bei Oxydation von In-Amalgam erhalten wurden, konnten wir für n nicht den Wert 3, sondern etwas kleinere Werte erhalten. Für diese Diskrepanz zwischen den experimentellen und theoretischen Wert kann man mehrere Erklärungen finden.[35–39]

Die polarographisch erhaltene Daten bearbeiteten wir nach der Methode von DeFord und Hume:[9]

$$F_0(A) = \text{antilog}\left[0{,}4343\,\frac{nF}{RT}(E^s_{1/2} - E^k_{1/2}) + \frac{I_s}{I_k}\right] \qquad (7)$$

Mit $E^s_{1/2}$ ist das Halbwellenpotential des Metallions in Abwesenheit von Liganden, mit $E^k_{1/2}$ das Halbwellenpotential des Komplexes, mit I_s und I_k die entsprechende Diffusionskonstanten der freien und komplexen Ionen bezeichnet.

In der Lösung die einen Überschuß des Liganden in Bezug auf das Metallion enthält, gilt bei konstanter Ionenstärke folgende Beziehung für $F_0(A)$:

$$F_0(A) = 1 + \beta_1 C_A + \beta_2 C_A^2 + \beta_3 C_A^3 + \ldots + \beta_Q C_A^Q \qquad (8)$$

wo β_1, β_2, ... β_Q die entsprechende Bruttostabilitätskonstanten, C_A die Gleichgewichtskonzentration des Liganden in der Lösung annähernd gleich der analytischen Konzentration bedeutet. Die Berechnung des β_n-Wertes aus dieser allgemeinen Gleichung wurde durch das Leden-Verfahren durchgeführt.[40]

Das für die Berechnung von $F_0(A)$ notwendige Halbwellenpotential $E^s_{1/2}$, konnten wir nicht experimentell bestimmen weil diese Kationen in Abwesenheit von Acetaten irreversibel reduziert werden, darum bestimmten wir $E^s_{1/2}$ durch Extrapolation der Gleichung $E^k_{1/2} = f(C_A)$ auf $C_A = 0$. Die Stromdiffusionskonstanten erhielten wir aus der Gleichung:

$$I_k = \frac{i_d}{c \cdot m^{2/3} \cdot t^{1/6}} \qquad (9)$$

wo c die Konzentration des Cd^{2+}-, bzw. In^{3+}-Ions, m die Geschwindigkeit des Quecksilberausflusses aus der Kapillare, t die Tropfzeit des Hg, i_d den Grenzdiffusionstrom in μA, welcher sich mit der Zusammensetzung der Grundlösung ändert, bezeichnet. Die Kapillarkonstante hatte in Fall der Cadmium-Acetationen den Wert $m^{2/3}t^{1/6} = 2{,}50$, bei den Indiumacetatkomplexen $2{,}55\ mg^{2/3}\ sec^{-1/2}$. Die Empfindlichkeit des Galvanometers war $5 \cdot 10^{-3}$ μA/mm. Den Wert für die Stromdiffusionskonstante in Abwesenheit von Acetaten, I_s, bestimmten wir durch Extrapolation der Kurve $I_k = f(C_A)$ auf $C_A = 0$.

Bei graphischer Darstellung von F_1 (A) und F_2 (A) (Abb. 3) wurden Gerade erhalten die auf die Existenz von nur zwei Komplexen, $Cd(CH_3COO)^+$ und $Cd(CH_3COO)_2$ hinzeigen. Durch Extrapolation der Kurven $F(A)$ auf $C_A = 0$ wurden als Konstanten der Komplexe die Werte $\log \beta_1 = 1.49$ und $\log \beta_2 = 2{,}42$ erhalten. Ein Vergleich der erhalten und in der Literatur befindlichen Werten der Cadmiumacetatkomplexe gibt Tabelle 1.

Die $F_q(A)$ Werte der Indiumacetatkomplexe in Funktion der Ligandenkonzentration sind in Abb. 4 und 5 gegeben. Es wurde gefunden daß bei Acetatkonzentrationen $C_A \leq 0{,}1M$ sich fünf Komplexspezien bilden; in Abb. 6 sind die Ionenfraktionen der In(III)-Ionen, gebunden in verschiedenen Komplexen. dargestellt. Die erhaltene Werte der Stabilitätskonstanten der Indiumacetatkomplexen bei $0 \pm 0{,}05°$ sind in der Tabelle 2 gegeben.

DISKUSSION

Von den Arbeiten, die über die Zusammensetzung und Stabilität der Cadmiumacetatkomplexe berichten, sollte man nur die Ergebnisse vergleichen, die

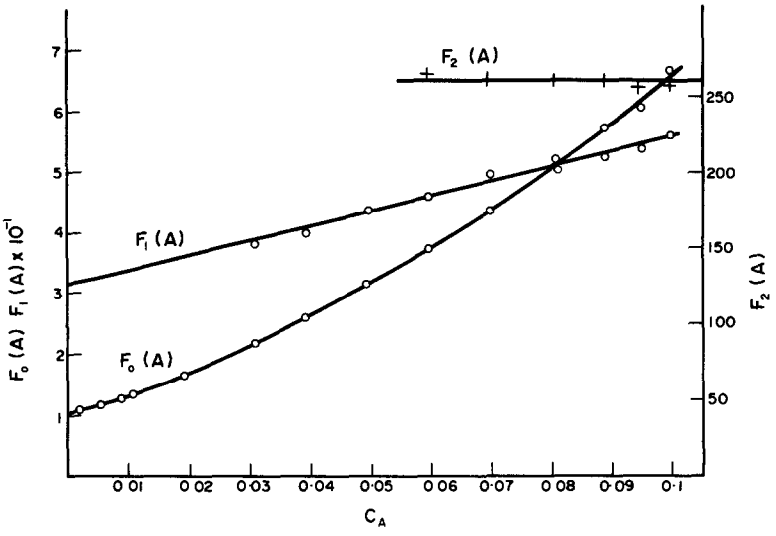

Abb. 3. Werten für F_0(A), F_1(A) und F_2(A) der Cadmiumacetatkomplexen als Funktion der Ligandenkonzentration.

Tabelle 1. Stabilitätskonstanten für Cadmiumacetatkomplexen

	T, °C	μ	log β_1	log β_2	log β_3	log β_4
Diese Arbeit:	0°	0,1				
(*a*) curve-fitting			1,40	1,95	—	—
(*b*) Lösung der Gleichung			1,43	1,96	—	—
(*c*) polarographisch			1,48	2,42	—	—
Bartham und Aditya[41]	25°	0	1,7	—	—	—
Yasuda *et al.*[42]	25°	0,1	1,50	—	—	—
Tanaka und Kato[30]	15°	0,2	1,43	—	—	—
Jacques[43]	25°	0,5	2,0	2,70	3,30	—
Ferrel *et al.*[44]	25°	0,5	1,7	—	—	—
Leden[45]	25°	3	1,3	2,28	2,42	2,20
Martin und Rossotti[46]	25°	3	1,33	2,19	—	—
Aditya und Prasad[47]	30°	?	1,75	2,75	—	—
Medved und Filipovic[29]	25°	2	1,60	2,04	2,04	2,33

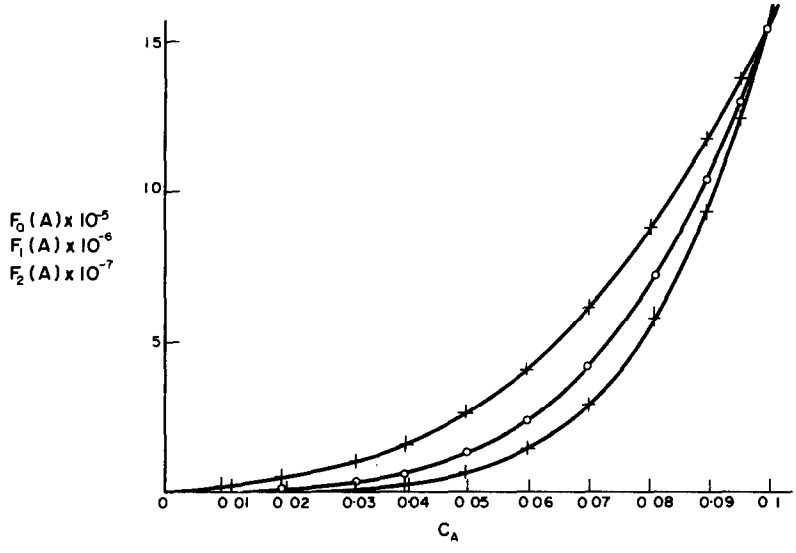

Abb. 4. Werte für F_0(A), F_1(A) und F_2(A) der Indiumacetatkomplexen als Funktion der Ligandenkonzentration.

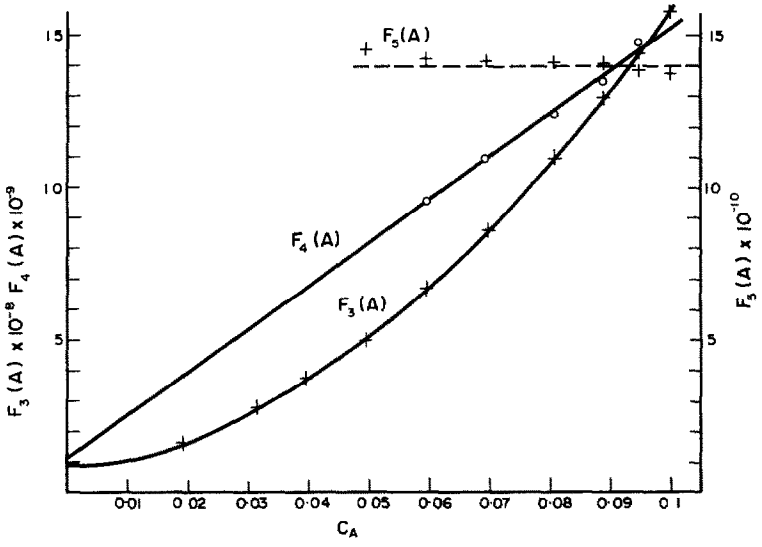

Abb. 5. Werte für $F_3(A)$, $F_4(A)$ und $F_5(A)$ der Indiumacetatkomplexen als Funktion der Ligandenkonzentration.

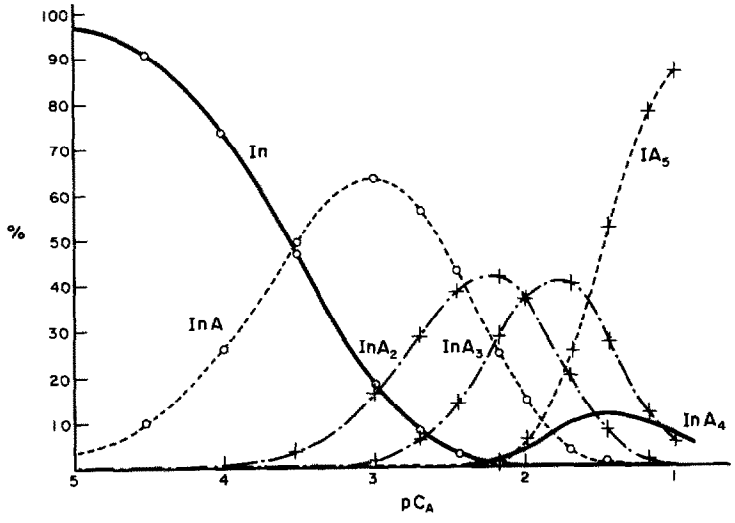

Abb. 6. Ionenfraktione der Indiumazetatkomplexe als Funktion der Acetatkonzentration.

sich auf Lösungen mit kleinen Molbrüchen des Acetats und bei niedrigerer Ionenstärke beziehen, da diese zwei Faktoren hervorragenden Einfluß auf die Zahl und Stabilität der gefundenen Komplexe ausüben.

Sunden[48] hat das Indiumacetatsystem potentiometrisch untersucht und sechs Komplexe gefunden (siehe Tabelle 2). Die Tatsache, daß wir einen Komplex weniger gefunden haben, kann durch die unterschiedliche Konzentrationsbereiche erklärt werden, da Sunden Acetatkonzentration von 2*M* verwendete.

Durch Vergleichen dieser Ergebnisse von zwei unterschiedlichen Verfahren, aber bei sehr änlichen Bedingungen (μ, T) erhält man den Eindruck, daß für das Cadmiumacetatsystem, bei der Papierelektrophoreses die Komplexe weniger Stabil sind im Vergleich zu den polarographisch erhaltenen Gleichgewichten. Eine von den möglichen Erklärungen dieses

Tabelle 2. Stabilitätskonstanten der Indium-acetatkomplexen

	T, °C	μ	log β_1	log β_2	log β_3	log β_4	log β_5	log β_6
Diese Arbeit:	0°	0,1						
(*a*) curve-fitting elektrophor.			3,52	5,93	7,91	9,00		
(*b*) Lösung der Gleichung			3,54	5,86	7,89	9,23		
(*c*) polarographisch			3,54	5,95	7,95	9,04	11,15	
Sunden[48] potentiometrisch	20°	2	3,51	5,95	7,90	9,08	9,30	10,3

verschiedenen Verhaltens der gleichen Systeme in Lösung (bei polarographischen Untersuchungen) und am Papier (bei der Elektrophorese), ist die Möglichkeit einer schwacher Adsorption oder Bindung an die Papierbestandteile einer von der Spezien aus den System CH_3COOH–CH_3COO^-–H^+–$Me(CH_3COO)_q$–Me^{n+}, wodurch das Gleichgewicht zwischen den gebildeten Komplexionen gestört wird. Auch die Möglichkeit einer Wirkungsweise des Trägers (Papier) ist nicht ausgeschlossen. Durch Komplexbildung ändern sich die Grösse, Gestalt und Ladung der Ionen, auch kann es zu verschiedenen Interaktionen zwischen den Komplexen und Papier kommen.

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SIMULTANEOUS DETERMINATION OF *N*-UNSUBSTITUTED AND *N*-SUBSTITUTED NITROAZOLES AND CRITERIA FOR THEIR IDENTIFICATION—III

CHROMATOGRAPHIC SEPARATION AND POLAROGRAPHIC DETERMINATION OF HALO-NITROIMIDAZOLES

D. DUMANOVIĆ, R. MAKSIMOVIĆ and J. ĆIRIĆ
Research Laboratory "Galenika", Zemun, Yugoslavia

and

D. JEREMIĆ
Faculty of Science, University of Belgrade, Yugoslavia

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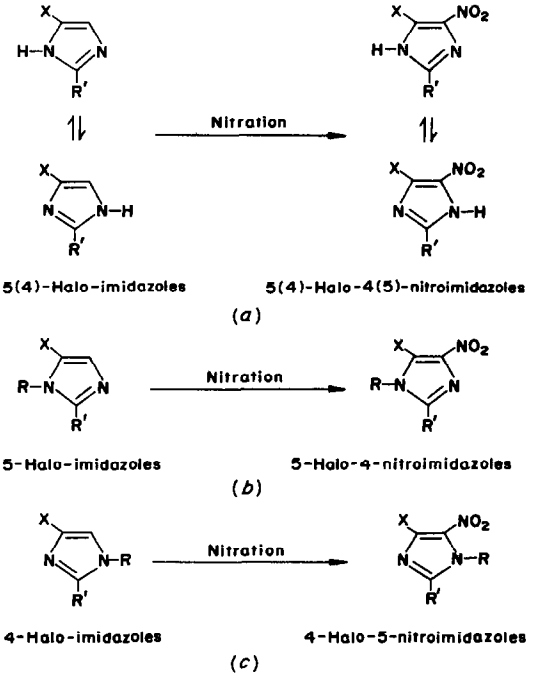
Summary—Methods for identifying and determining halo-nitroimidazoles appearing together during synthetic processes, regardless of the preparation methods, are proposed. Polarographic determination can be used in all synthetic processes when halo-nitroimidazoles have been obtained by nitration of the halo-imidazoles. When the halo-nitroimidazoles have been obtained from 5(4)-halo-4(5)-nitroimidazoles by substitution of the imino hydrogen atom, and when only one *N*-substituted derivative has been obtained in a reaction mixture, simultaneous polarographic determination of both compounds is possible, but only when an alkaline medium is used as supporting electrolyte. In some cases, simultaneous polarographic determination of all three compounds present in a reaction mixture during *N*-substitution processes [one 5(4)-halo-4(5)-nitroimidazole and two *N*-substituted isomers] is also possible with alkaline supporting electrolyte. Explanations are given of the phenomena on which the simultaneous polarographic determination is based. When simultaneous polarographic determination cannot be used to determine the amount of each polarographically-active compound present in a reaction mixture, the compounds can be separated chromatographically and then determined individually by polarography.

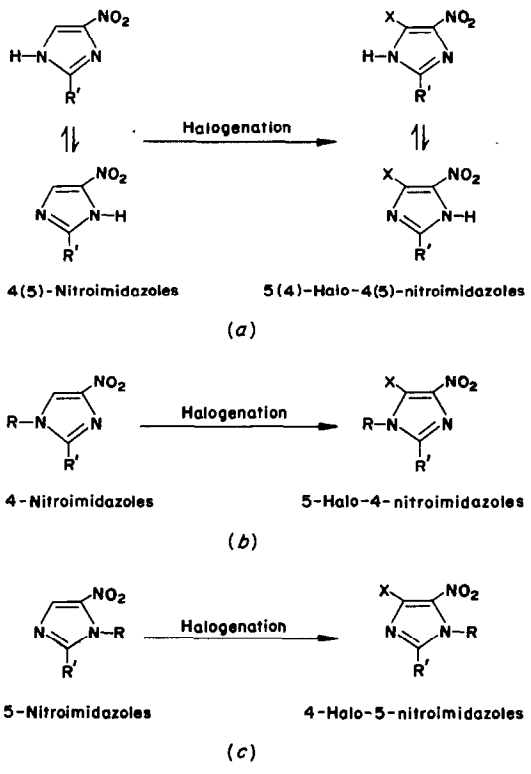
In previous papers[1,2] 0·1*M* alkali was proposed as the medium for simultaneous polarographic determination of nitroimidazoles or nitropyrazoles in reaction mixtures occurring during the *N*-substitution reactions. The method proposed was used to follow the alkylation of 4(5)-nitroimidazoles, *N*-unsubstituted 2-nitroimidazoles, *N*-unsubstituted 4-nitropyrazoles and 3(5)-nitropyrazoles to give their *N*-substituted derivatives. As the different alkyl substituents were without much influence on the $E_{1/2}$ values, we recommended the method even for mixtures of nitroimidazoles or nitropyrazoles which had not yet been studied.

However, halo-nitroimidazoles could not be determined under the same experimental conditions because 5-halo-4-nitroimidazoles are reduced at two different half-wave potentials, and the more positive wave, in some cases, is at nearly the same potential as for the corresponding 4-halo-5-nitroimidazoles. Furthermore, the waves of 5(4)-halo-4(5)-nitroimidazoles are not always well defined in alkaline medium.

The main purpose of the present work was to find methods for following the syntheses of halo-nitroimidazoles, regardless of the preparation methods.



Scheme 1.



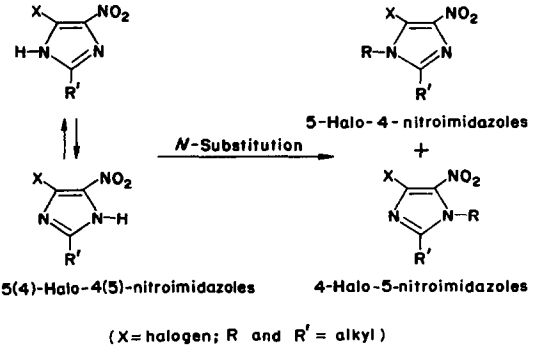
Scheme 2.

In general, halo-nitroimidazoles can be prepared in three different ways: by nitration of halo-imidazoles[3–14] (Schemes 1*a,b,c*), by halogenation of nitroimidazoles[15–19] (Schemes 2*a,b,c*), and by substitution of the imino hydrogen atom of 5(4)-halo-4(5)-nitroimidazoles[10,12,16,18–20] (Scheme 3).

EXPERIMENTAL

Compounds

The substances studied were prepared in the research department for synthetic chemistry of the Pharmaceutical and Chemical Factory "Galenika", Zemun. The physical properties of the substances corresponded to those given in the literature. Three newly synthesized bromo-nitroimidazoles were 2-isopropyl-5(4)-bromo-4(5)-nitroimidazole, white crystals, m.p. 220–221° (recrystallization from ethanol); 1-methyl-2-isopropyl-5-bromo-4-nitroimidazole,



Scheme 3.

white crystals, m.p. 82° (recrystallization from 50% aqueous ethanol); 1-methyl-2-isopropyl-4-bromo-5-nitroimidazole, white crystals, m.p. 49–50° (recrystallization from aqueous ethanol). The structures of the newly synthesized compounds were determined by infrared, NMR and mass spectroscopy.

Chromatographic separations

For chromatographic separations of two compounds having the nitro-group in the same position in the molecule, five different developers were tested so that the best for a given purpose could be chosen, *e.g.*, for a pair of 4(5)-nitroimidazoles (Scheme 2*a*) developers 3, 4 and 5, especially 4, can be recommended. For 4-nitro compounds (Scheme 2*b*) developer 3 is the best, and developer 2 is recommended for 5-nitro compounds (Scheme 2*c*). For a mixture of three compounds (Scheme 3), developers 1 and 2 are proposed.

In Table 1, R_f values are shown for the compounds investigated.

Procedure. Make a solution of the test compound in methanol (1% w/v), and place 0·010 ml on a thin-layer plate. Let the spot dry, place the plate in the developing tank, and chromatograph at room temperature by the ascending technique (about 15 cm) run). Use unactivated 0·25-mm thick layers of silica gel HF_{254} in an atmosphere saturated with the vapour of the developer. After the separation, air-dry the plate and use a needle to mark the position of the spot (visible under short-wave ultraviolet illumination, 254 nm). Spray the same plate with tin(II) chloride solution [1·5 ml of 15% tin(II) chloride solution mixed with 7·5 ml of conc. hydrochloric acid, and diluted with 90 ml of water; this solution is freshly prepared before use], dry it with hot air and then spray it with *p*-dimethylaminobenzaldehyde solution (1 g of reagent dissolved in a mixture of 100 ml of ethanol and 3 ml of conc. hydrochloric acid). After drying, a coloured spot of the nitroimidazole or halo-nitroimidazole appears. All 4-nitro derivatives give a yellow colour, 4(5)- and 5-nitro compounds are yellow–red. This differentiation in colours is probably due to different diazo coupling reactions.[21]

This procedure is used only for the purpose of identification; the experimental conditions for analysis of mixtures will be given later.

Polarography

The polarographic behaviour of all the compounds was examined in 0·5*M* sulphuric acid, acetate buffer (pH 4·68), phosphate buffer (pH 6·85), borate buffer (pH 9·23), 0·1*M* sodium hydroxide and Britton–Robinson buffers over the pH range 1·83–9·30.

5(4)-Bromo-4(5)-nitroimidazoles, with a methyl, ethyl, propyl or isopropyl group in position 2, give two reduction waves in acidic media but only one in slightly acidic, neutral or alkaline media (Fig. 1). 5(4)-Bromo-4(5)-nitroimidazole and 5(4)-chloro-4(5)-nitroimidazole, which have a hydrogen atom in position 2, have a more intricate polarographic behaviour (Fig. 2). The 4-halo-5-nitroimidazoles examined also give two reduction waves in acidic media, and only one wave in neutral and alkaline media (Fig. 3). The 5-halo-4-nitroimidazoles give on wave in slightly acidic and neutral media. In alkaline media the main wave splits into two waves of different height, the sum of which equals the corresponding wave in neutral media (Fig. 4).

The stock solutions ($10^{-3}M$) of all compounds studied were made with water. In some cases, especially when the solutions of 5(4)-halo-4(5)-nitroimidazoles were prepared, the water solution had to be moderately warm. All fundamental measurements, except those designed to investigate the effect of concentration, were carried out with low concentrations of the depolarizers ($2 \times 10^{-4}M$). The solutions examined were prepared by mixing 2 ml of aqueous stock solution ($10^{-3}M$) with 8 ml of the buffer solution, or with

Table 1. Chromatographic separations

Compound	R_f values Developer 1	2	3	4	5
4(5)-Nitroimidazole	0·0	0·0	0·45	0·25	0·45
5(4)-Bromo-4(5)-nitroimidazole	0·0	0·0	0·61	0·0	0·64
5(4)-Chloro-4(5)-nitroimidazole	0·0	0·0	0·64	0·0	0·63
2-Methyl-4(5)-nitroimidazole	0·0	0·0	0·40	0·53	0·60
2-Methyl-5(4)-bromo-4(5)-nitroimidazole	0·0	0·0	0·65	0·16	0·71
2-Isopropyl-4(5)-nitroimidazole	0·17	0·08	0·69	0·66	0·53
2-Isopropyl-5(4)-bromo-4(5)-nitroimidazole	0·0	0·16	0·91	0·24	0·69
1-Methyl-4-nitroimidazole	0·12	0·09	0·31	0·76	0·81
1-Methyl-5-bromo-4-nitroimidazole	0·24	0·16	0·45	0·86	0·91
1-Methyl-5-chloro-4-nitroimidazole	0·19	0·15	0·42	0·86	0·90
1,2-Dimethyl-4-nitroimidazole	0·21	0·12	0·40	0·80	0·70
1,2-Dimethyl-5-bromo-4-nitroimidazole	0·39	0·20	0·59	0·90	0·85
1-Methyl-2-isopropyl-4-nitroimidazole	0·62	0·12	0·66	0·85	0·83
1-Methyl-2-isopropyl-5-bromo-4-nitroimidazole	0·81	0·26	0·84	0·92	0·91
1-Methyl-5-nitroimidazole	0·55	0·22	0·51	0·90	0·80
1-Methyl-4-bromo-5-nitroimidazole	0·49	0·42	0·67	0·93	0·90
1-Methyl-4-chloro-5-nitroimidazole	0·46	0·42	0·67	0·93	0·89
1,2-Dimethyl-5-nitroimidazole	0·67	0·21	0·60	0·92	0·77
1,2-Dimethyl-4-bromo-5-nitroimidazole	0·59	0·41	0·75	0·93	0·87
1-Methyl-2-isopropyl-5-nitroimidazole	0·90	0·36	0·87	0·94	0·94
1-Methyl-2-isopropyl-4-bromo-5-nitroimidazole	0·89	0·64	0·93	0·94	0·93

Developer 1, diethylamine.
Developer 2, benzene–methanol (90:5).
Developer 3, benzene–diethyl ether–acetic acid–methanol (30:30:9:5).
Developer 4, chloroform–methanol–ammonia solution (85:14:1).
Developer 5, chloroform–methanol–formic acid (85:10:5).

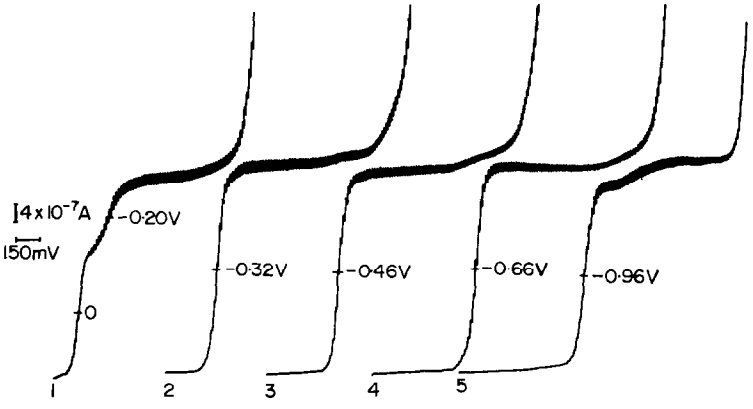


Fig. 1. Polarographic waves of 2-methyl-5(4)-bromo-4(5)-nitroimidazole at different pH values. *1*–0·5*M* H_2SO_4; *2*–acetate buffer pH 4·68; *3*–phosphate buffer pH 6·85; *4*–borate buffer pH 9·23; *5*–0·1*M* NaOH. Concentration of the compound $2 \times 10^{-4}M$. Starting potential for curve *1* is +0·15 V *vs.* S.C.E.; for curves *2*, *3*, *4* it is 0 V *vs.* S.C.E.; for curve *5* it is −0·15 V *vs.* S.C.E.

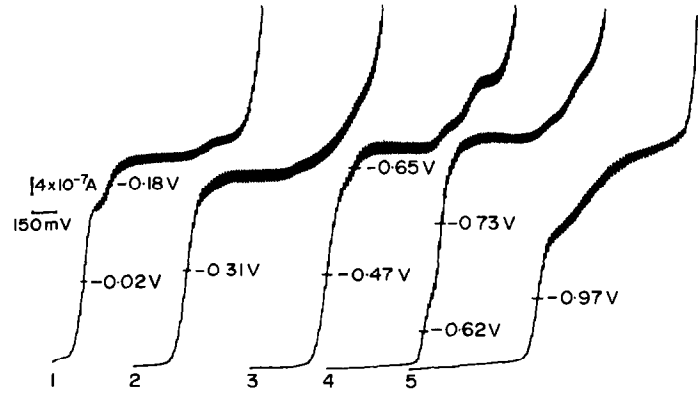


Fig. 2. Polarographic waves of 5(4)-bromo-4(5)-nitroimidazole at different pH values. Conditions as for Fig. 1.

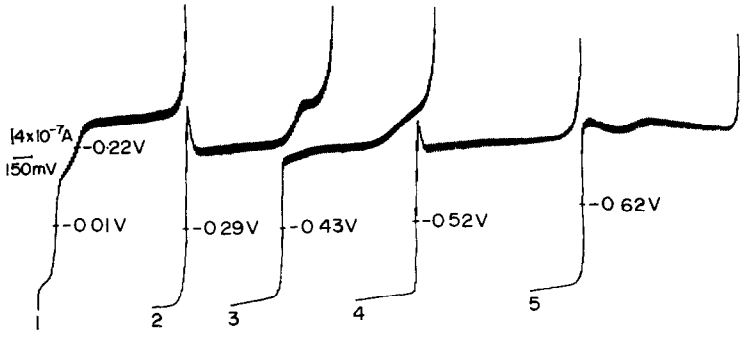


Fig. 3. Polarographic waves of 1,2-dimethyl-4-bromo-5-nitroimidazole at different pH values. Conditions as for Fig.1.

3 ml of water and 5 ml of 1*M* sulphuric acid, or with 3 ml of water and 5 ml of 0·2*M* sodium hydroxide.

The direct proportionality between wave height and the square root of effective mercury reservoir height, and the computed temperature coefficients, indicate that the reduction waves of the compounds studied are predominantly diffusion-controlled over the pH range investigated.

It was found for all halo-nitroimidazoles investigated that over the range from 5×10^{-5} to $5 \times 10^{-4}M$, the heights of the waves are a linear function of the concentration, at any pH value.

The half-wave potentials of the nitroimidazoles and corresponding halo-nitroimidazoles are shown in Table 2. From these data it can be seen that the $E_{1/2}$ values of 5(4)-halo-4(5)-nitroimidazoles and 5-halo-4-nitroimidazoles are almost identical over the whole pH range, except in alkaline media, and they are only slightly more negative than those of 4-halo-5-nitroimidazoles.

When halo-nitroimidazoles have been obtained by nitration of halo-imidazoles (Schemes 1*a*,*b*,*c*) polarographic determination of a halo-nitroimidazole in any one reaction mixture is possible, because in all these cases there are always only two compounds, of which the starting compound has no nitro group in its molecule and accordingly is not polarographically active.

Since the synthetic reaction conditions and composition of the solutions are different in each case, the content of halo-nitroimidazole should be determined by the method of standard addition, instead from a calibration curve.

Procedure. Weigh a sample of reaction mixture, dissolve it in distilled water, and make up to 100 ml, so that the concentration of the polarographically-active compound is about $10^{-3}M$ or lower. Transfer a 1-ml portion to a polarographic cell, add water (2 ml) and a suitable buffer (7 ml). Deareate the solution with nitrogen for 5 min, and record the polarogram over a suitable voltage range, which depends on the buffer used.

Transfer another 1-ml portion of the sample solution to a polarographic cell, add 2 ml of $10^{-3}M$ standard solution of the halo-nitroimidazole being determined, and 7 ml of the buffer solution, and proceed as before. Evaluate the polarograms by using the equation $\% = (100hc)/(h'w)$ where $\%$ = amount of the halo-nitroimidazole present in the mixture, h = wave-height for the sample, c = weight of the standard added (g), w = weight of the sample in the cell (g), h' = wave-height for the standard (*i.e.*, increase in the wave-height when standard is added).

RESULTS AND DISCUSSION

Simultaneous polarographic determination

In reaction mixtures according to Scheme 3, three compounds can be expected. However, very often only two are found to be present: a 5(4)-halo-4(5)-nitroimidazole and the corresponding 4-halo-5-nitroimidazole or 5-halo-4-nitroimidazole. In such cases, when it is chromatographically established that a reaction mixture contains only one *N*-substituted derivative besides the *N*-unsubstituted one, it is possible to determine both compounds simultaneously, using 0·1*M* sodium hydroxide as supporting electrolyte (Figs. 5 and 6).

The possibility of simultaneous polarographic determination is based on the ability of 5(4)-halo-4(5)-nitroimidazoles to dissociate to the corresponding anions, the $E_{1/2}$ values of which are strongly shifted to more negative potentials. *N*-Substituted derivatives have no imino hydrogen atom and cannot be dissociated. This makes possible the simultaneous polar-

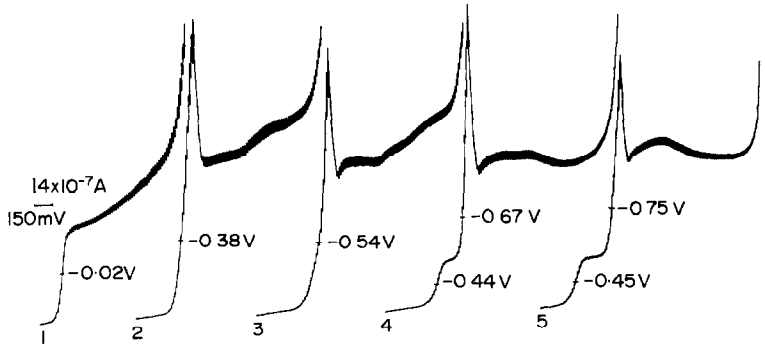


Fig. 4. Polarographic waves of 1,2-dimethyl-5-bromo-4-nitroimidazole at different pH values. Conditions as for Fig. 1.

Table 2. $-E_{1/2}$ as a function of pH

Compound	$-E_{1/2}$ vs. S.C.E., V													
	0·5M H_2SO_4	Acetate buffer pH = 4·68	Phosphate buffer pH = 6·85	Borate buffer pH = 9·23	0·1M NaOH	pH (Britton–Robinson buffer) 1·83	2·23	3·20	4·20	5·03	6·06	7·04	8·22	9·30
4(5)-Nitroimidazoles														
4(5)-Nitroimidazole	0·04	0·41	0·59	0·70	0·95	0·21	0·24	0·32	0·40	0·46	0·55	0·60	0·62	0·71
2-Methyl-4(5)-nitroimidazole	0·03	0·39	0·57	0·67	0·94	0·16	0·19	0·28	0·36	0·42	0·52	0·55	0·61	0·68
2-Isopropyl-4(5)-nitroimidazole	0·02	0·37	0·54	0·66	0·93	0·16	0·19	0·29	0·34	0·39	0·53	0·58	0·60	0·66
5(4)-Halo-4(5)-nitroimidazoles														
5(4)-Bromo-4(5)-nitroimidazole	0·02 0·18	0·31 0·48	0·47 0·65	0·62	0·97	0·14 0·38	0·16 0·40	0·23 0·46	0·28 0·48	0·33 0·53	0·41 0·60	0·49	0·58	0·74
5(4)-Chloro-4(5)-nitroimidazole	0·05 0·22	0·34	0·50 0·67	0·76	0·98	0·15 0·41	0·18 0·44	0·23 0·43	0·31 0·48	0·37 0·53	0·57	0·60	0·63	0·79
2-Methyl-5(4)-bromo-4(5)-nitroimidazole	0·00 0·20	0·32	0·46	0·66	0·96	0·14 0·39	0·17 0·43	0·23	0·29	0·33	0·41	0·48	0·60	0·69
2-Ethyl-5(4)-bromo-4(5)-nitroimidazole	0·00 0·18	0·31	0·46	0·67	0·96	0·14	0·18	0·24	0·30	0·35	0·42	0·49	0·58	0·68
2-Propyl-5(4)-bromo-4(5)-nitroimidazole	0·01 0·20	0·34	0·46	0·66	0·95	0·14 0·33	0·17 0·36	0·24	0·30	0·35	0·41	0·47	0·57	0·67
2-Isopropyl-5(4)-bromo-4(5)-nitroimidazole	0·01 0·20	0·34	0·49	0·68	0·96	0·15 0·36	0·19	0·24	0·30	0·36	0·43	0·50	0·58	0·69
4-Nitroimidazoles														
1-Methyl-4-nitroimidazole	0·05	0·40	0·58	0·68	0·73	0·20	0·23	0·29	0·36	0·43	0·51	0·56	0·63	0·69
1,2-Dimethyl-4-nitroimidazole	0·04	0·39	0·56	0·69	0·75	0·16	0·20	0·29	0·33	0·42	0·52	0·57	0·62	0·69
1-Methyl-2-isopropyl-4-nitroimidazole	0·04	0·40	0·57	0·69	0·76	0·19	0·21	0·29	0·36	0·44	0·53	0·59	0·64	0·70
5-Halo-4-nitroimidazoles														
1-Methyl-5-bromo-4-nitroimidazole	0·06	0·35	0·50	0·47 0·68	0·47 0·75	0·16	0·17	0·22	0·29	0·32	0·45	0·50	0·48 0·59	0·46 0·67
1-Methyl-5-chloro-4-nitroimidazole	0·08	0·35	0·53	0·65	0·69	0·18	0·20	0·26	0·33	0·39	0·44	0·49	0·60	0·66
1,2-Dimethyl-5-bromo-4-nitroimidazole	0·02	0·38	0·54	0·44 0·67	0·45 0·75	0·17	0·21	0·27	0·33	0·39	0·46	0·54	0·44 0·63	0·44 0·69
1-Methyl-2-isopropyl-5-bromo-4-nitroimidazole	0·05	0·41	0·55	0·48 0·69	0·48 0·77	0·19	0·22	0·28	0·34	0·44	0·50	0·46 0·57	0·46 0·62	0·46 0·69
5-Nitroimidazoles														
1-Methyl-5-nitroimidazole	0·02	0·29	0·46	0·57	0·61	0·12	0·13	0·21	0·25	0·33	0·42	0·48	0·54	0·58
1,2-Dimethyl-5-nitroimidazole	0·02	0·27	0·45	0·58	0·64	0·10	0·12	0·18	0·24	0·32	0·40	0·47	0·52	0·57
1-Methyl-2-isopropyl-5-nitroimidazole	0·01	0·27	0·45	0·58	0·64	0·07	0·11	0·17	0·25	0·32	0·43	0·47	0·53	0·59
4-Halo-5-nitroimidazoles														
1-Methyl-4-bromo-5-nitroimidazole	0·05 0·22	0·28	0·45	0·53	0·61	0·09	0·12 0·36	0·18	0·23	0·29	0·36	0·42	0·45	0·53
1-Methyl-4-chloro-5-nitroimidazole	0·06 0·22	0·29	0·43	0·55	0·59	0·13 0·44	0·17	0·21	0·26	0·31	0·42	0·48	0·53	0·57
1,2-Dimethyl-4-bromo-5-nitroimidazole	0·01 0·22	0·29	0·43	0·52	0·62	0·09 0·38	0·13 0·42	0·19	0·26	0·32	0·39	0·45	0·48	0·52
1-Methyl-2-isopropyl-4-bromo-5-nitroimidazole	0·01 0·23	0·31	0·49	0·56	0·65	0·11 0·40	0·14 0·45	0·21	0·27	0·35	0·43	0·48	0·53	0·56

$E_{1/2}$ values are corrected by comparison with the half-wave potential of thallium in 0·1M KCl.

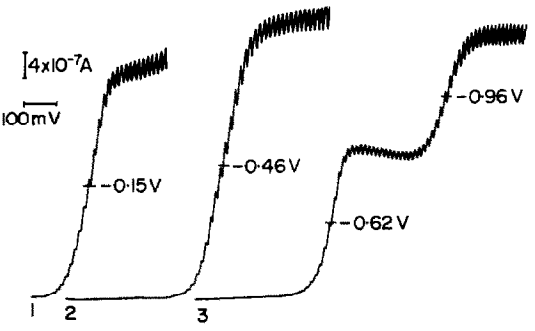


Fig. 5. Polarographic waves of equimolar mixtures of 2-methyl-5(4)-bromo-4(5)-nitroimidazole and 1,2-dimethyl-4-bromo-5-nitroimidazole at different pH values. *1*–pH 1·81; *2*–7·04 (Britton-Robinson buffers; *3*–0·1*M* NaOH. Concentration of each compound $10^{-4}M$. Curves *1* and *2* start at 0 V *vs.* S.C.E. Curve *3* starts at −0·2 V *vs.* S.C.E.

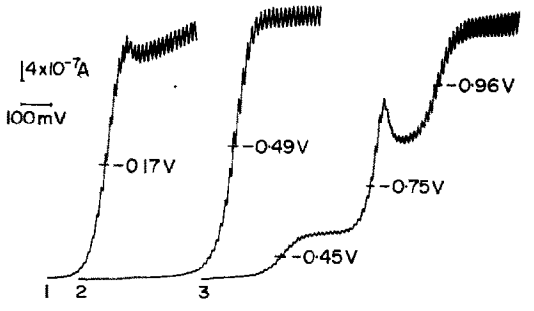
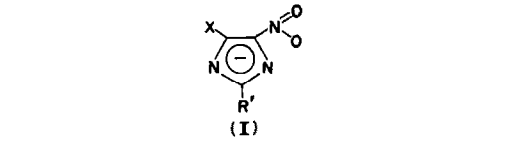


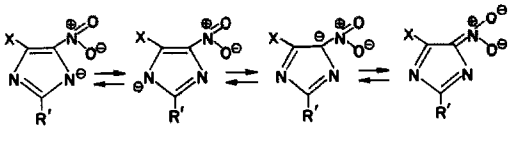
Fig. 6. Polarography of equimolar mixtures of 2-methyl-5(4)-bromo-4(5)-nitroimidazole and 1,2-dimethyl-5-bromo-4-nitroimidazole at different pH values. Conditions as for Fig. 5.

ographic determination of any pair of nitroazoles, one of which is an *N*-unsubstituted nitroazole and the other a corresponding *N*-substituted derivative.

The strongly negative shift of the $E_{1/2}$ of 5(4)-halo-4(5)-nitroimidazoles, when an alkaline medium is used as a supporting electrolyte, is due to their transformation into the anions, which have to be represented, not as the usual form (I), but as a resonance hybrid (II), where the contribution of the last resonance structure is quite important.



(I)



Resonance in 5(4)-halo-4(5)-nitroimidazole anions (II)
(X = halogen; R' = alkyl)

Only when the anions have been represented in this way can the shift of their $E_{1/2}$ to more negative values, their light-absorption at longer wavelengths, and their stability in alkaline media be understood.

As during the substitution of the imino hydrogen atom three compounds can be present in a reaction mixture (Scheme 3), we shall examine and explain the possibilities for their simultaneous polarographic determination.

From the $E_{1/2}$ values of different nitroimidazoles[1] and nitropyrazoles[2] it follows that the nitro-group's electron density strongly depends upon the position of the group in the ring. The electron density of the nitro-group increases with proximity to the pyridine nitrogen atom. Thus, the electron density of the nitro-group in the *ortho* position to the pyridine nitrogen atom (4 and 3 positions in imidazoles and pyrazoles, respectively) is greater than when it is in the *meta* position (position 5). This difference in the electron density of the nitro-group, together with the shift in $E_{1/2}$ on dissociation of 4(5)-nitroimidazoles and 3(5)-nitropyrazoles to the corresponding anions, makes possible the simultaneous polarographic determination of three compounds [*e.g.*, of a 4-, 5- and 4(5)-nitroimidazole[1] or a 3-, 5- and 3(5)-nitropyrazole[2]], but only when an alkaline medium is used as supporting electrolyte.

The halo-nitroimidazoles investigated behave similarly. From Table 2 it can be seen that the $E_{1/2}$ values of 5(4)-halo-4(5)-nitroimidazoles and corresponding 4(5)-nitroimidazoles are almost identical. The same holds for the 4-halo-5-nitroimidazoles and corresponding 5-nitroimidazoles. However, the 5-halo-4-nitroimidazoles do not show the same polarographic behaviour as the corresponding 4-nitroimidazoles. In alkaline media 5-halo-4-nitroimidazoles give two reduction waves, but only the more negative wave occurs at almost the same potential as that of the corresponding 4-nitroimidazoles. The more positive wave of the 5-halo-4-nitroimidazoles is in some cases at nearly the same potential as that for the corresponding 4-halo-5-nitroimidazoles. The difference ($\Delta E_{1/2}$) for a mixture of a 5-halo-4-nitroimidazole (first reduction wave) and a 4-halo-5-nitroimidazole is much smaller than the difference between the half-wave potentials for pure solutions of each separately (compared the $E_{1/2}$ values in Fig. 7 and in Table 2). Probably the adsorption of depolarizer and/or the reduction product must play an important role. This behaviour of 5-halo-4-nitroimidazoles limits the possibilities of simultaneous polarographic determination.

When the simultaneous polarographic determination can be applied, the first and third reduction waves correspond to a 5-halo-4-nitroimidazole, the second wave to a 4-halo-5-nitroimidazole and the fourth to a 5(4)-halo-4(5)-nitroimidazole (Fig. 7). The procedure for this determination and for that when only one *N*-substituted derivative is present besides a 5(4)-halo-4(5) nitroimidazole in a reaction mixture, is as follows.

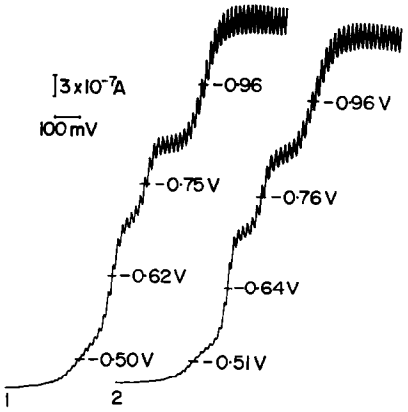


Fig. 7. Polarographic waves of equimolar mixtures of 2-methyl-5(4)-bromo-4(5)-nitroimidazole, 1,2-dimethyl-5-bromo-4-nitroimidazole and 1,2-dimethyl-4-bromo-5-nitroimidazole (curve *1*); 2-isopropyl-5(4)-bromo-4(5)-nitroimidazole, 1-methyl-2-isopropyl-5-bromo-4-nitroimidazole and 1-methyl-2-isopropyl-4-bromo-5-nitroimidazole (curve *2*). Concentration of each compound $10^{-4}M$. Supporting electrolyte 0·1*M* NaOH. The curves start at −0·2 V *vs.* S.C.E.

Procedure. Weigh a sample from the reaction mixture, dissolve it in distilled water and make up to 100 ml, so that the concentration of all polarographically-active compounds is about $10^{-3}M$ or lower. Transfer a 2-ml portion to a polarographic cell and add water (3 ml) and 0·2*M* sodium hydroxide (5 ml). Deaerate the solution with nitrogen for 5 min and then record the polarogram over the range from −0·2 to −1·4 V *vs.* S.C.E.

Transfer another 2-ml portion of sample solution to a polarographic cell, add 1 ml (or 1·5 ml if only two compounds are present) of $10^{-3}M$ standard solution of each compound present in the sample examined, and 5 ml of 0·2*M* sodium hydroxide, and proceed as before. From the polarograms obtained calculate the amount of each compound present in the reaction mixture.

Chromatographic separation and polarographic determination

In *N*-substitution processes according to Scheme 3, when the starting compound is 5(4)-bromo-4(5)-nitroimidazole or 5(4)-chloro-4(5)-nitroimidazole and three compounds are present in the reaction mixture, the components cannot be determined simultaneously.

Furthermore, when halo-nitroimidazoles are prepared by halogenation of nitroimidazoles (Schemes 2*a*,*b*,*c*) then in the reaction mixtures there are two polarographically-active substances with the nitro-group in the same position, and again the simultaneous polarographic determination cannot be applied. The substances with the nitro-group in the same position in the molecule have nearly the same $E_{1/2}$ regardless of the substituents in positions 1, 4 and 5, which do not have the great influence on the electron density of the nitro-group that is needed for the simultaneous determination.

In such cases, chromatographic separation followed by polarographic determination has proved very useful.

Procedure. Weigh a sample from the reaction mixture, dissolve it in methanol and make up to 10 ml, so that the concentration of all polarographically-active compounds is between 3×10^{-3} and $10^{-2}M$. Put 0·10- or 0·20-ml portions of this solution on the starting line of the thin-layer plate (10 × 20 cm) in very close-set spots. After the chromatographic separation, locate the bands under short-wave ultraviolet illumination (254 nm) and mark them with a needle. Scrape off each band and some adjacent silica gel with a razor blade, weigh each and put them into 10-ml standard flasks, add water (2 ml), mix for 10 min, make up to 10 ml with a suitable buffer, mix again, transfer to a polarographic cell and record the polarogram. Compare the wave-height of the sample with that of a standard solution containing the same weight of silica gel as the test sample, and proceed as before.

The criteria for distinction between N-*unsubstituted halo-nitroimidazoles and their* N-*substituted derivatives*

N-Unsubstituted halo-nitroimidazoles, because of their pseudo-acidic character, have lower R_f values in a basic developer (diethylamine) than do the corresponding *N*-substituted derivatives. 4-Halo-5-nitroimidazoles are stronger bases than the corresponding 5-halo-4-nitroimidazoles and hence have the highest R_f values in the same developer. In all the developers tested, the 5-halo-4-nitroimidazoles studied here gave a yellow colour with tin(II) chloride and *p*-dimethylaminobenzaldehyde reagent on silica gel thin-layers. Under the same treatment 5(4)-halo-4(5)-nitroimidazoles and 4-halo-5-nitroimidazoles give a yellow, yellow-red or red colour.

5(4)-Halo-4(5)-nitroimidazoles in alkaline media (*i.e.*, 0·1*M* sodium hydroxide) show a strong negative shift of $E_{1/2}$, compared with the corresponding *N*-substituted derivatives. 5(4)-Halo-4(5)-nitroimidazoles and 5-halo-4-nitroimidazoles have almost the same $E_{1/2}$ values over the whole pH range (except in alkaline media). The $E_{1/2}$ values of 4-halo-5-nitroimidazoles are slightly more positive.

N-Unsubstituted halo-nitroimidazoles do not decompose on standing in 0·5*M* sodium hydroxide, whereas *N*-substituted ones do.

All these facts also apply to the nitroimidazoles studied earlier.[1] However, the rate of degradation of 4-halo-5-nitroimidazoles in comparison with the degree of degradation of the corresponding isomers could not be used as a criterion for distinction between these isomers, as was proposed for the nitroimidazoles.[1] This is probably due to the degradation reactions of the *N*-substituted halo-nitroimidazoles being quite different.

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BASICITY OF NITROPYRAZOLES AND THEIR SIMULTANEOUS SPECTROPHOTOMETRIC DETERMINATION

D. DUMANOVIĆ and J. CIRIĆ

Research Laboratory "Galenika", Zemun, Yugoslavia

and

A. MUK and V. NIKOLIĆ

Boris Kidrič Institute of Nuclear Sciences Vinča, Beograd, Yugoslavia

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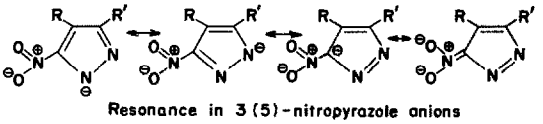
Summary—The protonation constants of some 1-, 3(5)-, 3-, 4- and 5-nitropyrazoles have been determined, and compared with those of nitroimidazoles. The effect of the position of the nitro group in the pyrazole and imidazole ring is discussed. The *ortho* effects of the nitro group in pyrazole and imidazole are compared and found to have identical values. The effect of the nitro group on protonation constants is greater when the nitro group is close to the pyridine nitrogen atom. This, together with the ability of *N*-unsubstituted nitropyrazoles to dissociate to give nitropyrazole anions, with an accompanying shift of the spectra to longer wavelengths, permits the simultaneous spectrophotometric determination of nitropyrazoles.

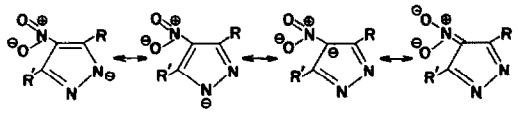
In earlier investigations of the nitropyrazoles it has been shown that mixtures of different nitropyrazoles can be simultaneously analysed by polarography.[1] The protonation constants of various nitro compounds, especially nitroimidazoles,[2–5] are dependent on the position of the nitro group in the ring. Initially, only 4-nitro derivatives of pyrazole were investigated[6] because it was believed the nitro group could be only in position 4,[7–9] or 1.[10] Subsequently a series of 3(5)-nitropyrazoles were synthesized,[11–16] and some of these have been used as the starting materials for the preparation of new 3- and 5-nitropyrazoles.[17]

The introduction of a nitro group at different positions in the pyrazole ring, strongly and differently decreases the values of the protonation constants, and strongly but not differently[18] increases the dissociation constants. As only *N*-unsubstituted nitropyrazoles can be dissociated and as these constants are almost identical for different nitropyrazoles, they probably cannot be used for correlations with the structure. For the reason given later, we decided to study the basicity of nitropyrazoles in preference to the acidity. Further, the basicity is a common characteristic of all nitropyrazole derivatives, *N*-unsubstituted as well as *N*-substituted. Nitropyrazoles with the nitro group in every possible position for the pyrazole ring [1, 3(5), 3, 5, 4 (*N*-unsubstituted and *N*-substituted)], were available, so it was of interest to compare the influence of the different positions of the nitro group on the protonation constants, and compare the results with those found for nitroimidazoles.[3]

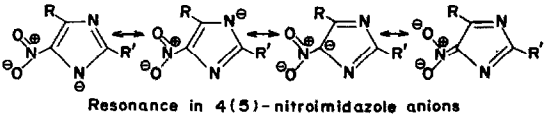
The reason why the values of dissociation constants could not be used for correlation with structures, is their similarity, *e.g.*, 3(5)-nitropyrazole 9·81,[18] *N*-unsubstituted 4-nitropyrazole 9·67,[18] and 4(5)-nitroimidazoles, 9·20 for R and R′ = H;[3] 9·67 for R = H and R′ = CH_3;[19] 9·61 for R = H and R′ = $CH(CH_3)_2$.[19] The almost identical values are the result of the transformation of *N*-unsubstituted nitroazoles into the corresponding anions, during the process of dissociation. These anions can be regarded as resonance hybrids, where the contribution of the last resonance structure, for each hybrid, is quite important. All these anions



Resonance in 3(5)-nitropyrazole anions



Resonance in 4-nitropyrazole anions



Resonance in 4(5)-nitroimidazole anions

(R and R′ = alkyl or aryl)

are similar, spatially as well as electronically, and this is the reason for the identical values of dissociation constants for such different compounds. As only the

Table 1. Ultraviolet absorption data for nitropyrazoles (λ_{max} in nm), ϵ in l.mole^{-1}.cm^{-1})

Compound	Medium, λ_{max}, log ϵ_{BH^+} for cation	Medium, λ_{max}, log ϵ_B for neutral molecule	Medium, λ_{max}, log ϵ_{B^-} for anion
Pyrazole	12·0*M* H_2SO_4, 215, 3·76	pH = 6·1, 210, 3·61	
1-Nitropyrazole	16·0*M* H_2SO_4, 216, 3·81	1*M* H_2SO_4, 267, 3·91	
4-Nitropyrazole	17·1*M* H_2SO_4, 234, 3·85	1*M* H_2SO_4, 274, 3·89	pH = 11·7, 320, 4·11
1-Methyl-4-nitropyrazole	17·1*M* H_2SO_4, 242, 3·90	1*M* H_2SO_4, 281, 3·97	
1-Ethyl-4-nitropyrazole	17·2*M* H_2SO_4, 242, 3·87	1*M* H_2SO_4, 281, 3·96	
3(5)-Nitropyrazole	17·1*M* H_2SO_4, 225, 3·88	1*M* H_2SO_4, 258, 3·83	pH = 11·5, 315, 3·87
1-Methyl-3-nitropyrazole	17·1*M* H_2SO_4, 237, 3·82	5*M* H_2SO_4, 273, 3·83	
1-Ethyl-3-nitropyrazole	17·0*M* H_2SO_4, 242, 3·86	5*M* H_2SO_4, 274, 3·85	
1-Methyl-5-nitropyrazole	17·1*M* H_2SO_4, 235, 3·88	1*M* H_2SO_4, 275, 3·87	
1-Ethyl-5-nitropyrazole	17·0*M* H_2SO_4, 228, 3·99	1*M* H_2SO_4, 277, 3·91	

last resonance structures satisfy Hückel's rule of aromaticity, they have to be the major ones. Furthermore, they best explain the stability of the anions, their absorption at longer wavelengths and their more negative values of $E_{1/2}$.[1,20] From the aforesaid it is clear that for correlations with the structure it is important to know the values of the protonation constants of different nitropyrazoles.

EXPERIMENTAL

Compounds

All nitropyrazoles studied were prepared in the Research Laboratory "Galenika", Zemun. 1-Nitropyrazole, 4-nitropyrazole, 1-methyl-4-nitropyrazole and 3(5)-nitropyrazole had the melting points and properties reported in the literature. The newly synthesized compounds were 1-ethyl-4-nitropyrazole, white crystals, m.p. 64–64·5°; 1-methyl-3-nitropyrazole, whilte crystals, m.p. 85–86°; 1-methyl-5-nitropyrazole, pale yellow liquid, b.p. 82°/12 mmHg, n_D^{20} 1·5314; 1-ethyl-3-nitropyrazole, slightly creamy white crystals, m.p. 31–32°; 1-ethyl-5-nitropyrazole, pale yellow liquid, b.p. 85°/12 mmHg, n_D^{20} 1·5154.

Apparatus

Spectrophotometric measurements were carried out on a Beckman Model DK-1A, a Perkin-Elmer Model 402 and a Unicam Model SP-500.

Procedure

The values of the protonation constants, pK_{BH^+}, were calculated from the recorded spectra of nitropyrazoles by the standard spectrophotometric method.[3,21] The nitropyrazoles were dissolved in appropriate sulphuric acid solutions, the acidities of which were expressed as Hammett functions H_0.[21–23]

RESULTS AND DISCUSSION

The data for the absorption spectra of the nitropyrazoles studied are reported in Table 1. The nitro group shifts the absorption maxima of the neutral molecules to longer wavelengths (by 50–70 nm). The nitro group also shifts the spectra of the protonated ionic forms of all nitropyrazoles to longer wavelengths (by 10–30 nm), with the exception of 1-nitropyrazole, the maximum of which, at 216 nm, is very close to that of the pyrazole.

The effects of each substituent, or a pair of substituents, on the protonation constants (basic ionization constants) are shown in Table 2. This effect is expressed as a ratio between the protonation constants of the substituted pyrazole and that of pyrazole as the "zero" reagent [$b = \log (K/K_0)_{BH^+}$]. Table 2 presents our results for nitropyrazoles and the literature data for nitroimidazoles.[3] The results obtained for the effect of substituents, pyrazoles *vs.* imidazole, interpreted by the least-squares method, give equation (1), $b_{pyrazole} = 0{\cdot}85b_{imidazole} - 0{\cdot}7$ when all the results are used for calculation, and equation (2) $b_{pyrazole} = 0{\cdot}92b_{imidazole}$ for the results without the effects of the

Table 2. pK_{BH^+} values of pyrazoles and imidazoles and effects of substituents on these values

Pyrazoles			Imidazoles		
pK_{BH^+}	Substituent(s)	Effect of substituent(s), *b*	Effect of substituent(s), *b*	Substituent(s)	pK_{BH^+}
2·52[6]	none			none	6·95[3]
2·09[6]	1-CH_3	−0·43	0·30	1-CH_3	7·25[3]
2·00[6]	1-C_2H_5	−0·52	0·35	1-C_2H_5	7·30[24]
−1·96[6]	4-NO_2	−4·48	−4·83	5-NO_2, 1-CH_3	2·12[3]
−2·21	4-NO_2, 1-CH_3	−4·73			
−2·16	4-NO_2, 1-C_2H_5	−4·68			
−2·38	5-NO_2, 1-CH_3	−4·90			
−2·35	5-NO_2, 1-C_2H_5	−4·87			
−4·21	1-NO_2	−6·73	−7·11	4(5)-NO_2	−0·16[3]
−4·66	3(5)-NO_2	−7·18	−7·53	4-NO_2, 1-CH_3	−0·58[3]
−4·64	3-NO_2, 1-CH_3	−7·16	−7·76	2-NO_2	−0·81[3]
−4·78	3-NO_2, 1-C_2H_5	−7·30	−7·43	2-NO_2, 1-CH_3	−0·48[3]

Table 3. Effect of the nitro group in dependence on its position in the ring

Pyrazoles			Imidazoles		
Position of nitro group	b	Mean, b	Mean, b	b	Position of nitro group
4	−4·48	−4·31		−5·13	5
	−4·30				
	−4·16				
5	−4·47	−4·41			
	−4·35				
1	−6·73		−7·47	−7·11	4
				−7·83	
3	−7·18	−6·90	−7·74	−7·76	2
	−6·73			−7·73	
	−6·78				

methyl and ethyl groups. From equation (2) it can be seen that the slope of 0·92 (±0·08) is close to unity. The difference in the effects of 1-CH_3 and 1-C_2H_5 groups in pyrazole and imidazole can be explained by the different effect on the pyridine nitrogen atom when it is closer to an alkyl group (position 2 in pyrazole ring).

From the values of the substituent effects, the values of the nitro group effects (the mean value) are calculated and are shown in Table 3. The effect of the nitro group depends on its position in the ring, being stronger when it is close to the pyridine nitrogen atom. So, in pyrazole, positions 1 and 3 are equivalent, with values −6·7 and −6·9, respectively. In other positions the effect of the nitro group is less strong but still significant (−4·3 for 4-nitro and −4·4 for 5-nitropyrazoles).

The *N*-unsubstituted nitropyrazoles and nitroimidazoles with the nitro group in an asymmetric position with respect to both nitrogen atoms [3(5)-position in pyrazoles and 4(5)-position in imidazoles] are predominantly in the tautomeric form with the proton on that hetero-atom which is most influenced by an electron withdrawing group (the nitro group). So, in solution, 3(5)-nitropyrazoles are predominantly in the 3-nitro-[1] and 4(5)-nitroimidazoles in the 4-nitro forms,[2,25] as is confirmed by the values of the protonation constants in Table 2. Accordingly, mean value for the 3-nitro position in pyrazole includes the value of 3(5)-nitropyrazole, and mean value for the 4-nitro position in imidazole includes the value of 4(5)-nitroimidazole (Table 3).

Certain positions in the pyrazole and imidazole rings can be considered as analogous, *vis.* positions 4 and 5 in pyrazole and position 5 in imidazole; positions 1 and 3 in pyrazole and positions 2 and 4 in imidazole.

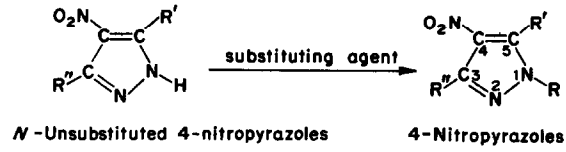
Additionally, from Table 3 it is possible to see the order of the nitro group effect:

Pyrazole 4-NO_2 = 5-NO_2 < 1-NO_2 ⩽ 3-NO_2

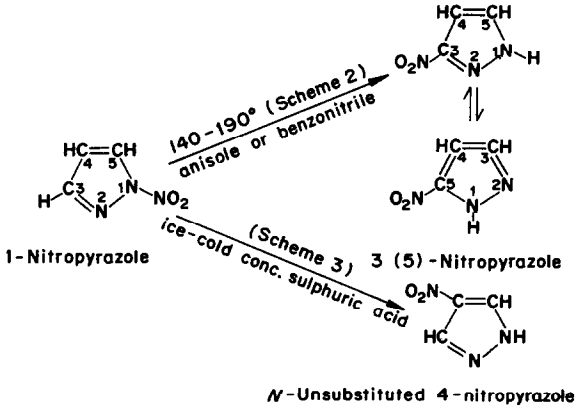
Imidazole 5-NO_2 < 4-NO_2 ⩽ 2-NO_2

The *ortho* effect of the nitro group, defined as a difference in effect of the nitro substituent in *ortho* and *meta* position to the pyridine nitrogen atom, for pyrazoles and imidazole, can be calculated from the results given in Table 3. The *ortho* effect of the nitro group in pyrazoles, expressed as the difference between the values for a 1- or 3-nitropyrazole and a 4- or 5-nitro derivative, is about −2·5. In the case of imidazole the *ortho* effect values, calculated from the data of Gallo *et al.*[3] is also about −2·5 (the difference between the values for a 2- or 4-nitroimidazole and a 5-nitroimidazole). These differences, together with the ability of *N*-unsubstituted nitropyrazoles to give nitropyrazole anions form the basis of a method for simultaneous spectrophotometric determination in the following cases.

(*a*) In every reaction mixture containing only one *N*-substituted nitropyrazole together with an *N*-unsubstituted one (Schemes 1–3) it is possible to determine both compounds simultaneously, at two different wavelengths, using a suitable alkaline medium.



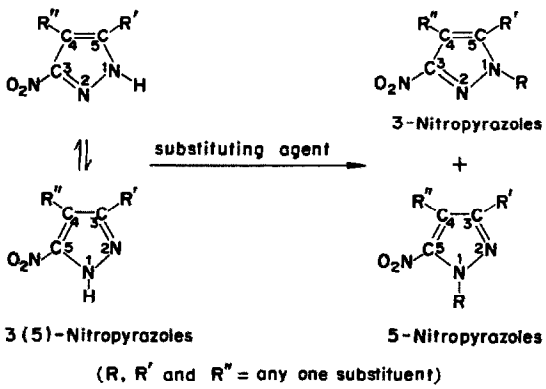
Scheme 1.



Schemes 2, 3.

(*b*) In the rearrangement process of 1-nitropyrazole to *N*-unsubstituted 4-nitropyrazole (Scheme 3) the rate of the process can be followed, at two different wavelengths, in two acidic media. This determination is based on the difference in protonation constants of 1-nitropyrazole and *N*-unsubstituted 4-nitropyrazole, pK_{BH^+} − 4·21 and −1·96, respectively.

(*c*) In reaction mixtures obtained during the substitution of the imino hydrogen atom (Scheme 4). all three compounds can be determined spectrophotometrically, or spectrophotometrically after chromatography. The determination is based on the different basicity of the 3- and 5-nitropyrazoles and the ability of 3(5)-nitropyrazoles to form corresponding anions, in a suitable alkaline medium, with absorption maxima shifted to longer wavelengths.



Scheme 4.

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THE SUCCESSIVE DETERMINATION OF CHLORIDE, FLUORIDE AND SODIUM IN SINGLE SAMPLES OF ORTHOPHOSPHATE MINERALS BY MEANS OF ION-SENSITIVE ELECTRODES

E. J. DUFF and J. L. STUART

Department of Preventive Dentistry, Turner Dental School, The University, Manchester M15 6FH, England

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Summary—A buffer system composed of perchloric acid, citric acid and triethanolamine has been used for the successive determination of chloride, fluoride and sodium in a single sample of an orthophosphate mineral. The conventional sodium-sensitive glass electrode compares favourably with the more expensive Orion sodium-sensitive electrode.

Following the introduction of the fluoride-sensitive electrode,[1] a number of other ion-sensitive electrodes have been manufactured, including those sensitive to chloride and sodium. Many of these electrodes have a detector membrane composed of a crystalline matrix through which conduction occurs by an ionic-electronic mechanism,[2] in contrast to the glass electrode where the species being determined develops a charge on the membrane surface. Although electrodes are finding widespread use, most of the published work relates to the determination of a single ionic species in a sample. Little attention has been paid to the determination of more than one ion in a single sample.

We have recently described methods for the determination of fluoride[3] and chloride[4] in orthophosphate samples, utilizing a buffer prepared from mixed perchloric and citric acids and triethanolamine (TEA) in which the acid used for dissolution formed an integral part of the buffer solution. We have extended these methods to include the successive determination of chloride, fluoride and sodium in a single orthophosphate sample. The determination of an alkali metal ion precludes the use of alkali metal salts in the buffer solution, but TEA, and possibly other organic amines, will give adequate buffering action.

EXPERIMENTAL

Apparatus

Radiometer PHM 52 digital pH-meter and Pye Dynacap pH meter. Orion 94.17A solid-state chloride-sensitive electrode. Orion 94.09A solid-state fluoride sensitive electrode. Orion 96-11-00 combination solid-state sodium-sensitive electrode. E.I.L. 1048-11451 sodium-sensitive glass electrode. Corning Glassworks 476200 "Monovalent Cation" electrode. Pye Ingold sodium-sensitive glass electrode. Pye Ingold E02 combination pH electrode. Cambridge Instrument Co. 42528 ceramic plug calomel reference electrode with a salt bridge of saturated potassium nitrate solution. Radiometer K601 ceramic plug mercurous sulphate reference electrode. Orion 90-01 sleeve-type calomel reference electrode. Radiometer K401 ceramic plug calomel reference electrode.

Reagents

All reagents were analytical grade except where stated. Demineralized water was used throughout.

Dissolution acid. Citric acid (420 g) dissolved in a mixture of 70–72% perchloric acid (83 ml) and water (700 ml) and the whole diluted to 1 litre.

Solution for pH adjustment. General-purpose grade triethanolamine (266 ml) dissolved in water and diluted to 1 litre. This should be prepared daily in the quantities required.

Standard solutions of sodium chloride and fluoride were prepared by appropriate dilution of 0·2*M* stock solutions.

Procedure

Weigh accurately about 200 mg of the calcium orthophosphate to be analysed into a 100-ml polyethylene beaker. Add 5 ml of dissolution acid and agitate gently until dissolved. Add 5 ml of demineralized water and 5 ml of TEA solution to give a pH near 2·5. Measure the e.m.f. of this solution with the chloride-sensitive electrode and the Cambridge 42528 or Radiometer K601 reference electrode. Remove the electrodes, add 10 ml of TEA solution to increase the pH to near 5·2 and measure the e.m.f. with the fluoride-sensitive electrode and the Orion 90-01 reference electrode. Add another 10 ml of TEA solution to raise the pH to 8 and measure the e.m.f. with a sodium-sensitive electrode and the Orion 90-01 reference electrode, or the Orion 96-11-00 sodium-sensitive combination electrode alone. Read the chloride, fluoride and sodium content of the samples from calibration curves prepared by using standard solutions in place of the 5 ml of demineralized water. The volume of reagents used may be reduced in proportion, provided that sufficient dissolution acid is present to dissolve the solid sample.

RESULTS AND DISCUSSION

Selection of optimum electrode conditions

Because alkali metal salts may not be used in the buffer systems, TEA-based buffer systems developed for the individual determination of fluoride and chloride appeal as a logical alternative. These solutions

are capable of giving the pH adjustment above 7 required[5] for the determination of sodium with a sodium-sensitive electrode. Their high buffer capacity is demonstrated by the fact that addition of 5 ml 5*M* ammonia solution to the 30 ml of perchloric acid/citric acid/TEA buffer at pH 8·2 did not change the pH. The high pH needed to overcome hydrogen-ion interference[6] in the sodium determination necessitates the presence of a calcium complexant to prevent the precipitation of a basic calcium orthophosphate. Citrate is effective for this purpose, and TEA serves as a complexant for transition metal ions[7] such as iron and manganese as well as assisting with calcium complexing at neutral pH where the complexing action of citrate is poor. This buffer system also gives sensitivity and detection limits for fluoride (Table 1) and chloride[8] which are generally comparable with those obtained by using trisodium citrate for pH adjustment.[3,4] A 0·33*M* perchloric acid/0·33*M* citric acid/0·66*M* TEA solution was used to explore the possibility of carrying out all the determinations at pH 7. However, at calcium concentrations $>0{\cdot}01M$ the amount of complexants present was insufficient to prevent precipitation and/or complex formation between calcium and halide ions. The decision was therefore taken to use 5 ml of 1*M* perchloric acid/2*M* citric acid solution as the dissolution acid and to ascertain the optimum pH for the determination of each ion in TEA buffer.

Ion determinations

Chloride determinations. The optimum electrode response from the Orion 94–17A electrode was found to be in the pH range 1·0–3·0. Below pH 1·5, electrode instability became serious: the most reproducible results were obtained at pH 2·5. Although the perchloric acid used was free from chloride contamination, determinations carried out in direct sunlight showed a gradual change in e.m.f., which was not noticed in fluoride determinations. This change was attributed to the photochemical decomposition of perchloric acid or the light-sensitivity of the $AgCl/Ag_2S$ detector crystal.[9] It is therefore desirable to use subdued lighting during the measurements.

Comparison of TEA and trisodium citrate buffer systems showed that at pH 2·5, linear near-Nernstian response was obtained down to $3{\cdot}3 \times 10^{-4}M$ and $1{\cdot}1 \times 10^{-4}M$ chloride respectively. The difference is relatively insignificant. Below these limits, a non-linear but reproducible response was obtained down to $5 \times 10^{-5}M$ chloride, although the time required to reach equilibrium was usually at least 15 min. The spectrophotometric comparison method[10] attempted suffered severe interference from orthophosphate ions and no comparisons could be made.

Table 1. Uptake of fluoride by various orthophosphates after reaction with 0·1*M* NaF: comparison of citrate buffer and TEA buffer

Sample	F^- found, % HCl/Na_3citrate	 $HClO_4$/citric acid/TEA
$BaHPO_4$	0·017	0·017
$Co_3(PO_4)_2\ 8H_2O$	0·045	0·043
$CaHPO_4$	0·157	0·158
$Cd_3(PO_4)_2$	0·736	0·736
$FePO_4$	1·61	1·60
$MgHPO_4\ 3H_2O$	2·42	2·39
$Mn_3(PO_4)_2$	2·34	2·31
$Ni_3(PO_4)_2\ 7H_2O$	0·078	0·076
$Sr_5OH(PO_4)_3$	2·75	2·68
$SnHPO_4$	2·06	2·10
$Zn_3(PO_4)_2\ 4H_2O$	0·089	0·090

Fluoride determination. The fluoride-sensitive electrode could be used in TEA-buffered solutions in the pH range 5·5–7·5: the optimum pH was 5·2. Linear near-Nernstian response was obtained down to $5{\cdot}0 \times 10^{-6}M$ fluoride with a reproducible but non-linear response below this limit.

The response was similar at this pH in both TEA and trisodium citrate buffers. At other pH's the lower limit of response in TEA buffer was $1{\cdot}7 \times 10^{-6}M$ at pH 7. In trisodium citrate buffer, the corresponding limits were 2×10^{-6}, $8{\cdot}5 \times 10^{-5}$ and $5 \times 10^{-4}M$: these differences were considered insignificant except for determinations at very low fluoride concentrations.

Sodium determination. The oldest and possibly best known ion-sensitive electrode is the pH glass electrode. At high pH the electrodes are also sensitive to alkali metal ions. This sensitivity, the alkali error, has been utilized in the formulation of special glasses which enhance the error and permit the construction of glass electrodes sensitive to metal ions. The properties of these electrodes have been described by Eisenman[11] and they have found extensive use in the electrochemical determination of sodium and potassium. They are more or less non-selective for alkali metal ions, although the Orion sodium-sensitive combination electrode has a high selectivity for sodium relative to potassium ($K_{NaK} = 1 \times 10^{-3}$) and lithium

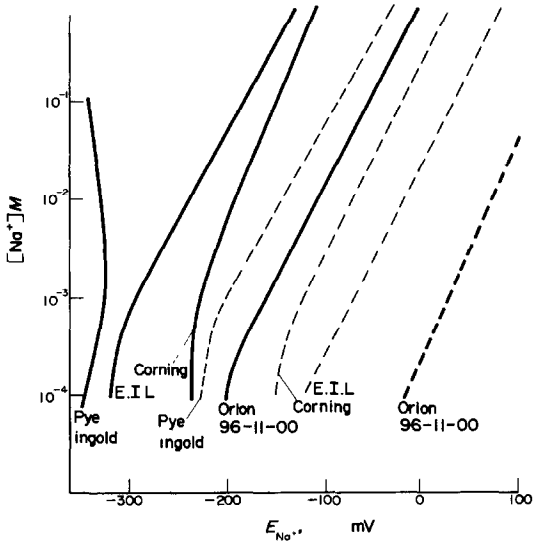

Fig. 1. Response of various sodium sensitive electrodes in aqueous sodium chloride solution (---) and TEA buffer (——).

($K_{NaLi} = 2 \times 10^{-3}$). This electrode is, however, very sensitive to silver ($K_{NaAg} = 350$) and hydrogen ions ($K_{NaH} = 100$).

TEA has been used previously as a pH-buffer in the determination of sodium:[12] its use has the disadvantage of possibly introducing impurities which may account for the departure from linear response at sodium concentrations between 10^{-4} and $10^{-5}M$. All the sodium-sensitive electrodes used were pretreated by soaking in 1*M* sodium chloride solution for at least 72 hr before use, in order to obtain maximum sensitivity by ensuring that the membrane surfaces were saturated with sodium ions. Calibration curves for the electrodes used in this study are shown in Fig. 1 for aqueous unbuffered solutions and TEA-buffered solutions. The response times were fairly rapid at pH 7·3 or above (equilibrium reached in 2 min) except for the Pye-Ingold electrode, which was sluggish, erratic and generally gave non-reproducible responses in TEA-buffered solutions. At pH below 7·3, electrode response time was considerably above 2 min, regardless of the sodium activity.

The Orion 96-11-00 combination electrode showed the fastest response time but the EIL electrode, at a quarter of the price (including a reference electrode), was almost as sensitive though slightly less selective. The Corning "Monovalent Cation" electrode was as sensitive as the EIL electrode but was badly affected by the presence of other univalent species, expecially potassium. The Orion and EIL electrodes gave a detection limit of $4 \times 10^{-4}M$ (10 ppm) in TEA buffer at pH 8·2, which was slightly above that expected from the manufacturers' data. The electrode method is much less sensitive than flame emission spectroscopy; comparative analyses of samples of fluoroapatite $Ca_5F(PO_4)_3$ [synthesized by the transformation of brushite ($CaHPO_4.2H_2O$) in sodium fluoride solutions[13]] by flame emission spectroscopy and by sodium-sensitive electrode gave results which agreed reasonably well (Table 2). Attempts were made to reduce the volume of the test solution by using 4*M* TEA in an effort to lower the detection limit but only half the volume specified in the procedure. Under these conditions, the response was linear down to only *ca.* $2 \times 10^{-3}M$ sodium.

Interferences

Fluoride–chloride interference. The possible mutual interference of fluoride and chloride was investigated by variation of the fluoride:chloride ratio from 200:1 to 1:200. No interferences were found.

Table 2. Comparison of mean sodium content (%, 6 replicates) of solid samples of fluoroapatite as determined by flame emission spectroscopy* and by an Orion sodium-selective electrode

Sample	1	2	3	4
Na by flame emission	0·107	0·09	0·120	0·117
Na by electrode	0·115	0·097	0·108	0·102

* Unicam SP 90 spectrophotometer with an SP 93 flame emission attachment.

Table 3. Typical analytical data obtained by this method in a study of the synthesis of amorphous calcium phosphate trihydrate in the presence of fluoride

Time, *hr*	0	0·25	0·5	1	2	4	24	48
$[Cl^-]$, *μg/ml*	3·72	3·80	3·75	3·69	3·60	3·62	3·72	3·68
$[F^-]$, *μg/ml*	20·0	21·7	21·0	20·3	6·7	1·9	2·0	1·5
$[Na^+]$, *mg/ml*	0·33	0·33	0·32	0·32	0·32	0·31	0·27	0·25

Results are average of 6 determinations. Relative standard deviations: Cl^- 1·1%; F^- = 0·9%; Na^+ = 3·3% (Orion), 2·0% (EIL).

Calcium and orthophosphate interference. The low solubility of calcium orthophosphates except under very acid conditions requires the presence of a suitable complexant for calcium, such as citrate[14,15] to prevent precipitation. Even so, precipitation sometimes occurs near neutral pH, which is prevented by the TEA. The citrate concentration at pH 8·2 is 0·286*M*, which completely inhibits precipitation when the calcium concentration is below 0·1*M*. Orthophosphate showed no interference at a similar level.

Interference with the chloride electrode. To 3 ml of standard chloride solution were added 2 ml of 1*M* solution of the nitrate or sulphate of the cation being compared for interference, and the e.m.f. measured after 3 min was compared with that of a solution containing 2 ml of demineralized water in place of the 2 ml of metal ion solution used. No interference was found from Mg, Sr, Ba, Cd, Mn(II), Fe(III), Co(II), Ni and Zn. Copper(II) nitrate and sulphate both caused a decrease in the apparent chloride content (Fig. 2). This effect may be similar to the interference of chloride with the copper sensitive electrode.[16,17] The decreased sensitivity is caused by damage to the detector membrane, which may be repaired by soaking overnight in 0·1*M* silver nitrate.

Bromide also interferes if its molar ratio to chloride exceeds a certain value.[8,18] Attempts to remove this by nitric acid oxidation[19] were not successful.[8]

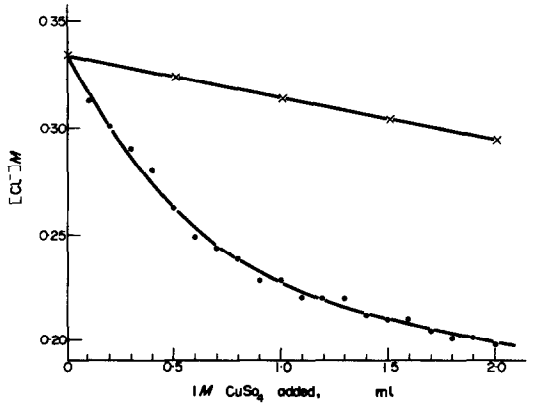

Fig. 2. Interference of copper(II) in chloride determination (5 ml of 0·334*M* NaCl, 5 ml of 1*M* $HClO_4$/2*M* citric acid, 5 ml of 2*M* TEA plus *x* ml of 1*M* $CuSO_4$). ×—[Cl^-] calculated; ●—[Cl^-] found.

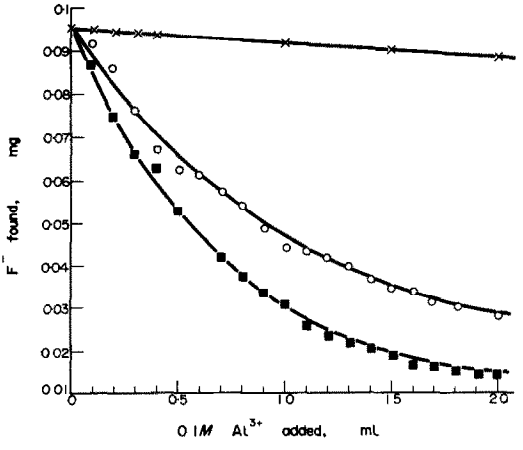

Fig. 3. Effect of Al^{3+} on F^- recovery. ×—F^- calculated; ■—F^- found, TEA buffer; ○—citrate buffer.

although nitrate itself does not appear to interfere with the determination.

Interference with the fluoride determination. The manufacturers' literature states that the only interference with the fluoride determination is from the hydroxide ion. Whilst this may be true, many metal cations form stable fluoro-complexes in aqueous media, reducing the ionic fluoride concentration.[20] The use of citrate and TEA in the buffer solution reduces the number of species which complex; aluminium probably causes the greatest interference, especially as the stability of AlF_4^- and AlF_6^{3-} is greater than that of most other aluminium complexes.[21]

We have compared (Fig. 3) the interference of aluminium in the fluoride determination by our present method and by our citrate method. The results indicate that the citrate method is possibly the superior for dealing with aluminium ions, although neither method is particularly good. Possibly the best method for determining fluoride in the presence of aluminium is the g.l.c. method[22] where the fluoride is converted into the trimethylfluorosilane derivative and detected by either the flame-ionization or the electron-capture method. Even this method gives up to 50% lower fluoride recoveries in the presence of aluminium.

Interference with sodium determination. None of the metal ions tested for chloride interference affected the sodium determination when 2 ml of a 1*M* solution of the ion were added to 3 ml of 0·01*M* sodium solution.

Application

The method was used to determine chloride, fluoride and sodium on ground human teeth. The results for chloride and sodium showed good agreement with the ranges quoted in the literature,[23,24] but the sodium content (0·92%) was very much higher than the 0·07% quoted by Jenkins.[24] We also applied the method to the analysis of orthophosphates other than calcium after their equilibration in 0·1*M* sodium fluoride at 80° for 1 month: the results obtained are indicated in Table 1.

Conclusions

The technique described enables chloride, fluoride and sodium to be rapidly determined on a single sample of an orthophosphate mineral. The use of a potassium or other alkali-metal cation-sensitive electrode would also appear to be feasible, but the use of bromide or iodide electrodes in place of the chloride electrode in this buffer system is limited by the possibility of complexing of the silver halide membrane with the TEA in the buffer. The expensive Orion combination sodium electrode has few advantages over the cheaper EIL electrode except in the presence of moderate amounts of other alkali-metal cations.

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DRYING AND WEIGHING OF STANDARD REFERENCE MATERIALS FOR TITRIMETRIC ANALYSIS, AND THE STATUS OF THE FARADAY CONSTANT AS AN INTERNATIONAL STANDARD

TAKAYOSHI YOSHIMORI

Faculty of Engineering, Science University of Tokyo, Kagurazaka, Shinjuku-ku, Tokyo, Japan

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Summary—A review is given of the methods of drying standard reference materials, and handling them after drying. The status of the Faraday as an international reference standard for titrimetric analysis is also discussed.

Many chemicals and "pure" elements have been proposed and investigated as standard reference materials for titrimetric analysis (SRMs). These materials should have properties such as high purity and homogeneity, definite composition, ability to give a complete, simple and stoichiometric reaction with a titrant, and should be easy to dry and handle. The first group of properties are associated with the selection of the materials and also depend on the manufacturers. The drying and handling, however, are the concern of the user. At every weighing of the materials, atmospheric moisture and water from other sources can influence the purity. Therefore, many procedures for drying the materials before weighing have been described in the literatures. However, we sometimes find great differences in the procedures, though the materials have high purities and crystalline structures. The hygroscopicity of materials, deplored by Lundell[1] over forty years ago, is still an undissolved problem, even for the SRMs. Thus, if the SRM potassium dichromate, for example, contains 0·05% of water, the concentration of a standard solution prepared from it will be low by 0·05%; and so will the results of any application of the "dilute" standard solution.

Recently, the Commission on Electroanalytical Chemistry, Analytical Chemistry Division of IUPAC, proposed the use of the Faraday constant as the international standard for analytical chemistry.[2] Although the constant is more suitable than standard materials, its use does not mean there is no need for SRMs. They are the practical standards for use in laboratories and industry.

This paper summarizes the drying conditions for SRMs given in the literature, and suggests the optimum conditions for the dehydration of each material. The status of the Faraday constant as the international standard for titrimetric analysis is also discussed.

DEHYDRATION AND WEIGHING OF SRMs

State of water in solids

According to Erdey[3] there are six types of water in solids, as follows.

(1) Loosely bound water

(*a*) Water bound by adhesion or retained in holes. It can be removed by exposure in the ordinary atmosphere.

(*b*) Occluded water, usually contained in holes and cavities in the crystals and sometimes called decrepitation water.

(*c*) Adsorbed water. The water simply adsorbed on the surface of materials may be removed by slight heating (100–130°). The water adsorbed in microscopic and submicroscopic cavities and channels can, however, be removed only by heating to dull redness (about 600°).

(2) Strongly bound water

(*d*) Crystalline water. This forms part of the stoichiometric composition. The SRMs containing water of this kind, *e.g.*, borax, will be considered separately.

(*e*) Structural water. This is the kind of water which is evolved by heating salts such as potassium hydrogen sulphate or sodium hydrogen carbonate.

(*f*) Water contained in the molecular-sized channels of zeolitic compounds. This is the type of water contained in compounds such as activated alumina, silica gel and aluminium silicates.

In view of the crystalline character of the SRMs discussed in this review, water of types (*a*), (*e*) and (*f*) will not be considered, because the methods and problems of determination of such kinds of water have been discussed and reviewed by Harris.[4]

Adsorption of water on crystal surfaces is one of the most important sources of contamination of the materials. In many cases, this phenomenon is discussed in contrast with the combined water in

solids.[5,6] Langmuir's adsorption theory (monolayer adsorption) is sometimes used for these discussions. The theory is, however, useful only for unwettable solids (benzoic acid for example). This kind of water may be removed very easily by heating the sample at about 110°, and so does not disturb the determinations.

According to Yoshimori and Tanaka,[7] however, the water on the surfaces of single crystals of sodium chloride grown from the molten salt (Stockberger's process) amounted to 0·2–0·5 $\mu g/cm^2$, an order of magnitude higher than the amount (about 0·05 $\mu g/cm^2$) calculated for monolayer adsorption, indicating that the water was adsorbed not as a monolayer (Langmuir theory) but as polylayers [Brunauer–Emmett–Teller (B.E.T.) theory[8]]. In that case the adsorption curve should be shown not by curve 1 but by curve 2 of Fig. 1. Curve 2 is the same as that of combined water,[5,9] and indicates the difficulty of removing the water completely. Moreover, the ions or molecules in the first layer of the crystal surface may be in the hydrated form, and in some cases crystalline water is also possible. Therefore, the water molecules of these types cannot be so easily removed, though sometimes they may be removed by heating the sample to much higher temperature than 110°. The removal of water from sodium carbonate, by preheating at 105°, cooling in a desiccator, then heating at 250 °,[10] indicates the possibility of the presence of this kind of water.

The occluded and adsorbed water in microscopic and submicroscopic cavities and channels may cause very serious difficulties in drying some SRMs. For example, Knoeck and Diehl[11] state that the difference between their results of coulometric assay of potassium dichromate and 100·000% depends largely on the occluded water. Although the microscopically visible cavities in large crystals may be removed by cutting the crystals into small pieces,[12] water in the ultramicroscopic cavities and channels cannot be dealt with so easily. Melting of the stable SRMs may be the most effective method to remove this water.

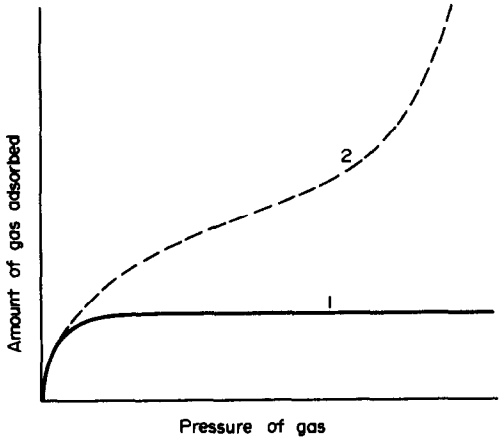

Fig. 1. Adsorption of a gas on a solid surface.

Occluded water in fine crystals or in SRMs which decompose on heating cannot be removed completely by these methods.

Heating temperatures for various SRMs

Obviously the chosen heating temperature for an SRM should be as high as possible, and the SRM should be pulverized before heating, if it was purified by recrystallization. As shown by Nelson and Hulett,[13] prolonged heating at relatively lower temperature does not give better-dehydrated materials. Therefore, the heating temperatures given in the literature will be reviewed and discussed.

Arsenic trioxide. This can be highly purified by sublimation and dried at 105–110°.[14–17] Sometimes the sublimed reagent is collected in a porcelain dish and cooled in a desiccator containing calcium chloride.[18] Dehydration of the reagent in a vacuum desiccator for 24 hr[14,15,19] or over sulphuric acid[20] has also been recommended.

When the reagent is dissolved in alkali, it usually first floats on the surface of the solution. This phenomenon indicates that the oxide may adsorb some gases on its surface and thus be protected from moisture. According to Hillebrand *et al.*[14] the oxide adsorbed only 0·014% of water during storage in an atmosphere of 90% relative humidity for 2 weeks, and could be weighed in an open container. Kolthoff *et al.*[21] and Laitinen[22] recommend this reagent for the standardization of various standard solutions, because of the simple reaction with permanganate and ease of drying. The only disadvantage of the reagent is its poisonous nature.

Benzoic acid. Although the acid needs alcohol for its dissolution and the solution creeps up the wall of the container, it has been used for a long time as a standard. Since the acid is not so hygroscopic,[23,24,27] the drying methods shown in the literature are rather simple and in good agreement. Two methods are usually preferred, one being drying in a vacuum desiccator for 48–72 hr[25] and the other being melting the acid at 130–140°, decanting the melt into a platinum dish, crushing the cooled melt and storing it in a desiccator.[23–26] Weaver[27] showed that the acid had adsorbed only 0·07% of water after storage in a glass bottle for more than a year. According to Yoshimori and Matsubara's coulometric investigation,[25] the pure reagent (used in Japan as the standard for the calorie) has a purity higher than 99·99% and may be dried either in a vacuum desiccator or by the melting method.

Potassium dichromate. Although this is a useful standard for titrimetric analyses, the drying procedures shown in the literature differ very appreciably. Melting of the reagent is sometimes recommended,[28–30] but nearly all authors warn about the formation of a green compound [chromium(III) oxide]. Drying at temperatures above 150° is preferred by many authors. For example 300°,[31] 260°,[32] 200°[29,33] and 150–200°[34,35] have been recommended.

and 140–150° has also been used.[36–40] The reagent is usually pulverized in an agate mortar before heating. These recommendations indicate the presence of the occluded water in the crystals of the reagent. Marinenko *et al.* dried the reagent by two different methods for their coulometric assay: (*a*) heating at 130° for 6 hr then cooling over phosphorus pentoxide[41] (*b*) heating at 110° for 24 hr and cooling over magnesium perchlorate.[42] Knoeck and Diehl[11] used method (*b*) and made the comment quoted earlier. Heating at 120° has also been used.[43,44] According to Japanese Industrial Standards (JIS), Yoshimori *et al.* dried the compound at 120° for 3 hr and assayed the Japanese SRM by precise coulometric titration,[45] coming to the same opinion as Knoeck and Diehl. Yoshimori *et al.* also purified the reagent by zone-refining;[46] this will be discussed later.

Water in the reagent has sometimes been determined. For example, Sappenfield *et al.* found 0·018% of occluded water by heating the SRM (NBS 136c) at 260°.[32] Knoeck and Diehl found 0·019% of water after heating the same reagent for 10 days at the same temperature.[11] Schwab and Wichers found 0·027 and 0·021% of water by the vacuum extraction method.[47] According to the specification of SRM 136c (NBS), a weight loss of 0·005% may be found on heating at 105° for several hours and about 0·01% loss on longer heating. Yoshimori and Sakaguchi[10] determined the water content of the SRM after heating it at various temperatures and indicated that the reagent may be dried by melting it at about 400°, and then cooled over magnesium perchlorate, if the reagent is completely free from organic matter. The water content of the weighed out SRM may be decreased to less than 0·005% if it is heated to higher than 250° for more than 3 hr in good ventilation and then cooled in a desiccator over magnesium perchlorate.

Potassium hydrogen phthalate. This has been used for a long time as a standard acid–base titration and pH. The heating temperatures shown in the literature are in rather good agreement, 100–125°.[11,19,23,25,26,48–57] Heating time is in the range 1–24 hr. Pulverizing the reagent before drying is also advisable, to remove the occluded water. Decomposition of the reagent occurs at temperatures over 125°,[51] or on prolonged heating.[57] It was shown that the dried reagent did not contain more than 0·003% of water.[51,53]

Sodium carbonate. Recently the Society for Analytical Chemistry[58] and IUPAC[59] recommended this reagent as a primary standard. The wide variety of drying procedures for this is summarized by Laitinen.[60] The reagent can be completely dehydrated by melting it at about 850° in an atmosphere of carbon dioxide. On cooling the melt, the atmosphere should be gradually changed to one of air.[60] The carbonate is sometimes dried by heating at 500–650°[16] or 350–400°[48] in a platinum dish, but contamination by sulphurous gases must then carefully be prevented. According to Yoshimori and Sakaguchi, the reagent may be dried nearly completely by heating it at 600° under good ventilation.[10] On the other hand, Smith and Croad warned that there was more than 1% decomposition of the reagent if it was heated at 310–315°[61] and Hillebrand *et al.* also stated that it could decompose at temperatures above 270°.[62] According to Newkirk and Aliferis, however, this decomposition is caused by reaction of the reagent with siliceous materials present as impurity or with the container.[63] IUPAC,[59] the Society for Analytical Chemistry[58] and Woodward and Redman[64] recommended heating it at 270 ± 10° in platinumware. A temperature of 260–300° has been recommended by many authors.[62,65–73] Balis *et al.* prefered 240°.[74] On the other hand, Kolthoff warned that the dried reagent adsorbed 0·05–0·1% of water during cooling and weighing.[75]

The reagent is usually purified as the bicarbonate, which is then converted into the carbonate by heating. The decomposition of the bicarbonate may be completed at a temperature higher than 160°.[76,77] Pulverizing of the reagent in an agate mortar is also recommendable. Yoshimori and Sakaguchi showed[10] that the reagent contained less than 0·005% of water when it was dried at above 250° and cooled in air over magnesium perchlorate. If sulphuric acid was used as the desiccant, the water content was higher, and use of the acid is not recommended as suitable. Heating at lower than 200° is always unsatisfactory.

The major problem with this standard is the choice of indicator for the titration, and the present author feels he cannot recommend this reagent as a primary standard.

Sodium chloride. This salt may be dried at above 500°.[16,78,79] Melting in platinumware and in an electric furnace is also recommended.[80–82] Sörensen indicated that heating at below 300° for more than 24 hr was not enough to remove the water completely and recommended heating at 380° for much longer than 12 hr.[83] Marinenko and Taylor found that the amount of impurities in the salt was less than 0·004%.[82] They also dried the finely pulverized salt at 130° or 200° for 18 hr in their study of coulometric assay of the salt.[84] All the procedures indicate the presence of water in the cavities of the crystals. Therefore, heating at about 110°[85] is not enough. A temperature higher than 400° is preferable. The use of a single crystal of the salt[7] is advisable for practical purposes (see later).

Sodium oxalate. According to the investigations by Sörensen[86] and the NBS,[87] this reagent is stable up to 240–250° and begins to decompose at above 250–270°.[87] Although the weight loss of the reagent (NBS SRM) amounted to 0·0008% and 0·009% on heating at 105° for 74 hr and at 240° for 24 hr respectively, it may be dried in practice by heating at 105° for 2 hr.[87] On the other hand, Sörensen found that the reagent contained 0·1, 0·033, 0·02 and less than 0·01% of water after heating at 125°, 180–200°, 200–210° and

240° respectively.[83,88] According to the NBS investigation, small crystals of the reagent dried at 240° took up 0·01% of water when exposed to an atmosphere of 70% relative humidity.[87]

The present author considers that the pulverized reagent may be dried rather completely at somewhat higher temperature than 200°. Because of the complex nature of the reaction between oxalate and permanganate, Kolthoff *et al.*[21] and Laitinen[22] prefer arsenic trioxide to this reagent, and the present author has the same opinion.

Decomposition of the reagent to sodium carbonate may be completed at the melting point of sodium carbonate.[89,90]

Sulphamic acid. This was recommended by Butler, Smith and Audrieth[91] as the acid standard, but has sometimes been considered as a secondary standard because its purity was not certified.[90,92] A few years ago, IUPAC[59] and the Society for Analytical Chemistry[93] recommended the acid as a primary standard, and gave methods for its purification and drying. Since the acid reacts with moisture at above 60°, dehydration in a vacuum desiccator at room temperature is recommended.[16,59,93,94]

Using the appreciable crystal growth of the acid, Yoshimori and Tanaka prepared some large crystals (10–16 g) and determined their purities by precise coulometric titration: the purities, however, were somewhat (0·02–0·05%) less than 100%.[12]

Problems in selecting the heating conditions

The differences between the heating procedures given in the literature for a reagent may have various causes. First, the method of preparation of the reagent is important. For example, fine crystals have a large amount of adsorbed water and a small amount of occluded water and may be dried at rather lower temperature. On the other hand, coarse crystals contain much water in their cavities and must be heated at higher temperature. This is why a pulverized reagent is usually recommended and there is better agreement about the drying conditions. Secondly, the effects of impurities should be considered. For example, if potassium dichromate contains traces of organic matter, it cannot be dried at high temperature, but otherwise may be dried by melting at 400°. Thirdly, the heating conditions are of practical importance. The uniformity of the temperature[4] and the ventilation in the heating apparatus affect the heating time. Harris[4] stated that good ventilation decreased the necessary heating time by about 60–70%. Heating time may also be influenced by other factors such as amount of sample, heat capacity of the container, rate of heating and thickness of the reagent layer through which the vapour passes. In many cases these conditions are not shown in detail. Thus, the disagreement about drying conditions is not unusual.

Generally speaking, the heating temperature should be as high as possible[10,13,95] when the reagents are stable on heating. However, the decomposition temperature indicated by a thermobalance is usually too high. For example, Duval showed[96] that potassium dichromate began to decompose on the thermobalance at 650°. According to the experience of the present author, however, the reagent decomposes appreciably at 500° under static heating conditions. Wendlandt stated[97] "the use of the thermobalance has only contributed to this confusion". The problem may be caused by the rate of heating[97–99] and the lack of the sensitivity of the balance.[100]

Conditioning of hydrated reagents

Oxalic acid and borax are of practical importance. Oxalic acid is stable in an atmosphere of 5–95% relative humidity,[26] and may be stored in a desiccator containing a saturated solution of sodium bromide. According to Schoorl,[101] the recrystallized acid contains 0·2–0·3% of occluded water, and he proposed a method for its purification. First the recrystallized acid is dehydrated completely over phosphorus pentoxide and then rehydrated over a saturated solution of sodium bromide. The condensed water amounts to about 0·01%.[26,101] Since the acid has a relatively low molecular weight, some authors do not recommend it as a primary standard.

Borax has a high equivalent weight and is a useful standard even though a certified reagent is not obtainable. The decahydrate is neither deliquescent nor efflorescent in an atmosphere of 39–99% relative humidity.[102] Menzel recommended storage over a saturated solution of sodium chloride and sucrose (RH 70%).[103] Storage over a saturated solution of sodium bromide may also be used.[102] The use of this reagent as a standard substance is highly recommended by Kolthoff *et al.*[102]

METALLIC STANDARDS

Pure metals are sometimes used as primary standards. For example, the Society for Analytical Chemistry recommended the I.C.I. scheme for using silver as the ultimate standard for titrimetric analysis.[104,105] Although a beautiful system for standardizing various solutions was developed, the error of the titration may be increased as more steps are introduced in the chain of standardizations. The other problem in the use of silver is its purity, which is certified only on the basis of determination of the impurities. Woodward and Redman stated that their standard silver (99·999% pure, Johnson Matthey) contained nearly 50 ppm of gaseous impurities.[106] Here, we have to remember the opinion of Barnard.[107] He stated that the sum of analytical results of 0·001 and 0·0002% is 0·001%, not 0·0012% when we consider the precision of their measurements. Thus, the present author considers that strict proof of a purity higher than 99·999% is impossible.

The effect of surface contamination may sometimes be a very important source of decrease in the purity of a metal. For example, Hashitani *et al.*[108] showed

that the oxygen on the surface of high-purity uranium increased by about 30 ppm after exposure of the metal to air for 30 min. Kammori *et al.*[109] and Goto *et al.*[110] measured the amounts of oxygen on the surface of various metals and Yoshimori *et al.* measured the amounts of water.[111] More comprehensive information on this problem is obtainable from the monograph edited by Melnick *et al.*[112] The results indicate that the amounts of surface contaminants depend largely on the treatment of the surface, *i.e.*, the nature of the oxide film of the metal, roughness of the surface, and the method of polishing. In particular contamination from polishing materials (alumina powder for example) was shown by Kammori *et al.*[109] to be practically important, because it may be caused accidentally.

PROBLEMS IN COOLING AND WEIGHING PROCEDURES

Desiccants and desiccators

The appreciable discrepancies in the vapour pressures of various desiccants reported in the literature[113,114] indicate the difficulties in the evaluation of heterogeneous reaction rates. The surface area and the state of the water adsorbed on the surface of a desiccant may be quite different for each reagent and method of practical use. For instance, we cannot always obtain the best drying conditions over phosphorus pentoxide, because a film of meta- or polyphosphates is formed on its surface.

In a recent study, Yoshimori and Sakaguchi showed that there is not much difference between magnesium perchlorate (commercial, not completely dehydrated) and concentrated sulphuric acid, and also pointed out the disadvantage of the latter as the desiccant for alkaline material (sodium carbonate).[10] The vapour pressure of the concentrated acid should also be considered.[115]

According to the literature, silica gel has very low water vapour pressure. This pressure, however, cannot be held for a long time, and also may vary from products to products. Above all, we must not forget that the blue colour of the indicator in the gel does not strictly indicate its condition. In the author's experience, the blue gel does not turn pink in a calcium chloride desiccator, and it may be possible that anhydrous calcium chloride is a better desiccant than silica gel.

In the author's opinion, heated SRMs should be cooled over magnesium perchlorate. The heating conditions (discussed above) and the practical handling of the desiccator for cooling are more important than the choice of desiccant in obtaining a drier SRM.

Since moist air is lighter than dry, the atmosphere in a desiccator does not reach equilibrium immediately the lid is closed. Booth *et al.*[116] showed that equilibrium was attained only about 2 hr after closing the lid. Hempel[117] proposed about 80 yr ago a desiccator in which the desiccant was kept over the sample. King[118] and Harris[4] proposed desiccators in which a desiccant was placed either round the sides and beneath a sample, or above and below a sample respectively. However, Strouts *et al.*[119] stated that the desiccant in a desiccator is useless for cooling the heated sample to be weighed. Peck[120] combined four small desiccators into one block, each of them containing only one crucible.

Although the power of a desiccant is very important in dehydration of a sample at room temperature, it is not so essential when a heated sample is being cooled. The following conclusion may be drawn.

(*a*) The required amount of sample should be put in a weighing bottle before dehydration.

(*b*) Heated material should be cooled in its own desiccator containing a good desiccant (magnesium perchlorate).

(*c*) The dried sample should be weighed as fast as possible.

(*d*) Subdivision of large samples after the dehydration should be avoided.

METHOD OF WEIGHING

An SRM is usually dehydrated and weighed in the same container. Therefore, we cannot forget the considerations about the condition of the container. The hygroscopicities of some container materials proposed in the literature[6] have been measured at room temperature. Yoshimori *et al.*[111] measured the water evolved when various glasses that had been washed and dried at 105° and then stored in hygrostats for several hours were heated at 300°. The results are shown in Table 1, and indicate that the Langmuir theory is applicable only to fused quartz and that the B.E.T. theory is preferable for borosilicate and hard glasses (also for platinum and stainless steels).[111,121] Soft glasses evolved much water on heating. Since soft glass has least tendency to become electrostatically charged, some authors recommend this as the material of a weighing bottle,[122] but it should be avoided for the most precise work.

The use of a counterpoise consisting of an empty container of the same size, shape and material, nearly

Table 1. Determination of the water evolved from various glasses by heating at 300°C[111]

Kind of glass	Relative humidity,* %	Water found, $\mu g/cm^2$
Quartz	53	0·03
	68	0·05
Hard glass	53	0·16
	68	0·19
Pyrex glass	53	0·20
	68	0·24
Soft glass	53	4·1
	68	7·1
Vycor glass	58	0·27

* Approximate values.

the same weight and treated in the same way as the sample-container, is advisable to decrease the effect of adsorption of moisture on the surface of the bottles.[12,25,46,99] A single-pan substitution balance is not recommended for the most precise work.

THE USE OF SINGLE CRYSTALS*

As early as a 100 yr ago, a single crystal of Iceland spar was already recommended as a primary standard for titrimetric analysis.[123] The preparation and use of single crystals have, however, been tried only recently. Bates *et al.*[124] at NBS prepared single crystals of benzoic acid and compared their purities with those of potassium hydrogen phthalate (SRM) and dehydrated pure oxalic acid. More recently, Marinenko and Taylor[125] evaluated the Faraday constant by using single crystals of benzoic and oxalic acids coulometrically, and compared the results with those previously obtained. Madej and Rokosz[126] prepared crystals of potassium hydrogen phthalate, borax, cadmium sulphate, *etc.*, but the crystals have not yet been assayed. In the author's laboratory, single crystals of sodium chloride[7] and sulphamic acid[12] were prepared and assayed, and the surface water or the weight loss during the dehydration process was also measured. Saito *et al.* also prepared single crystals of arsenic trioxide and assayed them.[127] They also zone-refined potassium dichromate.[46] All their assays were done by precise coulometric titration. With only one exception (arsenic trioxide 100·003 ± 0·009%), these single-crystal samples were not completely pure, though purer than 99·95%. The surface water of the crystals measured did not exceed 0·003%.

The results shown above indicate that a single crystal is not the purest material, and that the purity may differ from crystal to crystal. The main source of the difference may be water occluded in crystals grown from solution, or impurities in crystals grown from a melt. Therefore, single crystals may be useful, not as the ultimate and international standards, but as the practical or working standards, without the problems of drying.

THE FARADAY CONSTANT AS THE INTERNATIONAL STANDARD FOR VOLUMETRIC ANALYSIS

The experimental results and opinions cited above indicate that no materials obtainable at present are completely pure, and that in most cases they cannot be weighed without contamination by atmospheric moisture. Therefore, it is much better to abandon the use of a "material" as the ultimate and international standard for analytical chemistry. Even if an ultimate standard material should be selected by international consensus, it could not be held permanently, because it must be consumed for the standardization of other standards.

The idea of using the Faraday constant as the international standard was first proposed by Tutundžič, and recently proposed again by the Commission on Electroanalytical Chemistry of IUPAC.[2] The history of the proposal and the many advantages of the Faraday are discussed in that report. The present author gives here some experimental results and discussions that are not in the report.

Strictly speaking, the fundamentals of gravimetric and titrimetric analysis are different. In gravimetric methods, the content of a material in a sample is calculated more or less directly by using the atomic weights of the elements concerned. Therefore, the results obtained may be referred to the basic SI units if the isotopic composition of the elements concerned is known. On the other hand, the concentration of a standard solution must be determined in terms of the SRM used for either the preparation or the standardization of the solution. Therefore the results of any titrimetric analysis always include a factor corresponding to the purity of the SRM used. The isotopic composition of the elements concerned also affects the results. Thus, the results of titrimetric analysis and of many instrumental methods using calibration curves cannot be referred directly to the SI units. If we select one material (for example, silver prepared by the method of Richards[128]) as the primary and ultimate standard, we are deciding on the prototype of titrimetric analysis, and the atomic weight of the material (the silver) should be known with highest precision. However, the accuracy of any derived standard must be somewhat lower. In contrast to a prototype, the Faraday constant is useful not only for the direct assay of SRMs for practical use but also for the direct standardization of many standard solutions without use of SRMs. Therefore, the accuracy of titrimetric analysis should become better. Lingane[129] has already pointed this out, and Yoshimori *et al.*[45] have tried the direct standardizations successfully. Some other results obtained in the author's laboratory will be shown here.

The Industrial Inspection Institute of Japan certifies the purities of many SRMs, by comparison with their own standard materials and also cross-checking against the SRMs from NBS. Several Japanese SRMs and one SRM from NBS were assayed by precise coulometric titration in the author's laboratory, and the results obtained are summarized in Table 2. From these results, there appear to be no problems in using the Faraday constant as the international standard for titrimetric analysis.

The effect on commercially important standard reference materials if the Faraday is used must also be considered. In addition to the results referred to in the IUPAC report,[2] some precise coulometric results obtained in the author's laboratory may provide support for the proposal of the Committee. They include measurements of the purities of single crystals

* Strictly speaking, in this review the words "single crystal" mean transparent and sometimes microscopically clear crystals.

Table 2. Summary of the results obtained in the author's laboratory by precise coulometric titration

Sample	Certified value,* %	Results by coulometry, %	s, %	Refs.
NaCl	99·99	99·986	0·037	52
$K_2Cr_2O_7$ (*a*)	99·99	99·983	0·008	45
(*b*)	99·99	99·985	0·006	
H_2NSO_2OH	99·90	99·918	0·016	52
	99·91	99·929	0·017	
Na_2CO_3	99·99	99·991	0·044	52
C_6H_5COOH†	—	99·991	0·010	25
	—	99·993	0·009	
$KHC_8H_4O_4$	100·00	99·999	0·008	25
$KHC_8O_4O_4$ (NBS 84g)		99·999	0·007	25

* Certified in the Industrial Inspection Institute of Japan.
† Standard for the calorie.

of sodium chloride[7] and sulphamic acid,[12] of zone-refined potassium dichromate,[46] assays of commercial tin metals[130] and of high-purity uranium[131] and also the precise determination of total iron in several iron ores.[132] Many of these results were compared with those obtained by analysis for impurities, or with the certified values for the samples, and indicated that the method is useful not only for the analysis of SRMs but also for the analysis of the samples of practical importance.

In order to be referred to the system of basic SI units, the Faraday constant should be defined as the electric charge of one mole of electrons. This has not been emphasized in the IUPAC report. By this definition, however, the international standard for titrimetric analysis becomes permanent and is freed from such variables as the atomic weight of silver, the isotopic compositions of all elements, the unavoidable troubles discussed in the earlier sections of this review, and so on.

Most of the results of chemical analysis are calculated not as a molar fraction (mole %) but as a weight fraction (% w/w). If the Faraday is used as the ultimate reference, the amount of an element determined by coulometric analysis is connected with a basic SI unit, the mole. However, the mole concept is scarcely applicable to mixtures of unknown composition, and is strictly applicable only to absolutely pure single substances. Thus, the content of a material must be calculated by using the atomic weights of the elements concerned, and cannot be more precise than the values of the International Atomic Weights. In the most careful gravimetric work the precision is some tens of ppm[108] and the results are based on another basic SI unit (the kilogram): this degree of precision is comparable to that of some atomic weights and of the present value of the Faraday.[133]

For these reasons, the status of the Faraday constant in the field of analytical chemistry should be the same as that of the table of International Atomic Weights. Thus, the results of titrimetric and some instrumental methods of analysis should have the same international standing as those of gravimetric methods.

CONCLUSION

The Faraday constant, which is defined as the electric charge of one mole of electrons should be used as the ultimate and international standard for titrimetric and some instrumental analyses. However, the usefulness of the SRMs at present available will be unchanged, because they are necessary as the practical working standards in all laboratories and industries.

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SPECTROPHOTOMETRIC DETERMINATION OF TUNGSTEN IN ORES AND STEEL BY CHLOROFORM EXTRACTION OF THE TUNGSTEN–THIOCYANATE–DIANTIPYRYLMETHANE COMPLEX

ELSIE M. DONALDSON

Mineral Sciences Division, Mines Branch, Department of Energy, Mines and Resources, Ottawa, Canada

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Summary—A method for determining up to about 6% of tungsten in ores and mill products is described. It is based on the extraction of the yellow tungsten(V)–thiocyanate–diantipyrylmethane ion-association complex into chloroform from a 2·4*M* sulphuric acid–7·8*M* hydrochloric acid medium containing ammonium hydrogen fluoride as masking agent for niobium. The molar absorptivity of the complex is 1510 $l.mole^{-1}.mm^{-1}$ at 404 nm, the wavelength of maximum absorption. Moderate amounts of molybdenum and selenium may be present in the sample solution without causing appreciable error in the result. Interference from large amounts is avoided by separating these elements from tungsten by chloroform extraction of their xanthate complexes. Large amounts of copper interfere during the extraction of tungsten because of the precipitation of cuprous thiocyanate. Common ions, including uranium, vanadium, cobalt, titanium, arsenic and tellurium, do not interfere. The proposed method is also applicable to steel.

The preparation and characterization of certified reference ores is a continuing facet of the Canadian Certified Reference Materials Project. As part of this project, the author was asked to participate in the interlaboratory programme for the certification of three tungsten ores CT-1, BH-1 and TLG-1. In preliminary work, a modification[1] of a spectrophotometric thiocyanate method developed by Freund *et al.*[2] was investigated. In this method, tungsten is reduced to the quinquevalent state with stannous chloride, in a 3·6*M* sulphuric acid–5·8*M* hydrochloric acid medium, and the absorbance of the anionic tungsten(V)–thiocyanate complex is measured directly in an aqueous medium[2] or after extraction of the complex into an organic solvent (isopropyl ether or n-amyl alcohol).[1] However, this method did not yield consistent results for the ores when measurement was made both in aqueous media and after extraction of the complex. It is known that thiocyanate methods based on the formation of the anionic tungsten complex are subject to interference from coloured ions and from molybdenum, vanadium, niobium, titanium and cobalt when measurement is made in an aqueous medium, and to even greater interference from molybdenum, vanadium, niobium and titanium after extraction of the complex.[3,4] Consequently, a method was sought that would be more specific and reliable and would be applicable to the determination of both small and moderate amounts of tungsten in ores.

Recently, a more specific and sensitive thiocyanate method was described for the determination of tungsten in steel[5–7] and steel-making materials.[8] It involves chloroform extraction of the neutral ion-association complex formed between tungsten(V)–thiocyanate and tetraphenylarsonium chloride from an 8*M* hydrochloric acid medium and subsequent photometric measurement of the extract. Of the interfering elements mentioned above, only niobium and moderate amounts of molybdenum interfere. Interference from niobium is obviated by washing the tungsten extract with ammonium hydrogen fluoride solution[5–7] or by extracting tungsten from a fluoride medium.[8] Because of its relative specificity, this method was considered in the present work. However, preliminary experiments carried out with tetraphenylarsonium chloride and a widely used analogous compound, diantipyrylmethane,[9,10] showed that the latter functioned equally well for formation of an ion-association compound with the anionic tungsten–thiocyanate complex. Moreover, the tungsten–thiocyanate–diantipyrylmethane complex is more soluble in chloroform than the corresponding tetraphenylarsonium chloride complex. Consequently, this reagent was utilized in the present work, which describes the successful determination of tungsten in ores, mill products and steel. Interference from large amounts of molybdenum is avoided by separating it from tungsten by chloroform extraction of its purple-red

xanthate complex,[11–14] and from niobium by masking with ammonium hydrogen fluoride.

EXPERIMENTAL

Apparatus

Funnels for filtering the extracts were made from broken 20-ml pipettes by cutting the bulb in half.

Reagents

Standard tungsten solution, 25 μg/ml. Dissolve 0·8973 g of sodium tungstate dihydrate in water and dilute to 500 ml. Dilute 5 ml of this stock solution to 200 ml with water. Prepare fresh as needed.

Diantipyrylmethane, 1% solution in 20% hydrochloric acid. Dissolve 0·5 g of 4,4′-methylenediantipyrene in 25 ml of water containing 10 ml of concentrated hydrochloric acid and dilute to 50 ml with water. Prepare fresh every 2 days.

Stannous chloride, 45% w/v solution. Dissolve 22·5 g of stannous chloride dihydrate in concentrated hydrochloric acid and dilute to 50 ml with the same acid. Prepare fresh as required.

Potassium thiocyanate, 20% w/v solution. Prepare fresh every seven days.

Potassium ethyl xanthate, 20% w/v solution. Prepare fresh as required.

Ammonium hydrogen fluoride, 10% w/v solution.

Tartaric acid, 7·5% and 50% w/v solutions.

Sodium hydroxide, 50% w/v solution.

Hydrochloric acid, 8M.

Chloroform, analytical reagent grade, containing 1% of thioglycollic acid. Prepare fresh as required. Pure chloroform is also needed.

Procedures

Calibration curve. By burette, add 1, 2, 4, 6, 8 and 12 ml of standard 25 μg/ml tungsten solution to six 125-ml Erlenmeyer flasks and dilute each solution to approximately 15 ml with water. Add 15 ml of water to a seventh flask; this constitutes the blank. Add 10 ml of concentrated sulphuric acid, 20 ml of concentrated hydrochloric acid and 5 ml of 45% stannous chloride solution to each flask, mixing thoroughly after each addition, then place the flask in a boiling water-bath for 30 min. Remove the flask and cool the solution to 10–15° in an ice-bath.

Transfer each solution to a 125-ml polypropylene separatory funnel, marked at approximately 75 ml, and wash the flask three times with cold concentrated hydrochloric acid contained in a plastic wash-bottle. Add the washings to the funnel and dilute the resulting solution to the mark with cold concentrated hydrochloric acid. Add 10 ml of 10% ammonium hydrogen fluoride solution, 10 ml of 20% potassium thiocyanate solution (Note 1) and 2 ml of 1% diantipyrylmethane solution to each funnel, stopper and mix thoroughly. Add 10 ml of chloroform containing 1% thioglycollic acid, stopper tightly and shake for 2 min. Allow several min for the layers to separate, then drain the chloroform layer into a 60-ml glass separatory funnel. Extract twice more, by shaking for 2 min, using 0·5 ml of diantipyrylmethane solution each time, and 5- and 3-ml portions of chloroform, respectively (Note 2). Wash the aqueous phase by shaking it for 30 sec with 3 ml of chloroform. Combine the extracts, add 10 ml of 8*M* hydrochloric acid and shake for approximately 30 sec. Allow several min for the layers to separate, then filter the chloroform extract through a thick wad of cotton-wool into a dry 25-ml volumetric flask. Wash the aqueous layer twice with 2–3-ml portions of chloroform containing thioglycollic acid, filter the washings into the volumetric flask and dilute to volume with chloroform containing thioglycollic acid (Note 3). Determine the absorbance of the blank and each of the first four tungsten extracts, at 404 nm, against a reference solution of chloroform containing thioglycollic acid, using 20-mm cells. Determine the absorbance of the blank and each of the last five tungsten extracts in a similar manner, using 10-mm cells. Correct the absorbance value obtained for each tungsten–thiocyanate–diantipyrylmethane extract by subtracting that obtained for the blank. Plot μg of tungsten *vs.* absorbance for each series of measurements.

Ores and mill products. Depending on the expected tungsten content, transfer 0·2–1 g of powdered sample to a 50-ml Vycor crucible, add 5 g of fused sodium bisulphate (Note 4) and mix. Cover the crucible and fuse the mixture over a low flame for 3–4 min to ensure the complete decomposition of tungsten minerals. Allow the melt to cool for 3–4 min, then transfer the crucible and cover to a covered 400-ml beaker containing 100 ml of 7·5% tartaric acid solution. Heat gently until the dissolution of the melt is complete, remove the crucible and cover after washing them thoroughly with 7·5% tartaric acid solution, and evaporate the solution to 140–150 ml. Filter the hot solution (Whatman No. 40 paper) into a 200-ml volumetric flask and wash the beaker, paper and residue thoroughly with 7·5% tartaric acid solution. Discard the paper and residue. Cool the filtrate to room temperature and dilute to volume with 7·5% tartaric acid solution. Run a blank determination through the whole procedure.

Transfer a suitable aliquot (up to 10 ml) of both the blank and sample solutions, containing not more than 0·25 mg of molybdenum, to 125-ml Erlenmeyer flasks. Dilute to approximately 15 ml with water and proceed with the determination of tungsten as described above.

If the aliquot taken for analysis contains more than 0·25 mg of molybdenum, transfer identical aliquots of the blank and sample solutions to 60-ml separatory funnels, add 4·5 ml of 8*M* hydrochloric acid and dilute to approximately 25 ml with water. Add 2 ml of 20% potassium ethyl xanthate solution, mix thoroughly, then add 10 ml of chloroform and shake for 1 min. Allow the layers to separate, then drain off and discard the chloroform layer. Repeat the extraction, using 0·3–0·5 ml of xanthate solution and 5 ml of chloroform each time, until the chloroform layer is colourless (Note 5). Transfer the aqueous layer to a 125-ml Erlenmeyer flask and heat gently to remove residual chloroform. Evaporate the solution to approximately 15 ml, then proceed with the reduction and subsequent determination of tungsten as described above.

Steel. Transfer 0·2–1 g of sample to a 400-ml beaker, add 20 ml of concentrated hydrochloric acid, cover and heat gently until the sample has dissolved. Add 5 ml of concentrated nitric acid, heat until the destruction of carbides is complete, then remove the cover, add 3 or 4 drops of concentrated hydrofluoric acid and evaporate the solution to dryness to remove nitric acid. Add 5 ml of concentrated hydrochloric acid and approximately 25 ml of water to the residue and heat to dissolve the salts. Add 30 ml of 50% tartaric acid solution, cool the solution to room temperature and carefully add 25 ml of 50% sodium hydroxide solution. Cool the resulting solution to room temperature, transfer to a 200-ml volumetric flask and dilute to volume with water (Note 6). Run a blank determination.

If the separation of molybdenum is not necessary (*i.e.*, less than 0·25 mg), transfer suitable aliquots of both the blank and sample solutions (Note 7) to 125-ml Erlenmeyer flasks and proceed with the reduction and subsequent determination of tungsten.

If the separation of molybdenum is necessary, transfer suitable aliquots of both the blank and sample solutions to 60-ml separatory funnels, add 5·5 ml of 8*M* hydrochloric acid, dilute to 25 ml with water and proceed with the xanthate–chloroform extraction (Note 8) and subsequent determination of tungsten as described above.

Notes

1. Sodium thiocyanate cannot be used in place of potassium thiocyanate, because a dense white precipitate of sodium sulphate forms in the solution.
2. Because of the high acid content of the solution, some salts may precipitate during extraction; this does not interfere with the extraction of tungsten.
3. If the blank or tungsten extracts are slightly opalescent, or become opalescent on standing, filter a suitable portion of the extract through two dry Whatman No. 42 filter papers before the spectrophotometric measurement.
4. Potassium pyrosulphate is not recommended for fusion of the sample because of the insolubility of potassium tartrate, which crystallizes from the final solution on cooling and standing. This can cause low results for tungsten because of occlusion.
5. A three-stage extraction with a total volume of 4 ml of 20% potassium ethyl xanthate solution is sufficient for the separation of 5 mg of molybdenum (also 5 mg of arsenic, selenium or tellurium).
6. If a precipitate of hydrous oxides is present, allow the suspension to settle before an aliquot is taken for the tungsten determination.
7. If the sample is a high-tungsten steel, further dilution will be necessary before an aliquot is taken for the tungsten determination. In this case, transfer a suitable aliquot of the blank and sample solutions to 100-ml volumetric flasks, add 5 ml of 50% sodium hydroxide solution, dilute to volume with 7·5% tartaric acid solution, then proceed as described.
8. If the sample contains nickel, vanadium or cobalt, a colourless extract will not be obtained after the complete separation of molybdenum. These elements are partly co-extracted as xanthates which continue to colour the extract.

RESULTS

Extraction of the tungsten(V)–thiocyanate–diantipyrylmethane complex

Previous investigators[5,6] found that an approximately 7*M* or more hydrochloric acid medium is necessary for the efficient extraction of tungsten–thiocyanate ion-association complexes into chloroform, following the reduction of tungsten in concentrated (12*M*) hydrochloric acid media with stannous chloride[5] or with a mixture of stannous and titanous chlorides.[6] Because the reduction of tungsten in a more dilute acid medium was considered more suitable for analytical purposes, preliminary experiments were carried out to determine the feasibility of extracting the tungsten–thiocyanate–diantipyrylmethane complex from a sulphuric–hydrochloric acid medium, following the reduction of tungsten with stannous chloride in a 3·6*M* sulphuric acid–5·8*M* hydrochloric acid medium, according to the method described by Freund *et al.*[2] In these tests, thioglycollic acid, which is soluble in chloroform, rather than quinol dissolved in ethyl alcohol,[6] was added to the chloroform to reduce interfering organic peroxides that would re-oxidize the tungsten complex. The results of these tests, which were carried out in a fluoride medium, showed that up to at least 300 μg of tungsten could be quantitatively extracted, in three stages, from an approximately 8*M* hydrochloric acid medium containing the volume of sulphuric acid recommended for reduction by Freund *et al.*,[2] with 2, 0·5 and 0·5 ml of 1% diantipyrylmethane solution. However, the extracts become turbid almost immediately after filtration and dilution to volume with chloroform containing thioglycollic acid. Ethyl alcohol could not be used to clarify the extracts because of the instability of the complex in chloroform–ethyl alcohol media. It was subsequently found that turbidity can be avoided by washing the extracts with 8*M* hydrochloric acid. Beer's law is obeyed over the range investigated. The absorbance of the complex remains constant for at least 24 hr. The molar absorptivity of the complex is 1510 $l.mole^{-1}.mm^{-1}$ at 404 nm, the wavelength of maximum absorption.

Reduction of tungsten

Although Freund *et al.*[2] claimed that in 3·6*M* sulphuric acid–5·8*M* hydrochloric acid media a 5-min heating period at 100° was sufficient for the complete reduction of tungsten in pure tungsten solutions, later investigators[1] found that 30–60 min may be required when an appreciable amount of phosphate is present in the sample solution. In the present work, approximately 30 min are required for solutions containing tartaric acid and matrix elements.

Separation of molybdenum by extraction of its xanthate complex

The interference of molybdenum in the determination of tungsten by the thiocyanate method is known to be greater in the presence of iron because of an interelement effect.[1,6,7] To reduce this effect, iron can be separated from molybdenum by extraction of its chloro-complex into methyl isobutyl ketone[7] or isopropyl ether[1] before the formation of the tungsten–thiocyanate complex. Both molybdenum and tungsten can also be separated from iron by chloroform extraction of their α-benzoinoxime complexes.[7] In the present work, it was considered that the complete removal of molybdenum from tungsten would result in a more reliable method, and published data[11–14] on the extraction of molybdenum(V) xanthate indicated that this method might provide a simple and effective means of separating moderately large amounts of molybdenum from tungsten.

Preliminary experiments with tungsten solutions (1000 μg) containing tartaric acid showed that at least 10 mg of molybdenum, depending on the amount of potassium ethyl xanthate employed, can be readily extracted into chloroform, in three successive stages, from 0·5–3*M* hydrochloric acid. Extraction at lower and higher acidities was not investigated. Complete recovery of the added tungsten was obtained in all the tests and analysis of the final solutions showed that less than 30 μg of molybdenum remained in the aqueous phase after extraction. Subsequent work showed that, in the range of acid concentration (1·5–2*M*) chosen, cobalt, nickel and vanadium are partly extracted and arsenic, selenium and tellurium are completely extracted as the xanthates. Copper forms

Table 1. Effect of diverse ions on the extraction of tungsten (200 μg)

Diverse ion taken, mg	W found, μg	Diverse ion taken, mg	W found, μg
Fe(III) 50	200	U(VI) 10	196
Mo(VI) 2	213	Nb(V) 10	196
Mo(VI) 0·5 + Fe(III) 50	220	Zn(II) 20	197
Mo(VI) 0·35 + Fe(III) 50	213	Cu(II) 10	196
Mo(VI) 0·30 + Fe(III) 50	206	Ni(II) 10	199
Mo(VI) 0·25 + Fe(III) 50	200	Bi(III) 10	198
Mo(VI) 5	195†	Sb(V) 10	199
Mo(VI) 5 + Fe(III) 50	198†	Al(III) 10	196
Se(IV) 10*	60	Mn(II) 10	200
Se(IV) 2	128	Ti(IV) 10	205
Se(IV) 1	153	Zr(IV) 10	196
Se(IV) 0·5	187	Cd(II) 10	197
Se(IV) 0·25	198	Cr(VI) 10	202
Se(IV) 5	200†	As(III) 10*	199
Co(II) 10	197	Te(IV) 10*	197
V(V) 10	202	P(V) 10	196

* Removed, in elemental state, by filtration through glass-wool before extraction of tungsten.
† After xanthate–chloroform extraction.

a bright yellow precipitate, which is insoluble in chloroform and remains above the chloroform layer, but is decomposed completely during evaporation and boiling of the aqueous layer to destroy excess of xanthate.

Effect of diverse ions

Tests carried out with moderate amounts of coloured ions, common ions and ions that are known to interfere in tungsten thiocyanate colourimetric methods by forming coloured extractable thiocyanate complexes, showed that, for the quantity of each ion tested (Table 1), none, except molybdenum and selenium, interfered in the extraction and subsequent determination of tungsten by the proposed method. However, up to approximately 0·25 mg of molybdenum and selenium can be present in the aliquot taken for extraction without causing appreciable error. It is not known how selenium interferes but interference from larger amounts can be avoided by separating it from tungsten by xanthate–chloroform extraction. Although arsenic and tellurium (also selenium) are reduced to the elemental state during the reduction of tungsten, interference from these precipitated elements during the extraction procedure can be avoided by removing the precipitates by filtration of the solution through glass-wool before the extraction of tungsten. Large amounts of copper interfere during extraction because of the precipitation of cuprous thiocyanate.

Table 2. Recovery of tungsten from synthetic tungsten ore samples

Total W present, %	W found, %	
	In presence of Mo	After separation of Mo
0·179	0·172	0·168
0·329	0·326	0·322
0·579	0·584	0·572
1·079	1·064	1·056
2·079	2·040	2·064
4·079	4·064	4·080

Ten determinations of tungsten in the ore (TLG-1) by the proposed method gave an average result of 0·079% (*cf.* Table 3).

Applications

The proposed method was applied to the analysis of a series of synthetic mixtures of a scheelite ore to which 0·5% of molybdenum was added and in which the tungsten varied from 0·10 to 4·00%. The standard tungsten solution was added to the samples just before dissolution of the sodium bisulphate melt. It was also applied to standard reference steel samples and to the three tungsten ores, CT-1, BH-1 and TLG-1, currently undergoing certification for tungsten. For each of these ores, tungsten was determined according to the directives of the Mines Branch's Canadian Certified Reference Materials Project, *i.e.*, by using five subsamples from each of two bottles. The results of these analyses are given in Tables 2–4.

DISCUSSION

Table 2 shows that the results obtained for the synthetic scheelite ore samples, containing 0·5% added molybdenum, agree favourably with the total calculated amount of tungsten present, both when tungsten was determined in the presence of molybdenum and after its separation by xanthate–chloroform extraction. The results obtained (Table 3) for the reference ores are in reasonably good agreement with the aver-

Table 3. Determination of tungsten in standard reference ores

Sample*	Laboratory A†		Laboratory B†		Laboratory C†		This work	
	Average value and range, % W	Standard deviation, %	Average value and range, % W	Standard deviation, %	Average value and range, % W	Standard deviation, %	Average value and range, % W	Standard deviation, %
CT-1 Scheelite ore	1·056 (1·019–1·078)	0·020	1·018 (0·98–1·04)	0·023	1·038 (1·01–1·05)	0·015	1·041 (1·024–1·056)	0·009
BH-1 Wolframite ore	0·409 (0·381–0·444)	0·018	0·416 (0·412–0·420)	0·004	0·439 (0·42–0·46)	0·010	0·410 (0·404–0·414)	0·003
TLG-1 Scheelite ore	0·077 (0·069–0·086)	0·006			0·084 (0·077–0·089)	0·003	0·079 (0·074–0·082)	0·003

* The molybdenum contents of CT-1, BH-1 and TLG-1 are 0·032, 0·023 and 0·002%, respectively.
† Tungsten determined by a thiocyanate method involving measurement of the anionic complex in aqueous media. The average value is the arithmetic mean of 10 values.

Table 4. Determination of tungsten in N.B.S. and B.C.S. steels

Sample	Nominal composition, %	Mo, %	Certified value and range, % W	W found, %
NBS-50a Chromium–tungsten steel	0·3 Mn, 0·5 Si, 3·5 Cr, 1·0 V, 0·1 Cu, 0·1 Ni, 0·04 As	0·009	18·25 (18·16–18·34)	18·2
NBS-50B Tungsten–chromium–vanadium steel	0·3 Mn, 0·3 Si, 0·1 Cu, 0·1 Ni, 4·1 Cr, 1·0 V, 0·04 As	0·401	18·05 (17·95–18·14)	17·9
NBS 101E Chromium–nickel steel	1·8 Mn, 0·4 Si, 0·4 Cu, 9·5 Ni, 18·0 Cr, 0·04 V, 0·2 Co	0·426	0·056	0·054†
NBS-123a Chromium–nickel steel (niobium-bearing)	0·8 Nb, 0·04 V, 0·5 Si, 18·1 Cr	0·12	0·11*	0·108
NBS-123b Niobium–tantalum stabilized stainless steel	0·8 Nb, 0·2 Ta, 0·5 Si, 0·05 V	0·17	0·18*	0·182
NBS-134A Molybdenum–tungsten high-speed steel	0·2 Mn, 0·3 Si, 0·1 Cu, 0·1 Ni, 3·7 Cr, 1·3 V	8·35	2·00 (1·97–2·05)	2·03†
NBS-153 Cobalt–molybdenum–tungsten steel	0·2 Mn, 0·2 Si, 0·1 Cu, 0·1 Ni, 4·1 Cr, 2·0 V, 8·5 Co	8·38	1·58 (1·54–1·61)	1·55†
NBS-155 Chromium–tungsten steel	1·2 Mn, 0·3 Si, 0·1 Cu, 0·1 Ni, 0·5 Cr, 0·02 V	0·039	0·517 (0·508–0·526)	0·517
BCS-220/1 Tungsten–molybdenum high-speed steel	5·1 Cr, 2·1 V, 0·1 Co, 0·2 Si, 0·3 Mn, 0·2 Ni, 0·2 Cu, 0·03 As	5·20	6·86 (6·78–7·00)	6·78
BCS-246 Niobium–molybdenum 18/12 stainless steel	0·8 Nb, 18·8 Cr, 12·1 Ni, 0·1 Cu	2·89	0·22 (0·19–0·23)	0·223†
BCS-271 Mild steel	0·1 Cr, 0·1 Sn	$0{\cdot}19_0$	$0{\cdot}01_5$ (0·013–0·019)	0·016
BCS-273 Mild steel	0·1 Cr, 0·2 Cu, 0·1 Sn, 0·05 V	0·045	$0{\cdot}28_0$ (0·271–0·282)	0·287
BCS-281 Low-tungsten steel	0·1 Si, 0·1 Mn	0·02	0·70 (0·68–0·73)	0·696
BCS-282 Low-tungsten steel	0·1 Si, 0·1 Mn, 0·1 Cr, 0·02 V	0·02	1·30 (1·28–1·32)	1·29

* N.B.S. provisional result.
† Molybdenum removed by xanthate-chloroform extraction.

age results hitherto reported in the interlaboratory programme of certification. Also, those obtained for the National Bureau of Standards and British Chemical Standards samples of steel are in good agreement with the certified values. The precision of the results for the ores CT-1, BH-1 and TLG-1 (Table 3) is superior, in most cases, to that for sets of results obtained by using thiocyanate methods based on measurement of the anionic tungsten complex.

The proposed method is suitable for samples containing up to approximately 6% of tungsten but material containing larger amounts can also be analysed with reasonable accuracy. It is more sensitive than the thiocyanate methods mentioned above, considerably more selective, and reasonably specific as far as common ions are concerned.

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MICRODETERMINATION OF PHENOLS, CARBOXYLIC ACIDS AND PHENOLIC ACIDS BY POTENTIOMETRIC AND VISUAL TITRATIONS IN DIMETHYLFORMAMIDE

SAAD S. M. HASSAN and M. T. M. ZAKI

Research Microanalytical Laboratory, Department of Chemistry, Faculty of Science, Ain Shams University, Cairo, Egypt

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Summary—Potentiometric titration of phenols with sodium methoxide in dimethylformamide, with a glass–calomel electrode system, is limited to monohydric phenols substituted with electron-attracting groups and dihydric phenols in which the two —OH groups are substituted in isolated benzene rings. Brilliant Orange has proved to be a suitable indicator in the titration of all types of mono- and dihydric phenols. Titan Yellow is recommended as indicator for the titration of carboxylic acids. Simultaneous visual titration of —OH and —COOH groups is also described. A detailed study with 62 structurally different compounds covering the various groups is reported, and a suitable procedure for the microdetermination of each class of these compounds with an error of ±0·2% absolute or less is presented.

Titration of weak acids in dimethylformamide (DMF) is usually performed potentiometrically owing to the lack of a suitable indicator.[1–3] However, Azo Violet and Thymol Blue have been recommended as indicators for the visual titration of imides and compounds containing active methylene,[4] while dithiazanine iodide[5] and Bromophenol Red[6] have been advocated for some phenols and aryl arsonic acids, respectively.

The present investigation was undertaken because potentiometric titration with methoxide in DMF is not successful with all types of phenolic compounds and many of the known indicators, including those mentioned above, are not suitable to detect the end-points for the various types of phenolic compounds. In addition, little is known about the titration of dihydric phenols and phenolic acids in non-aqueous solvents.

EXPERIMENTAL

Reagents

All reagents were of analytical grade unless otherwise specified. Standard sodium methoxide solution (0·04*M*), was prepared as previously described[6] and was standardized by titration with different weights (4–8 mg) of benzoic acid in 20 ml of anhydrous neutral dimethylformamide, with Brilliant Orange or Titan Yellow as indicator. Methanolic solutions (0·3% w/v) of the indicators were used. Methanol, isopropyl alcohol, and t-butyl alcohol were distilled over barium oxide. Benzene and dioxan were kept over sodium metal and pyridine over sodium hydroxide pellets for 24 hours before distillation under ordinary pressure. Chloroform was used without purification. DMF is commercially available of sufficient purity to require no further purification. The solvent is neutralized by the addition of 0·04*M* sodium methoxide solution to 100-ml aliquots of the solvent until the Brilliant Orange or Titan Yellow used as indicator changes its colour (0·3–0·7 ml of the methoxide solution is usually needed per 100 ml of DMF).

All phenolic, carboxylic and phenolic acid samples used were provided as standard compounds with purity not less than 98%, and those of unknown purity were purified by crystallization repeated several times.

Apparatus

Potentiometric titrations were done with a Radiometer PHM 22r pH-meter, Radiometer GK 282C/0 calomel electrode filled with saturated potassium chloride in absolute methanol, and Radiometer G 202B glass electrode. The microtitration vessel and automatic microburette were similar to those described by Maurmeyer *et al.*[4] The ion-exchange column (25 × 1·2 cm) was made of Dowex 50W-X8 (100–200 mesh) in the hydrogen form. The exchange capacity was 1·7 m equiv/ml of the wet resin. The column was washed with several 20-ml portions of 0·1*M* hydrochloric acid, followed by double-distilled water until no chloride ion was detected in the effluent and finally by 20 ml of anhydrous neutral dimethylformamide.

Procedures

Determination of phenols and carboxylic acids. Weigh accurately 3–8 mg of the sample, transfer it to the reaction vessel and dissolve it in 10 ml of neutral anhydrous dimethylformamide. Adjust the flow of nitrogen to about 100 bubbles/min. Add 2 drops of Brilliant Orange indicator for phenols or Titan Yellow for carboxylic acids. Titrate with 0·04*M* sodium methoxide until the colour of Brilliant Orange changes from yellow to violet or that of Titan Yellow from yellow to orange.

Both the carboxylic and the phenolic groups in phenolic acids are determined concurrently by using Brilliant Orange as indicator in one run to determine both types of group, and Titan Yellow in a second run to determine the carboxyl group.

Alternatively, use 20 ml of DMF and titrate potentiometrically, with passage of nitrogen during the titration. The electrodes should be at least 2 mm below the surface and about 5 mm apart.

Simultaneous determination of phenolic and carboxylic groups. Weigh accurately 3–8 mg of the sample and transfer it to the titration vessel. Dissolve it in 10 ml of anhydrous

DMF and add 2 drops of Titan Yellow indicator. Titrate with sodium methoxide solution until the indicator changes colour. Pass the solution through the cation-exchange column and elute with 10 ml of DMF added in portions. Add 2 drops of Brilliant Orange indicator to the effluent and titrate again with the methoxide solution until a violet colour appears. Carry out a blank and calculate the —COOH and —OH contents according to the equations:

$$\%\text{—COOH} = V_1 \times M \times 45 \times 100/W,$$

$$\%\text{—OH} = (V_2 - V_1) \times M \times 17 \times 100/W$$

where V_1 and V_2 are the volumes of sodium methoxide solution consumed in the first and second titrations, respectively, M is the molarity of the methoxide solution and W is the weight of sample in milligrams.

RESULTS AND DISCUSSION

Determination of monohydric phenols

Potentiometric titration. The titration curves for unsubstituted phenols and those substituted with electron-donating groups have no clear inflection at the equivalence points (Fig. 1). Phenols substituted with electron-attracting groups give titration curves similar to those for carboxylic acids (Fig. 2). The shape of the curves appears to be related to the acidic behaviour of these phenols. Determination of trinitrophenol, 2,4-dinitrophenol, 3,5-dinitro-4-hydroxy-6-methoxyquinoline, 2,4,6-tribromophenol, *o*-nitrophenol, and 1-nitroso-2-naphthol by titration with sodium methoxide in DMF, with a glass–calomel electrode system, shows results accurate to ±0·1% with an average recovery of 98·8%.

A relationship between the shift in half-neutralization potential and degree of neutralization of these

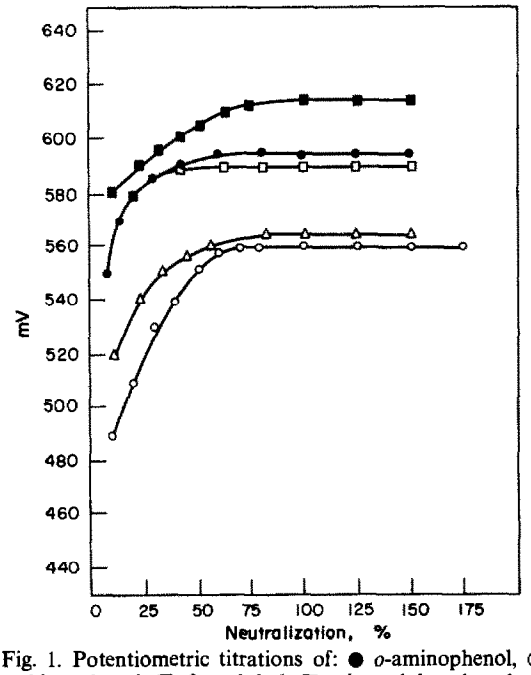

Fig. 1. Potentiometric titrations of: ● *o*-aminophenol, ○ *p*-chlorophenol, □ β-naphthol, ■ *p*-benzylphenol and △ 8-hydroxyquinoline in dimethylformamide with sodium methoxide (glass–calomel electrode system).

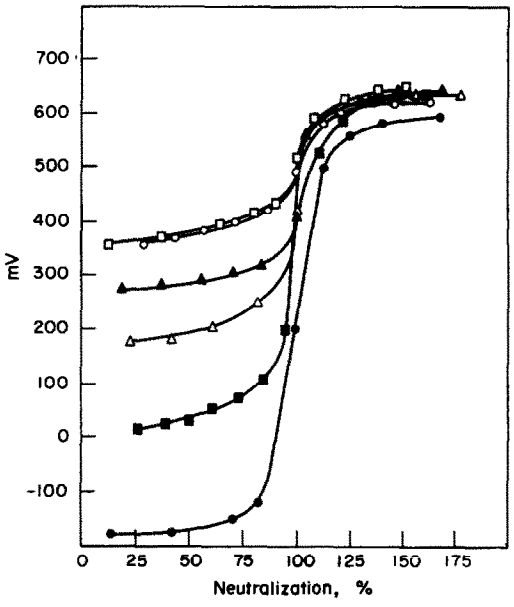

Fig. 2. Potentiometric titrations of: ● picric acid, ■ 2,4-dinitrophenol, △ 3,5-dinitro-4-hydroxy-6-methoxyquinoline, ▲ 2,4,6-tribromophenol, ○ *o*-nitrophenol and □ 1-Nitroso-2-naphthol in dimethylformamide with sodium methoxide (glass–calomel electrode system).

phenols was obtained by the procedure suggested by Streuli.[7] The half-neutralization potential (HNP) of benzoic acid was arbitrarily assigned a value of zero and the HNP values of phenols were referred to it to obtain ΔHNP values. This relation illustrates the relative acidities of phenols with respect to benzoic acid in dimethylformamide. A considerable enhancement of the acidity of the phenols in DMF is clear. There is a linear relationship between pK_a (in aqueous medium) and ΔHNP values for the phenols in DMF. The slope of this line, 60 mV/pK_a unit, can be used to determine the resolving power of DMF as a solvent.[8]

Brilliant Orange has a transition interval of 500–650 mV and is suitable for phenols or acids with $pK_a > 3$; Titan Yellow has its transition interval at 350–500 mV and is suitable for $pK_a < 5$.

Visual titration. *p*-Benzylphenol and *p*-hydroxydiphenyl were titrated in various solvents with sodium methoxide, and a great variety of indicators covering a wide range of pH. The results obtained show that pyridine, dioxan, dimethylformamide, isopropyl alcohol, t-butyl alcohol, benzene and chloroform are not suitable as solvents with Thymol Blue, Titan Yellow, phenolphthalein, thymolphthalein and Diphenol Purple as indicators. However, quantitative neutralization is detected by using DMF as a solvent and Brilliant Orange as indicator.

To confirm the applicability of this indicator, 10–50 μmole of 20 phenolic compounds of different nature were determined and the results are quoted in Table 1. The results show an average recovery of 99·8% and a mean absolute error of ±0·1%. 1-Nitroso-2-naphthol, *p*-aminophenol, *m*- and *p*-nitro-

Table 1. Microdetermination of some monohydric phenols by titration with sodium methoxide in DMF, using Brilliant Orange indicator

Sample	—OH, % Calculated	Found	Recovery, %
Phenol	18·09	18·0	99·5
		18·0	99·5
α-Tetralol	11·49	11·4	99·2
		11·5	100·1
α-Naphthol	11·81	11·7	99·1
		11·8	99·9
β-Naphthol	11·81	11·8	99·9
		11·8	99·9
p-Chlorophenol	13·22	13·2	99·8
		13·2	99·8
2,4,6-Tribromophenol	5·14	5·1	99·2
		5·1	99·2
5,7-Dibromo-8-hydroxyquinoline	5·61	5·6	99·8
		5·6	99·8
4-Bromosalicaldehyde	8·46	8·4	99·3
		8·5	100·5
4-Bromophenol	9·83	9·7	98·7
		9·7	98·7
o-Iodophenol	7·73	7·7	99·6
		7·7	99·6
m-Hydroxybenzaldehyde	13·93	13·8	99·1
		14·0	100·5
p-Hydroxybenzaldehyde	13·93	14·0	100·5
		14·0	100·5
Salicylaldoxime	12·41	12·3	99·1
		12·4	99·9
8-Hydroxyquinoline	11·72	11·6	99·0
		11·7	99·8
p-Hydroxydiphenyl	10·00	9·9	99·0
		9·9	99·0
p-Benzylphenol	9·24	9·2	99·6
		9·2	99·6
o-Cresol	15·74	15·7	99·7
		15·7	99·7
p-Fluorophenol	15·17	15·1	99·5
		15·2	100·2
2,4-Dichlorophenol	10·49	10·4	99·1
		10·4	99·1
Hydroxybenzthiophene	11·33	11·3	99·7
		11·3	99·7

phenols and 2,4-dinitrophenol develop a colour in DMF and cannot be determined under these conditions. *o*-Hydroxyacetophenone and *o*-hydroxybenzaldehyde do not show a clear end-point.

Determination of dihydric phenols

Potentiometric titration. Curves with practically no inflection (jump not exceeding 10 mV) at the equivalence point are obtained with dihydric phenols in which the two —OH groups are in the same benzene nucleus or in two benzene rings fused together (*e.g.*, catechol, resorcinol and 2,6-dihydroxynaphthalene). However, the potentiometric curves of dihydric phenols in which the two —OH groups are substituted in two isolated benzene rings (*e.g.*, 4,4′-dihydroxybenzophenone, 2,2′-dihydroxy-6,6′-dinaphthyldisulphide, 2,2′-dihydroxy-4-methoxybenzophenone and 2,2′-dihydroxydiphenyl) exhibit one sharp inflection point with a jump of 30–300 mV, corresponding to the consumption of one mole of titrant per mole of compound. On this basis, determination of 10–50 μmole of these compounds gives results with an average recovery of 98·9% and a mean absolute error of ±0·2%.

Visual titration. Structurally different dihydric phenols were titrated with sodium methoxide in DMF, with Brilliant Orange as indicator. Compounds containing two —OH groups in the same benzene nucleus (*e.g.*, catechol, resorcinol, 3,5-dihydroxytoluene, 2,4-dihydroxyquinoline and 2,4-dihydroxyacetophenone) and those containing two —OH groups in two adjacent fused aromatic rings (*e.g.*, dihydroxynaphthalene derivatives) quantitatively consume one mole of methoxide per mole of compound. In addition, compounds containing two —OH groups in two isolated systems and engaged in intramolecular hydrogen bonding (*e.g.*, 2,2′-dihydroxydiphenyl and di-β-naphthol) behave similarly. Results accurate to ±0·1% absolute with a mean recovery of 99·8% are obtained (Table 2). The potentials at half-neutralization (*i.e.*, for titration of one phenol group) fall within the transition range for Brilliant Orange.

These results show that one of the two hydroxyl groups in these compounds is active and the other one is too weak to be titrated quantitatively in DMF. This is in agreement with the finding of other workers that compounds having two or more ionizable hydroxyl groups often show a marked difference in their degree of ionization;[9] one hydroxyl group is 10^4 times more acidic than the other, as confirmed by methylation, and their potentiometric curves are similar to those associated with monohydric phenols.[7]

However, compounds containing two —OH groups which are in two isolated aromatic systems but not involved in hydrogen bonding (*e.g.*, 4,4′-dihydroxydiphenyl, 4,4′-dihydroxybenzophenone and 2,2′-dihyd-

Table 2. Microdetermination of some dihydric phenols by titration with sodium methoxide in DMF, using Brilliant Orange indicator

Sample	—OH, % Calculated	Found*	Recovery, %
Catechol	30·91	30·7	99·3
		30·8	99·6
Resorcinol	30·91	30·9	100·0
		30·9	100·0
3,5-Dihydroxytoluene monohydrate	23·94	23·8	99·4
		23·9	99·8
2,4-Dihydroxyquinoline	20·86	20·7	99·2
		20·8	99·7
2,4-Dihydroxybenzophenone	16·35	16·3	99·7
		16·3	99·7
1,5-Dihydroxynaphthalene	21·25	21·1	99·3
		21·2	99·8
1,7-Dihydroxynaphthalene	21·25	21·2	99·8
		21·2	99·8
2,6-Dihydroxynaphthalene	21·25	21·2	99·8
		21·2	99·8
Chromotropic acid (disodium salt)	9·34	9·3	99·6
		9·3	99·6
2,2′-Dihydroxydiphenyl	18·28	18·1	99·0
		18·2	99·6
Di-β-naphthol	11·89	11·8	99·2
		11·8	99·2
2,2′-Dihydroxy-6,6′-dinaphthyldisulphide	9·71	9·7	99·9
		9·7	99·9
4,4′-Dihydroxybiphenyl	18·28	18·2	99·6
		18·2	99·6
4,4′-Dihydroxybenzophenone	16·35	16·3	99·7
		16·3	99·7

* Based on the consumption of one mole of sodium methoxide per mole of compound, except the last three compounds which consume two moles of methoxide per mole of compound.

Table 3. Microdetermination of some mono- and dicarboxylic acids by titration with sodium methoxide in dimethylformamide

Acid	Calculated	—COOH, % Found						
		Potentiometric	Thymol Blue	Titan Yellow	Brilliant Orange	Phenolphthalein	Thymolphthalein	Diphenol Purple
Benzoic	36 89	36 6	36 6	36 7	36 9	36·9	36·7	36 7
		36·7	36·9	37 0	36 9	37 0	36·9	36 7
o-Methoxybenzoic	29 61	29·3	29 3	29 5	29·5	29·4	29 8	29 4
		29 4	29 4	29 7	29·6	29·6	29 8	29 5
p-Chlorobenzoic	28·74	28 5	28 5	28·5	28·8	28 6	28·6	28·5
		28 5	28 6	28 6	28 8	28·7	28·8	28 6
Benzilic	19 74	19 5	19 7	19 6	19 8	19 9	19 6	19·7
		19·6	19 8	19 7	19 8	19 9	19 7	19·8
3-Nitrophthalic	42·65	42 5	42 5	42·7	42·7	42 6	42·8	42 5
		42·6	42 6	42·8	42 7	42·7	42 6	42·6
Succinic	76 27	75·9	75 8	76 2	76 1	75 8	76 1	76·3
		76 0	76 2	76·5	76 3	76·0	76 4	76·3
Malic	67 16	66·9	67·2	66 9	67 0	67 1	67 0	66·9
		66 9	67 2	67 1	67 3	67 1	67·1	67 2
Tartaric, monohydrate	54 22	53 8	54·0	54·3	54·1	54 1	53 9	54·0
		54·1	54 1	54·2	54 2	54 2	54·0	54·0

roxy-6,6′-dinaphthyl disulphide) consume two moles of titrant per mole of compound, probably because these compounds behave as two separate units, owing to free rotation around the single bond connecting the two isolated systems. The results obtained (Table 2) show an average recovery of 99·9% with a mean absolute error of ±0·1%. Phenolic compounds having coloured salts (*e.g.*, hydroquinone, chlorohydroquinone, 1,4-, 1,5-, and 1,8-dihydroxyanthraquinones) are not easily titrated under these conditions.

Determination of mono- and dicarboxylic acids

Potentiometric titration. Titrations of some carboxylic acids with sodium methoxide in DMF, with glass–calomel and platinum–calomel electrode systems, show sharp and clear inflections at the equivalence points with the former electrode system. Dicarboxylic acids show two clearly resolved inflections. Determination of some carboxylic acids, with a glass–calomel electrode system, shows an average recovery of 99·4% and a mean absolute error of ±0·2% (Table 3).

Visual titration. Thymol Blue, Titan Yellow, phenolphthalein, thymolphthalein, and Brilliant Orange are suitable indicators for the titration of all types of carboxylic acids with sodium methoxide in DMF, dioxan, benzene or chloroform, but end-points are not detectable when Titan Yellow is used with benzene media or Diphenol Purple is used with dioxan, benzene or chloroform. Because the salts of many carboxylic acids are insoluble in dioxan, benzene and chloroform, these solvents are excluded and DMF is recommended. Determination of some acids in DMF, with various indicators, are shown in Table 3. Titan Yellow is the best indicator for the neutralization point of the —COOH group without interferences from the phenolic group.

Determination of phenolic acids

Potentiometric titration. Compounds containing both carboxylic and phenolic groups (*e.g.*, 1-hydroxy-2-naphthoic acid, *m*- and *p*-hydroxybenzoic acids and 3,4-dihydroxybenzoic acid) show titration curves similar to those of the corresponding carboxylic acids. The neutralization of the phenolic group is not indicated in these curves. Titration of these phenolic acids as monocarboxylic acids shows an average recovery of 99·3% and a mean absolute error of ±0·2%.

Visual titration. Because Brilliant Orange proved to be a suitable indicator for the neutralization points of both —COOH and phenolic —OH groups and Titan Yellow for that of the —COOH group, attempts were made to determine phenolic acids by sequential titration in DMF, using these indicators. The results obtained with Brilliant Orange show that (*i*) *o*-hydroxybenzoic acid consumes one equivalent of titrant per mole, probably because of intramolecular hydrogen bonding; (*ii*) *m*- and *p*-hydroxybenzoic acids consume two equivalents of titrant per mole, probably because the —COOH and —OH groups are not engaged in hydrogen bonding; (*iii*) 2,3-, 3,4-, and 3,5-dihydroxybenzoic acids consume two moles of titrant per mole, because of the difficulty in obtaining two

Table 4. Titration of some phenolic acids with sodium methoxide in dimethylformamide, using Brilliant Orange and Titan Yellow indicators

Acid	Moles of sodium methoxide consumed per mole of compound	
	Brilliant Orange	Titan Yellow
m-Hydroxybenzoic	2 002	1 002
	2 003	1·002
p-Hydroxybenzoic	1·998	1 003
	2 009	1 000
2,3-Dihydroxybenzoic	2·004	0·994
	2·002	0·999
3,4-Dihydroxybenzoic	1 995	1·005
	2·003	1·007
3,5-Dihydroxybenzoic	1 989	1 000
	1·999	1 005
o-Hydroxybenzoic	1·002	1 005
	1·000	1 001
1-Hydroxy-2-naphthoic	0·998	0·990
	0 996	0 995
2-Hydroxy-1-naphthoic	0 993	0 999
	0 989	0 993

Table 5. Simultaneous microdetermination of the carboxylic and hydroxylic groups in some phenolic acids by visual titration with sodium methoxide in dimethylformamide

	—COOH			—OH		
Acid*	Calculated, %	Found, %	Recovery, %	Calculated, %	Found, %	Recovery, %
		32·5	99·7		12·3	99·8
p-Hydroxybenzoic	32·61	32·6	100·0	12·32	12·3	99·8
		32·5	99·7		12·3	99·8
		32·5	99·7		12·2	99·0
m-Hydroxybenzoic	32·61	32·6	100·0	12·32	12·3	99·8
		32·7	100·3		12·3	99·8
		29·2	99·9		22·0	99·6
2,3-Dihydroxybenzoic	29·22	29·2	99·9	22·08	22·0	99·6
		29·3	100·3		22·1	100·1
		29·1	99·6		22·0	99·6
3,5-Dihydroxybenzoic	29·22	29·2	99·9	22·08	22·1	100·1
		29·3	100·3		22·2	100·5

* Two moles of sodium methoxide are consumed per mole of these compounds when Brilliant Orange is used as indicator and 1 mole per mole with Titan Yellow as indicator.

phenate groups on the same benzene nucleus. On the other hand, Titan Yellow does not indicate neutralization of the phenolic —OH group (Table 4).

It is possible, therefore, to determine phenolic acids by titration with sodium methoxide in DMF, using Brilliant Orange to detect the end-point of the reaction of both —COOH and —OH groups in one run, and Titan Yellow to detect the end-point for the —COOH group in another run.

Trials were also made of determination of the —COOH and —OH groups in some phenolic acids simultaneously in one run. It was found that this could not be done by titrating first with Titan Yellow as indicator and then with Brilliant Orange added after the first end-point, because the Brilliant Orange formed a deep red compound with the alkaline form of the Titan Yellow indicator, probably from a coupling reaction with the latter. It was found, however, that addition of a mineral acid to Titan Yellow, or passage of the indicator in the alkaline form through a cation-exchanger in the hydrogen form produced a rearrangement of the indicator[10] to a form that did not interact with Brilliant Orange. The determination was thus finally achieved by titrating the —COOH group with sodium methoxide in DMF, using Titan Yellow as indicator. The reaction mixture was then passed through a cation-exchange column in the hydrogen form and eluted with DMF. The phenolic —OH and —COOH groups were titrated in the effluent, with Brilliant Orange as indicator. The results quoted in Table 5 show an average recovery of 99·9% for both functions in some hydroxybenzoic acid derivatives. This procedure, however, is not applicable to *o*-hydroxy acids or phenolic acids having salts which are insoluble in DMF (*e.g.*, 3,4-dihydroxybenzoic acid).

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DETERMINATION OF 1,4-BENZODIAZEPINES IN BIOLOGICAL FLUIDS BY DIFFERENTIAL PULSE POLAROGRAPHY

M. A. BROOKS and J. A. F. de SILVA

Department of Biochemistry and Drug Metabolism, Hoffmann -La Roche Inc., Nutley, N.J. 07110, U.S.A.

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Summary—The determination of various 1,4-benzodiazepines and their metabolites by differential pulse polarography is reviewed and compared with that by other methods, and the general applicability of the polarographic methods, in terms of simplicity and flexibility, is demonstrated.

Since the introduction of Librium™*, chlordiazepoxide hydrochloride, in 1960, a large number of 1,4-benzodiazepine compounds have been investigated as tranquilizers, anti-depressants, and sedatives. The 1,4-benzodiazepines are usually present in trace amounts following therapeutic administration because they undergo extensive biotransformation and/or tissue distribution. Many sophisticated analytical procedures have been developed,[1–3] such as electron-capture gas chromatography (E.C.-G.L.C.), radioimmunoassay (R.I.A.) and spectrofluorimetry, for the determination of these drugs in biological fluids in order to study their metabolism and pharmacokinetics. More recently polarography has been used to determine the 1,4-benzodiazepines in biological fluids. These assays are based on the ease of polarographic reduction of the 4,5-azomethine functional group common to all 1,4-benzodiazepines. This polarographic activity was first documented by Oelschlager[4] and Senkowski *et al.*[5] The mechanism of the polarographic reduction of this series of compounds has recently been verified.[6–9]

The renaissance of polarography for the determination of drugs in biological fluids is due to the advent of commercial instrumentation capable of performing sophisticated techniques such as differential pulse polarography (D.P.P.) which has superior sensitivity and selectivity to d.c. polarography.[10] With D.P.P., easily interpretable gaussian peaks are obtained for the reduction of the 4,5-azomethine group, which can be used to determine the compounds with a concentration limit of 50–100 ng/ml. In addition, many of the 1,4-benzodiazepines possess other functional groups capable of undergoing polarographic reduction. Each of the functional groups is reduced at a particular potential, depending upon the various substituents in the compound and these potentials can be used as an aid in identification of metabolites and to ensure selectivity in an analytical method. The technique is suitable for determining blood or plasma levels of chlordiazepoxide and its metabolites[11] following therapeutic administration, and of diazepam and its *N*-desmethyl metabolite[10] following repeated administration. D.P.P. can also be used to assay the urinary excretion of most 1,4-benzodiazepines following therapeutic or repeated administration. The analysis of blood or plasma for all 1,4-benzodiazepines and their metabolites at levels below 50 ng/ml can typically only be performed by employing E.C.-G.L.C.[1–3] or R.I.A.[12]

When concentration is not a limiting factor (*i.e.*, it is $\geqslant$100 ng/ml) the polarographic determination of the intact 1,4-benzodiazepines is usually preferred to other more complicated assays which require derivative formation. *e.g.*, the spectrofluorimetric determinations of flurazepam[13] and chlordiazepoxide[14,15] and their metabolites. Since polarographic assays are relatively easy to develop, they can also be used as "intermediate" blood-level assays in monitoring preliminary pharmacokinetic studies on various animal species where doses are typically as high as 5–10 mg/kg of body weight, while the more difficult and sensitive E.C.-G.L.C. or R.I.A. procedures are being developed.

Polarographic investigations performed on ten 1,4-benzodiazepines (Fig. 1, Compounds [I]–[II-C], [III], and [V]–[X]) have primarily dealt with the mechanism of polarographic reduction and its applications to the determination of the compound in pharmaceutical formulations.[4–9,16–33] Applications dealing with their determination in blood or plasma have for the most part not been sufficiently sensitive to measure the drug after therapeutic or repeated doses nor capable of measuring toxicological levels of the drug unless exceedingly large samples were employed.[17,28,34,35] Assays for diazepam by D.P.P.[36] and cathode ray polarography,[37] though of high sensitivity, are not able to distinguish between the parent compound and its *N*-desmethyl metabolite. More recently D.P.P.

* TM signifies registered trademark.

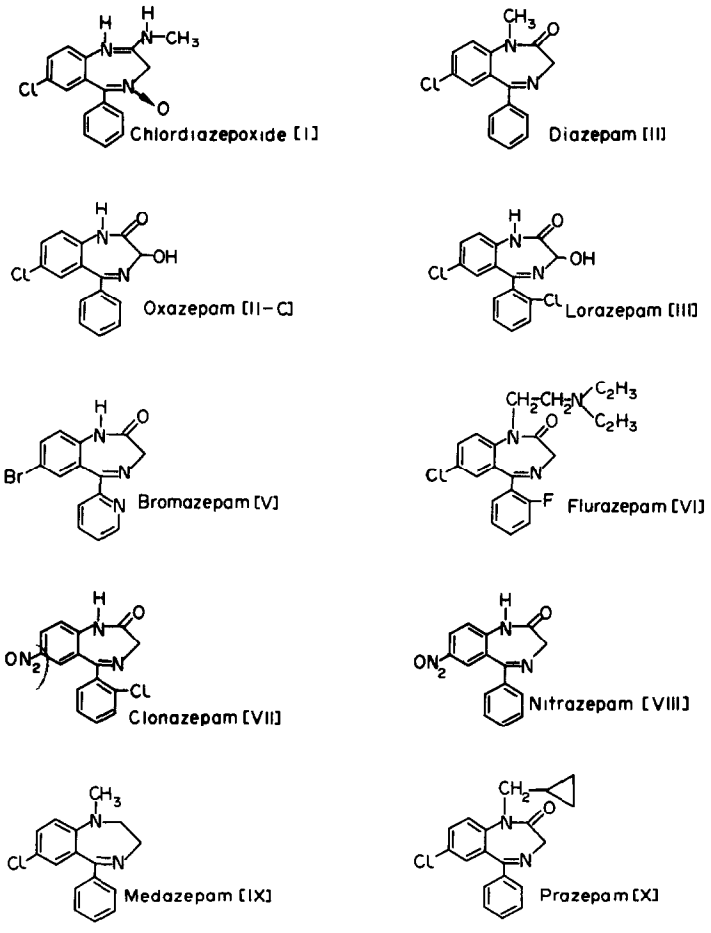


Fig. 1. 1,4-Benzodiazepines reported in the polarographic literature.

assays have been reported which are capable of determining low levels of chlordiazepoxide and its metabolites in plasma,[11] diazepam and *N*-desmethyldiazepam in plasma,[10] lorazepam in urine,[38] and bromazepam,[39] flurazepam[40] and their major metabolites in urine. An assay has also been proposed for the determination of clonazepam[41] following repeated administration.

This paper will review those polarographic assays reported for the determination of the 1,4-benzodiazepines in biological fluids and will discuss the advantages and disadvantages of each, compared to other methods of analysis.

Chlordiazepoxide

Chlordiazepoxide hydrochloride, 7-chloro-2-methylamino-5-phenyl-3*H*-1,4-benzodiazepine-4-oxide-hydrochloride, [I], marketed as Librium™, is extensively used as an anti-anxiety drug. The compound is metabolized in man to form two major biotransformation products detectable in blood, *viz.* *N*-desmethylchlordiazepoxide [I-A] and demoxepam [I-B] (Fig. 2).[13,14,42]

Colorimetric assays employing the Bratton–Marshall chromophore[43–47] and an ultraviolet spectrophotometric assay[48] have insufficient sensitivity to analyse for the compound following therapeutic administration. Spectrofluorimetric assays[14,15] employing selective extraction, hydrolysis and photochemical rearrangement to yield fluorescent derivatives have been used to assay chlordiazepoxide and its two metabolites with a sensitivity of 0·1–0·2 μg/ml, using a 2-ml specimen of plasma. The assay[15] is quite complicated in that after initial selective extractions,

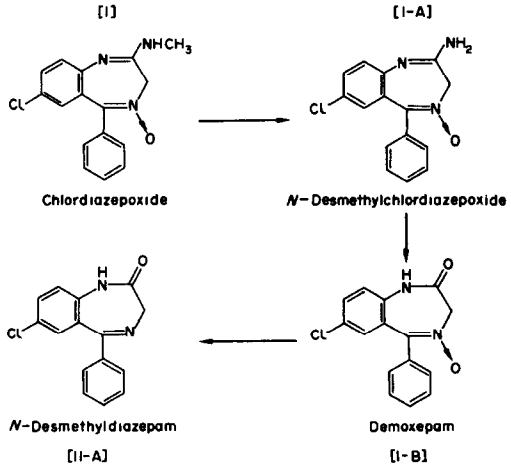


Fig. 2. Metabolism of chlordiazepoxide in man.

Table 1. Plasma levels of chlordiazepoxide and its metabolites following a single 30-mg oral dose

Time, *hr*	Chlordiazepoxide [I], *μg/ml*	*N*-Desmethyl-chlordiazepoxide [I-A], *μg/ml*	Demoxepam [I-B], *μg/ml*
1	1·55	0·08	n m *
1 5	2·39	0 18	n m
2	2·12	0·29	n m
3	1 07	0·15	n m.
4	1 28	0 26	n m.
6	1 19	0·39	n m
8	0 97	0 56	n m
12	0·75	0·39	n m.
24	0 16	0·33	n m
30	0 11	0·32	n m
48	0 06	0 13	0 05†
72	n m.	n m.	0·08†

* n.m. = <0·05 μg/ml for [I] and [I-A], <0·1 μg/ml for [I-B], in a 2-ml sample.

† Estimated concentration (peak height <1·0 cm).

three separate fractions must be processed simultaneously through different analytical procedures. The determination is somewhat cumbersome in that the concentration of chlordiazepoxide is calculated from the difference between measurements of the sum of chlordiazepide and its *N*-desmethyl metabolite and of the *N*-desmethyl metabolite itself. Electron-capture gas chromatography can be used to assay chlordiazepoxide and its two major metabolites *via* acid hydrolysis to the corresponding benzophenone,[49] and chlordiazepoxide as the intact drug.[50] The latter assay,[50] sensitive to levels as low as 0·5 ng/ml for chlordiazepoxide in plasma, can determine the levels of chlordiazepoxide that follow a single 5-mg dose, but does not determine the two major metabolites. Studies dealing with the mechanism of polarographic reduction[4,6,7,9,16–18] and the determination of the compound in pharmaceutical formulations[29] have been reported.

Toxicological assays employing d.c. polarography which either determine chlordiazepoxide in an extract from 10 ml of sample (blood, urine or gastric contents) at a sensitivity of 1·0 μg/ml,[34] or directly in serum diluted with 0·1*M* sulphuric acid, at a sensitivity of 13 μg/ml,[17] have been reported. However, neither assay can distinguish the parent drug from metabolites present.

A D.P.P. assay[11] with a sensitivity of 0·05–0·1 μg/ml and using a 2-ml sample has been employed to determine levels of chlordiazepoxide and its metabolites in plasma following 30-mg single and repeated oral doses (Tables 1 and 2). The assay involves selective extraction of the compounds into diethyl ether from plasma buffered to pH 9·0, followed by thin-layer chromatographic separation. The compounds are eluted from the thin-layer chromatogram with methanol, after evaporation of which the residues are dissolved in 0·1*N* sulphuric acid and analysed by D.P.P. for the 4,5-azomethine (see Table 3). The overall recovery of chlordiazepoxide and its metabolites is 62 ± 4% (S.D.*). The assay is selective by virtue of the TLC separation and by the fact that each compound may be identified by its distinctive peak potential (E_p). More specific information can be obtained by analysis of a full D.P.P. scan (from 0·0 to −1·3 V *vs.* S.C.E.) which shows additional reduction peaks for the N_4-oxide in all three compounds, and the 1,2-azomethine group in chlordiazepoxide and *N*-desmethylchlordiazepoxide (see Fig. 3). The D.P.P. assay has the distinct advantage over the fluorometric assay[15] of being able to determine the three compounds as such without photochemical conversion into analytically useful derivatives, and of determining each individually and thus avoiding the cumbersome calculations of the fluorescence assay.

D.P.P. can also measure diazepam [II] and its major blood metabolite *N*-desmethyldiazepam [II-A] which are well resolved by TLC from each other and from chlordiazepoxide and its two major blood metabolites [I-A, I-B] (see Table 3). *N*-Desmethyldiazepam [II-A] has recently been identified as a minor blood metabolite of chlordiazepoxide, with steady-state levels of about 0·2 μg/ml after continued oral administration of 30 mg of Librium™.[51] The simultaneous assay of these five compounds is useful in toxicological analysis when the ingestion of both Librium™ and Valium™ is suspected.

* Standard deviation.

Table 2. Plasma levels (μg/ml) of chlordiazepoxide and its metabolites following repeated administration*

Day No.	Interval after dose, *hr*	Chlordiazepoxide [I]		*N*-Desmethylchlordiazepoxide [I-A]		Demoxepam [I-B]	
		D.P.P.	Fluor.	D.P.P.	Fluor.	D.P.P.	Fluor.
22	1	1·65	1·42	0·41	0·33	0·43	0·42
22	2	1·63	1·46	0·41	0·29	0·46	0·42
26	1	1·45	1·36	0·40	0·32	0·50	0·48
26	2	1·28	1·18	0·33	0·26	0·53	0·49
30	1	1·57	1·48	0·35	0·33	0·49	0·48
30	2	1·58	1·35	0·37	0·32	0·50	0·55
34	1	1·43	1·50	0·31	0·26	0·43	0·52
34	2	1·33	1·35	0·41	0·27	0·46	0·47
36	1	1·34	1·41	0·36	0·28	0·40	0·48
36	2	1·23	1·23	0·37	0·27	0·41	0·62

* The subject received 10-mg oral doses three times a day for 21 days, and a single 30-mg oral dose once a day thereafter. Plasma was obtained 1 hour and 2 hours after the dose.

Table 3. T.L.C. and D.P.P. parameters for the assay of 1,4-benzodiazepines

Designation	Compound	T.L.C system	R_f	Supporting electrolyte	E_p, V vs. S.C.E (4.5-azomethine)
[I]	Chlordiazepoxide	(1)	0·20	(1)	−0·600
[I-A]	*N*-Desmethylchlordiazepoxide	(1)	0·05	(1)	−0·590
[I-B]	Demoxepam	(1)	0·32	(1)	−0·640
[II]	Diazepam	(1)	0·57	(1)	−0·640
[II-A]	*N*-Desmethyldiazepam	(1)	0·44	(1)	−0·645
[II-A]	*N*-Desmethyldiazepam	(2)	0·44	(1)	−0·645
[II-B]	3-Hydroxydiazepam	(2)	0·56	(1)	−0·665
[II-C]	Oxazepam	(2)	0·33	(1)	−0·660
[III]	Lorazepam	—	—	(2)	−0·620
[IV]	7-Chloro-1,3-dihydro-5-(2′-chlorophenyl)-2*H*-1,4-benzodiazepin-2-one	—	—	(2)	−0·645
[V]	Bromazepam	—	—	(3)	−0·535
[V-A]	3-Hydroxybromazepam	—	—	(3)	−0·555
[V-B]	2-Amino-5-bromobenzoylpyridine	—	—	(3)	−0·630
[V-C]	3-Hydroxy-5-bromobenzoylpyridine	—	—	(3)	−0·635
[VI]	Flurazepam	(3)	0·49	(4)	−0·800
[VI-A]	Monodesethylflurazepam	(3)	0·23	(4)	−0·780
[VI-B]	Didesethylflurazepam	(3)	0·34	(4)	−0·785
[VI-C]	Hydroxyethylflurazepam	(3)	0·75	(4)	−0·815
[VI-D]	*N*-Desalkylflurazepam	(3)	0·81	(4)	−0·785
[VI-E]	*N*-Desalkyl-3-hydroxyflurazepam	(3)	0·66	(4)	−0·830
[VI-F]	*N*-1-Flurazepam-acetic acid	—	—	(4)	−0·825
[VII]	Clonazepam	(4)	0·68	(2)	−0·575
[VII-A]	3-Hydroxyclonazepam	(4)	0·26	(2)	−0·575
[VII-B]	7-Amino-5-(2-chlorophenyl)-1,3-dihydro-2*H*-1,4-benzodiazepin-2-one	(4)	0·48	(2)	−0·580
[VII-C]	3-Hydroxy-7-amino-5-(2-chlorophenyl)-1,3-dihydro-2*H*-1,4-benzodiazepin-2-one	(4)	0·15	(2)	−0·580
[VII-D]	7-Acetamido-5-(2-chlorophenyl)-1,3-dihydro-2*H*-1,4-benzodiazepin-2-one	(4)	0·32	(2)	−0·640
[VII-E]	3-Hydroxy-7-acetamido-5-(2-chlorophenyl)-1,3-dihydro-2*H*-1,4-benzodiazepin-2-one	(4)	0·08	(2)	−0·625

T.L.C. systems

(1) Quantum Q4F chromatoplate; $CHCl_3$:acetone (60:40).
(2) Brinkman Silica Gel 60 chromatoplate; $CHCl_3$:CH_3OH (90:10).
(3) Quantum Q4F chromatoplate; (*a*) benzene–CH_3OH:HAc (90:10:10)
(*b*) acetone–NH_4OH (conc.) (100:0·5).
(4) Brinkman Silica Gel G chromatoplate; benzene:n-propranol:NH_4OH (conc.) (80:20:1).

Supporting electrolytes

(1) 0·1*N* H_2SO_4.
(2) 0·1*N* HCl.
(3) 1*M* phosphate buffer (pH 5·5).
(4) 1*M* phosphate buffer (pH 4·0).

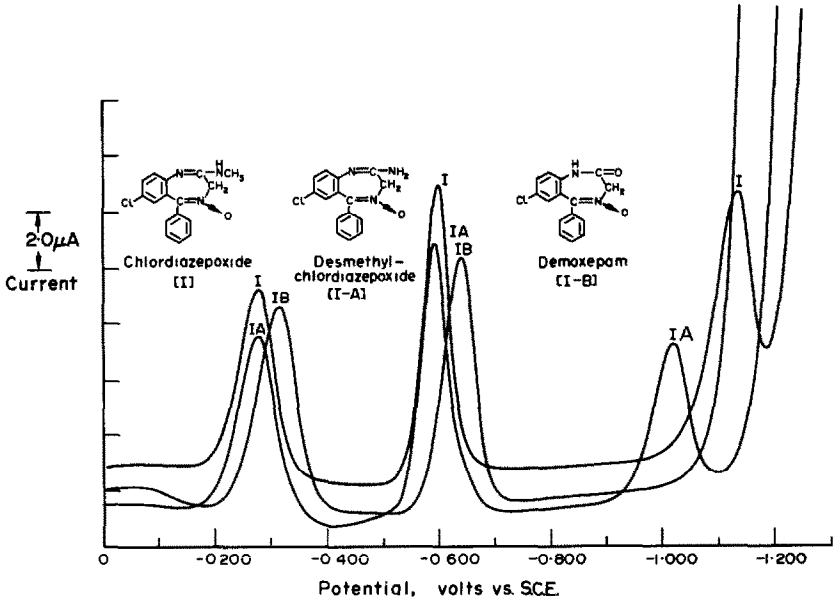


Fig. 3. D.P.P. of chlordiazepoxide and its metabolites in 0·1 *N* H_2SO_4.

Diazepam

Diazepam, 7-chloro-1,3-dihydro-1-methyl-5-phenyl-2*H*-1,4-benzodiazepin-2-one, [II], is a psychotherapeutic agent which is the active ingredient in Valium™. The major metabolic pathways are demethylation and hydroxylation, yielding *N*-desmethyldiazepam, [II-A], a major blood metabolite, and glucuronides of *N*-desmethyldiazepam, 3-hydroxydiazepam (temazepam), [II-B], and oxazepam, [II-C], the major urinary metabolites (Fig. 4).[52]

Gas chromatographic assays for the determination of diazepam and its *N*-desmethyl metabolite in blood have been reported, the flame-ionization detector being used for toxicological analysis[53] and the electron-capture detector for measuring therapeutic levels following single and repeated administration.[49,54–56] E.C.-G.L.C.[49,54] and R.I.A.[12] are the only methods capable of determining both diazepam (the peak levels of which range from 0·1 to 0·2 μg/ml) and the *N*-desmethyl metabolite (the steady-state levels of which are less than 0·03 μg/ml) in blood following therapeutic administration.[57]

Studies dealing with the polarographic reduction mechanism[6–9,19,20] and the determination of diazepam in pharmaceutical dosage forms[29,30] have been reported. Toxicological assays employing d.c. polarography with sensitivity limits of 1 μg/ml for 10-ml samples of blood,[34] and with a sensitivity limit of 20 μg/ml for cadaver blood diluted with supporting electrolyte[35] have been reported. Assays employing D.P.P.[36] and cathode ray polarography[37] which are capable of determining diazepam levels as low as 0·02–0·05 μg/ml have also been reported. However, neither assay determines the *N*-desmethyl metabolite, which is only extracted to a small extent by the non-polar solvents employed (benzene[36] and petroleum ether[37]). It is present in significant quantities several hours after single oral administration and in approximately equal concentration to diazepam itself (0·1–0·2 μg/ml) after repeated administration.[57] In toxicology, it is important to assay this metabolite, the concentration of which may be several times that of the parent compound, depending on the time interval between ingestion and sampling. Therefore, even if analysis shows therapeutic quantities of diazepam, an overdose is still a possibility, because most of the *N*-desmethyl metabolite will not be extracted.[36,37]

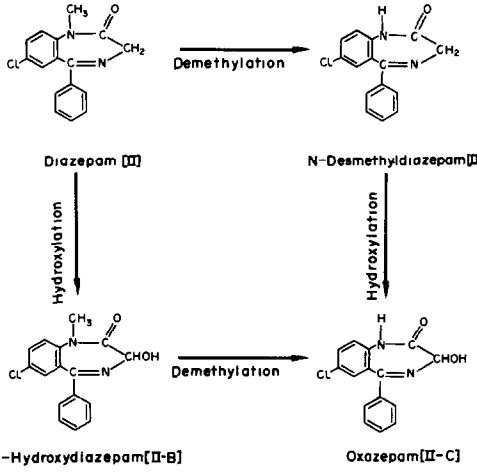


Fig. 4. Metabolism of diazepam in man.

Table 4. Plasma levels of diazepam and its major metabolite determined by differential pulse polarography following the suspected ingestion of about 1·0 g (one hundred 10-mg Valium™ tablets) of the drug

Date	Diazepam, μg/ml	*N*-Desmethyl metabolite, μg/ml
21 October	7·0	1·2
22 October	3·4	1·4
23 October	3·6	1·7
24 October	3·0	1·9
25 October	3·0	3·1
26 October	2·3	2·8
27 October	1·3	2·0
28 October	0·4	1·6
29 October	0·4	1·2

A D.P.P. assay which determines both diazepam and its *N*-desmethyl metabolite in blood with a sensitivity of approximately 0·4 μg/ml and employs extraction with a more polar solvent and a thin-layer chromatographic separation, has been reported.[10] Recent work has indicated that by use of plasma and the assay described for chlordiazepoxide[11] (see Table 3) a much cleaner extract is obtained, resulting in an increased sensitivity limit of 0·05–0·1 μg/ml for each compound. Thus the assay is capable of determining the levels of diazepam arising after 10-mg single administration, and of both the parent drug and the metabolite with the necessary selectivity for toxicological or therapeutic examination. The overall recovery is 80 ± 5·0% (S.D.). The utility of the assay was demonstrated in the determination of levels of diazepam and *N*-desmethyldiazepam in a subject who was suspected of having ingested about 1·0 g of diazepam (one hundred 10-mg Valium™ tablets), see Table 4. The assay is rapid and relatively easy to perform. However, therapeutic levels following single or repeated administration are determined, the levels of drug and metabolite approach the sensitivity limit of the assay and it is therefore preferable to use the more sensitive E.C.-G.L.C.[54] or R.I.A.[12]

A modification of the spectrophotometric assay for chlordiazepoxide[43] has been used for determining urinary levels of oxazepam [II-C], *N*-desmethyldiazepam [II-A] and 3-hydroxydiazepam conjugates [II-B] following administration of diazepam. These three metabolites account for approximately 25–30% of the dose administered.[52]

A D.P.P. assay using a TLC separation step can be employed to determine oxazepam, *N*-desmethyldiazepam and 3-hydroxydiazepam after they have been split off from their conjugates. The assay involves incubation of a urine sample at pH 5·3 with

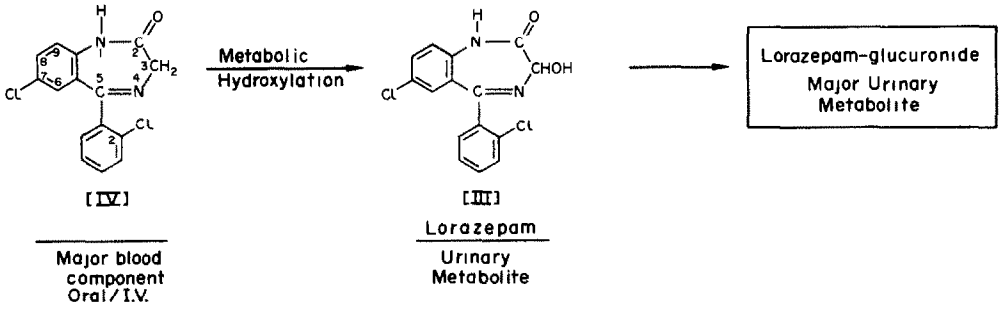


Fig. 5. Metabolism of compound [IV] to lorazepam and its further metabolism in man.[63]

the enzyme glusulase, adjustment of the pH to 9·0, extraction of the three compounds into ethyl acetate, and TLC. The compounds are eluted with 95% methanol, the solution is evaporated to dryness and the compounds are dissolved in 2 ml of 0·1*N* sulphuric acid and determined by D.P.P. for reduction of the 4,5-azomethine group (see Table 3). The recovery of oxazepam and *N*-desmethyldiazepam is approximately 90%, whereas the recovery of 3-hydroxydiazepam is approximately 60%. The assay has a sensitivity limit of approximately 0·25–0·50 μg/ml (1-ml sample), and can be used to monitor the urinary excretion of the three compounds following therapeutic doses of diazepam.

Two recent papers have reported use of polarography for studying the urinary metabolism of diazepam in man[58] and to identify and determine the biliary metabolites of diazepam in the rat.[59] In both assays the urinary metabolites are converted into their respective aminochloro- and methylaminochlorobenzophenones and their sum is determined polarographically *via* the total benzophenone peak. The results are comparable to those obtained by analysing the separated benzophenones by gas chromatography with a flame-ionization detector.[59]

Oxazepam

Oxazepam, 7-chloro-1,3-dihydro-3-hydroxy-5-phenyl-2*H*-1,4-benzodiazepin-2-one [II-C] (as a glucuronide), is the major urinary metabolite of diazepam (Fig. 4). Oxazepam possesses anti-anxiety activity and is the active ingredient in Serax™. The determination of oxazepam in blood involves E.C.-G.L.C. determination of its acid hydrolysis product, 2-amino-5-chlorobenzophenone.[60,61]

A modified spectrophotometric assay[43] can be used to determine oxazepam glucuronide following administration of oxazepam. A D.P.P. assay similar to that previously described for the analysis of the urinary excretion of diazepam, but excluding TLC separation, can be used for the determination of oxazepam in urine.

Lorazepam

Lorazepam [III] (Fig. 5), the 5-(*o*-chlorophenyl) analogue of oxazepam, is a sedative which is effective at relatively low doses. It is also the major urinary metabolite of the compound 7-chloro-1,3-dihydro-5-(2′-chlorophenyl)-2*H*-1,4-benzodiazepin-2-one ([IV], Fig. 5).[63] Blood levels of compound [IV][38,62] and lorazepam[63] following therapeutic administration can only be determined by E.C.-G.L.C. Lorazepam glucuronide is the major urinary metabolite in man after the oral administration of either compound. A spectrophotometric assay has also been employed to determine lorazepam in the dog after the administration of compound [IV], with a sensitivity of 0·5 μg/ml.[62]

The mechanism of polarographic reduction of lorazepam has been studied[6] and polarography used for automated determination of lorazepam in pharmaceutical dosage forms.[33] A D.P.P. assay has been

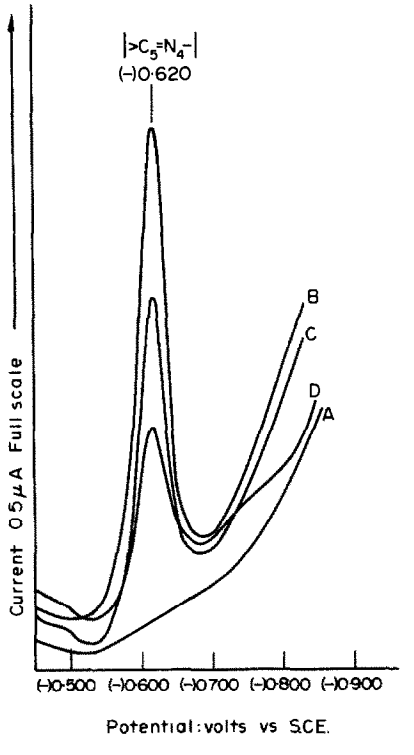


Fig. 6. D.P.P. of lorazepam in 0·1*N* HCl supporting electrolyte. (A) control urine blank, (B) authentic reference standard, (C) authentic standard recovered from urine, (D) patient's urine fraction taken in first 6 hr after dosing.

Table 5. Urinary levels of [IV] and its metabolite, lorazepam glucuronide, in man

Excretion period, *hr*	Subject 1		Subject 2		Subject 3	
	Total excreted as [IV]*, *μg*	Total excreted as [III]†, *μg*	Total excreted as [IV]*, *μg*	Total excreted as [III]†, *μg*	Total excreted as [IV]*, *μg*	Total excreted as [III]†, *μg*
0–6	1·94	16·5	1·01	14·8	1·49	30·8
6–12	1·86	27·2	2·46	35·0	0·79	44·1
12–24	2·95	75·5	3·54	81·6	0·99	41·8

* Determined by E.C.-G.L.C. as free or directly extractable drug.
† Determined by differential pulse polarography after hydrolysis with glucuronidase–sulphatase.

reported which can determine urinary lorazepam glucuronide in the range of 150–200 ng, in a 5-ml sample, after oral administration of [I], with an overall recovery of 65 ± 5·0% (S.D.).[38] The urine specimen is extracted at pH 9·0 with diethyl ether to remove compound [IV] and free lorazepam, which are then determined by E.C.-G.L.C. The specimen is then incubated with glusulase to split off lorazepam as described for diazepam. Lorazepam is extracted into diethyl ether at pH 9·0, the ether evaporated off, the residue dissolved in 100 μl of methanol, mixed with 2 ml of 0·1*M* hydrochloric acid, and analysed by D.P.P. for reduction of the 4,5-azomethine group (Table 3 and Fig. 6). The assay has higher sensitivity and selectivity than the spectrophotometric assay,[62] since it does not require formation of a derivative (the Bratton–Marshall chromophore). It was used to analyse the urinary excretion in man of lorazepam glucuronide following a 4-mg oral dose of compound [IV] (Table 5).

Bromazepam

Bromazepam, 7-bromo-1,3-dihydro-5-(2-pyridyl)-2*H*-1,4-benzodiazepin-2-one (Fig. 7, Compound [V]), is of clinical interest as an anti-anxiety agent. Metabolic studies[64–66] showed that the compound was transformed *via* hydroxylation and hydrolysis into 2-amino-5-bromobenzoylpyridine [V-B] and glucuronides of 3-hydroxybromazepam [V-A] and of 2-amino-3-hydroxy-5-bromobenzoylpyridine [V-C]. Blood levels of bromazepam were determined by E.C.-G.L.C. with a sensitivity of 5–10 ng/ml of blood following the administration of a 12-mg oral dose.[39] The analysis of the urinary excretion is more complicated, measurable levels of bromazepam, 3-hydroxybromazepam and the two benzoylpyridines requiring differential extraction procedures to separate the unbound from the bound fractions.

D.P.P. of bromazepam in pH 5·5 phosphate buffer gives three reduction peaks at −0·565, −1·280, and −1·350 V *vs.* S.C.E., the first due to the reduction of the 4,5-azomethine group and the other two to reductions of the pyridyl substituents. An assay was reported[39] which determines the urinary excretion of bromazepam and its metabolites by using the reduction peaks of the 4,5-azomethine group of bromazepam and 3-hydroxybromazepam, and that of the carbonyl group of the two benzoylpyridines. The assay

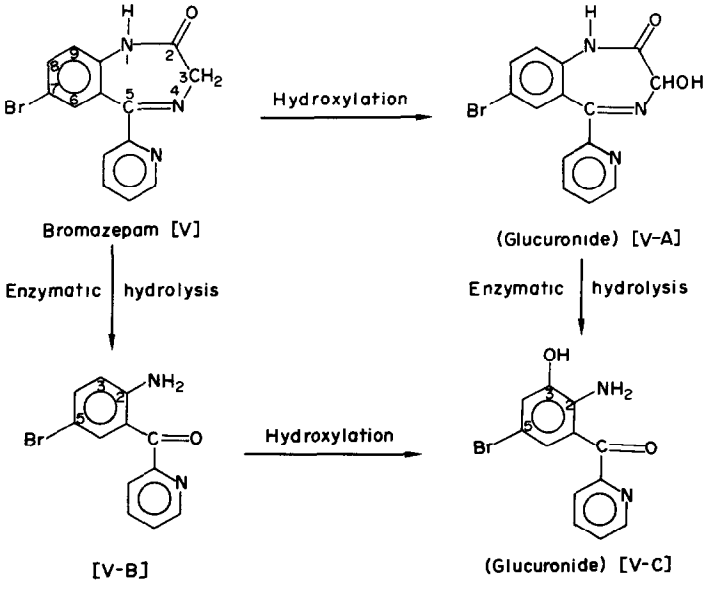


Fig. 7. Metabolism of bromazepam in man and in dog.

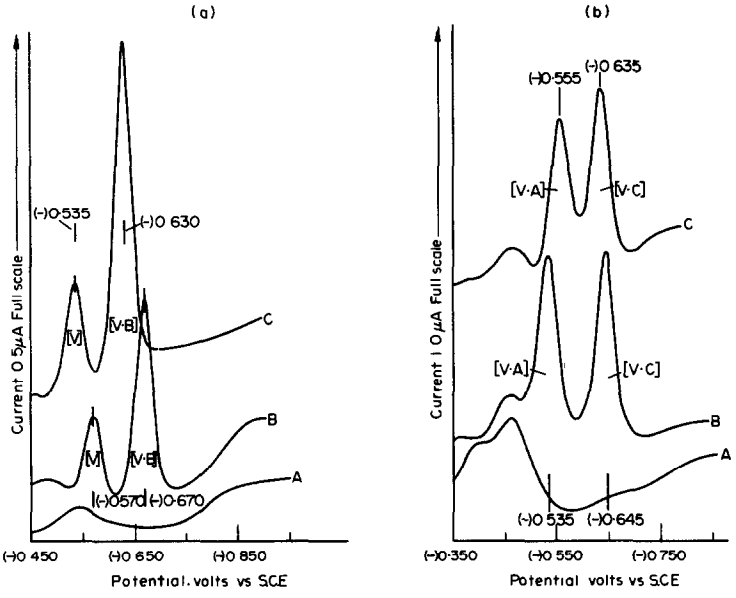


Fig. 8. Differential pulse polarograms of (*a*) bromazepam [V], and the aminobromobenzoylpyridine metabolite [V-B], and (*b*) the 3-hydroxy metabolites [V-A] and [V-C] obtained in 1·0*M* pH-5·5 phosphate buffer as the supporting electrolyte. (A) Control urine blank, (B) authentic standard mixture, (C) authentic compounds recovered from urine.

employs selective extraction of bromazepam and [V-B] with diethyl ether from urine buffered to pH 9·0, followed by incubation with glusulase at pH 5·5 to split off 3-hydroxybromazepam and 2-amino-3-hydroxy-5-bromobenzoylpyridine from their conjugates. The pH of the sample is then adjusted to 7·75 and these two compounds are extracted into diethyl ether. The residues from evaporation of the respective diethyl ether extracts are dissolved in 1·0*M* phosphate buffer (pH 5·5) and analysed by D.P.P., which yields two distinct peaks for the 1,4-benzodiazepin-2-one and the benzoylpyridine component in each fraction (see Table 3 and Fig. 8). The overall recovery of bromazepam and [V-B] is 80 ± 5% with sensitivity limits of 100 and 50 ng/ml of urine, respectively, while the recovery of 3-hydroxybromazepam and 2-amino-3-hydroxy-5-bromobenzoylpyridine is 45 ± 5% with sensitivity limits of 100 ng/5 ml of urine analysed. The assay was employed to analyse urinary excretion following the administration of single 12-mg oral doses (Table 6). The assay is not sufficiently sensitive to determine blood levels after the same dose.

Flurazepam

Flurazepam hydrochloride, 7-chloro-1-(2-diethylaminoethyl)-5-(2′-fluorophenyl)-1,3-dihydro-2*H*-1,4-benzodiazepin-2-one-dihydrochloride, [VI], the active ingredient in Dalmane™, is a hypnotic used for the treatment of insomnia. Studies on the biotransformation of flurazepam[67] showed that it was extensively metabolized in man to the desethyl [VI-A] and didesethyl [VI-B] metabolites, the hydroxyethyl [VI-C], *N*-desalkyl [VI-D] and the *N*-desalkyl-3-hydroxy [VI-E] metabolites (Fig. 9). In addition, both compounds [VI] and [VI-C] were metabolized extensively in the dog to an acidic compound [VI-F] by the oxidation of the alcohol side-chain to a carboxylic acid.

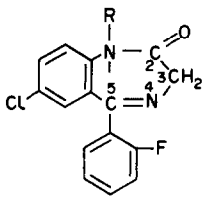
A spectrofluorimetric method[13] for assaying blood levels and urinary excretion of flurazepam and its metabolites which involves selective extraction, acid hydrolysis and cyclization to form highly fluorescent 9-acridanone derivatives has been reported. The assay has a sensitivity limit of 3–10 ng/ml for each compound (in a 4-ml blood sample) and higher sensitivity limits in urine, which are sufficient to measure blood levels and urinary excretion following therapeutic administration. The assay, however, is time-consuming and complicated.

An E.C.-G.L.C. assay has recently been reported,[40] which determines flurazepam and its major blood metabolites (hydroxyethyl-, *N*-desalkyl- and *N*-desalkyl-3-hydroxy-flurazepam) following therapeutic administration. These two assays[13,40] are the only procedures reported capable of determining the low levels of flurazepam and its metabolites (≤50 ng), which are typical after single and repeated oral administration of flurazepam. Two D.P.P. assays are also described;[40] the first for the analysis of urinary

Table 6. Bromazepam and its major urinary metabolites in man, determined by differential pulse polarography

	Fraction of dose, % excreted in 72 hr as				Recovery	
Subject	[V]	[V-A]	[V-B]	[V-C]	*mg*	% of dose*
1	2·5	22·6	0·35	46·6	8·65	72·1
2	1·9	27·8	0·75	29·9	6·91	57·6
3	1·8	34·8	0·21	39·5	9·19	76·6

* Dose was 12 mg.



R-Group

Flurazepam	$-(CH_2)_2-N-(C_2H_5)_2$	[VI]
Monodesethylflurazepam	$-(CH_2)_2-NH-C_2H_5$	[VI-A]
Didesethylflurazepam	$-(CH_2)_2-NH_2$	[VI-B]
N-1-hydroxyethylflurazepam	$-CH_2-CH_2OH$	[VI-C]
N-1-desalkylflurazepam	$-H$	[VI-D]
N-1-desalkyl-3-hydroxyflurazepam	$-H(3>CHOH$	[VI-F]
N-1-flurazepam acetic acid	$-CH_2COOH$	[VI-F]

Fig. 9. Flurazepam and its major biotransformation products in man and dog.

excretion of flurazepam following therapeutic administration, and the second for toxicological studies.

The toxicological assay which determines "total" benzodiazepines is a rapid diagnostic tool for the confirmation of drug ingestion and to obtain an estimate of the amount of drug ingested. In this assay, 0·1 ml of urine is diluted with 1·90 ml of 1*M* phosphate buffer (pH 7·0), and analysed by D.P.P. for the reduction of the 4,5-azomethine group. The peak for total benzodiazepines [at (−)0·955 V *vs.* S.C.E.] is measured and gives a sensitivity of 5 μg/ml of urine. This sensitivity is sufficient to confirm the ingestion of flurazepam, since 30–40% of the dose is usually excreted in the urine in the first 24-hr excretion period.[13,67]

The specific determination of the urinary metabolites of flurazepam by D.P.P. analysis employs a 5-ml urine sample which is extracted with diethyl ether at pH 11 to remove the free metabolites [VI–VI-C]. The urine sample is then incubated with glusulase to split the glucuronide of the hydroxyethyl metabolite [VI-C] (the major urinary metabolite), and the [VI-C] is then extracted into diethyl ether after pH adjustment to 9·0. The metabolites in the first extract are separated by TLC, dissolved out with 95% methanol, and the residues from evaporation are analysed by D.P.P. in 1*M* phosphate medium at pH 4 (see Table 3). The residue from evaporation of the second diethyl ether extract containing the hydroxyethyl metabolite is dissolved in pH 4·0 buffer (1*M* phosphate) and analysed directly by D.P.P. The assay was applied to determine the urinary excretion of flurazepam in man following a single 90-mg oral dose (Table 7). Results indicated that the desethyl [VI-A] and didesethyl [VI-B] metabolites were the major components in the non-conjugate fraction, accounting for 4–15% of the dose, and that flurazepam and metabolites [VI-C], [VI-D] and [VI-E] accounted for less than 0·5% of the dose. The hydroxyethyl metabolite [VI-C] in the conjugate fraction accounted for approximately 30% of the dose. The data are in good agreement with ^{14}C studies.[67] The D.P.P. assay has an advantage

Table 7. Urinary excretion of flurazepam and its major metabolites in 24 hr by humans who received single oral 90-mg doses of Dalmane™ [=75·8 mg of flurazepam (free base)]

Subject	Form excreted	Compound measured	Concentration, μg/ml	Equivalent amount of flurazepam, mg		Fraction of dose excreted, %	Direct assay for total benzodiazepines, %
1	Free	[VI-A]	0·17	0·35		0·5	
		[VI-B]	1·14	2·75		3·6	
	Conjugate	[VI-C]	9·30	22 5		29·7	
					Total	33·8	42 2
2	Free	[VI-A]	1·83	2 26		3·0	
		[VI-B]	6·57	8·78		11·6	
	Conjugate	[VI-C]	18 1	24·3		32·1	
					Total	46·7	50·2
3	Free	[VI-A]	2·14	1 73		2 3	
		[VI-B]	11·4	9 95		13·1	
	Conjugate	[VI-C]	25·8	22 6		29·8	
					Total	45 2	43·8

The sum of the amounts of flurazepam [VI] and metabolites [VI-C], [VI-D] and [VI-E] in the directly extractable (non-conjugate) fractions yielded a total of 0·44%, 0·36% and 0·54% for subjects 1, 2 and 3, respectively.

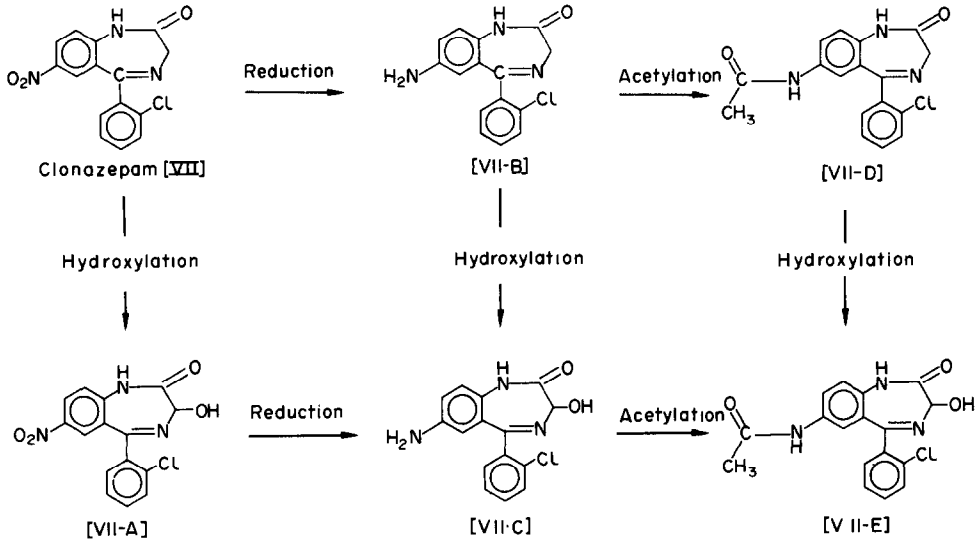


Fig. 10. Metabolism of clonazepam in man.

over the spectrofluorimetric assay[13] in being able to determine flurazepam and its metabolites as the 1,4-benzodiazepines themselves without time-consuming conversion into derivatives. The D.P.P. assay can also determine the desethyl and didesethyl metabolites of flurazepam which could not be determined by the spectrofluorimetric assay because of non-reproducible derivative formation.

Clonazepam

This compound, 7-nitro-5-(2-chlorophenyl)-1,3-dihydro-(2*H*)-1,4-benzodiazepin-2-one, [VII], is under investigation as an antiepileptic drug for the control of minor motor seizures, at doses of 1–2 mg daily. Clonazepam undergoes biotransformation *via* reduction, acetylation and hydroxylation to yield five metabolites[68] (see Fig. 10). E.C.-G.L.C. assays which measure the clonazepam as such,[69] as its benzophenone,[41] and as its *N*-1-methyl derivative[70] have been reported. These assays all give sensitivities of 1 ng/ml of blood.

A D.P.P. assay[41] was proposed for the determination of clonazepam and its five metabolites in urine, based on the ease of reduction of the 4,5-azomethine group (Fig. 11). Clonazepam and 3-hydroxyclonazepam (Fig. 10, Compound VII-A) also yield additional peaks for the reduction of the nitro-group. The metabolites, which are found mainly in the unbound form, are directly extracted into ethyl acetate from urine buffered to pH 9·0. The residue from evaporation of the ethyl acetate extract is separated by TLC and eluted into methanol, and the residue from evaporation of this solution is dissolved in 4 ml of 0·1*M* hydrochloric acid and analysed by D.P.P. reduction of the 4,5-azomethine group (Table 3). The sensitivity limit of the assay is 0·5–0·75 μg/ml for each component (5 ml of urine analysed). The assay was applied to the determination of urinary excretion of clonazepam following a single 2-mg oral dose. However, metabolites [VII-B], [VII-C], [VII-D] and [VII-E], which were detectable on the TLC plate (under short-wavelength ultraviolet light), could not be determined, because they were present in concentrations below the sensitivity limit of the assay. With use of the modified polarographic cell of smaller volume[10] and with elution solvents containing 5% water, such as used in the flurazepam assay,[40] it is expected that the sensitivity limit can be lowered to 0·1 μg/ml and that the levels found after 2-mg oral doses will be measurable.

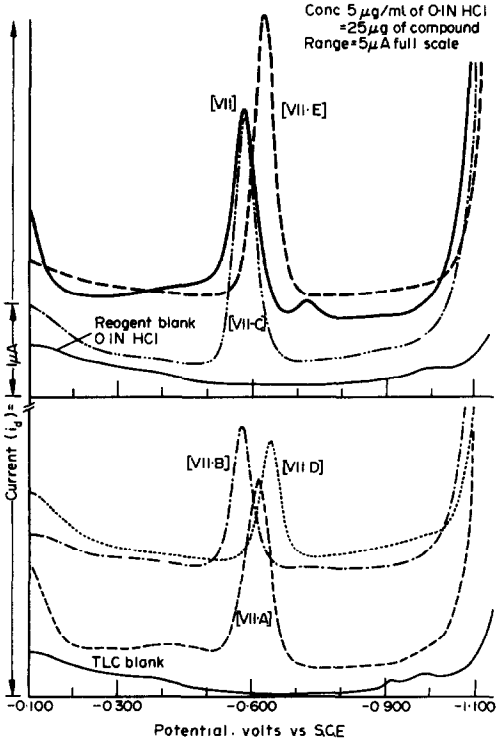


Fig. 11. D.P.P. of clonazepam and its metabolites in 0·1 *N* HCl.

Nitrazepam

Nitrazepam (Fig. 1), 1,3-dihydro-7-nitro-5-phenyl-2*H*-1,4-benzodiazepin-2-one, [VIII], is a hypnotic and sedative which is the active ingredient in Mogadon™ and is marketed in Europe. Colorimetric[71] and spectrophotometric[72] assays have been reported but are only adequate when high levels of the drug are present. A highly sensitive and specific spectrofluorimetric assay capable of determining levels of nitrazepam and its two major metabolites with a sensitivity of 0·010–0·025 μg/ml of plasma or urine has been reported.[73] E.C.-G.L.C. analysis has been used to determine blood levels of nitrazepam in the 0·001–0·005 μg/ml range, employing hydrolysis to the 2-amino-5-nitrobenzophenone[74] and the formation of the *N*-1-methylnitrazepam derivative.[70,75] These methods of assay[70,73–75] are the only ones sufficiently sensitive for determination of the drug following therapeutic administration.

Polarographic studies on the reduction mechanism of nitrazepam[5,6,9,26–28] and its metabolites[7,9,76] and on the determination of nitrazepam in pharmaceutical formulations[26] have been reported. Polarography has also been used to determine nitrazepam and its metabolites following TLC separation.[76] A d.c. polarographic method has been employed to analyse levels of nitrazepam in the range 0·5–80 μg/ml directly in serum.[28] The half-wave potential was −0·51 V *vs.* Ag/AgCl. The assay cannot determine therapeutic levels of the drug, but may be useful for the analysis of "total" benzodiazepines (nitrazepam and metabolites) in toxicological situations. A D.P.P. assay has not been reported, the blood levels following therapeutic administration being too low to be determined by this technique, but urinary excretion may be determined by using the assay described for clonazepam.[41]

Medazepam

Medazepam (Fig. 1), 7-chloro-2,3-dihydro-1-methyl-5-phenyl-1*H*-1,4-benzodiazepine, [IX], is marketed in Europe as Nobrium™, an anti-anxiety agent. Blood and urine levels of the parent compound and its metabolites *N*-desmethylmedazepam, diazepam, and *N*-desmethyldiazepam[77] are determined by E.C.-G.L.C. assay[54] with a sensitivity limit of 40–50 ng/ml, which is sufficient to monitor the drug after therapeutic administration. Polarographic investigations have dealt with the mechanism of reduction and the determination in pharmaceutical dosage forms.[24] Since the urinary excretion is similar to that after the administration of diazepam, the D.P.P. assay previously described can be employed.

Prazepam

Prazepam [X] (Fig. 1), which is an *N*-1-cyclopropylmethyl substituted analogue of diazepam is presently under study.[78] An investigation dealing with its polarographic reduction mechanism and the determination of the compound in pharmaceutical formulations has been reported.[22]

Conclusion

Polarography and, in particular, differential pulse polarography, has been demonstrated to be an excellent analytical method for the determination of 1,4-benzodiazepines in biological fluids. Polarography is of clinical utility because it possesses greater sensitivity than spectrophotometric assays, and comparable sensitivity to most spectrofluorimetric methods and gas-chromatographic assays based on use of the flame-ionization detector. The method does not, however, possess comparable sensitivity to electron-capture gas chromatography or radioimmunoassay. The technique in its present stage of development is extremely useful for simple and rapid measurement of urinary excretion of all the marketed 1,4-benzodiazepines. It is extremely useful when blood or plasma levels of the 1,4-benzodiazepines and their metabolites are in the range 50–100 ng/ml or higher as in toxicological situations. It is particularly useful in preclinical studies on animal species where relatively high doses (> 1 mg/kg of body weight) are usually administered, and also as an ancillary technique in metabolite identification.

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EXTRACTION OF BIVALENT VANADIUM AS ITS PYRIDINE THIOCYANATE COMPLEX AND SEPARATION FROM URANIUM, TITANIUM, CHROMIUM AND ALUMINIUM

V. YATIRAJAM and S. P. ARYA

Department of Chemistry, Kurukshetra University, Kurukshetra 132119, Haryana, India

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Summary—A simple method is described for the extraction of V(II) as its pyridine thiocyanate complex. Vanadate is reduced to V(II) in 1–2*N* sulphuric acid by zinc amalgam. Thiocyanate and pyridine are added, the solution is adjusted to pH 5·2–5·5 and the complex extracted with chloroform. The vanadium is back-extracted with peroxide solution. Zinc from the reductant accompanies the vanadium but alkali and alkaline earth metal ions, titanium, uranium, chromium and aluminium are separated, besides those ions reduced to the elements by zinc amalgam. The method takes about 20 min and is applicable to microgram as well as milligram amounts of vanadium.

Analysis for trace or higher amounts of vanadium is required when these are present along with titanium and/or aluminium in clays, bauxite, rutile, ilmenite, titanium slags, aircraft alloys; with uranium in uraninite, carnotite, reactor alloys; with chromium in chrome–magnetite refractories, fast-cutting tungsten steels to mention but a few examples in each case.[1,2] The three elements titanium, chromium and uranium interfere in all the titrimetric methods except the ferrous sulphate reduction method.[3] Even here, chromium interferes unless the less sharp end-point at room temperature is used, and requires separation for more than 2% and blank correction for less.[4a] These three elements and aluminium also interfere in most of the spectrophotometric methods for vanadium.[3] In the peroxide method, titanium interferes, though moderate amounts can be masked by fluoride (to the detriment of the colorimetric cells). Chromium in large amounts also interferes[5] and in small amounts has to be compensated for, at the cost of accuracy. In the phosphotungstovanadate method, titanium, chromium and uranium interfere[5] when present in more than traces.

Likewise, vanadium interferes[6] in most methods for aluminium, titanium, chromium, and uranium. Analysis for traces of vanadium requires its concentration from metals and oxides of these four elements, and for traces of these four elements, removal of vanadium from materials rich in it.[7] Thus, separation of vanadium from these elements is often required.

The few existing separation methods[3,4b] generally handle microgram amounts of vanadium and separate them from only one or two of the elements, aluminium, titanium, chromium, uranium, which must be present in comparable amounts to the vanadium.

Bivalent vanadium has not so far been quantitatively extracted. Like the other transition metal ions,[8,9] it might be expected to give an extractable pyridine thiocyanate complex. The present paper describes a simple method for extraction of such a complex and separation of vanadium even in macro amounts from large amounts of aluminium, titanium, chromium and uranium.

EXPERIMENTAL

Reagents and solutions

Vanadium solution. A stock solution (10 mg of V/ml) was prepared from sodium metavanadate and standardized by the oxine method;[3] suitable dilution gave 100- and 10-μg/ml vanadium solutions.

Zinc amalgam,[10] 2% w/w.

Pyridine. Used without further purification.

Solutions of other elements. Prepared by dissolving their soluble salts in water or dilute sulphuric acid to give 10 or 20 mg of element per ml.

Chloroform and other solvents were distilled before use. Other chemicals were of C.P. grade.

Separation procedure

Extraction of vanadium. To 15 ml of zinc amalgam in a 150-ml separating funnel, 5 ml of vanadate solution containing between 100 μg and 10 mg of vanadium, 2 ml of 10*N* sulphuric acid and 2 ml of 1*M* ammonium thiocyanate were added. Air in the funnel was displaced by carbon dioxide generated by addition of 0·3 g of sodium carbonate. The funnel was stoppered and shaken at moderate rate for at least 3 min. The stopper was removed and immediately a pinch of solid ammonium carbonate was added (to maintain the atmosphere of carbon dioxide) quickly followed by 1 ml of pyridine. The funnel was stoppered and swirled gently to mix in the pyridine. By addition of ammonium carbonate, initially pinches of solid and towards the end saturated solution drop by drop, the pH of the solution was adjusted to 5·2–5·5, tiny droplets (taken out with a thin glass rod) being tested periodically with short-range indicator paper. The solution was then shaken without delay for 5–10 sec with 10 ml of chloroform poured over the thin glass rod and the stopper, washing down

into the funnel any yellow or brown complex sticking to them.

The zinc amalgam was run off into a conical flask and kept under 1*M* hydrochloric acid till required again. The chloroform extract of the V(II) complex was run off into another 150-ml separating funnel. The aqueous phase was shaken with 0·5 ml of pyridine and extracted with two further 5-ml portions of chloroform. The chloroform layers were separated and added to the main chloroform extract in the separating funnel.

Back-extraction of vanadium. The organic phase was shaken for 1 min with an equal volume of water and 3 ml of 6% hydrogen peroxide. The chloroform was run off into another separating funnel and the back-extraction was repeated with half the volume of water. The combined extracts were made just alkaline and the pyridine was removed by extracting with 10 ml of chloroform. The solution was then treated with 0·5 ml of 7*M* alkali and boiled with 10 ml of 6% hydrogen peroxide for 6 min to oxidize the vanadium and thiocyanate.[11] The excess of peroxide was decomposed by acidification and continuing the boiling. The solution was cooled.

Determination of the elements

Any lower oxidation state of vanadium was reoxidized with 0·1*N* permanganate[12] till a faint pink colour persisted for 2 min, then 0·05*M* sodium nitrite was added to decolorize the solution and then 3 drops more. The excess of nitrite was decomposed by shaking vigorously with 0·5 g of urea and waiting for 5 min. More than 5 mg of vanadium was determined by titration with ferrous iron,[13] lower amounts by the peroxide[14a] or phosphotungstic acid[14b] methods. Traces of vanadium were determined by the ferron method.[15] Other elements were tested or determined by suitable conventional methods.[16] High degrees of extraction were measured by determining the lower concentration of vanadium in the aqueous phase and subtracting from the initial amount.

RESULTS AND DISCUSSION

Vanadate solution is most conveniently reduced to V(II) by zinc amalgam. Reduction is quantitative in 1–2*N* sulphuric or hydrochloric acid after 3 min of moderate shaking.[16a] The oxygen in the acid solution and the space above it in the separating funnel must be displaced beforehand by carbon dioxide, either from a generator or more simply, generated *in situ* by addition of sodium carbonate after the initial acidity has been increased by an equivalent amount. The carbon dioxide atmosphere must be maintained till the extraction is over. This is done by intermittent addition of ammonium carbonate, which also serves to neutralize the solution to the desired pH.

The pyridine should be added soon after the reduction and before neutralization of the acid. On formation of the pyridine thiocyanate complex, the violet colour of V(II) changes at about pH 3 to yellow at trace concentrations and brown at higher concentrations of vanadium. The complex is best extracted by chloroform or dichloromethane. Benzene, carbon tetrachloride, dichloroethane, isoamyl alcohol and isobutyl methyl ketone give decreasing extraction, in that order.

The extraction of the V(II)–pyridine–thiocyanate complex depends on the reagent concentration, pH of the solution and equilibration time, as shown in Table 1. Extraction is almost complete at pH 5·2–5·5, with 0·5–1·5 ml of pyridine, $\geq 0{\cdot}2M$ thiocyanate and 5–10 sec equilibration time, decreasing outside these ranges. Ammonium or potassium thiocyanate, sulphuric or hydrochloric acid can be used with the same results. As free pyridine is also extracted by chloroform, 0·5 ml of pyridine should be added before the second extraction with chloroform. The third extraction serves to remove any complex sticking on the glassware. Testing with short-range paper in the pH adjustment is convenient and oxidation is avoided by adding a pinch of ammonium carbonate immediately after opening the stopper and replacing it quickly after taking a tiny droplet of solution for testing.

Table 1. Dependence of V(II) extraction on various parameters [V = 10·0 mg, NH_4SCN (1*M*) = 2·0 ml, pyridine = 1·0 ml, pH = 7·6, aqueous phase and organic phase both 10 ml, contact time = 10 sec, unless varied; single extraction]

Pyridine, *ml*	0·2	0·5	0·8	1·0	1·5	2·0	3·0	4·0
Extraction, %	84·7	94·2	94·2	94·2	94·2	92·0	89·0	84·7
NH_4SCN, *M**		0·06		0·12		0·2–1·6		
Extraction, %		69·0		87·0			94·2	
pH	3·4	4·0	5·2	5·5	6·0	7·0	7·6	
Extraction, %	7·0	85·7	99·2	99·2	96·3	95·4	94·2	
Contact time, *sec*		5	10	15	30	60	120	
Extraction, %		94·2	94·2	93·7	91·3	89·8	88·0	

* In the final solution.

There is some difficulty in adjusting the reagent concentrations for different amounts of vanadium, as corresponding amounts of zinc, which also forms an extractable pyridine thiocyanate complex, are introduced from the reductant. However, the concentrations can be roughly calculated on the basis of the requirements for zinc.[17] The experimentally determined concentrations for different amounts of vanadium are shown in Table 2. The pyridine requirement for amounts much less than 10 mg of V is proportionately much larger. The degree of extraction at 10 μg/ml vanadium concentration is slightly lower though nearly complete. This may be due to some oxidation of vanadium in contact with the solution; similarly the extraction is lower for longer equilibration times.

Table 2. Reagent requirements for complete extraction of varying amounts of vanadium (pH = 5·2, contact time = 10 sec, aqueous phase and organic phase both 10 ml)

Vanadium, *mg*	Pyridine, *ml*	1*M* NH_4SCN, *ml*	Extraction, %
0·1	1·0	2·0	96·0
0·5–10	1·0	2·0	99·95
20	2·0	4·0	99·95
40*	3·0	8·0	99·95
100*	6·0	5·0†	99·95

* In 20 ml of aqueous phase.

† 4*M* NH_4SCN.

Back-extraction of vanadium

If the chloroform extract is shaken with 3–5*N* sulphuric acid under a carbon dioxide atmosphere, the vanadium is transferred to the aqueous phase, giving the solution the pink colour of the V(II)–thiocyanate complex. This confirms the bivalency of vanadium in the pyridine thiocyanate complex.

As the thiocyanate interferes in the oxidimetric methods for vanadium determination, the back-extraction is done with peroxide and the thiocyanate destroyed by boiling with alkaline peroxide.[11] The final decomposition of peroxide in acid solution reduces some vanadium which is best reoxidized with permanganate.[12]

Effect of anions

Complexing anions (citrate, fluoride, EDTA and oxalate) considerably lower the extraction of vanadium, but at 5 mg/ml anion concentration, the vanadium extraction is still above 90% at pH 5·2–5·5 (Table 3). Other complexing anions cause an extraction lower by only about 5% even at 100 mg/ml anion concentration. Sulphate and chloride have little effect.

Extraction of other elements

Ions which are reduced to the elements[16b,18] by zinc amalgam, such as nickel, copper, bismuth, lead, arsenic, selenium, tellurium, platinum, palladium, iridium, rhodium, silver, gold, are not extracted, provided the reduction is done at a suitable acidity. Under the proposed conditions, the extraction of zinc (from the reductant) is 99·1%, of cobalt(II) 99·9%, of chromium(VI) 91·0%, of iron(III) 59·2%, of molybdenum(VI) 38·0%, of tungsten(VI) 25·0%, of manganese(II) 5·5%, the initial oxidation state being shown in brackets. If entrained aqueous solution is removed by filtering the chloroform extract through filter paper moistened with the solvent, the extraction of aluminium is 0·9%, uranium 0·06%, titanium, potassium, barium and probably also other alkali and alkaline earth metal ions nil.

Table 3. Effect of anions on the extraction of V(II)–pyridine–thiocyanate complex (V = 1·00 mg/ml; mg of salt added per ml, *A* = 100, *B* = 10, *C* = 5)

Salt added	Extraction, %		
	A	*B*	*C*
Sodium chloride	99·95*	—	—
Sodium sulphate	99·95*	—	—
Sodium acetate	96·0	99·4	—
Sodium phosphate	95·8	99·3	—
Tartaric acid	94·5	98·5	—
Potassium citrate	55·0	88·3	92·4
Potassium hydrogen fluoride	37·7	84·6	93·3
EDTA	66·2†	92·0	96·3
Potassium oxalate	6·0	81·3	93·1

* 200 mg of salt per ml.
† 20 mg of salt per ml.

Table 4. Analysis of samples by the proposed method

Sample composition		
Other elements, *mg*	Vanadium, *mg*	Vanadium found, *mg*
U(50)	10·00	9·95
Al(60)	40·00	39·9
Al(15)	85·00	84·7
Cr(20)	10·00	9·95
U(20), Al(20), Cr(20), Ti(20)	10·00	9·95
Ti(20)	0·100	0·957

Back-extraction of vanadium and other elements

The chloroform phase containing the vanadium and other extracted elements is back-extracted with an equal volume of water at pH 5·5, containing peroxide, and again with half the volume of water. The vanadium is completely back-extracted and only 0·1% and 0·9% respectively of the initial chromium and aluminium accompany it. Repetition of the extraction procedure on the back-extract decreases to traces the chromium and aluminium accompanying vanadium.

Analysis of samples

In binary mixtures with 20 mg of titanium, uranium, aluminium or chromium, the extraction of vanadium is 97·0, 96·5, 95·5, 96·0% respectively, and is 94% from a mixture of all these elements. Therefore, the procedure is repeated on the aqueous phase to get complete extraction. With chromium and/or aluminium present, the extraction is repeated on the back-extract also, to decrease the co-extraction of these elements. As chromium is also highly extracted, as much additional pyridine and thiocyanate as needed for an equal amount of vanadium should be added. On extraction from a mixture with 50 mg of uranium and determination by titration with ferrous ion,[13] 9·95, 9·95, 9·95, 9·94 mg of vanadium are found instead of 10·00 mg present, showing good reproducibility. The method has been applied to a few samples with satisfactory results (Table 4).

The V(II)–pyridine–thiocyanate complex is shown to be quantitatively extracted by chloroform at pH 5·2–5·5. The extraction procedure takes about 20 min and effects the important separations of vanadium from titanium, uranium, chromium and aluminium, not possible by most of the existing methods of solvent extraction or even by the mercury electrolysis method[19] which separates most of the other elements from vanadium. Although zinc from the reductant accompanies vanadium, it does not interfere in most of the methods for vanadium determination and can be easily separated[16c] if desired. The method is simple, rapid, useful for both microgram and milligram amounts of vanadium and requires but ordinary chemicals. It can be used to complement the mercury electrolysis method for separation of all important elements from vanadium.

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SPECTROPHOTOFLUOROMETRIC DETERMINATION OF SOME ALKALOIDS CONTAINING A TERTIARY AMINE GROUP

A. D. THOMAS

Department of Chemistry, University of Aberdeen, Meston Walk, Old Aberdeen, Scotland

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Summary—The method developed involves the base-catalysed condensation of mixed anhydrides of organic acids, where a tertiary amine group functions as the basic catalyst. The product of the condensation reaction is highly fluorescent and allows the fluorometric determination of alkaloids containing a tertiary amine group, in the ng/ml range. The mixed anhydride system is simple to prepare and the fluorogenic reaction is completed within 15 min at 80°. The reaction is specific for, but does not distinguish between, different tertiary amines.

Although most alkaloids will exhibit native fluorescence, given the correct conditions,[1,2,3] a number of medically important alkaloids are either only weakly fluorescent (cocaine and pholcodine)[2,4] or non-fluorescent (pilocarpine and strychnine hydrochlorides).[2] Each of these four alkaloids contains at least one tertiary amine group (Fig. 1). The application of so-called "fluorogenic reactions", by which non-fluorescent compounds can be converted into fluorescent derivatives by chemical means, is well documented.[4–9] For example, reaction with 1-dimethylaminonaphthalene-5-sulphonyl chloride (DANS-Cl) allows the sensitive determination of primary and secondary amines and phenols, but not of tertiary amines.[9] Feigl[10] and a number of others[11,12] have reported that the reaction between a mixed anhydride and tertiary amines, or their chloride salts, yields a highly coloured product suitable for use as a spot-test for tertiary amines. The mixed anhydride is formed by reacting organic acids, such as malonic or citric acid, with acetic anhydride. These coloured products are also known to be fluorescent.[11]

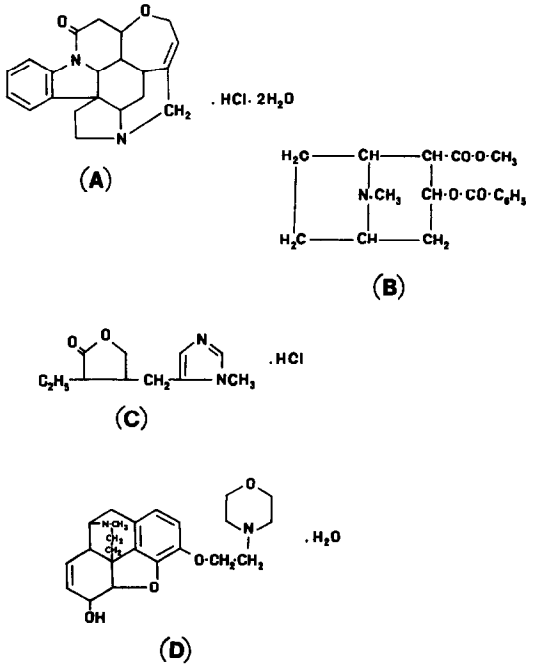

Fig. 1. Structures of alkaloids. (A) Strychnine hydrochloride; (B) cocaine; (C) pilocarpine hydrochloride; (D) pholcodine.

Pesez and Bartos[13] developed the aconitic acid/acetic anhydride system for the fluorometric determination of tertiary amines. The malonic acid/acetic anhydride system (hereafter called the MAA reagent) offers a number of advantages over the aconitic acid method in terms of stability of the fluorescent product and limit of detection for tertiary amines. Results obtained with the MAA method for the fluorometric determination of pholocodine, cocaine, strychnine hydrochloride and pilocarpine hydrochloride are presented and discussed below.

EXPERIMENTAL

Reagents

The alkaloids pholcodine, pilocarpine hydrochloride, strychnine hydrochloride, cocaine and cocaine hydrochloride were purified by recrystallization. Quinine sulphate was used as the fluorescent reference standard at all wavelengths. Laboratory reagent grade acetic anhydride and malonic acid, and doubly distilled spectroscopic grade 95% ethanol were used.

Malonic acid/acetic anhydride mixed anhydride system (MAA reagent). A 10% solution of malonic acid in acetic anhydride is prepared by dissolving the acid with heating. The reagent is stable for at least 7 hr.

Equipment

Fluorescence measurements were made with a Farrand Spectrofluorimeter with a 150-W xenon arc lamp, RCA IP 28 photomultiplier, Honeywell Electronic 15 chart-recorder, 10 × 10 × 45 mm quartz cells and 10-nm bandwidths.

All weighings were done on a Bunge microbalance and a Hamilton syringe was used for pipetting microlitre quantities. All glassware was cleaned by soaking overnight in dilute nitric acid, rinsed thoroughly with distilled water and then acetone, and allowed to dry.

Fluorogenic reaction

The sample [2–3 mg or its equivalent (1–2 mg for pholcodine)] of the alkaloid (or tertiary amine) is quantitatively transferred to a volumetric flask (25 or 50 ml) into which 3 ml of the MAA reagent are then pipetted. The flask is placed in a water-bath at 80° for 15 min, and then the reaction mixture is made up to volume with ethanol. A suitable aliquot (normally 50 μl) is diluted to 10 or 25 ml with ethanol and allowed to stand for 10 min and then its fluorescence is measured at the appropriate wavelength combination (Table 1). Calibration curves are prepared by taking a series of aliquots to produce the required concentration range.

Analysis of pharmaceutical preparations

The alkaloids to be determined will normally be in solution, so a suitable aliquot, equivalent to 2–3 mg of alkaloid, is transferred to the volumetric flask, followed by 1 ml of acetic anhydride and 3 ml of MAA reagent, and heated at 80° for 15 min. Standards, which should always be reacted at the same time and with the same MAA reagent, are treated first, with an amount of solvent equal to the aliquot of the sample, then with 1 ml of acetic anhydride and 3 ml of MAA reagent. Typically 50-μl aliquots of cocaine hydrochloride eye-drops were taken and 50 μl of 0·6% sodium chloride solution were added to the cocaine hydrochloride standard before reaction. Aliquots were taken directly from the eye-drop solutions but prior extraction of the alkaloid from the formulation was necessary for the pholcodine linctus[14] and nux vomica tincture.[15]

RESULTS AND DISCUSSION

Reaction conditions

As mentioned previously, a number of organic acids are capable of forming a coloured product with tertiary amines.[10–12] Malonic acid was preferred because it formed the most stable fluorescent product. The citric acid product exhibits a steady increase in fluorescence over a period of time. Although Pesez and Bartos[13] preferred aconitic acid, it was found to be unsatisfactory, as invariably a purple solution resulted on heating to dissolve the acid. Pesez and Bartos[13] used a different method of preparation for the mixed anhydride, which required over 30 min for completion. The mixed anhydride formed was stable for only some hours. A yellow solution occasionally results when malonic acid is dissolved in acetic anhydride; a fluorescent product is still obtained with tertiary amines but it is preferable to prepare a fresh solution. This coloration of mixed anhydrides has been observed previously[16,17] and is possibly due to traces of alkali on the glassware catalysing the condensation reaction.[10] The aconitic acid system is presumably more sensitive to alkali than the citric or malonic acid systems. On aging, the MAA reagent develops a yellow colour, which does not affect the fluorescence of the reaction product. Moreover the blank value does not increase significantly for this

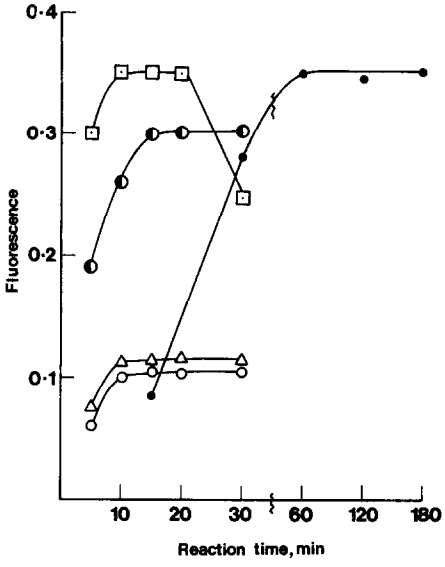

Fig. 2. Fluorescence *vs.* reaction time at various temperatures. ● Strychnine hydrochloride, 50°; ○ cocaine, 80°; △ pholcodine, 80°; ◐ strychnine hydrochloride, 80°; ⊡ pilocarpine hydrochloride, 80°.

"aged" solution. A 10% solution of malonic acid in acetic anhydride yields a more stable fluorescent product than the 2% solution recommended by Feigl[10] for spot-tests.

The variation of fluorescence intensity with reaction time for each alkaloid is shown in Fig. 2. Heating for 15 min at 80° was chosen for all alkaloids. Heating at lower temperatures required a reaction period of at least 1 hr. Although smaller volumes of the MAA reagent yield a slightly higher fluorescence intensity, 3 ml of the reagent were used to ensure that a sufficient excess was present when the alkaloid was dissolved in some other solvent, as in the analysis of pharmaceutical formulations. If no other solvent is present 1 ml of MAA reagent is sufficient.

The solution resulting from reacting the MAA reagent with tertiary amines has a deep golden orange colour, with a distinct green fluorescence. Normally 2–3 mg of the alkaloid are used but the pholcodine product is less soluble in acetic anhydride/ethanol and will precipitate if more than 2 mg of the alkaloid is taken. For reproducible and accurate results it is essential that both standards and samples are reacted with the same MAA reagent at the same time. If not, the concentration of malonic acid in acetic anhydride would have to be reproduced accurately each time a new solution was prepared.

Stability of the fluorescent product

The concentrated fluorescent product (*ca.* 50 μg/ml with respect to alkaloid) is stable for at least 3 hr with a small but definite increase in intensity over longer periods. Dilute solutions (≤0·1 μg/ml) show an initial increase in fluorescence (10–15%) which stabilizes after 10 min, although with an overall trend towards higher values (<5% over 3 hr). If a number

Table 1. Fluorescence characteristics and analysis of alkaloids

Alkaloid	Excitation/emission wavelengths, *nm*	Limit of detection,[18] *ng/ml*	Linear calibration range, *ng/ml*	Limit of determination, *ng/ml*	Standard deviation, *ng/ml*
Pilocarpine hydrochloride	395/450	2·8	2·8–280	2·8	2·1 (213)*
Pholcodine	395/450	0·5	2·8–230	2·8	1·7 (157)
Cocaine	395/475	0·1	0·6–11	0·6	0·2 (164)
Strychnine hydrochloride	420/450	0·5	7·7–280	7·7	0·7 (276)

* Value in brackets refers to the concentration of the solution (*ng/ml*) analysed to determine the standard deviation. A series of 15 solutions was analysed for each alkaloid.

of determinations are carried out simultaneously the solutions diluted initially have stabilized by the time all the solutions have been prepared, and fluorescence measurements can be made immediately. It is advisable to take readings within 3 hr of reaction, particularly for diluted solutions, although satisfactory results have been obtained with older solutions provided both standards and samples were prepared at the same time.

Fluorescence conditions, limit of detection and determination

The excitation/emission wavelengths together with the limits of detection and determination for each alkaloid are presented in Table 1. Typical fluorescence and absorption spectra are shown in Figs. 3 and 4. The limit of determination is defined as the smallest concentration which lies on the linear portion of the calibration curve. The limit of detection is as defined by Wilson,[18] a value of three times the standard deviation of the blank being used. Although the reagent blank will yield a fluorescent product on heating, the intensity is much less than for the fluorogenic reaction and the blank value is not significantly greater than the value for the solvent blank only. Quenching by self-absorption occurs at relatively low concentrations of alkaloid as is evident from the linear calibration range (Table 1). The method is therefore essentially a trace analysis technique.

Analysis of pharmaceutical products

Bearing in mind that the method is a trace technique, analysis of some commercial pharmaceutical formulations, containing the appropriate alkaloids at concentrations in the 0·1–2% range, was attempted. Quite reasonable results were obtained for three of the alkaloids (pholcodine, pilocarpine hydrochloride and strychnine, Table 2). Analysis of cocaine hydrochloride eye-drops was unsatisfactory because the alkaloid had been dissolved in a 0·6% sodium chloride solution, which appears to catalyse the condensation reaction. Although catalysis by cocaine hydrochloride will yield a more highly fluorescent product, the sodium chloride blank is only *ca.* 50% lower than the fluorescence obtained for the cocaine hydrochloride eye-drops, resulting in high values for the determination. The precision of the method for analysis of pharmaceutical preparations is illustrated by the results for the determination of the pilocarpine hydrochloride and cocaine hydrochloride eye drops (Table 2). Only one determination of the pholcodine linctus and nux vomica tincture (strychnine) was made because of the lengthy procedure required for extraction of the alkaloids.[14,15] Presumably the precision

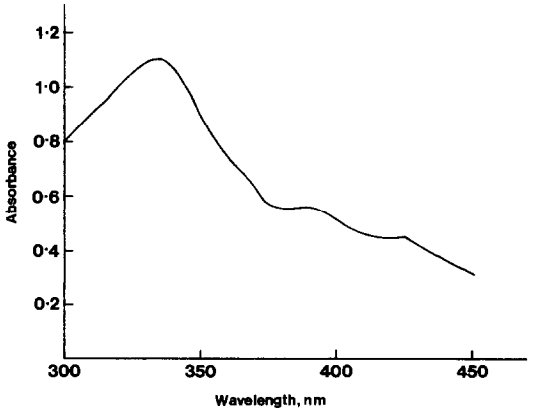

Fig. 3. Absorption spectrum of strychnine hydrochloride/MAA complex.

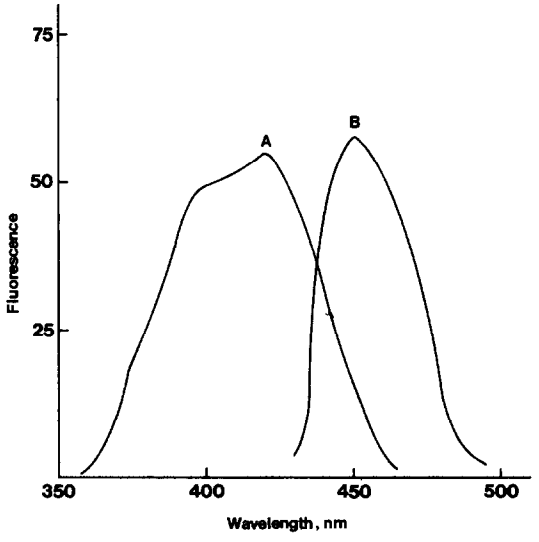

Fig. 4. Uncorrected excitation (A) and emission (B) spectra of strychnine hydrochloride/MAA complex.

Table 2. Analysis of some pharmaceutical preparations

Alkaloid	Nominal content, %	Content found %	R.S.D.* %
Nux vomica tincture (Strychnine)	0·120	0·118	
Pholcodine linctus	0·149	0·150	
Pilocarpine hydrochloride eye-drops	2·0	2·1	5·3
Cocaine hydrochloride eye-drops	2·0	2·3	3·5

* R.S.D. = relative standard deviation. Results derived from 15 separate determinations.

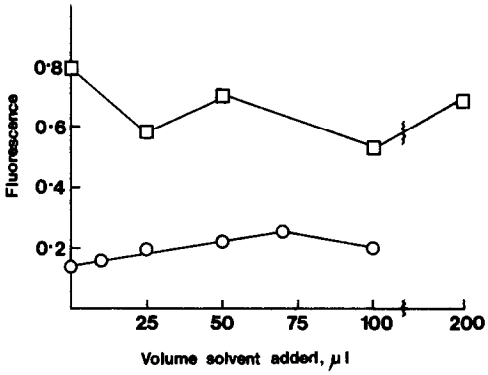

Fig. 5. Effect of various solvents on fluorescence intensity. ○ Water/pilocarpine hydrochloride; □ chloroform/pholcodine.

for these determinations would be of the same order as for the analysis of the eye-drops.

Interferences

Other solvents likely to be encountered during analysis for the alkaloids, either in pharmaceutical preparations (water or 0·002% benzalkonium chloride solution), or as the final solvents for an extraction procedure (chloroform), do not give high blank values. They do, however, affect the fluorescence intensity of the product (Fig. 5). This effect is reproducible, so addition of an amount of solvent equal to the aliquot of the alkaloid taken for analysis, as discussed above, allows an accurate and precise determination to be made. Alternatively, if the solvent is chloroform it can simply be evaporated and the MAA reagent added to the residue.

The method is not suitable for analysis of mixtures of tertiary amines as the reaction products formed with different tertiary amines have either identical or very similar fluorescence properties (Table 1, Fig. 2). Prior separation of the various amines would be necessary in such cases. For analysis of pharmaceutical preparations methods are available[14,15,19] for the separation of alkaloids from syrups, tinctures, or fillers such as magnesium stearate, lactose or starch which may interfere with the determination.

Comparison with other methods

Groth and Dahlen[20] claimed that the aconitic acid system gave the most sensitive reaction for tertiary amines, but their method was used for qualitative analysis only. Pesez and Bartos[13] developed a sensitive fluorometric method for determination of tertiary amines, using aconitic acid, but the fluorescent product formed is light-sensitive and stable for only 5 min. The fluorescent product from the MAA reaction is not light-sensitive and is stable for at least 3 hr. The limit of detection with the MAA system is about two orders of magnitude lower than for the aconitic acid system (Table 3). The value for the limits of detection and determination obtained with the MAA system for cocaine and strychnine hydrochloride is compared with the limits quoted for a number of other techniques in Table 3.

Reaction mechanism and products

The mechanism of the overall fluorogenic reaction has not as yet been fully elucidated but it seems apparent that the final product results from the base-catalysed condensation of mixed anhydrides.[11,12] The reaction is specific to tertiary amines because they retain their basic properties in an acetylating medium such as acetic anhydride, whereas primary and secondary amines do not. Groth and Wallerburg[12] have postulated a structure for the mixed anhydride of malonic acid and acetic anhydride, and suggested that the condensation product contained the basic catalyst, in their case pyridine, but did not identify the final product. Groth and Dahlen[20] identified the reactive compound for the aconitic acid/acetic anhydride system as α,γ-anhydroaconitic anhydride but once again the reaction product was not identified.

The fluorescent product formed by condensation of the MAA reagent with the various alkaloids has not as yet been identified. Thin-layer chromatography indicates that there is one product (or possibly two)

Table 3. Comparison of limits of detection (*ng/ml*) for MAA fluorometric method with those for some other techniques

Method	Cocaine	Strychnine	General tertiary amines
MAA/fluorometric	0·1	0·5*	
Aconitic acid/flurometric[13]			30
G.L.C[21] (ng/ml)	20		
Fluorimetry[14]	30×10^3		
Spectrophotometry[22]	20×10^3		
Spectrophotometry[23]		$1{\cdot}4 \times 10^3$†	
Radiometric[24]		200×10^3	
Non-aqueous[25] thermometric titration		33×10^3§	

* As the hydrochloride.
† As the sulphate.
§ Limit of detection in ng.

but the chromatograms have a number of other spots which seem to be associated with the MAA reagent. The NMR spectrum of the product contained one peak, identical to that for the MAA reagent. Elemental analysis was inconclusive owing to difficulties in recrystallizing the reaction product. Further attempts are being made to identify the fluorescent product.

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A PRELIMINARY STUDY ON THE EFFECT OF TIME ON APPARENT LEAD CONTENT OF EVAPORATED MILK AS DETERMINED BY NON-FLAME ATOMIC-ABSORPTION SPECTROMETRY

HUGH L. HUFFMAN, JR. and JOSEPH A. CARUSO®

Department of Chemistry, University of Cincinnati, Cincinnati, Ohio 45221, U.S.A.

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Summary—Analysis of several brands of canned evaporated milk at various times after opening showed increases in the lead content upon standing. Initially all samples had a lead content within the range 0·1–0·2 ppm. Upon standing, however, the lead concentration of anumber of samples doubled or tipled. Control samples obtained by pouring approximately half of the milk from a can into a polyethylene bottle immediately after opening showed no such increase. When atmospheric oxygen was ecluded by bubbling nitrogen through a sample, where was likewise no increase in lead for the sample. Bubbling oxygen through the samples produced an increase in the lead content of the milk left in the can but did not affect that of the milk in the polyethylene bottle.

Evaporated milk is a widely used substance known to contain lead as a contaminant where at least some of the contamination may be present in the milk as it comes from the animal. Shea[1] discusses possible sources of contamination as related to packaging the milk. Reports based on a U.S. Government[2] and an independent study[3] indicate lead levels ranging from 0·02 to 0·37 ppm with an average of 0·12 ppm and 0·01–0·43 ppm with an average of 0·13 ppm, respectively. Both of these studies showed the lead levels below the 0·5 ppm guideline.[4] A previous study in this laboratory utilized the high sensitivity and low detection limits of flameless atomic-absorption spectrometry to illustrate the potential of the technique for biological samples with complex matrices, such as canned milk.[5]

In a review of non-flame atomization in atomic-absorption spectroscopy (AAS) Amos[6] describes the various designs of filament and furnace atomizers presently in use and includes a detailed description of the carbon-rod atomizer used for this study. Additional descriptions of the carbon-rod atomizer are given by Brodie and Matoušek[7] and Matoušek;[8] Kurz *et al.*[9] describe the operation of the carbon-rod atomizer and the determination of its optimum settings. Determination of lead in milk by using a Perkin–Elmer graphite furnace without sample pretreatment is described by Manning.[10] In a collaborative study of lead in evaporated milk by AAS and anodic stripping voltammetry Fiorino *et al.*[11] used a pre-ashing AAS method. The AAS method reported here is considerably more rapid than this procedure.

Absolute sensitivities and absolute detection limits for the determination of lead by the carbon-rod atomizer are in the picogram range. Amos[6] reports that the absolute sensitivity and detection limit of the Varian–Techtron M-63 carbon-rod atomizer for lead are 2 and 5 pg. Matoušek[8] reports a sensitivity of 6·8 pg for lead at 217·0 nm, with the carbon-rod atomizer. Molnar *et al.*[12] report a detection limit of 75 pg for lead at 283·3 nm, using a graphite-rod atomizer in a Perkin–Elmer instrument.

EXPERIMENTAL

Apparatus

Measurements were made with a Jarrell–Ash Model 82-500 MVAA spectrometer equipped with a Varian Techtron Model 63 water-cooled "carbon-rod atomizer" complete with power supply and gas-control unit, the details of which are given elsewhere.[13] This unit may be used either with a carbon cup or carbon tube insert. Argon (flow-rate 6·5 ft^3/hr) was used as the inert sheathing gas for the flameless determinations. The voltage–time settings (V, sec) used for the "carbon-rod atomizer" with the tube insert were: predry, 3–30; dry, 4–20; ash, 5–20; atomize, 7–2. Slight variations may be needed for different instruments. Peak heights were recorded with a Hewlett–Packard Model 7101B strip-chart recorder which has a full-scale response time of 0·5 sec. All readings were made with minimum damping, minimum amplifier gain, and an unexpanded scale. In the worst case the baseline error in determining the peak height was 5%. A Jarrell-Ash hollow-cathode lamp was operated at 75% of the maximum recommended current with determinations made at the 283·3-nm lead absorption line. In addition, all solutions were measured at the non-absorbing lead line of 280·2 nm and when necessary background corrections were made by using the average absorption at this line. A 5-μl "Autopipette" precision pipetting device (1% tolerance on the volume delivered) with "non-wetting" polypropylene tips was used to inject the samples into the carbon tube. A "Pipetman" digital push-button microlitre pipette (1% tolerance with

reproducibility better than 0·1 μl) was used in preparing some of the spike solutions. Entrance and exit slits for the 0·5-m Ebert grating monochromator were fixed at 100 and 150 μm respectively. A wide-response photomultiplier tube, supplied by Jarrell–Ash with the instrument and which has a useful range of 1970–7800 Å, was mounted at the exit slit. "Uni-Seal" decomposition vessels (Haifa, Israel) with "Teflon" inserts, were used to oxidize the samples before analysis on the carbon rod. *In situ* ashing with the carbon-rod atomizer was shown to be unreliable, as previously reported.[5]

Reagents

"Baker Analyzed" lead nitrate, which was oven-dried at 120° and stored in a desiccator over anhydrous magnesium perchlorate, was used to prepare the 1000-ppm stock solution from which spike solutions for the standard additions method were prepared. Distilled water was passed through a "Crystalab Deeminizer" (Cole–Parmer) mixed-bed ion-exchange resin immediately before its use for preparing solutions or rinsing glassware. All glassware used in this study was soaked for a minimum of 12 hr in nitric acid (1 + 1) before use. Redistilled nitric acid (G. Frederick Smith Chemical Co.) was used in the digestion of the samples. Major-brand canned evaporated milk samples were purchased at random from the shelves of local supermarkets and shaken on an Adams Utility Shaker (275–285 oscillations/min) before sampling, to ensure homogeneity.

Procedure

After a 5–10 min shaking period the cans were opened by punching a single triangular hole and a smaller hole on opposite sides of the top of the can. A 1-ml sample was pipetted into the Teflon insert of the Uni-Seal decomposition vessel, 2 ml of redistilled nitric acid were added, the Teflon insert was sealed tightly in the stainless-steel vessel, and the entire assembly was placed in the oven at 140° for 2 hr. This was the minimum time for decomposition of the milk; longer times and higher temperatures led to destruction and concomitant leakage of the Teflon insert. During the digestion of the sample approximately half of the remaining milk was poured from the can into a clean dry polyethylene bottle and loosely covered with a double layer of "Kimwipes" tissues and kept adjacent to the can during the remainder of the experiment. The openings in the can were covered with a double layer of Kimwipes and secured with a rubber band, to keep out particulate matter while simultaneously allowing exposure to the atmosphere. Both polyethylene bottle and can were then placed in the refrigerator (3–4°). They were allowed 1 hr to return to room temperature before being sampled again. During shaking the can was covered with "Parafilm" secured with a rubber band. After decomposition, the sample was cooled to near room temperature (about 30 min), the acid digest was quantitatively transferred to a 10-ml volumetric flask, and diluted to volume. This solution was then directly injected into the carbon-tube insert of the carbon-rod atomizer for the flameless AAS determinations.

Two equally successful methods of spiking the samples were used. The first involved adding the lead nitrate spike with the milk in the Teflon insert and carrying it through the decomposition and subsequent dilution. The second employed spiking of the sample after digestion and dilution. Recoveries of aqueous lead nitrate standard solutions from the decomposition vessels ranged from 97·0 to 100·9% with an average recovery of 99·2%, indicating no significant loss of lead. A 1-ml aliquot from the 10-ml volumetric flask was spiked with an appropriate μl spike from a concentrated lead nitrate stock solution and the mixture was analysed immediately to minimize exposure to the atmosphere. Aliquots (5 μl) of the unspiked solution and at least two spike solutions were injected into the carbon tube and the programmed dry–ash–atomize sequence was initiated. Additional spike solutions were periodically analysed to ensure linearity for the analysis. Aqueous lead nitrate standard solutions were used to establish the maximum allowable spike concentrations for linearity. Spike solutions were generally equivalent to the range 0·1–0·4 ppm. A minimum of ten injections was used for each solution, the 283·3-nm lead resonance line being used for measurement. Before each injection the pipette tip was rinsed twice with the solution being injected. The same tip was used for all injections of a given solution, but a new tip was used for each new solution injected. As indicated earlier, a check of the 280·2-nm non-absorbing lead line was used to make background corrections, when appropriate. This correction varied from sample to sample and with carbon tube insert; most corrections were zero or near zero, with the maximum background correction being less than 15% of the peak height at the absorption line. Analyses were periodically checked with a new carbon tube.

General observations

During the course of this investigation several observations of general importance to non-flame analyses with the carbon-rod atomizer were made. In order to prevent splattering and subsequent loss of analyte and to gain reproducibility after injection into the carbon tube, it is necessary to employ a double drying step with a low-voltage predrying as the first step. The operator may have to vary the predrying time for different matrices or if the carbon-tube insert is not allowed to cool down properly after atomization. Replicate injections of a given solution give better reproducibility of peak heights if a systematic sequence is followed for injection of the aliquot after the atomization step. The first injection of a new solution generally gives a higher absorption signal than that of subsequent injections of the same solution. The pipette tips should be rinsed twice with the sample solution before each injection. It is also observed that the first few injections into a new tube give higher absorption peak heights but consistency develops after approximately ten injections.

The lifetime of a carbon-tube insert is unpredictable —tubes lasted from as few as 30 to as many as 250–300 injections. Irreproducibility is a key symptom of an aging tube. Another indication is a significant change in the slope of the standard-additions plot, which indicates a decrease in the sensitivity of the carbon tube with age. A frequent appearance of a double absorption peak indicates a possible interelement interference or aging of the carbon tube. When applicable, the 280·2-nm background correction is observed to be a larger fraction of the absorption peak height for a new tube, probably reflecting the greater sensitivity of an unused tube. Joselow and Singh[14] report a sensitivity loss of the Delves cup with use. Discussions of background corrections for flameless AAS analyses are given by Dick *et al.*[15] and Robinson *et al.*[16]

Addition of a spike to solutions already injected into the carbon tube gave irreproducible results. Simultaneous injection of a solution and a spike into the carbon tube followed by the predry, dry, ash, atomize sequence, did not give reproducible atomization peaks. Injection and drying of the spike solution followed by injection of the sample solution and initiation of the analysis sequence was also irreproducible. Reversal of the order of injection likewise gave irreproducible results. To gain reliable results the samples must be spiked before its injection into the carbon tube. Schramel[17] and Everett and West[18] also report that it is necessary to add the spike solution in the sample must be spiked before ints injection into the tions to obtain accurate results.

RESULTS AND DISCUSSION

In the flameless technique the sample is placed in the graphite tube through which the radiation from the hollow-cathode lamp passes. An appropriate electric current is passed through a resistive load, causing heating sufficient to dry, ash, or atomize the sample, depending on the amount of current passed. The atomizer is sheathed by a continuous flow of argon to protect it from atmospheric oxidation. Once the light-beam is focused on the atomizer and the sample is injected, the dry–ash–atomize sequence is initiated. Moisture or solvent is evaporated during the drying step and the volatile matrix is supposedly pyrolysed during the ashing step, leaving atomization of analyte to occur during the final step. For a sample containing a large amount of a volatile matrix such as organic matter, a non-atomic absorption peak usually occurs during the drying and ashing steps. Voltage settings regulating the power supplied to the graphite tube are determined such that there is no splattering during the drying step and the recorder trace returns to the baseline following the drying and ashing sequences. Diluted samples generally require slightly altered settings for drying and ashing.

Previous results in this laboratory demonstrated that *in situ* ashing in the carbon-rod atomizer result in loss of lead and thus organic matter must be removed before the injection into the carbon tube.[5] Dick *et al.*[15] found that some analytes were vaporized during ashing when the ashing temperature was too high. In this study wet-ashing in Uni-Seal decomposition vessels with redistilled nitric acid as the oxidant was used. The Teflon inserts for the vessels minimize retention of analytes and, with a tight seal, minimize loss of volatiles. This technique has the additional advantage of not requiring salts to be added for the digestion. Ranweiler and Moyers[19] used Teflon acid-digestion bombs in determination of metals in atmospheric particulate matter. Holak *et al.*[20] also used Teflon digestion vessels in their determination of mercury in fish by flameless AAS. Other investigators[21–23] have also reported rapid digestion procedures in Teflon vessels.

Schramel[17] described the relationship between the accuracy of flameless AAS analysis and some of the major components of a biological material wet-ashed with peroxide and sulphuric acid. He found considerable interferences in analysis for lead but noted that it is advantageous to use low concentrations of acids in order to minimize their fumes and concomitant molecular absorption and scatter during atomization. Hauck[24] reported that the influence of biological components on flameless AAS determinations can be minimized by adding nitric acid and by sample dilution. Since nitric acid is exclusively employed in this study for the digestion, which is followed by a tenfold dilution, it is believed that biologically-derived interferences with the lead determinations are minimal, if they exist at all. It was determined by titration that the nitric acid remaining after digestion was about half the original amount.

Since tin is present in the can coating as well as in the solder it is likely to be a trace contaminant in the milk. Thus an experiment was undertaken to determine if any tin interference was present at the 283·3-nm lead resonance line since tin has an emission line at 284·0 nm. Aliquots (5 μl) of 100, 1000, and 10,000-ppm tin solutions were analysed in the carbon tube at the lead 283·3-nm analytical line. The non-absorbing lead line at 280·2 nm was used to determine smoke corrections. The 100-ppm tin solution showed no absorption, but the other two indicated some absorption. This apparent absorption was found to be completely accounted for by the background correction determined at 280·2 nm. Shigematsu *et al.*[25] report that several cations in 1000-fold ratio to lead seriously interfere in the determination of lead with a carbon-tube atomizer but that most cations scarcely interfere when in 100-fold ratio to lead.

When aqueous lead nitrate standards were used, plots of per cent absorption *vs.* weight of lead were linear for up to 2 ng of lead and slightly curved for higher amounts. Per cent absorption was used instead of absorbance, in a least-squares determination of the intercept in the standard-additions method.[26] Dilutions and standard additions were such that the analytical responses were in the linear region. The standard deviation of the intercept was also calculated.[27] The results, with their standard deviations, are listed in Table 1, and are based on 25–30 injections into the carbon rod. The correlation coefficients varied from 0·88 to 0·99 with most of the values in the range 0·93–0·96. A hand plot of the median values for the standard addition solutions of a given sample usually gives the same intercept (within 0·03 ppm) as the least-squares computer analysis of the same data.

For those analyses which did not exhibit appreciable change in the concentration of lead, the mean deviations for both types of sample (*i.e.*, stored in the cans and in the polyethylene bottles) were calculated. These results are included in Table 1. For a total of 32 analyses on the six different samples the mean deviation of the results ranged from 0·01 to 0·03 ppm with an overall mean deviation of 0·02 ppm.

From Table 1 it is seen that all the samples studied were $<0{\cdot}5$ ppm for lead in evaporated milk. Of the five samples exposed to air or oxygen, sample E did not exhibit an increase in lead, even after it had been open for 144 hr. For sample C the lead concentration at first increases somewhat with time and then becomes constant. Samples C, D and E are of the same brand and have similar initial lead concentrations. Samples A, B and F exhibit increases in lead concentration at 20·6, 53·6, and 53·1 hr, respectively, after opening. These rapid increases are usually followed by a plateau and a subsequent gradual increase. Sample B-5 appears out of place, possibly indicating a loss of analyte. Samples B and C have only a slight increase in the pH of the milk in the can during the

Table 1.

Sample*	Pb *ppm*	Exposure	Time of exposure, *hr*	pH	Mean devn.,† *ppm*	Sample*	Pb, *ppm*	Exposure	Time of exposure *hr*	pH	Mean dev.,† *ppm*
A-1	0·18 ± 0·02	Ambient air	0		0·03	D-1	0·17 ± 0·02	N_2 atmosphere	0		0·02
AP-1	0·18 ± 0·02		2·8								
A-2	0·22 ± 0·03		6·1			DP-1	0·17 ± 0·02		8	6·22	
A-3	0·30 ± 0·03		12·1			D-2‡	0·28 ± 0·02		24·25		
A-4	0·40 ± 0·02		20·6			D-3	0·12 ± 0·02		48·5		
A-5	0·34 ± 0·03		27·6			D-4	0·14 ± 0·02		120·4		
A-6	0·47 ± 0·06		36·25			D-5	0·17 ± 0·01		146·4		
A-7	0·50 ± 0·04		213·9			DP-2	0·14 ± 0·01		168·6		
AP-2	0·26 ± 0·03		370·2								
AP-3	0·17 ± 0·03		383·6	6·06		E-1	0·15 ± 0·01	Ambient air	0		0·02
						EP-1	0·15 ± 0·02		3·8	6·19	
						E-2	0·10 ± 0·01		24·5		
B-1	0·15 ± 0·02	Ambient air	0	6·11	0·01	E-3	0·15 ± 0·01		48·1		
BP-1	0·14 ± 0·03		6·2	6·12		E-4	0·15 ± 0·01		72·8		
B-2	0·28 ± 0·02		53·6	6·12		E-5‡	0·42 ± 0·04		97		
B-3	0·22 ± 0·02		76·7	6·12		EP-2	0·12 ± 0·01		132·75	sour	
B-4	0·30 ± 0·04		101·4	6·15		E-6	0·18 ± 0·01		144·9		
BP-2	0·12 ± 0·02		105·7	6·11							
B-5	0·19 ± 0·02		220·25	6·16		F-1	0·10 ± 0·01	O_2 atmosphere	0		0·02
B-6	0·36 ± 0·03		901	6·18		F-2	0·10 ± 0·01		3·1		
BP-3	0·12 ± 0·02		1069·5			F-3	0·12 ± 0·02		6		
						F-4	0·14 ± 0·02		14·5		
C-1	0·11 ± 0·01	Ambient air	0	6·13	0·02	F-5	0·11 ± 0·02		30·1		
CP-1	0·13 ± 0·02		13·25	6·13		F-6	0·22 ± 0·03		53·1		
C-3	0·25 ± 0·03		83·7	6·16		F-7	0·28 ± 0·03		61·4		
CP-2	0·07 ± 0·02		116·1	6·15		F-8	0·33 ± 0·04		81·9		
C-4	0·27 ± 0·03		521·4	6·17		F-9	0·43 ± 0·03		113·5	6·18	
CP-3	0·11 ± 0·02		694·75			FP-1	0·14 ± 0·03		161	6·11	

* Samples identified with a P indicate a polyethylene container.

† Calculated from the analyses not showing any Pb concentration changes. For example, for sample A it was based on that calculated from the results in column 2 given by A-1, AP-1, A-2, AP-2, and AP-3.

‡ Possible contamination is suspected.

course of the experiment and no apparent change in their counterparts stored in the polyethylene bottles, whereas sample A shows a slight drop in the pH. Evaporated milk is a buffered system and shows only a slight increase in pH after opening, until it begins to sour; typically its pH changes from 6·02 to 4·84 from opening to souring. The pH of 0·1*N* lactic acid is 2·4, whereas cow's milk ranges from 6·3 to 6·6 and human milk ranges from 6·6 to 7·6.[28]

Since the increase in lead concentration of unsoured milk is not associated with a decrease in pH, it was suspected that the observed change might be caused by oxygen, with the lead possibly coming from the soldered joints of the can. However, further experiments are necessary to determine precisely the source of the lead. Sample D was analysed upon opening and the lead concentration was monitored, with nitrogen bubbling through the system *via* a gas dispersion tube. No significant concentration changes were found. A similar experiment was performed with oxygen bubbling through sample F and an increase was observed after 53·1 hr. The nitrogen and oxygen flow-rates were <1 ft^3/hr and adjusted so that there was no frothing of the samples out of their containers. Although these results point to an oxygen-related mechanism for the increase in lead concentration with time, microbiological activity is also a possible source for the change. Further studies to determine the mechanism are necessary. Pitting and discoloration of that portion of the cans in contact with the milk was noticed for all the samples except D and E for which the cans remained shiny. Samples from these cans exhibited no increase in lead concentration in the time observed. Sample D was kept under nitrogen, whereas sample E was exposed to the atmosphere and did not give an increase in lead concentration in the time interval studied.

It is worthy of note that all freshly opened samples as well as those kept in the polyethylene bottles agree well with previous results[2,3]. That is, they are generally within the range 0·1–0·2 ppm. In an earlier study by a similar technique[5] we reported values of 0·3–0·4 ppm for lead in evaporated milk. These values agree well with those obtained in this study for samples that had been exposed to the atmosphere for several days. This is not surprising, as in the previous study[5] the cans had been opened and stored in a refrigerator for 1–2 weeks before we arrived at a usable analytical procedure. Also the can-to-can variation of apparent trace-metal content necessitates a statistical sampling procedure involving composites of many samples before long-range conclusions can be reached.

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SIMULATION DES COURBES DE DOSAGE POTENTIOMETRIQUES PAR EMPLOI D'UNE EQUATION UNIVERSELLE

DOSAGE PAR ECHANGE D'UNE SEULE PARTICULE

JEAN DESBARRES et DENISE BAUER
ESPCI, Laboratoire de Chimie Analytique associé au C.N.R.S., 10 rue Vauquelin, 75231 Paris-Cedex 05, France

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Résumé—On montre que toutes les courbes de titrages potentiométriques sont décrites par la même expression mathématique, à condition d'exprimer sous certaines formes les courbes de réponse des diverses électrodes utilisables. Cette analogie est mise à profit pour l'écriture d'un programme qui permette la simulation des courbes de titrages en utilisant un petit calculateur et la détermination semi-quantitative des constantes d'acidité ou de formation de complexes ainsi que les potentiels normaux d'oxydo-réduction. Cette méthode permet également d'évaluer la concentration des solutions.

Il est d'usage de choisir pour réaliser des titrages des réactions aussi quantitatives que possible; la prévision des courbes correspondantes est alors aisée, à partir de formules approchées classiques en chimie analytique. Etant donné la facilité expérimentale avec laquelle sont réalisés dans la pratique les titrages potentiométriques, il est tentant d'étendre cette méthode à des réactions beaucoup moins quantitatives. Un problème se pose alors au chimiste quant à la précision que l'on peut atteindre par ce type de dosage. Le simple examen de la courbe ne permet pas de répondre à cette question. Cependant, il est possible d'évaluer la précision du titrage en faisant varier les paramètres des réactions (concentrations et constantes) et en examinant les perturbations résultantes sur la courbe théorique du dosage. Il est donc intéressant de disposer d'un moyen de générer facilement de telles courbes. Les possibilités du calcul électronique permettent, à l'heure actuelle, de résoudre ce problème dans le cas le plus général.[1–5]

Cependant, les méthodes utilisées sont souvent complexes et nécessitent l'emploi de calculateurs puissants. Pour le chimiste, il est pourtant d'un intérêt évident de disposer d'un moyen très accessible pour pouvoir simuler graphiquement et sans délai la courbe de dosage qu'il désire exécuter. Il peut ainsi choisir les conditions optimales de l'expérience. L'implantation des programmes sur un ordinateur puissant se révèle dans la pratique, un obstacle à l'emploi de telles méthodes. En effet, le petit nombre de paramètres nécessaires permet de se passer des cartes perforées et peut facilement faire l'objet d'une introduction manuelle par le clavier. De même, la rapidité du calcul est un facteur très secondaire. Par contre, les délais pour se rendre à un centre de calcul, pour perforer ou faire perforer les cartes, l'attente des résultats se révèlent souvent rédhibitoires. La solution la plus convenable est alors l'utilisation d'un petit organe de calcul équipé d'une unité graphique. Une telle installation, relativement économique, peut être disposée à proximité du poste de manipulation et accessible à tous. Soulignons enfin qu'une telle solution évite l'emploi de langages de contrôle plus ou moins bien connus des utilisateurs.

L'emploi de petits calculateurs nécessite cependant qu'un effort soit fait sur le choix des algorithmes et sur l'économie de place en mémoire. Un tel effort est également indispensable si l'on a recours, non plus à un mini-ordinateur, mais à un terminal de télétraitement, de façon à minimiser le coût des opérations.

La similitude est totale entre les courbes de dosage potentiométrique, qu'elles traduisent des phénomènes acide-base, d'oxydoréduction ou de formation de complexe. Il nous a donc paru intéressant d'expliciter un modèle mathématique unique permettant de décrire ces trois types de courbes de dosage tout en réalisant le meilleur compromis entre généralité et simplicité. Nous allons montrer ci-dessous qu'on peut traiter par la même formule toutes les courbes de dosage de mélanges de composés polyfonctionnels à la condition que ces titrages ne mettent en jeu qu'un seul type de particule. On peut ainsi traiter des dosages de mélanges d'acides ou de bases, de mélanges d'oxydants ou de réducteurs. Dans le cas des complexes, les dosages basés sur l'échange d'un seul type de ligand ou d'un seul type de cation par exemple, relèvent de la même formulation.

Par contre, ne seront pas abordés ici les dosages faisant intervenir à la fois, par exemple, l'acido-basicité et la formation de complexes, l'acido-basicité et l'oxydo-réduction, ou la formation de complexes pour plusieurs types de ligands.

EXPRESSION DES CONDITIONS D'EQUILIBRE DANS LE CAS D'UN DOSAGE POTENTIOMETRIQUE

Soit X la particule échangée (H^+ ou un ligand L par exemple). Pour éviter la prise en compte des coefficients d'activité, nous nous placerons en milieu de force

ionique constante. Nous pourrons alors rendre compte de l'équilibre en utilisant les concentrations [X] des espèces, et non leurs activités, à condition de leur associer les constantes apparentes k ou E° leur correspondant.

Nous supposerons en outre que nous disposons pour suivre la concentration de X d'une électrode dont le potentiel obéit à la loi:

$$E = -\frac{RT}{F}\{\log_e[X] - b\} \qquad (1)$$

où b est une constante. Nous supposons donc que le potentiel varie linéairement en fonction du logarithme népérien de la concentration en X. De (1) on tire

$$[X] = \exp\left(-\frac{EF}{RT} + b\right) = \exp(\mathscr{E})$$

avec

$$\mathscr{E} = -\frac{EF}{RT} + b$$

Considérons maintenant la réaction

$$T + X \rightleftharpoons TX$$

Si X est un proton ou un ligand, la condition d'équilibre est décrite généralement par la loi d'action de masses, soit:

$$\frac{[T][X]}{[TX]} = k \qquad (2)$$

Calculons le rapport [T]/[TX] à partir des relations (1) et (2) il vient:

$$\frac{[T]}{[TX]} = \frac{k}{[X]} = \frac{\exp(-pk)}{\exp(\mathscr{E})} = \exp[-(\mathscr{E} + pk^e)] \qquad (3)$$

en posant $pk^e = -\log_e k$.

Si X est l'électron, T est la forme oxydée et $[T, e^-]$ la forme réduite. Le potentiel de la solution à l'équilibre est donné par l'expression suivante:

$$E = E^\circ + \frac{RT}{F}.\log_e\frac{[T]}{[T, e^-]} \qquad (4)$$

qui remplace alors la relation (1). Posons

$$-\frac{EF}{RT} = \mathscr{E} \quad \text{et} \quad \frac{E^\circ F}{RT} = pk^e \qquad (5)$$

et calculons le rapport $[T]/[T, e^-]$, expression particulière à l'oxydoréduction du rapport [T]/[TX]. A partir de (4) et (5) il vient:

$$\frac{[T]}{[T, e^-]} = \exp[-(\mathscr{E} + pk^e)] \qquad (6)$$

Les expressions (3) et (6) sont formellement identiques, quelle que soit la particule échangée, proton, électron ou ligand.

ETABLISSEMENT DE L'EQUATION DE LA COURBE DE DOSAGE D'UN DIACIDE AH_2 PAR UNE DIBASE B

Les réactions s'écrivent:

$$H_2A \rightleftharpoons HA^- + H^+ \quad \text{avec} \quad k_{A_2} = \frac{[HA^-][H^+]}{[H_2A]}$$

$$HA^- \rightleftharpoons A^{2-} + H^+ \qquad k_{A_1} = \frac{[A^{2-}][H^+]}{[HA^-]}$$

$$H_2B^{2+} \rightleftharpoons HB^+ + H^+ \qquad k_{B_2} = \frac{[HB^+][H^+]}{[H_2B^{2+}]}$$

$$HB^+ \rightleftharpoons B + H^+ \qquad k_{B_1} = \frac{[B][H^+]}{[HB^+]}$$

Au début du dosage, le vase de réaction contient un volume V_A de H_2A à la concentration C_A. En un point quelconque du dosage, on ajoute un volume V_B d'une solution de concentration C_B en B. La conservation des espèces s'écrit donc:

$$\frac{V_A C_A}{V_A + V_B} = [H_2A] + [HA^-] + [A^{2-}]$$

$$= [A^{2-}]\left\{1 + \frac{[H^+]}{k_{A_1}} + \frac{[H^+]^2}{k_{A_1}k_{A_2}}\right\}$$

soit

$$\frac{V_A C_A}{V_A + V_B} = [A^{2-}]D_A \qquad (7)$$

et

$$\frac{V_B C_B}{V_A + V_B} = [B] + [HB^+] + [H_2B^{2+}]$$

$$= [H_2B^{2+}]\left\{1 + \frac{k_{B_2}}{[H^+]} + \frac{k_{B_2}k_{B_1}}{[H^+]^2}\right\}$$

soit

$$\frac{V_B C_B}{V_A + V_B} = [H_2B^+]D_B \qquad (8)$$

avec:

$$D_A = 1 + \frac{[H^+]}{k_{A_1}} + \frac{[H^+]^2}{k_{A_1}k_{A_2}}$$

$$= 1 + \exp[-(\mathscr{E} + pk^e_{A_1})] + \exp[-(2\mathscr{E} + pk^e_{A_1} + pk^e_{A_2})] \qquad (9)$$

$$D_B = 1 + \frac{k_{B_2}}{[H^+]} + \frac{k_{B_2}k_{B_1}}{[H^+]^2}$$

$$= 1 + \exp[(\mathscr{E} + pk^e_{B_2})] + \exp[2\mathscr{E} + pk^e_{B_2} + pk^e_{B_1}] \qquad (10)$$

Enfin H^+ réagit sur le solvant HY selon:

$$H^+ + Y^- \rightleftharpoons HY \quad \text{avec} \quad [H^+][Y^-] = k_S$$

posons

$$S = [Y^-] - [H^+] = \frac{k_S}{[H^+]} - [H^+].$$

La neutralité électrique de la solution s'écrit:

$$[H^+] + [HB^+] + 2[H_2B^{2+}] = [Y^-] + [HA^-] + 2[A^{2-}]$$

soit:

$$[H_2B^{2+}]\left[2 + \frac{k_{B_2}}{[H^+]}\right] = S + [A^{2-}]\left[2 + \frac{[H^+]}{k_{A_1}}\right]$$

ou encore

$$[H_2B^{2+}].N_B = S + [A^{2-}].N_A \qquad (11)$$

avec

$$N_A = 2 + [H^+]/k_{A_1} = 2 + \exp[-(\mathscr{E} + pk_{A_1})] \qquad (12)$$

$$N_B = 2 + k_{B_2}/[H^+] = 2 + \exp[\mathscr{E} + pk_{B_2}] \quad (13)$$

En combinant (11) avec (7) et (8) on arrive à:

$$\frac{V_A C_A N_A}{(V_A + V_B)D_A} + S = \frac{N_B V_B C_B}{D_B(V_A + V_B)} \quad (14)$$

Cette équation est celle de la courbe de titrage. Elle donne les variations du potentiel mesuré E, figurant ici par l'intermédiaire des fonctions N_A, N_B, D_A, D_B en fonction du volume V_B de réactif ajouté, mais cette relation n'est pas explicite. Par contre il est possible d'exprimer V_B en fonction de E soit:

$$V_B = \frac{V_A}{\dfrac{N_B C_B}{D_B} - S} \cdot \left(S + \frac{N_A}{D_A} C_A\right) \quad (15)$$

GENERALISATIONS

Composés polyfonctionnels

Il est facile de voir que les formules (14) et (15) restent valables si on dose un n-polyacide par une p-polybase. En effet, le raisonnement précédent reste le même. Seules les expressions (9), (10), (11) et (13) sont généralisées; elles deviennent:

$$D_A = 1 + \sum_{i=1}^{n} \exp\left[-i\mathscr{E} - \sum_{j=1}^{i} pk^e_{A_j}\right] \quad (16)$$

$$D_B = 1 + \sum_{i=1}^{p} \exp\left[i\mathscr{E} + \sum_{j=1}^{i} pk^e_{B_{(p-j)}}\right] \quad (17)$$

$$N_A = n + \sum_{i=1}^{n-1} (n-i).\exp\left[-i\mathscr{E} - \sum_{j=1}^{i} pk^e_{A_j}\right] \quad (18)$$

$$N_B = p + \sum_{i=1}^{p-1} (p-i).\exp\left[i\mathscr{E} + \sum_{j=1}^{i} pk^e_{B_{(p-j)}}\right] \quad (19)$$

Dosages de mélanges

De même, on peut étendre les formules (14) et (15) au cas du dosage d'un mélange de plusieurs acides par un mélange de plusieurs bases. Il existe, pour chaque composé une équation de conservation des masses qui conduira à une expression de N analogue à celle de (18) ou (19). D'autre part la neutralité électrique s'écrira:

$$S + \sum_k [A_k^{n-}].N_A = \sum_{k'} [H_p B_{k'}^{p+}] N_B$$

qui conduit à

$$\frac{V_B}{V_A + V_B} \cdot \sum_{k'} C_{B_{k'}} N_{B_{k'}}/D_{B_{k'}} = \frac{V_A}{V_A + V_B} \sum_k (C_{A_k}.N_{A_k}/D_{A_k}) + S \quad (20)$$

Soit

$$V_B = \frac{V_A.[S + \sum_k (N_{A_k}.C_{A_k}/D_{A_k})]}{\sum_{k'} (N_{B_{k'}}.C_{B_{k'}}/D_{B_{k'}}) - S} \quad (21)$$

Extension aux réactions autres que les réactions acide-base

Nous avons montré au-dessus que la même formulation rendait compte des phénomènes observés quelle que soit la particule échangée: proton, électron, cation métallique, ligand, *etc.* Les formules (16) et (18) sont donc valables dans tous les cas de dosages au cours desquels se produit l'échange d'un seul type de particule, c'est-à-dire le dosage d'un donneur TX_2 de la particule X par son accepteur A. Le cas inverse de dosage d'un accepteur A de la particule X par un donneur TX_2 se traite de la même façon, à condition de changer de signe l'argument de toutes les exponentielles.

C'est ainsi qu'on peut traiter par les mêmes formules le dosage d'un réducteur (T, ne^-) par un oxydant B. Dans ce cas, il n'y a pas réaction de e sur le solvant et la concentration de X, identique à e, est négligeable. S est donc égal à 0. Dans le cas du dosage par formation de complexe, un cation métallique M peut accepter un ligand X d'un complexe M'X; ou encore un ligand L peut recevoir un cation métallique X d'un autre complexe XL'. Alors X ne réagit généralement pas sur le solvant et S sera pris égal à [X].

Le dosage d'un acide fort, c'est-à-dire de la particule échangée elle-même (H^+), par une base faible est une simplification des cas précédents. L'anion associé à H^+ est une base infiniment faible; on donne alors arbitrairement à pK_A une valeur négative (en pratique -5 à -6). De la même façon, dans le cas du dosage d'un acide faible par une base forte, le cation associé à cette base est infiniment peu acide; on donne alors à pk_B une valeur arbitraire, supérieure à pk_S (en pratique $pk_S + 5$ ou $pk_S + 6$).

Enfin, le dosage direct d'un cation métallique par un ligand X est identique au cas du dosage de l'acide fort ou de la base forte, à la valeur de la fonction S près.

CONCLUSION

Etant donné la diversité des calculateurs programmables existants et vu la facilité de programmation de l'algorithme précédent, il nous paraît inutile d'indiquer l'implantation que nous en avons faite.

Un exemple d'emploi de cet algorithme a été décrit récemment;[6] il traite le cas d'un acide aminé à quatre fonctions, la dihydroxy-3,4 phénylalanine. Le titre, déterminé par pesée (0,010M) a pu être retrouvé avec une bonne approximation (5%). Du plus, la valeur de la constante d'acidité de la fonction acide la plus faible a pu être évaluée à partir de l'ajustement visuel entre courbes simulées et courbes expérimentales. Une telle technique a permis de montrer que ce pK était égal à 13,0 ± 0,5, en solution aqueuse.

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FUNDAMENTAL STUDIES ON IMPROVEMENT OF PRECISION AND ACCURACY IN FLAMELESS ATOMIC-ABSORPTION SPECTROSCOPY USING THE GRAPHITE-TUBE ATOMIZER

LEAD IN WHOLE BLOOD

V. P. GARNYS and L. E. SMYTHE

Department of Analytical Chemistry, University of New South Wales, Sydney, Australia

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Summary—Some fundamental aspects concerning the formation of ash on a pyrolytic graphite surface and the resulting effects on precision and accuracy in flameless AAS, have been examined for the determination of lead in whole blood. The nature and composition of the ash from whole blood and the state of the pyrolytic graphite surface have been observed with the aid of a scanning electron microscope and non-dispersive X-ray microprobe analyser. The use of nitric acid to separate the analytical peak from the matrix peak, an examination of high-temperature clearing of the matrix, and removal of ash remnants between each analysis are reported. A procedure to improve precision and accuracy in flameless AAS using the graphite-tube atomizer is reported.

Despite the development of simple and relatively inexpensive heated graphite furnaces for flameless AAS[1,2] and preliminary studies on their biological applications,[3,4] surprisingly few workers[5,6] have published methods on such a topical subject as the direct determination of lead in whole blood.

Kubasik *et al.*[5] applied 1 μl of whole blood diluted with 2 μl of Triton X-100 solution (5% v/v) to a Varian (CRA Model 61) Mini-Massmann furnace. The analysis was carried out under high temperature ashing (CRA instrument setting 7·5 V for 30 sec—approx. 900°) and fast atomizing (8 V for 1·5 sec) conditions. The authors noted that aqueous standards gave about one-third the absorbance of the blood standards and were unsatisfactory. They attributed the decreased absorbance to soaking of the purely aqueous standard into the graphite rod. However, no reason was advanced why blood diluted with Triton X-100 detergent to a lower surface tension than that of purely aqueous standards, did not soak into the graphite. Unfortunately, reliable comparisons of results were not possible in the normal range of 0·10–0·25 mg/l. for lead in whole blood, owing to the flame methods used for comparison.

Rosen[6] developed the technically difficult application of 0·5 μl of whole blood, encased between 0·3 μl and 0·2 μl of xylene, to the furnace of a Varian CRA Model 61. The analysis was carried out under very high ash temperature (CRA instrument setting 9 V for 15 sec—approx. 1000°) and fast atomization (8 V for 2·5 sec) conditions. The author demonstrated the good reproducibility of his method, but few precision data were available for the 0·10–0·20 mg/l. range, and curiously, incomplete recovery was obtained when EDTA-preserved blood was used for the direct determination. This incomplete recovery has been attributed to the EDTA inducing incomplete extraction by MIBK before the analysis.[7,8]

Unfortunately, both groups of workers appeared to be unaware that atomization temperatures should be set no higher than necessary, to minimize atom-cloud diffusion and slow amplifier-response effects.[1,4]

Subsequent work[9] and our observations have confirmed that higher atomization temperatures (2000–2300°) produce non-linearity in the working curve and decrease the precision of the analysis. More recently, measurement of the variation of the transient absorption signal of lead as a function of the time-constant of the amplifier–recorder system, has shown that spectrophotometer amplifiers with high time-constants may not have a linear response for fast signals.[10]

Complete studies of the accuracy of analysis of a whole-blood matrix have not yet been reported for the carbon rod method.[9] From several private communications it would appear that a large number of users have experienced difficulties in the use of flameless AAS for the direct determination of lead in blood.[11,12]

Various claims have been made regarding changes in sensitivity due to matrix accumulation,[4] the increased porosity of the carbon rod upon use causing decreased aqueous sensitivity,[5] the need for xylene to prevent soaking into the rod,[4,6] non-reproducible vaporization rates,[13] and large smoke peaks and pitting of the graphite tube.[9]

By coating of the surface of a new type of carbon tube[14] in the Varian CRA Model 63 with pyrolytic graphite, surface porosity effects have been minimized.

EXPERIMENTAL

Apparatus

The carbon-rod atomizer CRA Model 63 (Varian Techtron, Melbourne, Australia) was mounted in place of the burner in a Varian Techtron AA-5 spectrophotometer as described previously.[14] A Mace FBQ-100 Recorder (N.I.C. Instruments, Sydney, Australia) was operated at a chart-speed of 5 mm/sec with full-scale deflection of 10 mV. The AA-5 amplifier was operated in the minimally-damped absorbance mode. A lead hollow-cathode lamp (A.S.L., Melbourne, Australia) was operated at 8 mA and the most sensitive lead line at 217·0 nm was chosen. A hydrogen continuum lamp operating at 5 mA was used to measure the non-selective absorption. Solution aliquots of 1·5 µl were dispensed into the graphite tube through the inlet port with a 10-µl Hamilton syringe incorporating a Chaney adaptor and disposable Teflon tips (Diagnostics Division, Pfizer Inc., New York).

All electron micrographs were taken with a JEOL Model JSM-U3 Scanning Electron Microscope linked to a non-dispersive X-ray microprobe analyser (EDAX International Inc., North Carolina, U.S.A.).

All digestions were performed, and the digests stored, in 0·8-ml hinge-capped polyethylene containers free from heavy metals (Bactolabs Cat. No. NHP213038C; Camelec Pty. Ltd., Adelaide, South Australia, Australia).

A calibrated optical pyrometer (Leeds and Northrup Co., Pa., U.S.A.) was used to measure furnace temperatures at the axial centre of the furnace.

Reagents

Ultrapure 70% (11*M*) concentrated nitric acid (Aristar grade, B.D.H. Chemicals, U.K.) and twice-distilled water were used. The 15-ml polypropylene containers for blood collection were treated with 0·5 ml of heparin (injection grade B.P., 25,000 I.U./ml, pyrogen-free, preserved with 0·15% chlorocresol, Evans Medical Australia Pty. Ltd., Victoria, Australia).

Procedure

When capped, and heated to 70° by an infrared lamp, the 0·8-ml polyethylene containers acted as pressure digestion vessels for rapid digestion of 50 µl of whole blood with 50 µl of 70% nitric acid. When the reaction mixture was vortex-mixed immediately after the nitric acid addition, and intermittently during the digestion, a clear solution resulted which was suitable for trace metal analysis by flameless AAS. The procedure has been described more fully in another work.[15]

A 1·5-µl aliquot of the sample was dispensed into the graphite tube through the inlet port with the microlitre syringe and a preselected sequence of drying, ashing and atomization was initiated by means of the procedure described in another work.[15] Typical power supply settings were as follows: dry at 5–6 V for 20 sec, ash at 5·5–6·2 V for 20 sec, atomize 5·5–6 V for 4 sec. These settings corresponded to measured ashing temperatures of 350–500° and atomizing temperatures of 1700–1800° as shown in Fig. 1. Once the conditions had been optimized they were kept constant for the analysis batch. Nitrogen was used as the inert gas at a flow-rate of 3·5 l./min (setting 6) and the flow of room-temperature cooling water through the CRA 63 workhead was maintained at 2 l./min.

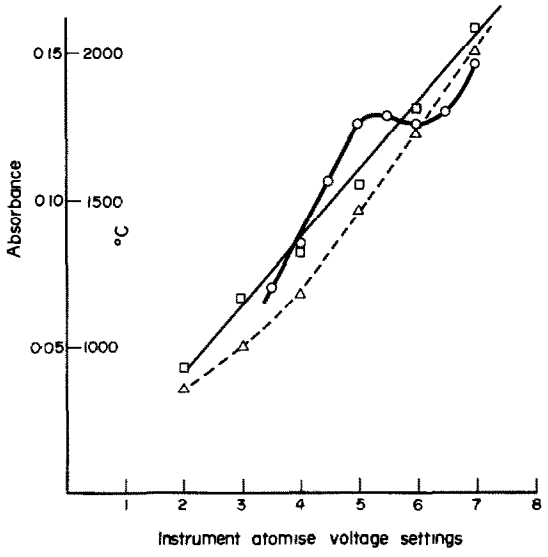

Fig. 1. The relationship of Pb absorbance at 217·0 nm with CRA63 power supply settings (—○—, 4 sec) superimposed on optical pyrometer temperature measurements at CRA63 power supply settings (—□—, 10 sec), (—△—, 4 sec)

Several blood samples were digested and used intermittently as quality-control standards to measure sensitivity drifts and also in the precision studies.

The outside surface temperature of the graphite-tube furnace was measured with an optical pyrometer. The inner surface was estimated to be about 100° higher than the outside of the furnace by observation through the inlet port and tube ends.

RESULTS AND DISCUSSION

When new, the pyrolytic coating on the graphite tube furnaces appeared to be impervious to aqueous lead standards in 0·2*M* and 6*M* nitric acid. However, nitric acid digests of whole blood, and whole blood diluted with twice its volume of Triton X-100 solution (5% w/v) consistently exhibited 30% reductions in sensitivity over seven consecutive atomizations when starting with a new tube. The ash matrix of 10 consecutive whole-blood digest atomizations was allowed to accumulate and was then stored for electron microscopic examination (Plate 4).

Another new tube was used to atomize 80 routine blood-digests for lead determination, regularly interspersed with 23 determinations of a blood-digest standard. The standard used in the second tube gave a mean absorbance of 0·097 and a relative standard deviation (RSD) of 8·5% over the 23 determinations. All analyses were performed in duplicate and duplicates agreed within 0·005 absorbance units. However, the interspersed standard showed overall variations of 0·020 absorbance units and a gradual decline in absorbance of 0·010 during the 100 atomizations. The absorbances for the aqueous standards also fell, but more erratically.

The overall accuracy and precision of results are dependent on three types of effects: application

effects; spectral and/or chemical effects; physical effects. Techniques for application of microlitre quantities of solution play a large part in attaining maximum accuracy and precision.[6,9,13] In this work, the contribution of application techniques was estimated by performing replicate determinations on the CRA63 with pure lead solutions in 0·2*M* nitric acid. The results of several hundred determinations indicated that, provided electrode contact, tube position, instrument conditions and decontamination were carefully optimized and maintained, R.S.D.'s of 3–4% at the 0·10-mg/l. lead level were readily attainable.

Spectral interferences from whole-blood matrix residues after ashing at below 600° can be serious unless steps are taken to reduce the non-atomic signal during atomization.[15] Ashing at above 600° can result in reductions in the atomic lead signal[16] and losses of the more volatile compounds, particularly in the presence of chlorides. The non-atomic signal can be reduced by such techniques as reduced sample size,[6] use of ramping atomization,[13] or by chemically treating the sample[15] to cause an alteration in the ash products so as to reduce the effect of non-atomic signals on the atomic signal. In this work, concentrated nitric acid was used to reduce the non-atomic component at the lead atomic-signal position. The non-atomic component remained low and constituted less than 10% of the signal obtained from whole bloods containing between 0·10 and 0·80 mg of lead per litre. Unless ashing conditions changed markedly, or there was an accumulation of matrix, spectral interferences remained constant and independent of the sample signal. As can be seen in Table 1, the ratio of non-atomic absorbance to total absorbance and the effect of variation in the non-atomic signal on the total signal, in all cases strongly favour use of the nitric acid predigest.

Figure 2 shows that only with the nitric acid predigest method can constancy of the non-atomic signal be assumed. With our single-beam instruments the low and constant non-atomic signals allowed a constant correction to be made and thus gave significant time-savings; users of double-beam instruments could remove the hydrogen-lamp after estimation of the non-atomic component and retain the advantages of double-beam operation.

A study of chemical interferences in the determination of lead in red blood-cells[9] found that interferences from vaious cations and anions were low or

Table 1. Comparison of the relative magnitudes of non-atomic signals and the effects on the total signal on the same set of samples

Matrix solution	Volume ratio	$\bar{x}_{NA}/\bar{x}_T$, %	$1s_{NA}/\bar{x}_T$, %
Whole blood:Triton X-100,	1:2	31·4	9·2
Whole blood:HNO_3,	1:1	7·7	2·3
Whole blood:HNO_3·H_2O,	1:1:1	7·0	1·5

$\bar{x}_{NA}$ = mean value of non-atomic absorbance.
$\bar{x}_T$ = mean value of total absorbance.
$1s_{NA}$ = standard deviation of non-atomic absorbance.

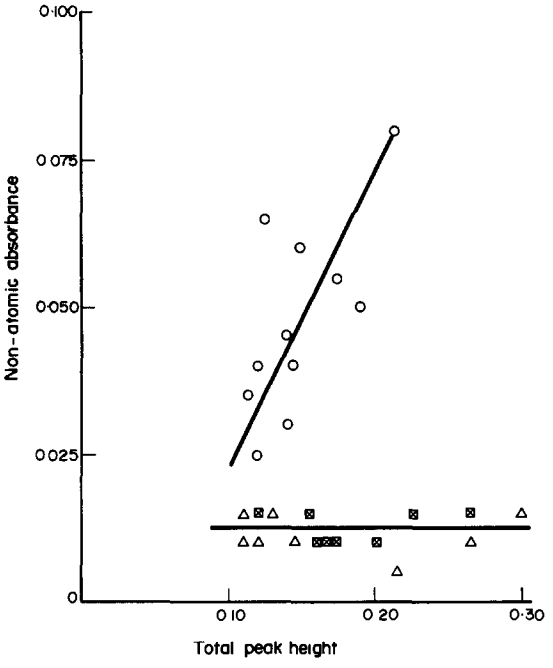

Fig. 2. The relationship of total peak height for lead at 217·0 nm with non-atomic component (H_2-lamp, 217·0 nm, centre of Pb-peak position) for whole blood:Triton X-100, 1:2 (—○—) whole blood:HNO_3, 1:1 (—△—) and whole blood:HNO_3:H_2O, 1:1:1 (—⊠—).

absent. Chemical interferences should not therefore affect the precision of the method, provided the applied matrix remains fairly constant, as was the case here. However, accumulation of less volatile elements such as Fe, Si, Al, B or their carbides formed by reaction with the graphite during atomization, could cause increasing chemical interference. Measurements showed that there was a considerable accumulation of iron on the tube after routine atomization of whole blood at *ca.* 1700° (CRA 63 power supply setting of 5·5 V for 4 sec). This setting on the CRA 61 reportedly also heats the furnace to 1700°.[10]

Iron accumulation was studied by atomizing four aliquots of the same sample sequentially on a new tube at 1700°. Between each atomization, the tube was cleared by heating to 2200° by setting the CRA 63 power supply atomization cycle to 7·5 V for 4 sec (2400° on the CRA 61[10]). After the fourth lead determination no 2200° clearing atomization was used and an iron lamp was substituted (248·3 nm, 5 mA) and the iron absorbances at 1700° measured. The 288·3- and 372·0-nm iron lines were too sensitive, so the 392·0-nm line had to be used.

The first clearing atomization at 1700° liberated the equivalent of only 5 mg of iron per litre from the 1·5-µl aliquot of 1:1 whole-blood:nitric acid digest solution naturally containing about 250 mg of iron per litre. Thus approximately 2% of the iron in the blood samples was atomized by each of the successive atomizations at 1700°. However, on reclearing of the tube at 2200°, subsequent atomizations at 1700° detected less than the equivalent of 0·002 mg/l.

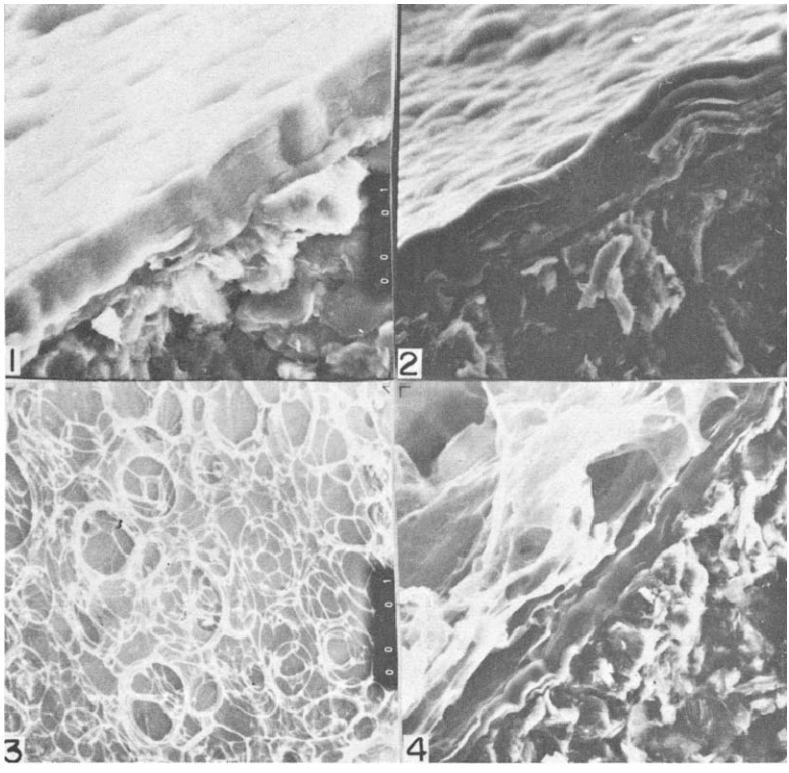

Plate 1. Pyrolytic graphite surface of an unused graphite tube, × 500. Note the dimpled surface and the even fracture edge of the pyrolytic coating. The coating is evenly bonded to the crystalline graphite body of the tube.

Plate 2. Pyrolytic graphite fracture surface after 46 atomizations at 2200°, × 250. Note the shrinking and increased brittleness of the pyrolytic graphite fracture edge causing poorer bonding to the crystalline graphite body of the tube. At several points the pyrolytic layer has lifted away from the crystalline main body. At no point were breaks observed in the pyrolytic surface.

Plate 3. One ash flake from a single atomization at 1700° of whole-blood digest, × 50. This flake was carefully removed from the tube and examined individually. This open structured "boil-holed" carbon net is thin enough for penetration by the microscope electron beam, and one or two layers may be distinguished below the top layer.

Plate 4. Ash build-up from 10 atomizations at 1700° of whole-blood digest, × 250. Note the development of enclosures within the highly irregular surface and bonding of the ash to the pyrolytic graphite surface at several points. EDAX scans showed low iron background but no metallic aggregates larger than 1 μm.

By clearing of the tube at 2200° after each sample and performance of the next analysis at 1700°, memory effects were avoided and any chemical effects that occurred would result directly from the sample being measured. In this way, for any one sample, all chemical effects should remain constant for a fixed set of atomization conditions. As has been demonstrated, application techniques can be controlled within 3–4% R.S.D. and spectral interferences in the nitric acid digests affect the total signal by 1·5–2·3% (R.S.D.) if a mean non-atomic correction is used. Chemical interferences due to memory effects are also eliminated by clearing less volatile elements at higher temperatures. Consequently the only cause of absorbance fluctuations greater than 6% and decreasing sensitivities must be due to physical effects. Physical effects are predominantly due to variations in furnace-heating rates, atomic-cloud diffusion characteristics, signal distortion due to slow amplifier responses, and surface effects.

Examination shows that some effects of heating rates, diffusion characteristics of different gases and instrument response-times on the determination of cobalt and gold in serum[10] have parallels in the determination of lead in whole blood. In our work, optimum atomization and spectral separation were obtained by varying the temperature programme of the tube. Provided heating conditions, gas flows and spectrophotometer conditions remained stable, we would expect the sum of all errors from these sources to approach the 3–4% R.S.D. precisions of pure aqueous standard solutions. However, results for whole-blood replicates during the life of a tube furnace yield 7–9% R.S.D.'s. Careful statistical analysis of the results obtained for gold, cobalt and lithium in blood plasma indicated that the procedural errors

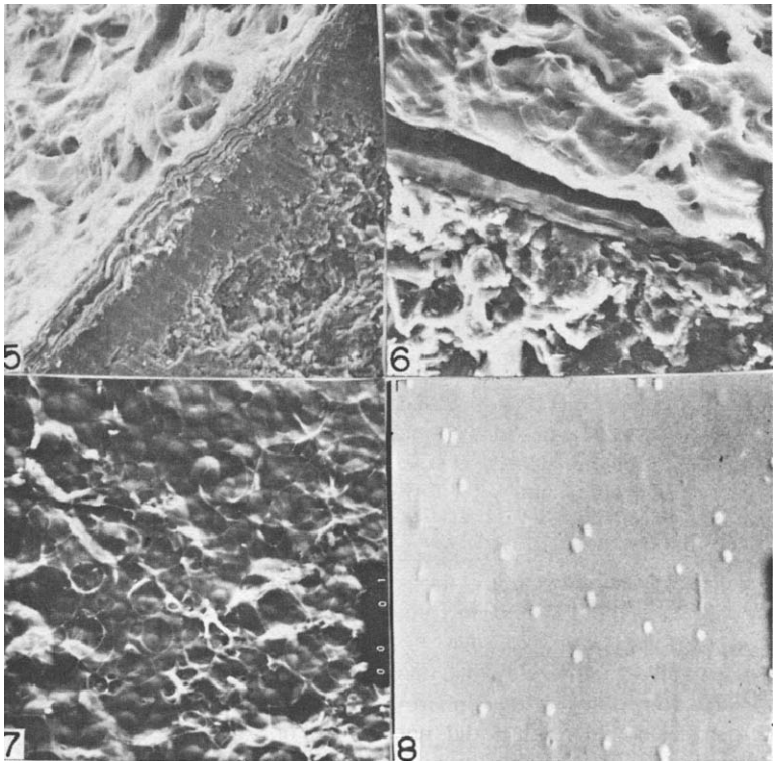

Plate 5. Ash build-up from 31 atomizations at 1700° of whole-blood digest with clearing atomizations at 2200° after each determination, × 87·5. The cut edge clearly shows sequential ash layering which eventually forms a ropy uneven surface from which the next sample is atomized. EDAX scans showed that no elements above atomic number 10 were present either overall or in aggregates larger than 1 μm.

Plate 6. Ash build-up from 120 atomizations at 1700° of whole-blood digest with clearing atomizations at 2200° after each determination, × 250. Note the dense ash layer forming large enclosures with passage holes leading from the enclosures. Also note the intact pyrolytic surface within the enclosures.

Plate 7. Pyrolytic graphite surface after 50 atomizations at 1700° of whole-blood digest, with the ash being cleared away after each determination and the contamination cleared by atomizing at 2200° before the next determination, × 125. Note the adhering monolayer of ash, which is transparent to the electron beam and reveals the intact pyrolytic surface beneath.

Plate 8. A high-magnification ($\times 10^4$) picture of the ash-flake surface shown in plate 3 (atomization at 1700°). The particles on the surface were too small for EDAX analysis, but their electron-beam opacity may indicate inorganic aggregates.

were significant and probably caused by alteration in the properties of graphite by repeated atomizations.[13] Similar conclusions were drawn early in our work when, despite the use of tubes coated with pyrolytic carbon, high R.S.D.'s were obtained. This suggested one of two mechanisms: either a breakdown of the pyrolytic coating, thus exposing underlying porous graphite, or, in some way, alteration of the surface characteristics by the blood matrix.

Because of its 100–200 Å resolution, 50–100 μm depth of field and its ability to produce high contrast easily, a scanning electron microscope was selected for observing the furnace surfaces. The attached EDAX X-ray analyser could also be used to identify matrix segregation.

From Plates 1–7, it is clear that at no time was there observed a break or a discontinuity of the pyrolytic graphite surface, even after severe heat treatment such as in Plate 2. From the nature of the fracture edges, it was clear that successive high-temperature ashings caused each layer within the layered pyrolytic coat to harden and to shrink slightly. This gave rise to an exfoliation effect as the pyrolytic coat contracted and buckled away from the underlying graphite. There also appeared to be no evidence that the underlying coarser graphite became appreciably more porous. However, uncoated graphite as used in the CRA 61 model carbon-rod furnace may behave differently, if the machined surface of the furnace walls become damaged.

Although precise measurement of the variation in the thickness of the pyrolytic carbon coating with respect to number of atomization firings was not possible from the uneven specimen fracture surfaces, an apparently linear decrease from 18 μm when new to 5 μm after 200 firings occurred in the measured coating thickness. It would appear that up to 250–300 firings should be possible before the pyrolytic coat becomes too thin. Our best results for the determination of lead in whole blood to date have been 307

firings before the standard blood result drifted below an arbitrary −10% from the mean analysed value.

By far the most enlightening aspect of the scanning electron microscope study, was the nature, structure and composition of the residual ash. Plate 4 shows the typical cavernous structure of ash accumulated when 10 whole-blood determinations were performed in succession by atomizing at CRA setting 5·5 V for 4 sec (*ca.* 1700°). Visual inspection of the tube showed a slightly roughened surface, presumably similar to that described by other workers as corrosion and pitting of the graphite.[5,9]

While high-temperature firing between each sample removed the less volatile matrix components, it did not prevent accumulation of residue, as can be seen in Plate 5 and particularly in Plate 6. With successive atomization of whole blood, the matrix deposit became more dense, continuous and impervious. In Plate 6, the accumulated matrix layer is seen to have lifted away from the pyrolytic graphite surface, forming a large enclosure or repository for applied solutions. A further interesting aspect in Plate 6 is the intact nature of the pyrolytic surface within the observed enclosure. Non-dispersive X-rays microprobe scans of the ash flakes and residues did not reveal any major segregation of elements of atomic weight greater than that of sodium. However, a slight enhancement was detected in the iron content of the ash after atomizations at 1700°. No elements were detected after atomizations at 2200°, thus suggesting that the ash is predominantly carbon.

From these observations the nature of the physical conditions preventing precise and accurate results were deduced and the following mechanism is proposed. Vaporization of pure aqueous lead nitrate from a clean pyrolytic graphite surface in an inert atmosphere should follow a normal decomposition sequence, which is probably

$$Pb(NO_3)_2 + C \xrightarrow[470°]{} PbO(s) + 2NO_2(g) + CO(g)$$

then

$$PbO(s) + C(s) \rightarrow Pb(g) + CO(g)$$

The decomposition of lead nitrate occurs[17] at 470° while the appearance temperature for lead in the second reaction has been measured as 727°.[16] The presence of excess of nitrate salts may slowly etch the graphite surface by CO formation. It is probable that after ashing of the whole blood/nitric acid matrix at 500–600°, very little $PbCl_2$ or $Pb(NO_3)_2$ would remain and that most of the lead would exist either in the oxide or the metallic state, imbedded in an open-structured film of carbon containing large amounts of iron, calcium and silicon oxides and carbides. Plate 3 illustrates the open net structure of the carbon film.

Electron microscope measurements showed the ash web to be 0·2–2 μm thick, which as our recovery experiments suggest, allows quantitative excape of the lead at 1700°. With each successive sample addition, a proportion would soak beneath the previous ash layer and be lost. From our measured absorbances over seven successive additions, about 28% of the sample may be lost in this way in the first few applications (Plate 4) until a reasonably continuous surface is built up, as in Plate 5. The release of atoms should then remain reasonably constant, perhaps slowly decreasing until the matrix residue film becomes too thick and begins to buckle and cause large enclosed "caverns", such as the 280 × 12 μm structure observed in Plate 6. The small 4–8 μm diameter holes would also readily conduct strongly creeping acid solutions into these enclosures but would not allow quantitative or reproducible escape of atomic vapour. The lower viscosity aqueous standards appeared to be more affected than whole-blood samples, thus resulting in more erratic and decreasing absorbances.

"Pipecleaner" technique

Removal of the ash after each determination by brisk cleaning with a wool-wound pipecleaner maintained a relatively clean, constant surface as shown in Plate 7. The matrix web remained open and was only 2 or 3 layers deep. The tube-cleaning procedure was followed by a 2200° atomization (CRA 63 instrument atomization setting at 7·5 V for 4 sec) to remove any accumulated less volatile matrix and to clear any contamination remaining from the pipecleaner. This simple and rapid procedure, applied before each determination, produced remarkable improvements in sensitivity and precision, as shown in Fig. 3. This figure also illustrates, in a cyclic manner, the accumulation of matrix ash, causing an overall decrease in absorbance of 28–37% at almost the same rate in all cases. In all cases the signal was restored after a 2200°

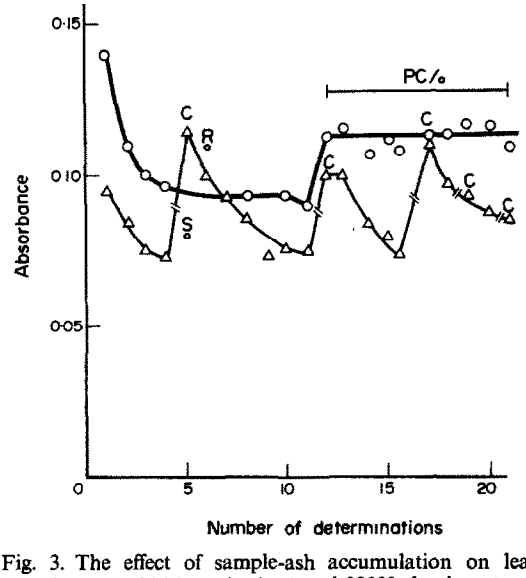

Fig. 3. The effect of sample-ash accumulation on lead absorbance at 217·0 nm (—△—) and 2200° clearing atomization (//, C) compared to the increased precision and accuracy of the "pipecleaner technique" (PC, —○—). S = sparking at electrode contact, R = reset of electrodes.

clearing atomization but fell again as the matrix again accumulated. When the same sample was applied to a new tube and only 2200° matrix-clearing was carried out after every 1700° sample-atomization, the absorbance fell by 28% but stabilized at a more reliable absorbance 27% higher than if no clearing atomization was used. Finally, when the ash was removed with a pipecleaner after each determination and any residual matrix elements were cleared at 2200°, nitric acid digests of whole blood gave 3·4% R.S.D. at the 0·1-mg/l. lead level and the signal was maintained at 90% of the first determination absorbance.

The pipecleaner technique could not return the signal completely to its first value, because of the presence of a thin layer of ash adhering to the pyrolytic surface. However, the residual layer (Plate 7) left after 25 sample determinations is so thin that it is transparent to the electron microscope. The preserved pyrolytic surface can be clearly seen below the ash film. The sharp edge of a stainless steel rod was required to remove this tenacious film.

CONCLUSION

Several interesting questions are yet to be resolved. These are: the action of nitric acid in almost eliminating the non-atomic component of the lead peak, the nature of the non-volatile inclusions seen in the ash under high magnification in Plate 8, and whether the predominantly carbonaceous ash can be removed or modified before the atomization. These questions are currently under study but the findings reported above lead to a procedure for improved precision and accuracy with the carbon-tube atomizer.

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EMISSIONSSPEKTROMETRISCHE ELEMENTBESTIMMUNG IM NANO- UND PICOGRAMM-BEREICH NACH VERFLÜCHTIGUNG DER ELEMENTE IN MIT MIKROWELLEN INDUZIERTE GASPLASMEN—I

EXTREM NACHWEISSTARKE QUECKSILBERBESTIMMUNG IN WÄSSRIGEN LÖSUNGEN, LUFT, ORGANISCHEN UND ANORGANISCHEN MATRICES

G. KAISER, D. GÖTZ, P. SCHOCH und G. TÖLG

Max-Planck-Institut für Metallforschung, Laboratorium für Reinststoffe, Stuttgart und Schwäbisch Gmünd, D.B.R.

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Zusammenfassung—Elemente wie z.B. B, F, Si, P, Cr, Ge, As, Se, Sb und Hg lassen sich emissionsspektrometrisch besonders nachweisstark und gut reproduzierbar bestimmen, wenn man sie direkt oder nach Umsetzung in flüchtige Verbindungen aus einem elektrisch heizbaren Graphitreaktionsgefäß in ein mit Mikrowellen induziertes Argonplasma verdampft und das emittierte Licht mit einem Spektralphotometer integrierend mißt. Dieser erste Beitrag befaßt sich mit der Bestimmung von Quecksilber, das, nachdem es in speziellen Säulenanordnungen quantitativ durch Zementieren oder elektrolytische Abscheidung an Kupfer-bzw. Amalgamierung mit Silber oder Gold angereichert wurde, durch Ausheizen der "Trägermetalle" in das Plasma verdampft wird. Alle Verfahrensschritte wurden mit ^{203}Hg optimiert, so daß noch 0,05 ppM Quecksilber in wäßrigen Lösungen (z.B. Trinkwasser, Oberflächenwässer, Abwasser), nach geeigneten Aufschlußverfahren in anorganischen und organischen Matrices und mit einer einfachen Anordnung auch in Luft mit hoher Sicherheit bestimmt werden können. Die absolute Nachweisgrenze—über alle Verfahrensschritte—beträgt 0,1 ng, der Variationskoeffizient für die Bestimmung von 1 ng $\leq$ 10%, die Analysendauer (Probenaufschluß ausgenommen) ca. 15 min.

In der extremen Spurenanalyse ist man häufig gezwungen, die Proben aufzuschließen, die zu bestimmenden Elemente von der Matrix abzutrennen oder gegebenenfalls aus einer größeren Probenmenge anzureichern.[1,2,3] Die aus diesen Verfahrensschritten resultierenden systematischen Fehler lassen sich sehr klein halten, wenn man die einzelnen Operationen eng miteinander koppelt.

Die Vorteile eines kombinierten Aufschluß- und Abtrennungsverfahrens, bei dem die zu bestimmenden Elementspuren verflüchtigt werden (Verdampfungsanalyse) sind schon lange bekannt.[4,5] Man nutzt sie heute z.B. auch bei zahlreichen flammenlosen Anregungstechniken in der AAS oder AFS.[6] Besonders günstige Bedingungen liegen vor, wenn die zu bestimmenden Elemente bei verhältnismäßig niedriger Temperatur quantitativ zu verflüchtigen und in einem zweiten unmittelbar folgenden Schritt in der Gasphase bei möglichst konstanten Anregungsbedingungen spektroskopisch zu bestimmen sind.

Beide Forderungen lassen sich leicht erfüllen; (1) wenn sich Elemente unmittelbar bei Temperaturen unterhalb 800° destillieren lassen, wie As, Se, Cd, Hg u.a., oder sich in wasserfreien Systemen als Halogenide bei Temperaturen unterhalb 500° vollständig in die Gasphase überführen lassen, wie z.B. B als BF_3, Si als SiF_4, Cr als CrO_2Cl_2 oder Ge, As, Se, Sn und Sb als Chloride bzw. Bromide; (2) wenn man dann die gasförmigen Reaktionsprodukte der zu bestimmenden Elemente in einem mit Mikrowellen induzierten Gasplasma zur Emission anregt. Ein konstantes Argonplasma z.B. erhält man bereits in Mikrowellenfeldern (2450 MHz) relativ niedriger Leistung (*ca.* 100 W), die sich mit käuflichen Generatoren und Resonatoren erzielen lassen, wenn das Plasma in einem Quarzrohr geführt wird.[7] Allerdings darf bei dieser niedrigen Leistung die Fremdmolekül-Konzentration einen bestimmten Grenzwert nicht überschreiten. So wird das Plasma z.B. schon durch verhältnismäßig kleine wasser-dampfmengen stark beeinflut, was bis zur Löschung führen kann.[8,9,10] Ebenso wird es bereits durch geringe Konzentrationen leicht ionisierbarer Elemente, wie Natrium oder Kalium gestört.[11]

Bestimmung des Quecksilbers

Obwohl für die Quecksilberbestimmung in den unterschiedlichsten Matrices zahlreiche nachweisstarke

Prinzipien bekannt sind (vgl. Tab. 1) zeigen jedoch die vielen Arbeiten[83,84] über immer wieder verbesserte Techniken, daß bei der Erfassung kleinster Mengen Quecksilber noch viele Probleme ungelöst sind. Zum Beispiel treten vor allem im pg- und unteren ng-Bereich immer wieder erhebliche systematische Fehler durch Verflüchtigung, Adsorption und Kontamination auf.[57–65]

Bestimmung in wäßrigen Lösungen. Bisherige Verfahren mit Mikrowellen-Plasmaanregung[8,66] schließen Störungen nur unbefriedigend aus: Das Quecksilber wird aus der wäßrigen Lösung nach Reduktion mit

Tabelle 1. Auswahl von Prinzipien zur Quecksilberbestimmung

Methode	NWG	Aufschluß	Anreicherung	Technik	Literatur
AAS 253,7 nm	1 ppM	Nassveraschung		Ausblasen nach Reduktion mit Sn(II), NH_2OH, u.a [12, 13, 68, 69]	12, 13, 68, 69
		$HNO_3/KMnO_4$	(*a*) Dithizon-Extraktion	Durchflußkuvette	
		$HNO_3/HClO_4$	(*b*) Elektrolyt.	(*a*) 1 × Durchgang	
		HNO_3/HBr	Abscheidung [14]	(*b*) Kreislauf [15]	14, 15
		HNO_3/V_2O_5	(*c*) Amalgamierung (Ag, Au), [16–19, 72]	Kuvette, statisch	16–19, 72
		$H_2SO_4/K_2S_2O_8$ u.a.	(*d*) Adsorption an $PdCl_2$ [20]	(*a*) Dosierung mit Spritze [21]	20, 21
	0,01 ppM		oder an mit methanol Jodlösung getrankte Glasfilter [22]	(*b*) Trager in Kuvette ausheizen	22
	1 ppM	O_2-Kolben [23]	(*a*) Dithizon-Extraktion [23]	Ausblasen	23, 24, 25
			(*b*) Amalgamierung [24, 25]		
		O_2-Strom [26]	Amalgamierung [26]		26
		H_2/O_2-Flamme [27]		(*a*) Durchflußküvette	27, 28
		Pyrolyse [28]		(*b*) Nach Absorption in $HNO_3/KMnO_4$: Ausblasen	
184,9 nm	0,01 ppM			Durchflußküvette [29]	
	0,04 ppM			Pt-Ösen-Technik [30]	29–31
				Zeeman-Effekt [31]	
AES	2 ng	Nassveraschung		HF-Anregung	
Plasmenanregung				Ausblastechnik [32]	32
253,7 nm	0,01 ppM			Mikrowellenanregung von Lösungen [8]	8
184,9	0,02 ng			Mikrowellenanregung Pt-Ösen-Technik [7]	7
AFS	0,05 ng			Kaltdampftechnik [33]	33
	0,5 ng	Nassveraschung mit Ausblastechnik	Amalgamierung [34, 35]	Kaltdampftechnik [85]	34, 35, 85
NAA	2,3 ng	Nassveraschung nach	Elektrolyt.	Kreislauftechnik	
^{203}Hg	bzw 0,5 ppM	Trägerzusatz	Abscheidung u.a	mit Schlauchpumpe [36]	36
^{197}Hg	keine Angabe	Nassveraschung nach Tragerzusatz	Saulenchromatographie (Kupferdibenzyldithiocarbamidat) [37] (Pd-Schwarz) [38]		37–40
		O_2-Strom	Nach Verdampfung Absorption an Se-Papier [39] oder in Charcoalsaule [40]		
Spektralphotometrie	~1 ppm	Nassaufschluß Pyrolyse	Amalgamierung [41]	Hg-Dithizonat (483 nm)	41
		Nassaufschluß	Saulenchromatographie [42]	Hg-Dithizonat (483 nm)	42
	~1 ppm			1,2-Diketobisthiobenzhydrazon (420 nm) [43]	43
	1,7 ng			Brillant-Grün [44]	44
	~10 ppM			Brillant-Gelb (460 nm) [45]	45
	0,4 ppm			Hg(II)-2-Mercaptobenzoat (264 nm) [46]	46
Fluorimetrie	10 ng/ml			mit Thiamin (440 nm) [47, 48]	47, 48
Katalytisches Verfahren	0,05 ng	wäßrige Losung	Abtrennung von Storelementen	indirekte, jodid-katalysierte Ce(IV)-As(III)-Reaktion (275 nm) Durchflußkuvette [49–51]	49–51
Gaschromatographie	50 ppM	waßrige Lösung	Saule: Äthylenglykoladipinsäurepolyester auf Suprasorb	über C_6H_5HgCl [52]	52
				Detektor ECD	
Elektrische Leitfähigkeitsänderung	50 pg	Nassveraschung	Amalgamierung	Ausblasen, Änderung der Leitfahigkeit von Au-Folie durch Amalgambildung [53]	53
Radio-release	0,25 µg/ml		Anreicherung auf Filterpapier	$^{110m}Ag_2S + Hg^{2+} = HgS + 2\,^{110m}Ag^+$ [54]	54
	1 ng/ml		Extraktion	HgX_2 + 2 Ag-dibuthyldithiocarbamat → Hg-dibuthyldithiocarbamat + 2 AgX [55]	55
Potentiometrisches Verfahren	20 ng/ml			Jodidselektive Elektrode [56]	56

$SnCl_2$ ausgetrieben; Wasserdampf und weitere flüchtige Produkte müssen vor der Anregung des Quecksilbers durch Adsorptions- bzw. Diffusionstechniken abgetrennt werden. Einerseits sind dabei systematische Fehler unvermeidlich, andererseits soll Quecksilber aus wäßrigen Lösungen nicht quantitativ ausgetrieben werden können.[67]

Die im Zusammenhang mit AAS-Bestimmungsverfahren empfohlene Methode, das Quecksilber aus wäßrigen Lösungen an Kupfer[14,70,71] bzw. an Gold[72] zu zementieren bzw. es elektrolytisch abzuscheiden, bringt bei den beschriebenen "statischen" Verfahren, wie eigene radiochemische Untersuchungen mit trägerfreiem ^{203}Hg ergaben, bei Quecksilber-Konzentrationen $\leq$ 10ppM ($M = 10^9$) nur noch schlechte Ausbeuten, die auch durch lange Elektrolysezeiten $\leq$10 h und Rühren mit Ultraschall nicht verbessert werden konnten.

Ebenso ist das Verhältnis von Elektrodenoberfläche zum Lösungsvolumen sehr ungünstig. Bei der beschriebenen Anordnung (vgl. Abb. 1) wird die wäßrige Lösung (max. 10ml) mit einer PTFE-Rotorpumpe mehrmals durch eine gegenüber dur Lösung kathodisch geschaltete, kleine, mit Kupfergaze gefüllte Säule bewegt. Der Vorteil dieser Abscheidungstechnik gegenüber den in der Literatur beschriebenen "statischen" Techniken liegt darin, daß die Kupfernetzsäule ähnlich wie eine Ionenaustauschersäule wirkt. Radiochemische Ausbeutebestimmungen ergaben, daß aus 10 ml einer 0,5*M* salpetersauren Lösung nach nur 5 min $\geq$ 50 pg Hg vollständig abgeschieden werden.

Nach der Quecksilber-Abscheidung wird die Kupfersäule in das Graphit-Töpfchen der spektrometrischen Bestimmungsanordnung (vgl. 8 in Abb. 2) überführt, das Quecksilber in das Argonplasma verdampft, und das emittierte Quecksilber-Licht bei 253,7 nm mit einem üblichen Spektralphotometer intergrierend gemessen.

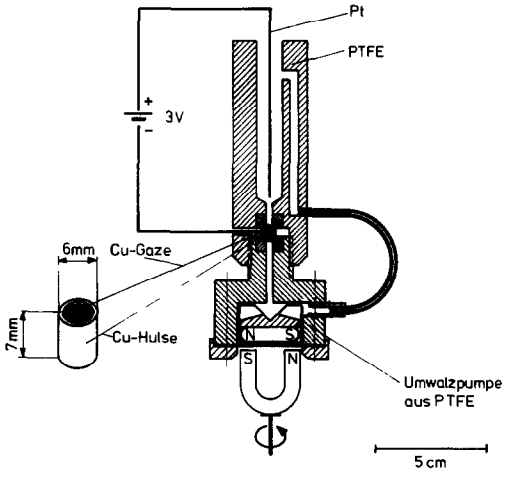

Abb. 1. Elektrolysezelle—elektrolytische Abscheidung von Hg_2^{2+}/Hg^{2+} an einer Kupfernetzsäule.

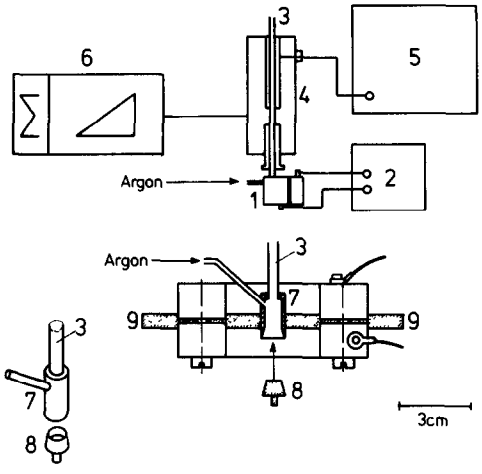

Abb. 2. Anregung von Quecksilberdampf im mikrowelleninduzierten Argon-Plasma zur emissionsspektrometrischen Quecksilberbestimmung. 1—Ofen mit Reaktionsgefäß (Graphit); 2—Regler zu 1; 3—Quarzrohrküvette; 4 Hohlraumresonator; 5—Mikrowellengenerator; 6—Spektrometer (Prisma); 7—Reaktionsgefäß (Graphit); 8–Probentöpfchen (Graphit); 9—Graphitelektroden.

Während bei der praktisch problemlosen spektrometrischen Bestimmung nur Ausheizzeit und Argongasmengenstrom optimiert werden mußten, erforderte die Ausarbeitung des Anreicherungsverfahrens eine genaue Untersuchung der Abhängigkeit der Abscheidung des Quecksilbers von der Umlaufgeschwindigkeit der Lösung sowie von Störeinflüssen durch Komplexbildner wie CN^-, Cl^-, Br^-, J^-, ÄDTE u.a. Auch mußten Störungen durch As(III), Cd(II) und Sb(III), die teilweise mit abgeschieden und verdampft werden, ausgeschlossen werden.

Organische Matrices. Bei solchen mit relativ hohen Mineralstoffanteilen (z.B. Schlamm), schließt man zur Bestimmung des Gesamtquecksilbergehaltes die Probe mit Salpetersäure (65%)–u.U. in Gegenwart von etwas Flußsäure—in einer PTFE-Bombe unter Druck auf.[73] Die durch Verdünnung auf eine Acidität von *ca.* 0,5*M* gebrachte Aufschlußlösung kann unmittelbar elektrolysiert werden. Organische Matrices wie Fleisch, Milchpulver u.a. (geringer Mineralstoffanteil) lassen sich problemlos mit aktiviertem Sauerstoff aufschließen.[74] Die Verbrennungsgase müssen zwei kleine Silber-bzw. Goldnetzsäulen (mit gleicher Dimensionierung wie die Kupfernetzsäule) passieren, die dicht in ein PTFE-Rohr mit Verschraubung eingespannt sind (vgl. Abb. 3). Das Quecksilber wird durch Amalgambildung quantitativ absorbiert. Die Säulen werden anschließend zur Freisetzung und Bestimmung des Quecksilbers direkt in den Graphittiegel des Plasma-Anregungssystems überführt (vgl. 8 in Abb. 2).

Anorganische Matrices. Für die Bestimmung von Quecksilber in Mineralien, Erzen, Gesteinen und Metallen, wird das Quecksilber in einer Verdampfungsapparatur (vgl. Abb. 4) im Trägergasstrom aus den Proben ausgetrieben und in zwei hintereinander-

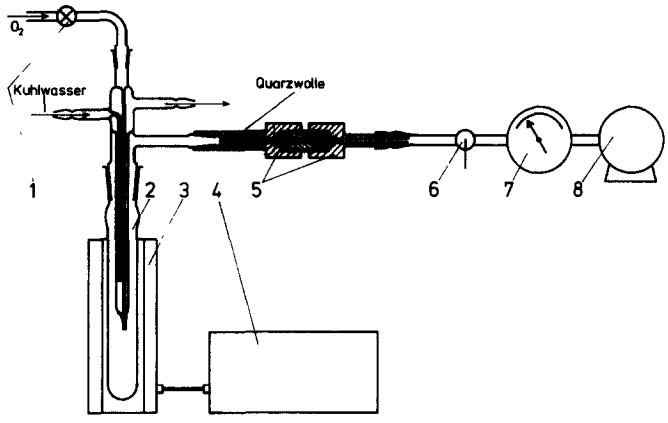

Abb. 3. Aufschluß von biologischen Matrices im mikrowelleninduzierten Sauerstoff-Plasma zur Anreicherung von Quecksilberspuren. 1—Nadelventil; 2—Aufschlußgefäß (Quarz); 3—Mikrowellenresonator; 4—Mikrowellengenerator; 5—PTFE-Halterung für 2 Goldnetzsäulen; 6—Belüftung; 7- Druckmeßgerät; 8—Vakuumpumpe.

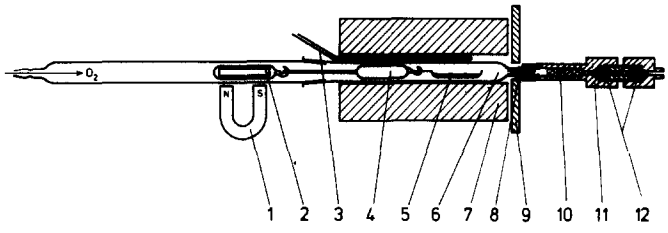

Abb. 4. Anordnung zur Abtrennung von ng- und pg-Mengen Quecksilber von nichtflüchtigen anorganischen Matrices durch Verflüchtigung. 1—Magnet, 2—eingeschmolzener Eisenstab; 3- Thermoelement; 4—Strömungskörper; 5—Probe; 6—Quarzrohr; 7 Ofen; 8—Silberwolle; 9—Asbestplatte; 10—Quarzwolle; 11 PTFE-Halterung für Goldnetzsäulen; 12—Goldnetzsäulen.

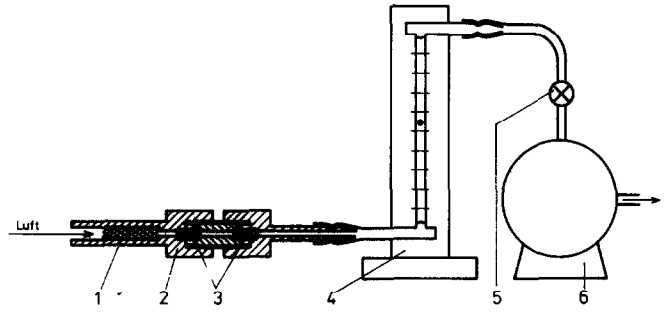

Abb. 5. Anordnung zur Anreicherung von Quecksilberdampf aus Luft und Abgasen. 1—Quarzwolle; 2- PTFE-Halterung für 2 Goldnetzsäulen; 3- Goldnetzsäulen; 4—Rotameter; 5- Nadelventil; 6—Vakuumpumpe.

geschalteten Silber- bzw. Goldnetzsäulen absorbiert.

Luft bzw. Abgase. In diesem Fall saugt man eine abgemessene Gasmenge mit geeigneter Geschwindigkeit durch zwei kleine Silber bzw. Goldnetzsäulen (mit gleicher Dimensionierung wie die Kupfernetzsäule), die in eine PTFE-Verschraubung eingespannt sind (vgl. vorhergehenden Abschnitt und Abb. 5).

In allen Fällen, bei denen das in den Säulen abgeschiedene Quecksilber in das Argonplasma verdampft wird, ist die absolute Nachweisgrenze des spektrometrischen Verfahrens von 0,1 ng ausreichend, um die Allgegenwartskonzentration des Quecksilbers in relativ kleinen Probenmengen (*ca.* 10 ml Wasser, max. 1 g Festsubstanz, 20 l. Luft) sicher und schnell zu bestimmen.

ERLÄUTERUNGEN ZU DEN EINZELNEN TEIL-VERFAHREN

Quecksilberverluste bei der Probennahme und -vorbereitung

Verluste durch Adsorption aus salpetersauren Lösungen. Adsorptionseffekte wurden wegen der Vielzahl der Abhängigkeiten (Zusammensetzung und pH-Wert der Lösung, Gefäßmaterial, chemische Vorbehandlung des Gefäßmaterials u.a.) nur soweit untersucht,

wie es für die Optimierung dieses Verfahrens (Geräte und Gefäße aus PTFE, salpetersaure Lösungen) erforderlich war. In Übereinstimmung mit anderen Autoren[57,58,62] wurde festgestellt, daß die Adsorption am geringsten ist, wenn der pH-Wert der Lösung $\leqslant 0{,}5$ liegt. Eine starke Abhängigkeit besteht außerdem von der chemischen Vorbehandlung der Gefäßmaterialen. Zweistündiges Ausdämpfen mit Salpetersäure (65%) zeigte die besten Ergebnisse (Abb. 6). Die Adsorption ist praktisch vernachlässigbar, wenn der Probenlösung *ca.* 0,1 mg/ml Kaliumcyanid bzw. Natriumbromid bzw. Kaliumjodid bzw. ÄDTE zugesetzt und sie nicht länger als 3 Tage aufbewahrt wird (Abb. 7). Die Wirkung von ÄDTE entspricht in saurer Lösung nicht derjenigen der anderen Komplexbildner.

Verluste durch Verflüchtigung. Die Quecksilberverluste durch Verflüchtigung aus salpetersauren Lösungen bei der Aufbewahrung in unverschlossenen Behältern hängen u.a. von der Zusammensetzung, vom pH-Wert und von der Temperatur der Lösung, vom Gefäßmaterial und von der Vorbehandlung des Gefäßmaterials ab.[58–61,63–65] Setzt man der zu untersuchenden 0,5*M* salpetersauren Lösung z.B. *ca.* 0,1 mg/ml Kaliumcyanid bzw. Natriumbromid bzw. Kaliumjodid zu, so sind die Verluste durch Verflüchtigung praktisch zu vernachlässigen (Abb. 8).

Probenvorbereitung

Wäßrige Lösungen. Um Verluste durch Adsorption und Verflüchtigung zu vermeiden (vgl. Abschn. oben) stellt man die Analysenlösung schon bei der Probennahme mit Salpetersäure (65%) auf eine Acidität von *ca.* 0,5*M* ein und fügt *ca.* 0,1 mg Kaliumjodid/ml zu.

Feststoffe. Sie sind im allgemeinen zu homogenisieren. Mix-bzw. Homogenisiergeräte dürfen nur verwendet werden, wenn Mischkammer und Schneide- bzw. Zerkleinerungswerkzeuge nicht aus Metall sind,

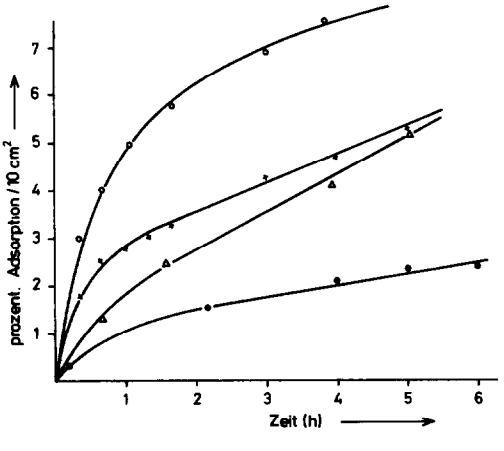

Abb. 6. Adsorption von Quecksilber aus wäßrigen Lösungen (0,5*M* HNO_3, 2 ppM $^{203}Hg^{2+}$) an PTFE und Fiolax-Glas. ○: Fiolax-Glas, mit 1*M* HNO_3 gespült; ×: PTFE, mit 1*M* HNO_3 gespült; △: Fiolax-Glas, mit HNO_3 (65%) ausgedämpft; ●: PTFE, mit HNO_3 (65%) ausgedämpft.

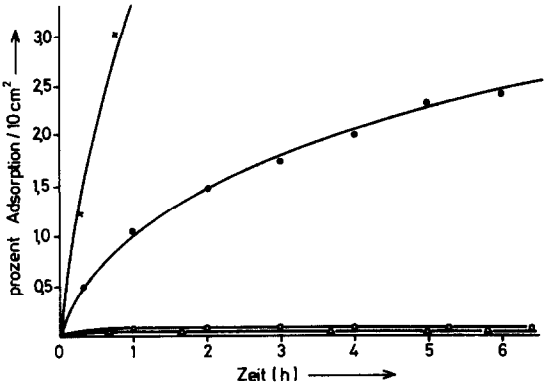

Abb. 7. Adsorption von Quecksilber aus wäßrigen Lösungen mit und ohne Zusatz von Komplexbildnern (0,5*M* HNO_3, 2 ppM $^{203}Hg^{2+}$) an PTFE und Fiolax-Glas. ×: Fiolax-Glas, ohne Zusatz; ●: PTFE, ohne Zusatz; ○: Fiolax-Glas, Zusatz: 0,1 mg/ml KJ; △: PTFE, Zusatz: 0,1 mg/ml KJ.

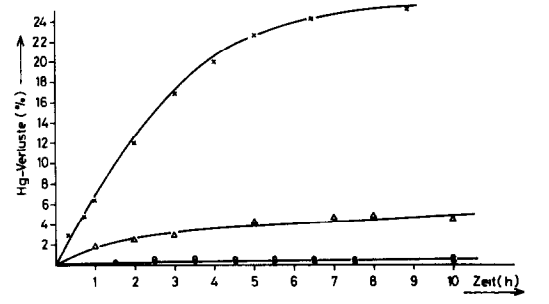

Abb. 8. Verflüchtigung von Quecksilber aus wäßrigen Lösungen (0,5*M* HNO_3, 2 ppM $^{203}Hg^{2+}$, PTFE-Gefäß 1,5 cm^2 Flüssigkeitsoberfläche ohne Bewegung, 20°C. ×: 0,5*M* HNO_3; △: Flußwasser; ○: 0,5*M* HNO_3 (Zusatz: 0,1 mg/ml KJ bzw. KBr bzw. KCN); ●: Flußwasser (Zusatz: 0,1 mg/ml KJ bzw. KBr bzw. KCN).

da sonst in Gegenwart von Elektrolyten (z.B. Natriumchlorid) Verluste durch Zementierung und Amalgambildung auftreten können. Die geringsten Verluste treten auf, wenn die durch flüssigen Stickstoff tief gefrorene Probe zerkleinert wird.

In manchen Laboratorien ist—abhängig von der Vorgeschichte des Laboratoriums—die Allgegenwartskonzentration des Quecksilbers meist relativ hoch. Es konnte nachgewiesen werden, daß Geräteteile (z.B. Glas, Quarz, PTFE) Blindwerte bis zu 5 ng/20 cm^2 aufweisen, wenn sie einen Tag normaler Laboratoriumsluft ausgesetzt sind (Quecksilberanreicherung im Staub). Erst in einem Reinstraum war ein "blindwertfreies" Arbeiten möglich. Deshalb muß z.B. bei der üblichen Kaltdampftechnik das Trägergas unbedingt speziell gereinigt werden, wenn sehr niedrige Gehalte bestimmt werden sollen.

Aufschlußtechniken

Druckaufschluß. Für die Bestimmung von Quecksilber in den verschiedensten Wässern ist ein Aufschluß meistens nicht notwendig. Sie können direkt nach Zusatz von Salpetersäure (65%) bis zu einer

Acidität von *ca.* 0,5*M* und eventuell von Komplexbildnern (z.B. Kaliumjodid oder Natriumbromid) nach Zentrifugieren elektrolysiert werden. Handelt es sich jedoch um stark verschmutzte Wässer, wie z.B. Industrieabwässer, muß damit gerechnet werden, daß das Quecksilber komplex gebunden (z.B. als Methyl- oder Phenylverbindung) bzw. in schwerlöslicher Form (z.B. HgS, HgSe) vorliegt. Diese Verbindungen lassen sich leicht mit Salpetersäure unter Druck zerlegen.[73] Generell lassen sich Methyl- bzw. Phenyl-Quecksilberverbindungen auch elektrolytisch abscheiden (Abb. 9), die Abscheidungszeit vergrößert sich dann jedoch gegenüber einer Standardlösung erheblich.

Biologische Matrices, wie Blut, Fisch, Milchpulver u.a., und solche mit höherem Mineralstoffanteil (z.B. Schlämme) lassen sich problemlos mit gereinigter Salpetersäure (65%), gegebenenfalls unter Zusatz von etwas gereinigter Flußsäure (40%), in einem Teflongefäß unter Druck aufschließen.[73] Nach dem Aufschluß wird die saure Aufschlußlösung mit bidest. Wasser auf eine Acidität von *ca.* 0.5*M* verdünnt und zur Abscheidung des Quecksilbers in die Elektrolysezelle überführt (vgl. Abb. 1).

Aufschluß im Sauerstoff-Plasma. Bei der Bestimmung von Quecksilber ist für die meisten biologischen Matrices auch für Kohle und Teer, wegen geringerer systematischer Fehler der Aufschluß mit im Mikrowellenfeld aktiviertem Sauerstoff[74] dem Druckaufschluß vorzuziehen.

Zwei Silbersäulen (Dimensionierung wie die Kupfernetzsäule), die mit Silberwolle oder engmaschigem Golddrahtgewebe dicht ausgefüllt sind, befinden sich in einer PTFE-Halterung mit Verschraubung, die mit einem Schliff unmittelbar an das Quarzaufschlußgefäß adaptiert ist (Abb. 3).

Für den Aufschluß eiweißhaltiger Matrices (z.B. Fisch, Fleisch, Milchpulver) ist in diesem Fall Gold als Absorptionsmaterial besser geeignet, weil die beim Aufschluß entstehenden Schwefelverbindungen die Silberoberfläche relativ rasch blockieren (Sulfid- bzw. Sulfitbildung). Die Verbrennungsgase werden

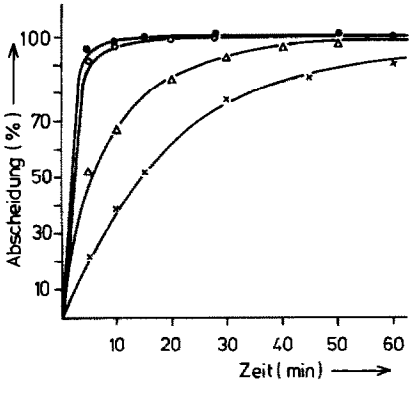

Abb. 9. Elektrolytische Abscheidung von Hg_2^{2+}, Hg^{2+} aus wäßrigen Lösungen (0,5*M* HNO_3, 2 ppM $^{203}Hg^{2+}$). ×: Abwasser; △: 0,5*M* HNO_3 (Zusatz: $C_6H_5{}^{203}HgCl$); ○: Abwasser nach Druckaufschluß; ●: Leitungswasser bzw. bidest. Wasser.

Tabelle 2. Verteilung von Quecksilber in den Absorptionssäulen beim Aufschluß von organischen Matrices im mikrowellen induzierten Sauerstoff-Plasma

Matrix	^{203}Hg zudosiert, *ng*	Quecksilber-Anteil in den Absorptionssäulen, % 1. Säule	2. Säule	3. Säule	4. Säule
Filterpapier 0,1 g	10	99	0,5	—	—
Bodenprobe 0,5 g	10	98,5	1	—	—
Bodenprobe 0,5 g + 0,5 mg Na_2S	10	99	1	—	—
Bodenprobe 0,5 g + 0,5 mg Na_2S + 0,5 mg Na_2SeO_3	1,0	99,5	0,5	—	—
Milchpulver 0,48 g	10	98,5	1	—	—
Mehl 0,54 g	10	98	1.5	—	—

während des Aufschlusses ständig durch die mit Absorptionsmaterial gefüllten Säulen abgesaugt. Man darf die Probe nicht zu schnell aufschließen, sonst können teerartige Pyrolyseprodukte auf das Absorptionsmaterial aufziehen und verhindern, daß das Quecksilber quantitativ in der ersten Säule absorbiert wird. Um zu kontrollieren, ob mit dieser Aufschlußtechnik das gesamte Quecksilber auch in Proben (z.B. Bodenproben) mit höherem Schwefel- und Selenanteil (HgS und HgSe) erfaßt und quantitativ in der Säule absorbiert wird, wurden 10 ng ^{203}Hg und eine 5000-fache Menge an Natriumsulfid und -selenit zu verschiedenen Matrices dosiert, die Proben 8 Tage unter Verschluß stehen gelassen und anschließend aufgeschlossen (vgl. Tab. 2). Die radiochemischen Untersuchungen ergaben, daß zwischen 97% und 99% des Quecksilbers in der ersten Säule abgeschieden wurden. Das Hintereinanderschalten von zwei Säulen ist auf jeden Fall zu empfehlen, um sicher zu sein, daß das gesamte Quecksilber festgehalten wird.

Verdampfung des Quecksilbers im Rohrofen. Aus anorganischen Probenmaterialien, vor allem aus Metallen aber auch aus Gesteinen und Erzen (hier eventuell Zuschläge erforderlich), kann das Quecksilber leicht in einer Verdampfungsapparatur bei max. 1100° ausgetrieben werden (vgl. Abb. 4). Die Absorptionssäulen sind in einer PTFE-Halterung mit Verschraubung eingespannt und mit einem Quarzrohr durch einen Schliff eng verbunden.

Die Probe (Einwaage je nach Matrix 0,5–3 g) wird in einem mit einem Weicheisenkern verbundenen Keramik- bzw. Platin-Schiffchen (8 × 53 × 6 mm) mit Hilfe eines Magnetes in den Verbrennungsofen eingeführt. Das verdampfte Quecksilber wird in den Absorptionssäulen angereichert und zur Bestimmung anschließend in den Graphittiegel des Plasma-Anregungssystems überführt (vgl. 8 in Abb. 2).

Vorbehandlung der Kupfer-, Silber- und Goldnetzsäulen

Kupfernetzsäule. Die Oberfläche des Kupfers muß oxidfrei sein, damit eine schnelle und quantitative Quecksilber-Abscheidung im pg-Bereich möglich ist.

Vor jeder Bestimmung saugt man deshalb *ca.* 7*M* Salpetersäure durch die mit engmaschigem Kupfernetz (1000 Maschen/cm^2) dicht gepackte Kupfernetzsäule. Dieses Abätzen wird in der Elektrolysezelle durchgeführt. Ein eventuell eingebrachter Blindwert läßt sich leicht durch kurzes Umschalten der Kupfersäule auf Anode mit einer Hilfselektrode aus Platin entfernen. Diese so gereinigte Kupfersäule dient unmittelbar zur kathodischen Abscheidung von Quecksilber aus der Analysenlösung.

Silber- bzw. Gold-Netzsäule. Quecksilber aus biologischen Matrices nach Aufschluß mit aktiviertem Sauerstoff und aus Luft absorbiert man mit einer Silbersäule, die mit Silberwolle oder mit engmaschigem Goldnetz gefüllt ist. Vor jeder Bestimmung muß durch die Silbersäule Salpetersäure (30%), sofern die Silberwolle durch Sulfid inaktiviert wurde, Salpetersäure (65%) oder konzentrierte Kaliumcyanid-Lösung gesaugt werden, um die Oberfläche wieder zu aktivieren. Man spült anschließend mit bidest. Wasser und glüht bei *ca.* 500° im Argonstrom "blindwertfrei". Bei Verwendung einer mit Goldnetz gefüllten Säule genügt Ausglühen bei *ca.* 500°.

Elektrolytische Abscheidung

Elektrolysezelle. Die elektrolytische Abscheidung von Quecksilber aus wäßrigen Lösungen erfolgt am besten aus salpetersaurer Lösung im Konzentrationsbereich von 0,1–1,5*M*.[14,36,71]

In der 10-ml-Elektrolysezelle aus PTFE (vgl. Abb. 1) bewegt der spezielle PTFE-Rotor mit eingesetztem Stabmagnet (Antrieb durch angekoppelten Rührmagneten) die Lösung ständig im Kreislaufsystem durch die als Kathode geschaltete Kupfernetzsäule. Der Lösungsdurchsatz hängt davon ab, wie dicht die Kupfersäule mit Kupfernetz ausgefüllt ist; er läßt sich jedoch leicht mit dem regelbaren Rührmagneten auf den optimalen Wert von ca. 6 l./h einstellen. Gegenelektrode ist eine Platin-Drahtelektrode in der Lösung. Die Elektrodenspannung wurde bei allen Abscheidungsversuchen mit einem Potentiostaten auf 3 V (Stromfluß zwischen 5 und 20 mA) eingestellt. Die Elektrolysezeiten für eine quantitative Quecksilberabscheidung sind Abb. 9 zu entnehmen.

Wie radiochemische Untersuchungen zeigten, muß bei Quecksilber-Konzentrationen von *ca.* 2 ppM bei Verwendung von normalem PTFE mit einigen Prozent Adsorptionsverlust durch die PTFE-Oberfläche (50 cm^2) gerechnet werden; er kann jedoch beträchtlich verringert werden, wenn die gesamte Anordnung aus leitfähigem Graphit-PTFE hergestellt und gegenüber der Lösung positiv geschaltet wird. Genaue Aussagen über das Ausmaß der Adsorptionsverminderung können noch nicht gemacht werden, da es stark von der jeweiligen mechanischen und chemischen Vorbehandlung der Oberfläche abhängt und für die Klärung noch umfangreiche Untersuchungen erforderlich sind.

Einfluß von Begleitstoffen bei der elektrolytischen Abscheidung. Die Quecksilberabscheidung aus saurer Aufschlußlösung kann—je nach Matrix—durch unterschiedlich große Mengen von Fremdkationen sowie Komplexbildnern wie CN^-, Cl^-, Br^-, J^-, ÄDTE u.a., beeinflußt werden. Es konnte jedoch radiochemisch nachgewiesen werden, daß diese Begleitstoffe bis zu einer Konzentration von 0,1 mg/ml die Abscheidung von 10 ng Quecksilber pro 10 ml nicht stören (vgl. Abb. 10).

Abscheidung von Quecksilberdampf aus Luft bzw. Abgasen. Zwei kleine Silbersäulen (gleiche Dimensionierung wie die Kupfersäule) werden in eine PTFE-Verschraubung (vgl. Abb. 5) dicht eingespannt und durch einen Polyäthylen-Schlauch mit einem Rotameter, einem Nadelventil und einer Membranpumpe verbunden. Bei Industrieabgasen verwendet man anstelle der Silberfüllung Golddrahtgewebe als Absorptionsmaterial um Störungen durch z.B. Schwefelwasserstoff und Schwefeldioxid auszuschalten. Die Konzentration des Quecksilbers liegt in atmosphärischer Luft (unbesiedelte Gebiete) zwischen 1 und 0,05 ppM[75,76] in solcher industrialisierter Gebiete ist sie jedoch wesentlich höher. Bei einer Nachweisgrenze des Verfahrens von 0,1 ng absolut und einem angenommenen Durchschnittswert von 0,05 ppM Quecksilber in Luft reichen 10 Nl Luft aus, um ein auswertbares Signal zu erhalten.

Die hier beschriebene Technik erfaßt nur Quecksilberdampf. Quecksilberverbindungen (z.B. metallorganische Quecksilberverbindungen) müssen in einem vorgeschalteten Kontaktofen verbrannt werden. Da für eine quantitative Umsetzung zu Silber- bzw. Goldamalgam die Verweilzeit des Quecksilbers in der Absorptionssäule ausschlaggebend ist, mußte der Mengenstrom des Analysengases optimiert werden. Durch Hintereinanderschalten von vier Säulen konnte festgestellt werden, daß bei einer Saugeschwindigkeit von 5 Nl/h der Quecksilberdampf der Laboratoriumsluft praktisch vollständig in der ersten Säule absorbiert wird. In der 2. Säule befanden sich nur noch 0,5–1%. Doch auch hier ist es ratsam, mit

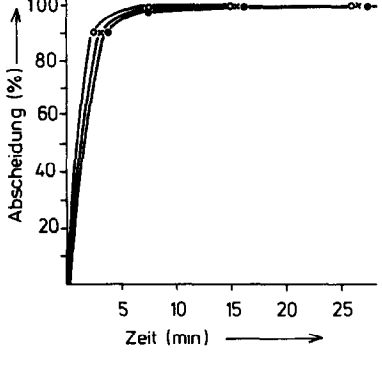

Abb. 10. Elektrolytische Abscheidung von Hg_2^{2+}/Hg^{2+} aus wäßrigen Lösungen mit Zusatz von Komplexbildnern und Fremdkationen (0,5*M* HNO_3, 2 ppM $^{203}Hg^{2+}$). ○: Zusatz je 0,1 mg/ml J^-, Br^-, CN^-; ●: Zusatz je 0,1 mg/ml Fe^{3+}, As^{3+}, Se^{4+}, Sb^{3+}; ×: Zusatz je 0,1 mg/ml Fe^{3+}, As^{3+}, J^-, CN^-.

2 Säulen zu arbeiten, um eventuelle Mängel, verursacht durch Reinigung und Ausheizen, rechtzeitig erkennen zu können.

Vor jeder Bestimmung muß die Silber- bzw. Goldfüllung "blindwertfrei" gemacht werden (vgl. Abschn. *Vorbehandlung der Silber- und Goldnetzsäule*). Andere Techniken, die Silber oder Gold in Draht oder Plättchenform oder auch als Graphittiegelüberzug zur Anreicherung von Quecksilberdampf aus verschieden gasförmigen Matrices verwenden,[18,19,77–79] müssen, da immer nur kleine Oberflächen vorliegen, mehrere hintereinandergeschaltete Absorptionsfallen einsetzen, wobei systematische Fehler nur schwer auszuschließen sind.

Emissionsspektrometrische Bestimmung des Quecksilbers

Nach Abscheidung in der Kupfernetzsäule. Nach der Elektrolyse wird die Kupfernetzsäule in der Elektrolysezelle zunächst mit bidest. Wasser und dann mit dest. Aceton gespült. Diese Spülflüssigkeiten müssen wieder vollständig aus der Säule entfernt werden, da sie die Anregung des Quecksilbers beeinflussen oder sogar das Plasma löschen. Man heizt die Kupfersäule im Graphittiegel des Plasma-Anregungssystems (vgl. 8 in Abb. 2) im Argonstrom bei 50° (1 min) aus. Wie radiochemische Untersuchungen ergaben, tritt beim Spül- und Trocknungsprozeß ein Quecksilberverlust von 2–3% auf. Durch rasches Erhöhen der Temperatur auf *ca.* 500° wird anschließend das Quecksilber nahezu schlagartig verdampft und mit dem Argonstrom ins Plasma überführt. Zum Aufheizen des Graphit-Reaktionsgefäßes wird ein Regelgerät (Temperatur- und Zeitprogrammierung) verwendet. Es kann aber auch ein regelbarer Trafo (prim. 220 V, 5A, sek. 10 V, 100 A) benützt werden.

Das Argon-Plasma wird bei Normaldruck durch ein Mikrowellenfeld induziert (3/4λ Resonator durch ein Koaxialkabel mit einem Mikrowellengenerator verbunden) und in einem alkaliarmen Quarzrohr (i.D. $1 \pm 0{,}1$ mm, ä.D. $4{,}3 \pm 0{,}1$ mm) geführt. Ein Argongasmengenstrom von *ca.* 100 ml/min hat sich für diesen Rohrdurchmesser als günstig erwiesen. Bei kleineren Gasmengenströmen ist das Plasma instabil, bei größeren ist es zwar stabil und verkraftet kleine Wasserdampfmengen, aber das Nachweisvermögen wird geringer. Das vom Plasma emittierte Quecksilberlicht wird mit einer Quarzlinse auf den Eintrittsspalt des Monochromators fokussiert und bei 253,7 nm gemessen und über einen Schreiber mit angeschlossenem Integrator ausgewertet. Diese Auswertung über die Peakfläche ist notwendig, da die Säulen nicht alle gleichmäßig dicht gepackt werden können und somit die Ausheizcharakteristik von Säule zu Säule variiert, was sich in unterschiedlichen Peakformen ausdrückt.

Das Plasma-Anregungssystem: Resonator, Ofenanordnung (bestehend aus Graphitreaktionsgefäß, Graphitelektroden und Aluminiumhalterung) und Quarzrohr (vgl. Abb. 2) ist an einen Präzisions-Koordinatentisch montiert. Dadurch ist eine exakte Abbildung des Plasmafadens auf den Eintrittsspalt des Monochromators möglich. Die gesamte Anordnung (Spektralphotometer und Plasma-Anregungssystem) ist auf einer optischen Bank aufgebaut.

Nach Abscheidung in Silber- und Goldnetzsäulen. Die Säulen können zur Verdampfung und Bestimmung des aus Luft bzw. Abgasen und aus Verbrennungsgasen (organische Substanzen) angereicherten Quecksilbers ohne weitere Vorbehandlung in den Graphittiegel des Plasma-Anregungssystems (8 in Abb. 2) überführt werden.

EXPERIMENTELLER TEIL

Geräte

Druckaufschlußapparatur. PTFE-Gefäß (Länge: 83,5 mm, i.D. 13,5 mm, ä.D. 24 mm) in Edelstahlbombe mit Heizblock und elektronischer Temperaturregelung*.[73]

Mikrowellenaufschlußapparatur. Mikrowellengenerator Typ Mikrotron 200† (Leistung: 200 W); Resonator Type 210 L†; Aufschlußgefäß aus Quarz‡; Vakuumpumpe (*ca.* 1 Torr); Golddrahtgewebe (1024 Maschen pro cm^2, 90% Au, 10% Pt), Firma Heraeus, Hanau, D.B.R. Silberwolle zur Elementaranalyse, Firma E. Merck AG, Darmstadt, D.B.R. Silbersäulen (Länge: 6 mm, i.D. 4,5 mm, ä.D. 6 mm), hergestellt aus Silberrohr (99,99% Ag).

Verdampfungsapparatur. Rohrofen Typ BR 1,8/25 (42 V, 10,7 A) mit Steuer- und Temperaturanzeigegerät, Firma Heraeus; Keramik-Schiffchen (Pythagoras 8 × 53 × 6 mm) Firma Haldenwanger, Berlin-West; 2 Quarzrohre (Suprasil, Länge 400 mm, ä.D. 13 mm), Firma Heraeus Schott Quarzschmelze GmbH, Hanau. PTFE-Verschraubung (Eigenanfertigung, Länge *ca.* 80 mm, i.D. *ca.* 3,5 mm, ä.D. *ca.* 25 mm, vgl. Abb. 4).

Homogenisiergerät. Typ Virtis 23, Firma The Virtis Company, Inc., Gardiner, New York, PTFE-Mischgefäße (Eigenanfertigung).

Elektrolysezelle und Zubehör. Elektrolysezelle* (vgl. Abb. 1); Kupfersäulen (Länge: 6 mm, i.D. 4,5 mm, ä.D. 6 mm) hergestellt aus Kupferrohr (99,99% Cu); Kupferdrahtgewebe (1000 Maschen pro cm^2), Firma Heraeus; Platindraht (0,5 mm Durchmesser, Länge 100 mm); Potentiostat, Firma Jaissle, Neustadt/Rems, D.B.R.

Plasma-Anregungssystem und Spektralphotometer. Mikrowellengenerator Typ Mikrotron 200†; Resonator, Typ 210 L†; Quarzrohr (Suprasil, Länge: *ca.* 30 mm, i.D. $1 \pm 0{,}1$ mm, ä.D. $4{,}3 \pm 0{,}2$ mm) Firma Heraeus Schott Quarzschmelze GmbH; Kleinstströmungsmesser (1,6–16 Nl Argon/h), Firma Krohne, Duisburg, D.B.R.; Ofenanordnung mit Graphitelektroden und Graphitreaktionsgefäß (Eigenanfertigung, an Varian–Techtron Atomabsorptionsspektrophotometer, Modell AA 5 adaptierbar, vgl. Abb. 2). Graphitelektroden (Länge: *ca.* 60 mm, Durchmesser 6 mm) und Graphitreaktionsgefäß (Länge: 20 mm, i.D. *ca.* 7 mm, ä.D. 10 mm, vgl. Abb. 2) wurden aus Graphitstäben Typ EK 576 bzw. 506 (Durchmesser 10 mm), Firma Ringsdorff Werke, Bonn–Bad Godesberg, D.B.R., hergestellt; Präzisions-Koordinatentisch, Firma Hahn und Kolb, Stuttgart, D.B.R.; Regelbares Versorgungsteil für Ofenanordnung (Eigenanfertigung, Trafo: prim. 220 V, 5 A,

* Forschungsinstitut Berghof, Tübingen, D.B.R.

† Firma Elektromedical Supplies, London. Ähnliche Geräte und Resonatoren stellt die Fa. Erbe-Elektromedizin, Tübingen, D.B.R. her.

‡ Glastechnische Werkstätte W. K. Becher OHG, Mainz, D.B.R.

sek. 10 V 100 A); Spektralphotometer (Prismenmonochromator M 4 Q III. Empfängergehäuse mit Photomultiplier, Anzeigegerät PMQ II) Firma Zeiss, Oberkochen, D.B.R.; Quarzlinse ($f = 50$ mm); Optische Bank (Länge: 1 m) Kompensationsschreiber Typ BD 5 (Meßbereich 0,1 V 20 μV), Firma Kipp und Zonen, Delft, Niederlande; Digital-Integrator, Typ Autolab 6300 (Spannungsbereich 0–1000 mV, linearer dynamischer Bereich 10, Empfindlichkeit 1000 Imp./mV-sec, Auflösung 1 μV-sec), Firma Spektra Physics, Santa Clara, U.S.A.

Reagenzien

Aufschlußsäuren. Salpetersäure (*ca.* 65%) hergestellt durch Destillation unterhalb des Siedepunkts;[80] Flußsäure (*ca.* 40%) in einer PTFE-Apparatur unterhalb des Siedepunkts destilliert.

Aceton. Dreimal über eine Füllkörperkolonne destilliert.

Gase. Argon (99,998%); unreineres Gas muß mit Molekularsieb (5 Å) Firma E. Merck AG, und mit Oxisorb [Chrom(III)oxid auf Kieselgel], Firma Messer—Griesheim GmbH, Düsseldorf, D.B.R., gereinigt werden; Sauerstoff (99,99%). Um Quecksilber aus den Gasen zu entfernen, werden sie zuerst durch einen Verbrennungsofen (600°, Silberkontakt) geleitet und das Quecksilber anschließend bei Zimmertemperatur an Silberwolle abgeschieden.

Kaliumjodid, p.a. Firma E. Merck AG. Durch Erhitzen auf 600° "quecksilberblindwertfrei" gemacht.

Quecksilberstandardlösung. Quecksilber (0,100 g) wird in einem 500-ml Quarzmeßkolben in 17 ml Salpetersäure (65%) gelöst und mit bidest. Wasser aufgefüllt. Die Lösung wird mit *ca.* 2,5 g Kaliumjodid versetzt und in einem PTFE-Gefäß aufbewahrt. Verdünntere Lösungen werden unmittelbar vor Gebrauch aus dieser Lösung hergestellt.

^{203}Hg-Standardlösung. Mit $^{203}Hg(NO_3)_2$ spezifische Aktivität 11,1 mCi/mg und 0,5*M* Salpetersäure werden Standardlösungen hergestellt mit Gehalten von 9 ng ^{203}Hg/5 μl (0,1 μCi/5 μl) und 0,9 ng ^{203}Hg/5 μl (0,01 μCi/5 μl).

Eichung des Verfahrens

Zementierung im Kupfertiegel. Es wurden 0,5–20 μl der Quecksilberstandardlösung (1,6 ng Hg/μl) mit einer Mikrobürette (System Spinco, Beckman Instruments) direkt in einen verkupferten Graphittiegel (vgl. 8 in Abb. 2) dosiert und das durch Zementierung abgeschiedene Quecksilber ins Plasma verdampft.

Elektrolytische Abscheidung. Aus Quecksilber-Standardlösungen (1,6 ng/10 ml–32 ng/10 ml) wurde das Quecksilber in der Kupfernetzsäule elektrolytisch abgeschieden.

Mikrowellen-Plasmaaufschluß. Es wurden 0,5–20 μl der Quecksilberstandardlösung (1,6 ng/μl) mit einer Mikrobürette, auf Filterpapier (*ca.* 50 mg) dosiert und im Sauerstoffplasma verbrannt.

Der Verlauf der nach diesen Techniken ermittelten Eichkurven folgt im untersuchten Bereich von 0,5–30 ng der linearen Funktion $y = ax + b$ wo a und b folgende Werte annehmen: $a = 0{,}85$, $b = 0{,}2$ (Reagenzienblindwert) bei den Eichkurven ermittelt durch Zementierung im verkupferten Graphittiegel bzw. durch Amalgamierung in der Silber bzw. Goldnetzsäule; $a = 0{,}85$, $b = 0{,}5$ bei der Eichkurve ermittelt durch elektrolytische Abscheidung in der Kupfernetzsäule (1 Einheit—1 cm—auf der Abszisse entspricht 1 ng Hg, 1 Einheit—1 cm—auf der Ordinate entspricht 100 Integrationseinheiten). Die relative Standardabweichung liegt bei allen drei Eichgeraden im 1-ng Bereich bei 5% und 10-ng Bereich bei 4%.

Durchführung des Verfahrens für Wasser, biologische und anorganische Matrices und Luft

Wasser (ohne Aufschluß). Vor der elektrolytischen Abscheidung des Quecksilbers wird die Kupferkathode "blindwertfrei" gemacht (vgl. Abschnitt: *Vorbehandlung der Kupfernetzsäule*). Von der Analysenlösung (mit gereinigter Salpetersäure (65%) auf *ca.* 0,5*M* Acidität eingestellt) werden 10 ml in die Elektrolysezelle überführt und 5 min bei einer Elektrodenspannung von 3 V elektrolysiert. Anschließend wird die Kupfernetzsäule in der Elektrolysezelle zuerst mit *ca.* 10 ml bidest. Wasser und dann dreimal mit je 5 ml dest. Aceton gespült und in den Graphittiegel des Plasma-Anregungssystems überführt (vgl. 8 in Abb. 2). Man trocknet *ca.* 2 min im Argonstrom bei 50° und verdampft das Quecksilber durch Erhöhen der Ofentemperatur auf *ca.* 500°. Das Meßergebnis wird digital ausgedruckt.

Abwasser und biologische Matrices nach dem Druckaufschluß. Je nach Verschmutzungsgrad werden 2–3 ml Analysenlösung mit 1 ml gereinigter Salpetersäure (65%) versetzt und in der PTFE-Druckbombe 1 h lang auf 150° erhitzt.[73]

Biologische Matrices werden, sofern notwendig, vor der Analyse in einem PTFE-Behälter mit flüssigem Stickstoff tief gekühlt, homogenisiert und gegebenenfalls gefriergetrocknet. Je nach Matrix werden zwischen 300 und 500 mg Trockensubstanz mit 1 ml gereinigter Salpetersäure (65%) und bei hohem Mineralanteil mit *ca.* 0,5 ml gereinigter Flußsäure (40%) versetzt und 1–1,5 h bei 150° in der PTFE-Bombe aufgeschlossen.

Die Aufschlußlösung wird mit bidest. Wasser bis zu einer Acidität von 0,5–1,5*M* verdünnt (Vol. max. 10 ml), in die Elektrolysezelle überführt und 5 min bei einem Potential von 3 V elektrolysiert. Die Kupfernetzsäule wird danach wie im vorhergehenden Abschnitt beschrieben weiterbehandelt und zur Bestimmung des Quecksilbers ins Plasma-Anregungssystem überführt.

Biologische Matrices mit Aufschluß im Sauerstoffplasma. Zwei "blindwertfreie" Absorptionssäulen (vgl. Abschnitt: *Vorbehandlung der Absorptionssäulen*) werden in die PTFE-Verschraubung eingesetzt und mit der Aufschlußapparatur verbunden (Abb. 3). Die homogenisierte und gegegebenenfalls gefriergetrocknete Probe (Einwaage 0,5–1 g) wird im Sauerstoffplasma aufgeschlossen. Nach dem Aufschluß (die Aufschlußdauer ist matrixabhängig) werden die Absorptionssäulen zur Bestimmung des Quecksilbers direkt in den Graphittiegel des Plasma-Anregungssystems (vgl. 8 in Abb. 2) überführt.

Anorganische Matrices. Zwei "blindwertfreie" Gold-Absorptionssäulen (vgl. Abschn. *Vorbehandlung der Absorptionssäulen*) werden in die PTFE-Verschraubung eingesetzt und mit der Verdampfungsapparatur verbunden (vgl. Abb. 4). Die Probe (Einwaage je nach Matrix 0,5–3 g) wird im Keramik- bzw. Platinschiffchen mit Hilfe der magnetischen Kopplung in den Verbrennungsofen eingeführt und das ausgetriebene Quecksilber in den Absorptionssäulen festgehalten. Die Säulen werden anschließend zur Bestimmung des Quecksilbers in den Graphittiegel des Plasma-Anregungssystems (vgl. 8 in Abb. 2) überführt.

Luft und Abgase. Zwei aktivierte und "blindwertfreie" Absorptionssäulen (vgl. Abschn. *Vorbehandlung der Absorptionssäulen*) werden in die PTFE-Verschraubung eingesetzt und mit der Membranpumpe und dem Kleinstströmungsmesser verbunden (vgl. Abb. 5). Je nach Verunreinigungsgrad werden zwischen 10 und 50 Nl (Gasmengenstrom 5 Nl/h) des zu untersuchenden Gases durch die Säulen gesaugt, die anschließend zur Bestimmung des Quecksilbers in den Graphittiegel des Plasma-Anregungssystems (vgl. 8 in Abb. 2) überführt werden.

ERGEBNISSE UND DISKUSSION

Das beschriebene Verfahren erlaubt die Bestimmung von Quecksilber in Wässern (z.B. Trinkwasser, Flußwasser, Abwasser), in organischen Matrices (z.B. Fleisch, Fisch, Milchpulver oder Schlamm und Bodenproben), in anorganischen Matrices (z.B. Metallen, Erzen, Gesteinen). Die Nachweisgrenze des

Tabelle 3. Bestimmung von Quecksilber in einigen Wasserproben

Wasserprobe 10 ml	^{203}Hg zudosiert, ng	ng	Quecksilbergefunden, $V\%(n = 10)$†
Leitungswasser	—	<0,1	
Leitungswasser	5,0	4,9	±5,2
Flußwasser*			
(Rems)	—	1,0	±6,9
(Rems)	5,0	6,2	±4,9
Abwasser*			
(Kläranlage)	—	0,5	±9,1
(Kläranlage)	5,0	5,4	±4,8

* Nach Druckaufschluß mit Salpetersäure.
† Relative Standardabweichung.

Tabelle 4. Bestimmung von Quecksilber in einigen biologischen Matrices

Matrix	Matrix-Einwaage, mg	^{203}Hg zudosiert, ng	Quecksilber-gefunden, ng	$V\%(n = 10)$‡
Magermilchpulver	480	—	0,5	±4,9
Magermilchpulver	400	10	9,8	±5,1
Magermilchpulver	400	3,3	3,4	±5,2
Mehl	543	—	1,3	±5,3
Mehl	410	10	10,2	±5,4
Bodenprobe (4361)*	209	—	11,5	±4,2
(4361)*	92	7	11,8	±4,1
Bodenprobe (4362)*	529	—	22,5	±3·9
Bodenprobe (4482)†	329	—	22,5	±4,1
Bodenprobe (4483)†	568	—	55	±3,8

Die Proben wurden im mikrowelleninduzierten Sauerstoff-Plasma aufgeschlossen (vgl. Abb. 2).
* Problennahme im Sandstein—Schwarzwald (Landschaft Schabenhausen).
† Probennahme im Sandstein—Schwarzwald (Landschaft Ertingen).
‡ Relative Standardabweichung.

Verfahrens liegt bei 0,1 ng. Sie erlaubt mit relativ kleinen Probenmengen (biologische Matrices 0,5–1 g, anorganische Matrices 0,5–3 g, Luft *ca.* 20 Nl) die Allgegenwartskonzentration des Quecksilbers zu erfassen.

Eine weitere Verbesserung der Nachweisgrenze wäre durch Verwendung eines empfindlicheren Photomultipliers—es wird von einer Nachweisgrenze von 10 pg berichtet[81]—oder durch Auswertung der 184,9 nm Resonanzlinie leicht möglich. Einige Autoren[82] geben eine *ca.* 10–50 fache Steigerung der Nachweisgrenze gegenüber der 253,7 nm Linie an. Die Allgegenwartskonzentration des Quecksilbers in Luft ist jedoch so hoch, daß sie bei Bestimmungen im unteren ng-Bereich erheblich als Blindwert ins Gewicht fällt. Es ist z.B. sehr schwierig Geräte und Gefäße "blindwertfrei" zu halten, wenn nicht in speziell gereinigten Räumen (z.B. "cleanrooms") gearbeitet wird. Somit ist es fraglich, ob Nachweisgrenzen <100 pg überhaupt praktisch ausgenützt werden können.

Alle Verfahrensschritte (von der Probennahme bis zur Überführung des Quecksilbers in den Plasma-Detektor) wurden mit ^{203}Hg anhand reiner Standardlösungen (ohne Matrix) und anhand verschiedener, mit ^{203}Hg markierter Matrices überprüft und

Tabelle 5. Bestimmung von Quecksilber in atmosphärischer Luft

Matrix (10 Nl)	Quecksilbergehalt, *ppM*	*V*, % ($n = 10$)
Normalluft (Wohngebiet)	0,06	±3,8
Laboratoriumsluft		
Lab. 1*	0,25	±3·6
Lab. 2†	0,5	±3·9
Lab. 3‡	0,65	±4,0

* Raum mit Ventilation.
† Raum ohne Ventilation.
‡ Gutventilierter Raum, mit einer Quecksilberdestillationsapparatur.

optimiert (spez. Aktivität der ^{203}Hg-Standardlösung: 0·1 μCi/9 ng; Szintillationszähler—NaJ/Tl, Bohrloch 5 × 5 cm). Bei Wasser und einigen biologischen Matrices (z.B. Bodenproben, Milchpulver, Mehl) wurden 10 ng ^{203}Hg zu den Proben dosiert und nach 3 Wochen analysiert. Dadurch sollten Bedingungen simuliert werden, wie sie unbekannten Proben entsprechen (vgl. Tab. 3 und 4). In Tabelle 5 sind die Ergebnisse einiger Luftanalysen zusammengestellt. Es handelt sich hierbei um Untersuchungen von Stadt- und Laboratoriumsluft. Die unterschiedlichen Quecksilbergehalte in den Laboratorien sind auf verschiedene Kontaminationsgrade (Quecksilberreinigung, Quecksilberdiffusionspumpe u.a.) zurückzuführen.

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SHORT COMMUNICATIONS

POTENTIOMETRIC DETERMINATION OF CHLORIDE IN INORGANIC ORTHOPHOSPHATES IN CITRATE-BUFFERED MEDIA

E. J. DUFF and J. L. STUART

Department of Preventive Dentistry, Turner Dental School, The University, Manchester, England

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The use of halide-sensitive electrodes for the determination of relatively low levels of halide ions in both geological and biological minerals possibly also provides one of the more accurate methods for determination of these ions in mineral deposits. Considerable efforts have been made to develop suitable methods for the determination of fluoride[1] in mineral deposits, but the use of other halide-sensitive electrodes has been somewhat neglected. It is well known that as a result of contact with chloride-containing ground waters, low but significant levels of chloride may be present in geological mineral deposits. Similar levels of chloride may be present in biological hard tissue as a result of contact with saline body fluids. We have been developing methods for the determination of halide ions in orthophosphates as part of an investigation of possible mechanisms of reactions involving calcified tissues.

One of the principal factors in any analysis using ion-sensitive electrodes is the choice of a suitable buffer system which will provide a constant ionic strength background and minimize the interference by other ions. In a previous contribution, we reported the use of a buffer composed of perchloric acid, citric acid and triethanolamine (pH 2·5) for the potentiometric determination of chloride.[2] This buffer system has been in use in these laboratories for several years without any apparent damage to the AgCl/Ag_2S membrane of the Orion 94-17A chloride-sensitive electrode. We do not yet know whether triethanolamine will in fact damage the membrane surface by formation of a silver complex, but it has become apparent that the use of triethanolamine which has been stored for a few months may lead to imprecise results. We have therefore tried using the buffer system previously described for the determination of fluoride,[3] modified by substitution of perchloric acid for hydrochloric acid.

EXPERIMENTAL

Reagents

Analytical grade chemicals and demineralized distilled water were used throughout.

Dissolution acid. Add 166 ml of perchloric acid to a solution of 420 g of citric acid in 700 ml of water and dilute to 1 litre.

Citrate solution. Dissolve 294 g of trisodium citrate dihydrate in water and dilute to 1 litre.

Standard chloride solutions. Dissolve 5·85 g of sodium chloride in water and dilute to 1 litre. Dilute further as required.

Procedure

Weigh accurately about 100 mg of the solid material to be analysed and dissolve it in 5 ml of the dissolution acid. Add 5 ml of water followed by 5 ml of the citrate solution. For the determination of chloride in aqueous solutions, use a 5-ml aliquot mixed with 5 ml of the acid mixture and 5 ml of the citrate solution. Stir the solution with a magnetic stirrer and measure the potential with a suitable potentiometer. A Radiometer PHM 51 expanded-scale pH-meter or a PHM 52 digital pH-meter, an Orion 94-17A chloride-sensitive electrode (AgCl/Ag_2S detector crystal) and either a Radiometer K601 $Hg/Hg_2SO_4/K_2SO_4$ reference electrode or a Cambridge Instrument Company type 42528 calomel reference electrode, filled with a saturated solution of potassium nitrate, were used in the present study.

RESULTS AND DISCUSSION

By the procedure described above, the e.m.f. may be measured within 5 min, provided that the chloride concentration is above $10^{-3}M$. Below this level, a somewhat longer equilibrium period is required. Stirring is hepful in achieving this equilibrium, but usually results in a stirring potential of ± 5 mV. Thus, for precision, it is necessary to stir all samples or none. The chloride content is found from a calibration curve.

The pH of the sample solutions prepared from solids was about 0·2 above that of samples where the chloride was already in solution, but this did not matter since variation of the pH from 2·0 to 3·5 produced little change in the e.m.f. The reproducibility at constant temperature or with automatic temperature compensation was ± 3 mV and often within ± 1 mV. The calibration curve, once established, could be used for months if two points were checked at regular intervals. The electrode typically showed a response of 56·7 mV/decade, which was linear down to about $1{\cdot}1 \times 10^{-4}M$ chloride in the buffered solution. The method could be used to determine down to about 1 ppm chloride.

Interferences

With the exception of some halide ions (see later), the Orion chloride-sensitive electrode suffered interference from few other species. Sulphide, cyanide and thiocyanate must be absent from the sample or removed before the chloride determination. No interference from PO_4^{3-}, NO_3^-, ClO_4^-, SO_4^{2-} or F^- was found, and group IA, IIA and most bi- and tervalent transition metal ions did not interfere when present in 1000-fold w/w ratio to chloride. The exceptions were Cu^{2+}, Al^{3+} and to a lesser extent, Fe^{3+}. Interference by copper has already been described.[4]

The interference of Al^{3+} was determined by the addition of 0·1-ml aliquots of aluminium sulphate solution, 0·1M in Al^{3+}, to standard samples and is compared in Table 1 with that for the earlier triethanolamine method. The citrate system has the better buffer capacity and the pH of the triethanolamine solutions was lower than that of the corresponding citrate solutions. In addition, the e.m.f. in the triethanolamine solution varied more with pH.

The Orion handbook for the 94-17A electrode[5] suggests that both bromide and iodide interfere seriously. We have earlier determined[6] that there is no interference by at least a 1000-fold molar ratio of fluoride, but that iodide must be at a level less than 1/500 and bromide at a level less

Table 1. Interference by Al^{3+} in determination of A^-

$[Cl^-]$ in standard, *M*	Critical ratio of $[Al^{3+}]/[Cl^-]$	
	citrate buffer	TEA buffer
10^0	1:25	1:25
10^{-1}	3:10	1:3
10^{-2}	2:3	1:1
10^{-3}	2:1	3:1

than 1/50 of that of the chloride ions. This interference renders the potentiometric determination of chloride suspect unless bromide and iodide are determined first and steps taken to remove or limit the interference. Examples of typical interference of bromide in the determination of chloride are shown in Table 2. The solid substrate was a fluoroapatite, prepared by the transformation of secondary calcium orthophosphate dihydrate in 0·1*M* sodium fluoride solution in the presence or absence of other halides, as indicated in the table. Attempts to eliminate bromide selectively were not successful. However, if the bromide is present in amounts only slightly in excess of the tolerable amount, the error is only about ± 10%. If it is known that there is a great excess of chloride over bromide and iodide in the sample, and an error of ± 5% may be tolerated, the presence of the additional halides may be ignored.

Factors affecting the selectivity limit

Solid-state membrane electrodes are generally able to detect ppm levels of a given species. Silver halide membranes, especially those containing Ag_2S have a detection limit lower than many other electrodes. With the Orion 94-17A chloride-sensitive electrode, a linear near-Nernstein response was obtained in citrate buffer down to $1{\cdot}1 \times 10^{-4}M$ Cl^-, slightly better than the limit of $3{\cdot}5 \times 10^{-4}M$ obtained in triethanolamine buffer. We have used the citrate buffer to determine levels of chloride down to $5 \times 10^{-5}M$ without apparent loss of precision. An additional advantage of the citrate buffer is that it may be stored for longer periods than the triethanolamine buffer, which unless prepared daily from reagent grade solutions (themselves stored in the refrigerator for not longer than 6 months) has limited buffer capacity. In our experience, the citrate buffer remains fully stable for several months. Studies showed that the free chloride content of the perchloric acid used was negligible, but care should be taken to carry out the determination away from direct sunlight which causes an apparent increase in the chloride content of the samples, possibly arising from the photochemical decomposition of the perchlorate.

Application of the method

We have applied this method to the determination of the chloride content of synthetic samples of fluoroapatite obtained by transformation of secondary calcium orthophosphate dihydrate (Table 3) and of the chloride content of phosphate rock samples (Table 4). Chloride recovery data are given in Table 5. The method has also been applied to the determination of chloride in hydrothermally synthesized silicate rocks. These samples were crushed, extracted with 0·1*M* perchloric acid for 24 hr at room temperature, and the extract analysed both by the method described here and by potentiometric titration at pH 2·0–2·5 with silver nitrate, the chloride-sensitive electrode being used. The results (Table 6) which agreed well, were the means of three determinations on separate 1-ml aliquots of the sample solutions. Because of the small volumes available, further determinations were not possible. The direct potentiometric determinations were made after a stabilization period of 5 min and agreed to better than ±2 mV. The titrimetric results agreed to within ±0·1 ml of $10^{-2}M$ silver nitrate and each determination took at least 15 min.

CONCLUSIONS

The use of citrate-buffered medium offers better sensitivity, more freedom from interferences and a greater chemical stability of the buffer system than is afforded by the triethanolamine system. Direct potentiometric determinations are rapid and convenient, but it must be remembered that the results depend on reading a logarithmic calibration graph. Whilst the results in the lower third of

Table 2. Spurious results given by 94-17A chloride electrode in presence of other halides

Sample	Apparent $[Cl^-]$, *ppm*	Remarks
1. $Ca_5F(PO_4)_3$ prepared in absence of any added Cl^- or Br^-	76	
2. $Ca_5F(PO_4)_3$ prepared from solution 0·1*M* in NH_4Cl	$1{\cdot}01 \times 10^3$	Cl^- substituting for F^- in apatite structure: Cl^- found represents substitution of 1·4% of F^- present and would be expected from preparative conditions used
3. $Ca_5F(PO_4)_3$ prepared from solution 0·1*M* in NH_4Br	$4{\cdot}4 \times 10^4$	Br^- interference with Cl^- electrode; expected Br^- content of order 3–600 ppm
4. $Ca_5F(PO_4)_3$ prepared from solution 0·1*M* in both NH_4Cl and NH_4Br	$4{\cdot}4 \times 10^4$	Expected Cl^- not greater than 1000 ppm; probable Br^- interference
5. Sample 3, fumed in HNO_3 to remove Br^-	$5{\cdot}8 \times 10^2$	Majority of Br^- lost in fuming
6. Sample 4, fumed in HNO_3 to remove Br^-	$9{\cdot}7 \times 10^2$	Majority of Br^- and possibly some Cl^- lost during fuming

Samples of fluoroapatite prepared by transformation of $CaHPO_4.2H_2O$ in 0·1*M* NaF [E. J. Duff, *J. Chem. Soc.* (*A*), 1971, 33] in the presence of chloride and/or bromide ions).

Table 3. Chloride content of fluoroapatites formed by transformation of $CaHPO_4.2H_2O$ in 0·1*M* NaF containing NaCl

Sample	Cl^-, %*	Std. den.	NaCl in supernatant solution, *M*
1	0·127	0·0102	0·5
2	0·069	0·0087	0·1
3	0·031	0·0011	0·05
4	0·012	0·0089	0·02

* Average of 6 analyses.

Table 4. Chloride content of some samples of phosphate rock from Morocco (M) and Newfoundland (NFL) (donated by Albright & Wilson Ltd., Marchon Div.)

Sample	Cl^-, %*	Std. den.	Source
1	0·0352	0·005	NFL
2	0·0571	0·006	M
3	0·0526	0·0067	M
4	0·0534	0·0057	M
5	0·0483	0·0061	M
6	0·0427	0·0010	M
7	0·0142	0·0045	M

* Average of 10 analyses.

Table 5. Recovery of Cl^- added to phosphate samples

Added, *mg*	Recovered, *mg*				
0·0355	0·039	0·039	0·038	0·039	0·034
0·0710	0·075	0·075	0·070	0·077	0·069
0·1056	0·110	0·110	0·105	0·110	0·104

Table 6. Chloride content of rock extract (means of three results)

Chloride, *mg/ml*	
Direct potentiometry	Titrimetry
0·135	0·140
0·280	0·278
0·550	0·548
0·206	0·200
0·248	0·247
0·462	0·471

each decade are readily comparable with those obtained by potentiometric titration, the precision and reproducibility of the results deteriorate rapidly towards the upper portion of each decade. It is therefore advisable to adjust the chloride content of the sample where this is possible, by appropriate additions such that the e.m.f. readings will fall in the lower third of the next higher decade of the calibration curve. Additionally, small errors in the reading of the calibration curve, compounded with minor variations in the measured e.m.f. may be the cause of the relatively high standard deviations obtained in Table 4.

Acknowledgement—We thank the United Manchester Hospitals Research Fund for the Radiometer PHM 52 digital pH meter. The work was carried out, in part, under a project supported by Colgate Palmolive Ltd.

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Summary—The chloride content of some inorganic orthophosphates and phosphate rock samples has been determined in a medium buffered to pH 2·5 with a mixture of perchloric acid, citric acid and trisodium citrate. The method has been compared with an earlier method which employed a mixture of perchloric acid, citric acid and triethanolamine. The present method is of similar reproducibility and does not suffer from decomposition of the reagents. The interference patterns of several metals are discussed.

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SPECTROGRAPHIC ANALYSIS OF BORON NITRIDE FOR TRACE IMPURITIES

B. R. VENGSARKAR, I. J. MACHADO and S. K. MALHOTRA

Spectroscopy Division, Bhabha Atomic Research Centre, Trombay, Bombay—400085, India

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Boron nitride in pure form is used as a dopant in semiconductor technology. Earlier, a d.c. arc method using an argon atmosphere was developed by Kravchenko[1] for the estimation of eleven impurities. This method uses boron nitride pellets, and two different exposure times and currents for recording the spectra, which makes it unwieldy

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and complicated. Kharitonova *et al.*[2] used a chemical method for the determination of impurity oxides in BN which is applicable to per centage concentrations of impurities. The present method simultaneously determines nine impurities (Al, As, Bi, Ca, Fe, Mg, Pb, Sb and Sn) in the concentration range from 2 to 1000 ppm in boron nitride, by a d.c. arc method. This method is simple, straightforward and quick for routine analysis and has achieved the desired limits. Because of the presence of Al, Ca, Fe and Mg in the boron nitride used for the preparation of standards, the limits obtained for these elements are high. It would be possible to lower the limits by using pure boron nitride free from these impurities.

EXPERIMENTAL

Equipment

The spectra were recorded on a Hilger large quartz Littrow spectrograph E492 having a reciprocal linear dispersion of 0·4 nm/mm at 240·0 nm. A d.c. arc source was used at 10 A to excite the sample for a period of 30 sec. The slit of the spectrograph was kept at 10 μm, and a 10% transmission filter was placed in front of it. The spectra were recorded on Kodak SA-1 plates and the spectrum line densities were measured with a Hilger non-recording microphotometer Model L-451. Finally, the ratios of intensity of impurity element lines to intensity of the internal standard element lines were calculated on a Respectra calculator (Dennert and Pape, Hamburg).

Preparation of standards

A set of synthetic standards covering the concentration range from 1 to 1000 ppm was prepared by diluting "Spexmix" standard (Spex Industries, Cat. No. 1000),[3] containing 1·28% of each impurity element, with the required amount of Ultra Carbon Corporation (U.C.C.) spectroscopically pure graphite powder. These were then ground with equal quantities of pure boron nitride. To these mixtures of boron nitride and graphite were added 2% of sodium fluoride (Johnson Matthey, "Specpure") as carrier and 1% of lanthanum oxide (Johnson Matthey, "Specpure") as an internal standard.

Procedure

A charge of 30 mg of the mixture prepared as described above was loaded in the cavity of a U.C.C. preformed 100-L graphite electrode used as an anode, and a 1/8-in. diameter pointed U.C.C. graphite electrode was used as a cathode. The charge was excited in a d.c. arc at 10 A for a period of 30 sec, the electrode gap being maintained at 3 mm during arcing. Working curves were drawn for various elements and their concentrations in the sample were determined.

Table 1. Analytical lines and concentration ranges

Impurity	Analytical line wavelength, *nm*	Amount in standard BN, *ppm*	Concentration range, *ppm*
Al	308 21	2	10–200
As	278·02	—	50–1000
Bi	306 77	—	5–200
Ca	317 93	30	50–1000
Fe	259 96	10	20–200
Mg	277 98	5	10–200
Pb	283·31	—	2–50
Sb	259 81	—	5–500
Sn	284 0	—	2–50

La 280·83 nm is used as an internal standard line for all the elements. Al, Bi and Ca are measured with the 10% transmission filter in position.

RESULTS AND DISCUSSION

Table 1 shows the analysis lines of different impurity elements and their concentration ranges with corrections for impurities in the standard boron nitride where necessary. These corrections were found by the method of standard additions.

Since boron nitride is refractory, different concentrations of carriers such as silver chloride, gallium oxide and copper oxyfluoride were tried along with graphite used as buffer; 2% of sodium fluoride as carrier mixed with equal quantities of graphite and boron nitride was found to give maximum sensitivity for all the impurities. It was observed experimentally that the burning of the arc was smooth and regular in the presence of sodium fluoride, thereby improving the precision of the method. The relative standard deviation of the method varied from 8 to 16% for different impurities. The iron content of a sample analysed chemically was 50 ppm; the value obtained by this spectrographic method was 54 ppm.

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Summary—A d.c. arc emission spectrographic method has been developed for the determination of nine trace impurities in boron nitride. The charge for exciting the sample contains equal quantities of boron nitride and graphite (containing 2% NaF as carrier and 1% La_2O_3 as an internal standard). The method is useful in the determination of impurities in the range 2–1000 ppm, with a mean relative standard deviation of 13%.

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EXTRACTION WITH LONG-CHAIN AMINES—X

COMPLEXOMETRIC DETERMINATION OF TITANIUM AFTER EXTRACTION OF ITS ASCORBATE COMPLEXES

JIŘÍ ADAM

Analytical Laboratory, Institute of Geological Sciences, Charles University, Prague 2, Albertov 6, Czechoslovakia

and

RUDOLF PŘIBIL

The J. Heyrovský Institute of Physical Chemistry and Electrochemistry, Czechoslovak Academy of Sciences, Prague 1, Jilská 16, Czechoslovakia

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Ascorbic acid (ASA), besides its reducing properties, has a tendency to form complexes with ter- and quadrivalent cations. Great attention has been paid to the coloured complexes of titanium, uranium, iron, molybdenum and vanadium, which have been studied spectrophotometrically and potentiometrically. For some metals, ascorbic acid has been proposed as a spectrophotometric reagent. Analytical applications of ASA have been reviewed by Pilipenko and Kladnitskaya.[1]

Ascorbic acid forms not one, but a number of complexes, with the above-mentioned metals, depending on the reaction conditions (pH, ASA concentration). The complex formation is in some cases accompanied by reduction. For example, iron(III) is reduced to Fe(II) by the addition of ASA, forming a colourless solution; vanadium is also reduced in the cold to the blue ASA–V(IV) complex. Uranium(VI) is reduced to uranium(IV) on boiling.

ASA complexes are negatively charged and it can therefore be assumed that they could be extracted with a suitable liquid anion-exchanger. We have used a chloroform solution of trioctylmethylammonium chloride (TOMA; Aliquat S-336), and found that the extraction of ASA complexes is strongly dependent on the acidity of the solution. With increasing pH—starting from pH 2—the following metals are successively extracted: uranium(VI), titanium (IV), vanadium(IV), iron(II), chromium(III) (after boiling with ASA), aluminium *etc.* The difference in pH for extraction of titanium and of iron or aluminium is large enough to permit extraction of titanium in the presence of both (up to 500 mg of Fe or Al). Other bivalent metals are not extracted at all and do not interfere.

This paper is purely analytical in content. The nature of the complexes in the aqueous phase was not studied because their composition is mostly known.[1] The composition of the complexes in the organic phase is difficult to estimate, because free ASA is also partly extracted (up to 25%). The method described is very simple and has been applied to the determination of larger amounts of titanium in special alloys and rocks.

EXPERIMENTAL

Reagents

A 5% solution of TOMA in chloroform was prepared from Aliquat S-336 (General Mills Corp. Kankakee, Illinois, USA). The solution was pre-equilibrated by shaking 500 ml of it for 5 min with 100 ml of 1*M* sulphuric acid and then with 100 ml of saturated sodium sulphate solution, this operation being prepared three times.

Solutions of the metals (0·05*M*) were prepared from the sulphates, except that of vanadium, which was prepared from ammonium vanadate. Other reagents include 0·05*M* EDTA, 0·05*M* DCTA, 0·05*M* bismuth nitrate, 0·05*M* zinc sulphate, 1*M* nitric acid, 30% hydrogen peroxide, conc. ammonia solution, 0·5% aqueous. Xylenol Orange solution, ascorbic acid and hexamine.

Extraction of metals

In preliminary experiments, extractions with TOMA were not quantitative and gave non-reproducible results. It was found that this was caused by use of the chloride form of the amine. Therefore its solution was equilibrated with sulphuric acid and sodium sulphate and only metal sulphate solutions were used.

A 3-ml portion of 0·05*M* cation solution was diluted to 20 ml and 0·5 g of ascorbic acid was added. The pH of the solution was adjusted by dropwise addition of conc. ammonia solution (pH-meter and glass electrode). The solution was transferred into a 150-ml separatory funnel, diluted to 50 ml and extracted with four 5-ml portions of 5% TOMA solution, and finally with 10 ml of pure chloroform. The organic phases were discarded. In the aqueous phase the unextracted cation was determined complexometrically. The extraction curves are shown in Fig. 1.

Titanium. A strongly acidic solution of titanium sulphate remains colourless after addition of ASA. During the neutralization with ammonia the solution turns slightly yellow at pH 2. The colour deepens to yellow-orange with increasing pH and reaches its maximum at pH 3·7. Above this pH the colour fades but the extraction curve does not change up to at least 9 (see Fig. 1).

Sommer[2] recommended for spectrophotometric determination of titanium with ASA the optimal pH 3·7–4·5 and a huge amount of ASA (1900 times that of titanium). Under these conditions the TiR_3^{2-} complex is mostly formed.

Uranium. An orange-red complex of uranyl ion with ASA is extractable at pH 2–2·5 and above.

Hadobàs *et al.*[3] give the composition of the U–ASA complex as 2:3 at pH 4·2. Sobkowska and Minczewski[4] assume the existence of 1:1, 1:2 and 1:3 complexes, formation of which is dependent on the ASA concentration.

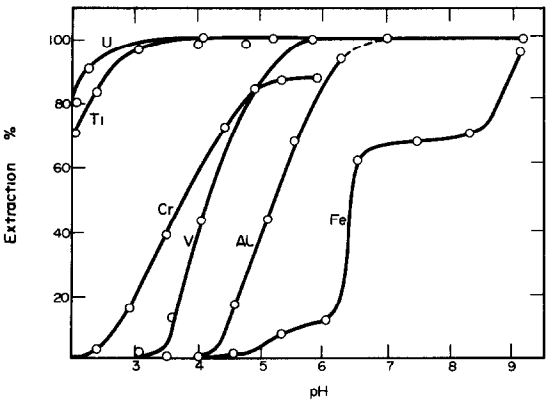

Fig. 1. Degree of extraction as a function of pH.

Iron(III). In acidic solution (pH 1) iron is reduced to the bivalent state and the solution remains colourless. At pH 4·5 a gray colour appears, which with increasing pH turns to brown-violet and dark violet. The coloured complexes are extractable with TOMA.

A solid complex of the composition FeR_2^- has been prepared.[5]

Aluminium. The colourless complex of Al and ASA can be partly extracted. At pH 5·5 up to 90% of the Al can be transferred into TOMA. Above this pH aluminium is precipitated and the extract is cloudy.

Vanadium. Acid solutions of vanadium(V) are reduced by ASA to vanadium(IV). The vanadium(IV) complex can be extracted at pH 3·6–9·3.

Chromium(III). At room temperature chromium(III) does not form a complex with ASA. On boiling, the green complex is formed,[6] which can be only partly extracted. (At optimal pH 5·5 the degree of extraction is 90%.)

Other cations. Ni, Co, Zn, Cd, Ca, Mg cannot be extracted under the conditions above. Gold and silver are reduced to the metallic state. Bismuth, zirconium, thorium and lead are precipitated.

Influence of ASA concentration on titanium extraction

Similarly a series of experiments with various amounts of ASA was carried out. It was found that at pH 3·7 the extraction of titanium from a volume of 70–100 ml is quantitanium up to 25 mg an addition of 0·5 g of ascorbic acid extraction with 10 ml of amine solution). For amounts of titanium up to 25 mg an addition of 0·5 g of ascorbic acid is sufficient if a double extraction is used.

Influence of anions

The extraction of titanium is quantitative only in sulphate solutions. Chlorides and nitrates have an adverse effect. In the presence of 200 mg of sodium chloride in 100 ml the extraction of 9 mg of titanium drops to 4·5%. The presence of 100 mg of potassium nitrate makes the extraction impossible. Potassium nitrate or nitric acid was therefore used for stripping the Ti—ASA complex into an aqueous phase as described below.

Procedure

To an acid solution in a small beaker containing up to 500 mg of aluminium and 100 mg of iron besides the titanium, add 0·5 g of ascorbic acid and adjust the pH to 3·7–3·8 with ammonia (pH-meter). Transfer the solution into a 150-ml separatory funnel, dilute to 70–100 ml and extract with two 10-ml portions of amine solution and then with 10 ml of pure chloroform. To the combined separate extracts add 20 ml of 1*M* nitric acid and shake for 1–2 min (the organic phase must become colourless). Transfer the nitric acid phase into a 250-ml titration flask, cool under tap-water to 15–16°, dilute to 150 ml, add an excess of 0·05*M* EDTA, and 1 ml of 30% hydrogen peroxide. After the addition of a few drops of Xylenol Orange titrate the solution slowly with 0·05*M* bismuth nitrate to red-violet. Typical results are shown in Table 1.

Table 1. Determination of Ti in the presence of Al and Fe

Taken, *mg* Fe	Taken, *mg* Ti	Found, *mg* Ti	Error, %	Taken, *mg* Al	Taken, *mg* Ti	Found, *mg* Ti	Error, %
7	2·32	2·44	+5·1	100	11·60	11·60	0
14	2·32	2·34	+0·8	100	6·96	6·75	−3·0
14	2·32	2·34	+0·8	250	11·60	11·55	−0·4
26	11·60	11·45	−1·2	250	6·96	6·98	+0·3
26	6·97	6·92	−0·7	500	11·60	11·52	−0·6
100	6·97	6·99	+0·3	500	6·96	6·96	0

Table 2. Determination of Fe or Al after titanium extraction

Taken, *mg* Ti	Taken, *mg* Fe	Found, *mg* Fe	Error, %	Taken, mg Ti	Taken, mg Al	Found, *mg* Al	Error, %
15·18	14·57	14·57	0	15·18	4·33	4·20	−3·0
15·18	29·14	29·12	−0·09	7·59	14·42	14·35	−0·4
15·18	17·87	17·70	−0·9	15·18	4·33	4·23	−2·3
15·18	35·74	35·74	0	15·18	4·33	4·27	−1·3
30·36	17·87	17·85	−0·1	7·59	7·21	7·21	0
7·59	35·74	35·74	0	7·59	7·21	7·23	+0·2
7·59	35·74	35·71	−0·08				

Determination of iron or aluminium after titanium extraction

The aqueous phase contains a large amount of ascorbic acid and iron(II) and aluminium ASA complexes. In the determination of aluminium ASA does not interfere, because on boiling the solution with an excess of EDTA or DCTA, the corresponding aluminium complex is formed quantitatively. Determination of the excessive of EDTA or DCTA by back-titration with zinc and Xylenol Orange does not present any difficulty.

DCTA is known to form the aluminium complex in the cold, but it reacts with the Al–ASA complex only partly if the solution is not heated, and gives low results. For the determination of iron, the ascorbic acid must be decomposed. Of several methods the following seemed to us the most suitable. The aqueous phase was boiled to eliminate traces of chloroform. Then 10 ml of 1*M* nitric acid were added and then 1 g of potassium bromide and 1 g of potassium bromate. After cooling, 1 g of sodium thiosulphate was added, and after 10 min an excess of EDTA. After adjustment of the pH to 5·5 with hexamine, the excess of EDTA was titrated with 0·05*M* zinc solution, with Xylenol Orange as indicator. Some results of both determinations are summarized in Table 2.

Practical applications

Determination of titanium in Ti–Al alloy (6·57% Ti). One gram of the sample was dissolved in 20 ml of conc. hydrochloric acid and a few drops of nitric acid, and the solution evaporated to 10 ml. After the addition of 5 ml of conc. sulphuric acid the solution was evaporated to white fumes. After cooling, the residue was dissolved in water and transferred to a 100-ml volumetric flask. Titanium was determined as described above, on 10 or 20 ml of the solution. Three analyses gave the results 6·58, 6·56, 6·59% Ti.

Determination of titanium in BCS alloy (40·40% Ti). This alloy contains Si (3·94), Cr (0·18), V (0·12), Al (7·30), Cu (0·52), Nb (0·08), Mn (1·64), C (0·04), P (0·048) and Fe (rest).

A 50-mg sample in a Teflon dish was dissolved with 20 ml of sulphuric acid (1 + 1) and 5 ml of hydrofluoric acid and evaporated to white fumes. Then 20 ml of *aqua regia* were added and evaporated to 10 ml. The solution was twice evaporated with sulphuric acid. The residue was dissolved in 20 ml of hot water, the solution filtered, and titanium determined in the whole volume as described. Found: 39·98 and 40·38% Ti.

Analysis of eclogite and biotite. Appropriate amounts of sample were decomposed with potassium pyrosulphate according to Harpham's procedure.[7] Titanium was determined as described above. In eclogite (2·03% Ti) the titanium content found was 2·03% (thrice) and in biotite (8·10% Ti), 8·08 and 8·10%.

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Summary—A highly selective extraction of titanium as its ascorbate complexes from slightly acidic medium into trioctylmethylammonium sulphate is described. After stripping into nitric acid, titanium is determined complexometrically. The method allows separation of titanium from large amounts of iron, aluminium and bivalent metals. The procedure for the determination of iron and aluminium after the titanium extraction is also given. The method has been applied to the determination of titanium in special alloys and minerals.

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AN EVALUATION OF SOLVENT MEDIATORS FOR ION-SELECTIVE ELECTRODE MEMBRANES BASED ON CALCIUM BIS(DIALKYLPHOSPHATE) SENSORS TRAPPED IN POLY(VINYL CHLORIDE) MATRICES

A. CRAGGS, L. KEIL, G. J. MOODY and J. D. R. THOMAS
Chemistry Department, UWIST, Cardiff CF1 3NU, Wales

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The selectivities of ion-selective electrodes prepared from calcium salts of dialkylphosphoric acids depend on the solvent mediator[1], for example, di-n-octylphenyl phosphonate produces a calcium ion-selective electrode, whereas decan-1-ol produces a "water hardness" (calcium, magnesium or bivalent ion) ion-selective electrode. Although the role of the mediator is recognized as more than just that of a solvent,[2,3] there have been few extensive studies of the effect of solvent mediators on ion-selective electrode character.

Garbett and Torrance[4,5] have examined the influence of various solvents on liquid-membrane electrodes based on calcium bis(di-n-decylphosphate) as sensor. However, poly(vinyl chloride) (PVC) matrix membranes impose an additional constraint and the present study with these membranes relates the extent to which primary aliphatic alcohols and certain plasticizing solvents might serve as mediators in conjunction with calcium bis(di-n-decylphosphate) or calcium bis(di-2-ethylhexylphosphate) as sensors.

EXPERIMENTAL

Electrodes

Ion-selective electrodes with membranes containing the liquid ion-exchanger (solvent mediator plus sensor) trapped in PVC were prepared as previously described.[6–10] The master membranes contained 0·36 g of solvent mediator and 0·036 g of calcium bis(dialkylphosphate) sensor in 0·17 g of PVC. However, because of the general insolubility of calcium bis(di-n-decylphosphate) in the membrane components a 1:1 w/w mixture of it with di-n-decylphosphoric acid was used for those membranes based on it. Such a procedure normally gave clear transparent membranes without the crystalline deposits characteristic of calcium bis(di-n-decylphosphate) alone, although the membrane sensor would still be expected to consist of a mixture of calcium bis(di-n-decylphosphate) and calcium dihydrogen tetrakis(di-n-decylphosphate).[7]

For comparison, membranes were also prepared from Orion (92-20-02) calcium liquid ion-exchanger (membrane I) and from Corning (476235) and Orion (92-32-02) bivalent liquid ion-exchanger (membranes II and III) with 0·40 g of the appropriate exchanger and 0·17 g of PVC.

Reagents

All chemicals were reagent grade except the di-n-octylphenylphosphonate and calcium bis(di-n-decylphosphate) which were synthesized.[6,11–13] Calcium bis(di-2-ethylhexylphosphate) was a gift from Corning Inc., U.S.A.

Procedures

All e.m.f. measurements were made relative to a Corning ceramic-junction saturated-calomel reference electrode (Cat. No. 476109) with a Corning Model 112 pH/millivoltmeter in conjunction with a Servoscribe Model RE4541 potentiometric recorder. Selectivity coefficients, K_{ij}, were determined by a mixed solution method,[14,15] with a fixed level of interferent, j.

Analysis of eclogite and biotite. Appropriate amounts of sample were decomposed with potassium pyrosulphate according to Harpham's procedure.[7] Titanium was determined as described above. In eclogite (2·03% Ti) the titanium content found was 2·03% (thrice) and in biotite (8·10% Ti), 8·08 and 8·10%.

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Summary—A highly selective extraction of titanium as its ascorbate complexes from slightly acidic medium into trioctylmethylammonium sulphate is described. After stripping into nitric acid, titanium is determined complexometrically. The method allows separation of titanium from large amounts of iron, aluminium and bivalent metals. The procedure for the determination of iron and aluminium after the titanium extraction is also given. The method has been applied to the determination of titanium in special alloys and minerals.

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A. CRAGGS, L. KEIL, G. J. MOODY and J. D. R. THOMAS
Chemistry Department, UWIST, Cardiff CF1 3NU, Wales

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Table 1. Constitution and properties of the membranes

Membrane number	Liquid ion-exchanger system: Solvent mediator	Sensor	Lower limit of detection* for Ca^{2+}, M	Remarks
I	Orion(92-20-02) calcium liquid ion-exchanger		4×10^{-6}	Pale yellow transparent, soft and rubbery membrane with no inclusions Good operational lifetime of $\gg 2$ weeks
II	Corning(476235) divalent liquid ion-exchanger		$4{\cdot}5 \times 10^{-5}$ for Ca^{2+} and Mg^{2+} 3×10^{-5} for Mn^{2+}	Clear transparent, semi-rigid membrane with surface exudate Good operational lifetime of >2 weeks.
III	Orion(92-32-02) divalent liquid ion-exchanger		10^{-4} for Ca^{2+}, Mg^{2+}, Mn^{2+}	Pale pink transparent, semi-rigid membrane with surface exudate Good operational lifetime of >2 weeks
IV	Di-n-octylphenyl phosphonate	Calcium bis(di-n-decylphosphate)/di-n-decylphosphoric acid (1.1 w/w)	$2{\cdot}4 \times 10^{-6}$	Transparent soft and rubbery but with tendency for gel-like inclusions in parts
V	Dinonylphthalate		6×10^{-7}	Transparent soft and rubbery membrane but slightly more rigid than membrane IV Unsteady readings in presence of interferents
VI	Decan-1-ol		—	Rigid membrane with extensive crystalline inclusions and considerable surface exudate. Unsuitable for electrodes
VII	Decan-1-ol (0·18 g) plus di-n-octylphenyl phosphonate (0·18 g)		$8{\cdot}5 \times 10^{-6}$	Transparent semi-rigid membrane with gel-like inclusions Some surface exudate
VIII	Di-n-octylphenyl phosphonate	Calcium bis (di-2-ethylhexylphosphate)	$2{\cdot}2 \times 10^{-5}$	Clear, transparent, soft and rubbery membrane with no inclusions. Good operational lifetime of >2 weeks
IX	Dinonylphthalate		$1{\cdot}2 \times 10^{-6}$	Soft, rubbery, but opaque membrane. Susceptible to electrical interference, *i.e.*, noisy output and with low slope; is generally unsuitable for ion-selective electrodes
X	Octan-1-ol		6×10^{-6}	The alcohol readily exudes from the membrane which has extensive crystalline deposits Lifetime ~ 4 days Not considered suitable for further study.
XI	Decan-1-ol		3×10^{-5} for Ca^{2+}, Mg^{2+}, Mn^{2+}	Cloudy white shrunken membrane with no exudate. Good operational lifetime of ~ 2 weeks.
XII	Dodecan-1-ol		Erratic response	State of membrane dependent on ambient conditions since the alcohol component solidifies with a drop in temperature.
XIII	Decan-1-ol (0·18 g) plus di-n-octylphenylphosphonate (0·18 g)		8×10^{-5}	Semi-rigid but completely transparent membrane Some exudate on surface

* Lower limit of detection is that activity of calcium ions (or ions of interest) at which the emf of the electrode deviates by 9 mV (that is, $18/z_j$, where z_j is the valence of the ion of interest) from the extrapolated linear section of the calibration plot.

RESULTS

The details of various membranes with alkan-1-ols as solvent mediators, or di-n-octylphenyl phosphonate or di-n-nonyl phthalate as plasticizing solvent mediators, and the electrodes assembled therefrom are summarized in Table 1 and the selectivity coefficients in Table 2. Calibration slopes of functional electrodes were near-Nernstian. The full range of alcohols included heptan-1-ol,

Table 2. Electrode selectivity characteristics of the membranes

Membrane number	Selectivity coefficient, K_{ij}*: K_{CaNa}	K_{CaK}	K_{CaMg}	K_{CaSr}	K_{CaBa}	K_{CaMn}	K_{CaCu}	K_{CaNi}	K_{CaZn}
I	1·05 (10^{-2})	1·2 (10^{-2})	$8{\cdot}6 \times 10^{-2}$ (10^{-3})	$5{\cdot}5 \times 10^{-2}$ (10^{-3})	$1{\cdot}4 \times 10^{-3}$ (10^{-3})	0·5 (10^{-3})	0·16 (10^{-3})	0·12 (10^{-3})	—
II	3·3 (10^{-2})	3·6 (10^{-2})	1 (all levels)	0·80 (10^{-3})	0·92 (10^{-3})	2 (10^{-3})	1·4 (10^{-3})	1·3 (10^{-3})	—
III	1·3 (10^{-2})	1·5 (10^{-2})	1 (all levels)	0·63 (10^{-3})	0·65 (10^{-3})	2 (10^{-3})	2·6 (10^{-3})	2·3 (10^{-3})	—
IV	0·19 (10^{-2})	0·56 (10^{-2})	$5{\cdot}2 \times 10^{-2}$ (10^{-3})	$3{\cdot}1 \times 10^{-2}$ (10^{-3})	$4{\cdot}0 \times 10^{-2}$ (10^{-3})	0·90 (10^{-3})	0·21 (10^{-3})	$5{\cdot}7 \times 10^{-2}$ (10^{-3})	—
V	0·56 (10^{-2})	2·4 (10^{-2})	0·14 (10^{-3})	0·14 (10^{-3})	0·76 (10^{-3})	1·0 (10^{-3})	1·3 (10^{-3})	0·76 (10^{-3})	—
VI	—	—	—	—	—	—	—	—	—
VII	1·6 (10^{-2})	0·52 (10^{-2})	0·55 (10^{-3})	0·21 (10^{-3})	0·29 (10^{-3})	—	0·86 (10^{-3})	0·71 (10^{-3})	—
VIII	46 (10^{-2})	14 (10^{-2})	$5{\cdot}7 \times 10^{-2}$ (10^{-3})	$4{\cdot}0 \times 10^{-2}$ (10^{-3})	$4{\cdot}8 \times 10^{-2}$ (10^{-3})	0·28 (10^{-3})	1·7 (10^{-3})	0·18 (10^{-3})	—
IX	—	—	—	—	—	—	—	—	—
X	—	—	—	—	—	—	—	—	—
XI	2·4 (10^{-2})	2·4 (10^{-2})	1 (all levels)	0·50 (10^{-3})	0·50 (10^{-3})	2 (10^{-3})	2 (10^{-3})	2 (10^{-3})	4·8 (10^{-3})
XII	—	—	—	—	—	—	—	—	—
XIII	1·4 (10^{-2})	1·4 (10^{-2})	0·52 (10^{-3})	0·17 (10^{-3})	0·17 (10^{-3})	1 (10^{-3})	0·66 (10^{-3})	0·26 (10^{-3})	—

* Figures in parentheses refer to levels (M) of j at which the coefficients were determined.

octan-1-ol, decan-1-ol, dodecan-1-ol and octadecan-1-ol, but data are not included in Tables 1 and 2 for membranes of extremely poor quality. For example, heptan-1-ol and octan-1-ol exude readily and in neither case was the membrane with calcium bis(di-n-decylphosphate) as sensor suitable for assembly into an ion-selective electrode. Dodecan-1-ol is sensitive to changes in ambient temperature and liable to crystallize from the membrane, whereas octadecan-1-ol merely gives a white sticky fibrous mass during attempted membrane fabrication.

In general, decan-1-ol was the most promising alcohol as solvent mediator, but with the calcium bis(di-n-decylphosphate) sensor even it fails to provide membranes suitable for ion-selective electrodes.

DISCUSSION

Weakly co-ordinating or non-co-ordinating solvents do not produce functional liquid–membrane ion-selective electrodes;[4] only liquid–membranes incorporating co-ordinating solvents such as alcohols, trialkyl phosphates and certain phosphonates appear to be functional.[4,5] This implies that the mediator not only dissolves the exchanger salt but also partly solvates the salt metal ion.[5] Thus, the solvent may affect electrode selectivity by influencing the formation constants and partition coefficients which define the ion-exchange between the calcium species in the liquid–membrane and the other cations in the sample solution.[4]

Whatever the reason, different solvent mediators are associated with significant differences in the selectivity of electrodes based on liquid ion-exchangers as sensors. Thus, the selectivity coefficient, K_{CaNa}, for a PVC calcium ion-selective electrode based on a neutral sensor containing two ether oxygen atoms and the carbonyl oxygen atoms of two amide and two ester groups, vary[3] from about 10 in dibutyl sebecate mediator to $< 10^{-2}$ in *p*-nitroethylbenzene. Garbett and Torrance[4,16] found that the response of electrodes with membranes based on calcium bis(di-n-decylphosphate) sensor admixed with alkan-1-ols (C_5—C_{10}) and isomers of octanol as mediators, varied from little selectivity for calcium, magnesium, nickel and copper with alkan-1-ols, to high copper selectivity (Cu $\gg$ Ca > Mg $\approx$ Ni) for certain branched-chain alkan-3-ols and alkan-4-ols. Electrodes with tri-n-alkyl phosphate (C_3—C_{10}) solvent mediators showed[4,16] that the lowest homologue gave an electrode which was marginally calcium ion-selective (Ca > Cu > Ni $\approx$ Mg), whereas the higher homologues gave somewhat better calcium ion-selectivity (Ca $\gg$ Cu > Ni $\approx$ Mg).

In the present investigation, the homologous alkan-1-ol solvent mediators have been disappointing in their ability to provide suitable PVC membrane electrodes, but the volatility and viscosity of mediators can also seriously impair the performance of conventional liquid-membrane ion-selective electrodes. For example, evaporation losses led to precipitation of exchanger salt with consequent blockage of the capillaries of the supporting membrane.[5] However, with those functional ion-selective electrodes that were obtained, interesting selectivity effects have been observed (Table 2). For example, membrane **V** gives an electrode with high selectivity towards copper.

The selectivity assessments for calcium-response in the presence of alkali metal ions emphasize the influence[15] of the power term, $(a_j)^{z/y}$, in

$$a_i = K_{ij}(a_j)^{z/y} \quad (1)$$

The rule that K_{ij} needs to be less than 1 for selective response to ion *i*, needs modification. Thus, even when $K_{ij} > 1$ there can be selectivity towards calcium if this is the primary ion, *i*. For example, with membrane **VIII** where $K_{CaNa} = 46$ and $K_{CaK} = 14$, the electrode is selective to calcium ions down to the $10^{-3}M$ range even though the alkali metal ion level is as high as $10^{-2}M$. Such a practical observation follows from equation (1). When *i* is bivalent and *j* univalent, K_{ij} needs to exceed the reciprocal of the activity of *j* before the electrode completely loses its selective response towards *i*.

The association of di-n-octylphenyl phosphonate as mediator with selectivity for calcium and of decan-1-ol with equal selectivity for calcium and magnesium is well illustrated by the series of electrodes made from membranes **VIII**, **XI** and **XIII**. Thus, membrane **XI**, based on decan-1-ol, shows little selectivity among the bivalent cations, while membrane **VIII**, based on di-n-octylphenyl phosphonate, is clearly selective for calcium. Membrane **XIII**, with equal weight proportions of the two mediators, exhibits an intermediate selectivity pattern. Such trends are also consistent with the selectivity patterns of membranes **I**, **II** and **III**, and thin-layer chromatography on Kieselgel G with benzene–acetic acid (9:1) as developer and ammonium molybdate/tin(II) chloride as detection reagent suggests that the liquid ion-exchanger of membrane **I** contains di-n-octylphenyl phosphonate or a similar mediator, and that of membranes **II** and **III** involves decan-1-ol. A comparison of the data for membranes **IV** and **VII** also demonstrates the effect of decan-1-ol in reducing selectivity among bivalent cations.

CONCLUSION

This investigation indicates that for the solvent mediators examined, the most useful ion-selective electrodes based on calcium bis(dialkylphosphate) sensors trapped in PVC require di-n-octylphenyl phosphonate as solvent mediator, whilst acceptable PVC matrix membrane electrodes selective for bivalent ions can be made with calcium bis(di-2-ethylhexylphosphate) as sensor and decan-1-ol as mediator. Although the presence of some di-n-octylphenyl phosphonate can reduce the rigidity of the membranes in the latter type of electrode, this must be controlled in order to avoid increase in selectivity for calcium and decrease in selectivity for other bivalent ions.

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Summary—This study on several alkan-1-ols, di-n-octylphenyl phosphonate and di-n-nonyl phthalate as solvent materials in ion-selective electrode membranes based on calcium bis(dialkylphosphate) sensors trapped in a PVC matrix indicates that the best electrodes are made with di-n-octylphenyl phosphonate. These are selective for calcium. The liquid alcohols readily exude from the PVC matrix, and solid alcohols are completely unsuitable for membrane fabrication. However, despite a tendency to be exuded, decan-1-ol gives acceptable electrodes responsive to bivalent cations if calcium bis (di-2-ethylhexylphosphate) is used as sensor. Several selectivity coefficients, K_{Caj}, greater than unity were found, but though such values for j = Na or K do not involve complete loss of selectivity towards calcium, a value of $K_{CaCu} = 13$ for a membrane with di-n-nonyl phthalate as mediator and calcium bis(di-n-decylphosphate) as sensor indicates greater selectivity for copper than for calcium.

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INDIRECT COMPLEXOMETRIC DETERMINATION OF BERYLLIUM

ARTHUR DE SOUSA

Brigus, Conception Bay, Newfoundland, Canada

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It is well known that beryllium cannot be titrated directly with EDTA and is therefore determined indirectly Misumi and Taketatsu[1] have described a procedure in which $[Co(NH_3)_6][H_2O)_2Be_2(CO_3)_2.(OH_3].3(H_2O)$ is precipitated and the solid complex is redissolved in a boiling solution of sodium hydroxide and, after acidification with hydrochloric acid, the Co is determined *via* EDTA titration. The complete formation of the precipitate is time-consuming and there is a risk of contamination by any nickel present and of adsorption of foreign ions. The precipitate cannot be used for gravimetric purposes. Several determinations made by the author, using this procedure and reagent grade solutions of beryllium sulphate gave low values for the Be, and when Cu^{2+}, Ni^{2+}, Cr^{3+} and Mn^{2+} were present, the values for Be were higher than those expected.

An improved method is described here. Beryllium is precipitated almost instantaneously from its solution at pH 5.2 by the addition of 20% diammonium hydrogen phosphate solution.[2,3,4] When precipitated under proper conditions, beryllium ammonium phosphate conforms strictly to the formula $Be(NH_4)PO_4$.[5] The precipitate is collected on a filter, washed and then dissolved in a hot solution of dilute hydrochloric acid. The solution is cooled, the pH is adjusted to 3.5 and the solution is passed through a resin column in the cationic form (Na^+) so as to retain Be^{2+} which if not removed from the solution would reprecipitate as $Be(NH_4)PO_4$ when the solution is made alkaline for titration.

$Na_2(NH_4)PO_4$ passing through the resin bed is collected and magnesium chloride solution is added to precipitate $Mg(NH_4)PO_4$, which is collected, washed, and dissolved in hot dilute hydrochloric acid. A known and excessive volume of 0.1*M* EDTA is then added to the solution to complex magnesium,[6] and the excess is back-titrated. As $Be(NH_4)PO_4$ is converted into $Mg(NH_4)PO_4$ and the Mg content determined by EDTA titration, that of Be can be obtained.

EXPERIMENTAL

Reagents

Diammonium hydrogen phosphate solution, 20% *w/v*.

Dilute hydrochloric acid (1 + 1).

Magnesium chloride solution 1M. $MgCl_2.6H_2O$ (11 g) is dissolved in a small volume of water, 280 g of ammonia solution (sp. gr. 0·90) are added and the solution is diluted to 500 ml with distilled water. The solution is allowed to stand for several hours and then filtered into a glass-stoppered bottle.

Ammonia solution (1 + 1).

EDTA solution 0·100M.

Magnesium chloride solution 0·100M. Standardized against the 0·100*M* EDTA.

Eriochrome Black T indicator. A 1% dry mixture with sodium chloride.

Apparatus

Resin column consisting of a glass tube 1·8 cm internal diameter, 20 cm long, filled to a height of 12 cm with Dowex 50W-X8 resin (Na^+-form, 20 mesh).

Procedure

Adjust the pH of the beryllium solution to 5·2 by adding dilute ammonia or dilute hydrochloric acid. Then add a slight excess of diammonium hydrogen phosphate solution. Filter off the precipitate on a porosity-4 sintered-glass

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Summary—This study on several alkan-1-ols, di-n-octylphenyl phosphonate and di-n-nonyl phthalate as solvent materials in ion-selective electrode membranes based on calcium bis(dialkylphosphate) sensors trapped in a PVC matrix indicates that the best electrodes are made with di-n-octylphenyl phosphonate. These are selective for calcium. The liquid alcohols readily exude from the PVC matrix, and solid alcohols are completely unsuitable for membrane fabrication. However, despite a tendency to be exuded, decan-1-ol gives acceptable electrodes responsive to bivalent cations if calcium bis (di-2-ethylhexylphosphate) is used as sensor. Several selectivity coefficients, K_{Caj}, greater than unity were found, but though such values for j = Na or K do not involve complete loss of selectivity towards calcium, a value of $K_{CaCu} = 13$ for a membrane with di-n-nonyl phthalate as mediator and calcium bis(di-n-decylphosphate) as sensor indicates greater selectivity for copper than for calcium.

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INDIRECT COMPLEXOMETRIC DETERMINATION OF BERYLLIUM

ARTHUR DE SOUSA

Brigus, Conception Bay, Newfoundland, Canada

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It is well known that beryllium cannot be titrated directly with EDTA and is therefore determined indirectly Misumi and Taketatsu[1] have described a procedure in which $[Co(NH_3)_6][H_2O)_2Be_2(CO_3)_2.(OH_3].3(H_2O)$ is precipitated and the solid complex is redissolved in a boiling solution of sodium hydroxide and, after acidification with hydrochloric acid, the Co is determined *via* EDTA titration. The complete formation of the precipitate is time-consuming and there is a risk of contamination by any nickel present and of adsorption of foreign ions. The precipitate cannot be used for gravimetric purposes. Several determinations made by the author, using this procedure and reagent grade solutions of beryllium sulphate gave low values for the Be, and when Cu^{2+}, Ni^{2+}, Cr^{3+} and Mn^{2+} were present, the values for Be were higher than those expected.

An improved method is described here. Beryllium is precipitated almost instantaneously from its solution at pH 5.2 by the addition of 20% diammonium hydrogen phosphate solution.[2,3,4] When precipitated under proper conditions, beryllium ammonium phosphate conforms strictly to the formula $Be(NH_4)PO_4$.[5] The precipitate is collected on a filter, washed and then dissolved in a hot solution of dilute hydrochloric acid. The solution is cooled, the pH is adjusted to 3.5 and the solution is passed through a resin column in the cationic form (Na^+) so as to retain Be^{2+} which if not removed from the solution would reprecipitate as $Be(NH_4)PO_4$ when the solution is made alkaline for titration.

$Na_2(NH_4)PO_4$ passing through the resin bed is collected and magnesium chloride solution is added to precipitate $Mg(NH_4)PO_4$, which is collected, washed, and dissolved in hot dilute hydrochloric acid. A known and excessive volume of 0.1*M* EDTA is then added to the solution to complex magnesium,[6] and the excess is back-titrated. As $Be(NH_4)PO_4$ is converted into $Mg(NH_4)PO_4$ and the Mg content determined by EDTA titration, that of Be can be obtained.

EXPERIMENTAL

Reagents

Diammonium hydrogen phosphate solution, 20% *w/v*.

Dilute hydrochloric acid (1 + 1).

Magnesium chloride solution 1M. $MgCl_2.6H_2O$ (11 g) is dissolved in a small volume of water, 280 g of ammonia solution (sp. gr. 0·90) are added and the solution is diluted to 500 ml with distilled water. The solution is allowed to stand for several hours and then filtered into a glass-stoppered bottle.

Ammonia solution (1 + 1).

EDTA solution 0·100M.

Magnesium chloride solution 0·100M. Standardized against the 0·100*M* EDTA.

Eriochrome Black T indicator. A 1% dry mixture with sodium chloride.

Apparatus

Resin column consisting of a glass tube 1·8 cm internal diameter, 20 cm long, filled to a height of 12 cm with Dowex 50W-X8 resin (Na^+-form, 20 mesh).

Procedure

Adjust the pH of the beryllium solution to 5·2 by adding dilute ammonia or dilute hydrochloric acid. Then add a slight excess of diammonium hydrogen phosphate solution. Filter off the precipitate on a porosity-4 sintered-glass

filter. Wash the precipitate three or four times with cold water, in which the precipitate is almost insoluble (12 mg/l. at 15°).[4] Dissolve the precipitate in hot hydrochloric acid (1 + 1). Wash the filter two or three times with water and add the washings to the beaker containing the dissolved precipitate. Dilute the solution to about 400 ml. Adjust the pH to 3·5 by adding ammonia solution (1 + 1). Pass the solution through the resin at a flow-rate not exceeding 2 ml/min. Faster flow-rates may lead to breakthrough of beryllium. Follow with 200 ml of water. Collect the solution coming through the column in the same beaker as the $Na_2(NH_4)PO_4$ solution. Evaporate the solution to 100–150 ml. Make the solution almost neutral by adding ammonia solution dropwise. Then to the cooled solution add dropwise (2 drops/sec) 10 ml of cold ammoniacal magnesium chloride solution with constant stirring. When the solution becomes cloudy, discontinue stirring and allow the precipitate to settle for at least 10 min. Collect the precipitate in a porosity-4 sintered-glass filter, wash the precipitate two or three times with ammonia solution (1 + 1) and then dissolve it by placing the filter and precipitate in a 250-ml beaker with enough hydrochloric acid (1 + 1) to cover the filter. Heat gently while stirring to dissolve the precipitate completely.

After the dissolution add a known and excessive volume of 0·100*M* EDTA and make the solution alkaline with ammonia. Back-titrate the excess of EDTA with 0·100*M* magnesium chloride after adding the indicator. The end-point is marked by the colour change from blue to red.

Calculations

Let N_1 ml be the total volume of 0·100*M* EDTA added and N_2 ml the volume of 0·100*M* magnesium chloride required for the back-titration. The beryllium content will be $(N_1 - N_2) \times 0{\cdot}9013$ mg.

RESULTS AND REMARKS

The procedure described gives very satisfactory results for routine analysis of beryllium metal, alloys and minerals. No interference from other ions has been observed after the precipitation of $Be(NH_4)PO_4$, its dissolution and ion-exchange treatment. The standardization of the magnesium chloride solution against the EDTA titrant must be accurately done. Typical results obtained for beryllium solutions and alloys are reproduced in Tables 1, 2 and 3 and show that the proposed method gives satisfactory results. Though the technique described may seem tedious, it gives good results in the beryllium industry where analyses are carried out in series.

Table 1. Pure beryllium solutions

Be taken, *mg*	Be found, *mg*	Difference, %
4·78	4·52	−5·5
8·05	7·97	−1·0
12·13	12·17	+0·3
21·07	21·00	−0·3
30·58	30·49	−0·3
47·15	47·03	−0·3
60·54	60·21	−0·5
73·80	73·68	−0·2

Table 2. Beryllium alloys

Alloy	Be taken, *mg*	Be found, *mg*	Difference %
Be 3% Cu 97%	5·50	5·70	+4·0
Be 3% Cu 97%	15·45	15·60	+1·0
Be 1% Cu 99%	12·13	12·23	+0·8
Be 3% Cu 97%	20·17	20·34	+0·8
Be 1% Cu 99%	16·45	16·50	+0·3
Be 2% Ni 98%	24·95	25·08	+0·5
Be 4% Ni 96%	21·72	21·90	+0·8
Be 5% Ni 95%	33·08	33·13	+0·5
Be 5% Ni 95%	30·92	31·02	+0·3
Be 7% Al 93%	20·25	20·35	+0·5
Be 5% Al 95%	70·12	70·24	+0·2
Be 4% Al 96%	80·72	80·90	+0·2

Table 3. Beryllium plus impurities

Impurities	Be taken, *mg*	Be found, *mg*	Difference %
5% Fe	100·00	99·98	−0·02
10% Fe	100·00	100·20	+0·20
5% Ti	100·00	100·07	+0·07
10% Ti	100·00	100·10	+0·10
15% Al	100·00	99·97	−0·03
20% Al	100·00	100·15	+0·15
2% Cr	100·00	100·08	+0·08
5% Cr	100·00	99·90	−0·10

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Summary—An indirect complexometric method is described for the determination of beryllium, which is selectively precipitated as $Be(NH_4)PO_4$, then dissolved in HCl, and the solution passed through an ion-exchange column to retain Be and allow PO_4^{3-} to pass through. Phosphate is precipitated as $Mg(NH_4)PO_4$ and Mg in the precipitate is titrated with EDTA. Be is obtained from the Mg content.

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UTILIZATION OF AN Hg^{2+}-SENSITIVE MEMBRANE-ELECTRODE IN THE COMPLEXOMETRIC DETERMINATION OF Bi^{3+}, Fe^{3+} AND Cr^{3+}

ELENA HOPÎRTEAN, C. LITEANU and RODICA VLAD

Department of Analytical Chemistry, University of Cluj, Cluj, Romania

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In a previous paper[1] we reported the behaviour of the I^--selective membrane-electrode as an Hg^{2+}-sensitive membrane-electrode.[2] The behaviour of the I^--selective electrode relative to Hg^{2+} was also studied by Hiiro *et al.*[3] This paper extends the analytical use of the Hg^{2+}-sensitive membrane-electrode (our own pattern[1]) by employing it as indicating electrode for the potentiometric complexometric titration of some tervalent cations (Bi^{3+}, Fe^{3+}, Cr^{3+}) for which no adequate electrodes exist.

EXPERIMENTAL

Apparatus and reagents

The Hg^{2+}-sensitive membrane-electrode (composition 3:1 molar ratio of AgI to Ag_2S) was used. The membrane-electrode potential was measured *via* the e.m.f. of the electrolytic cell

SCE ‖ salt bridge 10^{-1} *M* KNO_3–agar-agar ‖ test solution | Hg^{2+}-sensitive membrane-electrode

Potential measurements were performed at room temperature, with stirring, with a pH-meter accurate to ± 2 mV.

All reagents used were of *p.a.* purity.

Determination of Bi^{3+} and Fe^{3+}

The complexometric determination of Bi^{3+} and Fe^{3+} was performed by the substitution reaction with the Hg–EDTA complex (HgY^{2-}); the Hg^{2+} liberated is titrated with EDTA in the presence of the Hg^{2+}-sensitive membrane-electrode. ($K_{BiY^-} = 8{\cdot}71 \times 10^{27}$, $K_{FeY^-} = 1{\cdot}26 \times 10^{25}$ and $K_{HgY^{2-}} = 6{\cdot}31 \times 10^{21}$). Because the HgY^{2-} used contained a small excess of Hg^{2+}, a blank correction was needed.

Working procedure. To a solution containing Bi^{3+} or Fe^{3+} add excess of HgY^{2-} solution and approx. 0·5 g of hexamine to raise the pH to ~4. Heat the solution to 80–90°, cool, and titrate with EDTA in the presence of the Hg^{2+}-sensitive indicating electrode.

Determination of Cr^{3+}

The determination was performed by adding excess of H_2Y^{2-} to the Cr^{3+} solution and back-titrating with standard Hg^{2+} solution in the presence of the Hg^{2+}-sensitive membrane-electrode.

Working procedure. Add EDTA solution in excess to the Cr^{3+} solution, adjust the pH to ~4 with hexamine, boil the solution for 2–3 min, cool and titrate the excess of EDTA with standard Hg^{2+} solution.

RESULTS AND DISCUSSION

Table 1 lists the experimental results obtained for Bi^{3+} and Fe^{3+}. Each result is the mean of two determinations. Table 2 gives the results for Cr^{3+} (means of three determinations).

Table 1. Results of the complexometric determination of Bi^{3+} and Fe^{3+}, with the Hg^{2+}-sensitive membrane-electrode and HgI^{2-} solution

Cation	Taken, mg	Found, mg	Error, %	ΔE, mV*
Bi^{3+}	10.3	10.3	0	36
	5.18	5.22	+ 0.8	25
	0.518	0.514	− 0.8	18
Fe^{3+}	5.56	5.56	0	45
	1.38	1.34	− 3.0	20
	0.138	0.135	− 2.2	15

* For the range equivalence volume ± 1%.

Table 2. Results of the complexometric determination of Cr^{3+} by back-titration of the H_2Y^{2-} excess with standard Hg^{2+} solution

Cr^{3+}, mg		Error, %	ΔE, mV*
Taken	Found		
5.45	5.45	0	100
0.545	0.543	− 0.4	85
0.272	0.252	− 7	68

* For the range equivalence volume ± 1%.

The equivalence volumes were calculated by the Hahn–Weiler interpolation method.[4] The true Bi^{3+} and Fe^{3+} contents for calculation of the error were established by using Xylenol Orange and sulphosalicylic acid respectively to indicate the end-point in complexometric titrations of these ions at $10^{-2}M$ concentration. The potential jump at the equivalence point was estimated graphically.

From the results in Table 1 it is clear that both Bi^{3+} and Fe^{3+} may be determined with EDTA by using the Hg^{2+}-sensitive membrane-electrode for end-point detection. The Bi^{3+} determination is particularly accurate, the error obtained even at $10^{-4}M$ concentration being below 1%. Iron can also be determined satisfactorily at this level.

The true value of the Cr^{3+} content was also established by chemical end-point indication. From Table 2, the titration of Cr^{3+} gives an error of $<1\%$ at a concentration of $10^{-3}M$ and the potential jump at the equivalence point is 85 mV over 2% of the titration volume. Although at $2{\cdot}5 \times 10^{-4}M$ concentration the potential change at the equivalence point remains high (70 mV), the accuracy is no longer satisfactory.

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Summary—The paper reports the results obtained in the complexometric determination of Bi^{3+}, Fe^{3+} and Cr^{3+} by using an Hg^{2+}-sensitive membrane-electrode for the end-point indication. The determination of Bi^{3+} and Fe^{3+} is performed after addition of mercuric complexonate from which these cations release Hg^{2+}, by means of which the electrode senses the equivalence point. In the case of Cr^{3+} an excess of complexone is added and the surplus is titrated with a standard solution of Hg^{2+} in the presence of the Hg^{2+}-sensitive membrane-electrode.

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THALLIC PERCHLORATE IN ACID MEDIUM AS A REAGENT FOR OXIDIMETRIC DETERMINATION OF ASCORBIC ACID IN DRUGS AND FRUIT

DINESH GUPTA, P. D. SHARMA and Y. K. GUPTA
Chemical Laboratories, University of Rajasthan, Jaipur, India

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Use of thallium(III) as an analytical reagent has recently been described.[1,2] Both direct titration with *p*-ethoxychrysoidine as indicator and an indirect method by iodometric back-titration are possible. Determinations of ascorbic acid with cerium(IV),[3] ferricyanide,[4] bromine cyanide,[5] vanadium(V),[6] iodate,[7] copper(III)[8] and many other reagents[9–18] have been reported. Bromate[19] and other methods[20,21] have been suggested for its determination in drugs, and iodine[22] and iodate[23] have been recommended for its determination in fruits and vegetables. Several modified methods[24–27] have been suggested. A method for its determination in urine has been described.[28] A rapid pototentiometric method has also been reported.[29] The present method with thallium(III) as a reagent can be employed for the determination of ascorbic acid in drugs and fruit.

EXPERIMENTAL

Reagents

Thallic perchlorate was prepared by dissolving Tl_2O_3 in 60% perchloric acid and standardized iodometrically.[30,31] A 0·2% solution of *p*-ethoxychrysoidine in ethanol was prepared.

Procedures

For direct titrations the hydrogen-ion concentration of the reaction mixture should not be less than 0·5*M* during the titration. The solution was vigorously swirled after each addition of Tl(III). The end-point was marked by the disappearance of the pink colour of the indicator. Typical results are given in Table 1. Since ascorbic acid has a tendency to undergo aerial oxidation, all the determinations were carried out in an atmosphere of carbon dioxide. No indicator correction was necessary. In the indirect titration excess of thallic perchlorate was added to the sample and unreacted Tl(III) determined iodometrically.

Determination of ascorbic acid in vitamin C tablets. The tablets were ground to a fine powder and dissolved in water. The solution was not colourless and hence indirect titration was used. Filtration had no effect on the results (Table 2).

Determination of ascorbic acid in fruit. The edible portion of the fruit was crushed in a machine and the juice completely extracted. The solid material was separated by filtering the juice through a sieve and was washed several times. Ascorbic acid was determined by the indirect method because the juice was coloured. The results are given in Table 3.

Table 1. Estimation of ascorbic acid with thallic perchlorate

Direct titration, *mg*		Indirect titration, *mg*	
Taken	Found	Taken	Found
1·76	1·76	0·352	0·350
3·52	3·50	0·428	0·430
5·28	5·30	0·704	0·700
7·04	7·04	1·05	1·05
8·80	8·85	1·408	1·41
14·08	14·1	7·04	7·04
17·60	17·6	14·08	14·1
21·1	21·0	28·16	28·2
26·4	26·4	35·2	35·1
35·2	35·2	42·24	42·2
52·8	52·8		
70·4	70·4		
88·0	88·1		

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7·04	7·04	1·05	1·05
8·80	8·85	1·408	1·41
14·08	14·1	7·04	7·04
17·60	17·6	14·08	14·1
21·1	21·0	28·16	28·2
26·4	26·4	35·2	35·1
35·2	35·2	42·24	42·2
52·8	52·8		
70·4	70·4		
88·0	88·1		

Table 2. Estimation of ascorbic acid in vitamin C tablets with thallic perchlorate

Sample	Reported by the manufacturer, *mg*	Found, *mg*
"Redoxen"	500 (706463, Roche)	503 ± 1
"Redoxen"	200 (709182, Roche)	195 ± 3
"Celin"	500 (1631, Glaxo)	490 ± 3
"Chewcee"	500 (4102-584, Lederle)	498 ± 3
"Citravite"	500 (3010, Pharmed)	502 ± 2
"Cecon"	500 (33.205 YA Abott)	490 ± 6

Table 3. Estimation of ascorbic acid in fruit with thallic perchlorate

Fruit	Ascorbic acid. *mg*/100 *g* Reported	Found by iodimetry	Found by the present method
Tomato (round yellow)	20	20·1 ± 0·5	20·1 ± 0·4
Tomato (ovoid flat red)	22	22·4 ± 0·5	22·5 ± 0·5
Strawberry (yellow)	80	86 ± 2	85·9 ± 3
Strawberry (dark yellow)	80	83 ± 2	83·3 ± 3
Amla (green)	600	608 ± 3	610 ± 5
Amla (yellow-green)	600	591 ± 4	590 ± 5
Lemon (yellow)	—	179 ± 1	180 ± 2
Orange	—	81 ± 1	80 ± 1

Interferences

Citric, tartaric, succinic and malic acids, glucose, fructose and sucrose do not interfere. Cations such as Mn^{2+}, Cu^{2+}, Fe^{2+}, Ni^{2+}, Co^{2+}, Zn^{2+} and Ba^{2+} have no effect on the direct titration. Sulphate and nitrate are without any effect, but chloride interferes. The inhibition by chloride ions has already been reported.[32] It appears that the oxidation of ascorbic acid occurs *via* complex formation between it and Tl(III). The product, dehydroascorbic acid, is not oxidized by Tl(III).

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Summary—Thallic perchlorate is used for determination of ascorbic acid either by direct titration in acid medium (0·5*N*) or indirectly by addition of excess of the reagent and iodometric determination of the excess. The method is applicable to fruit juices and vitamin C tablets.

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SYNTHESIS AND METALLOCHROMIC PROPERTIES OF SOME NEW MONO- AND BISHYDRAZONES OF BENZIL AND 2,2′-PYRIDIL

A. A. SCHILT® and J. F. WU

Department of Chemistry, Northern Illinois University, DeKalb, Illinois 60115

and

FRANCIS H. CASE

Department of Chemistry, Temple University, Philadelphia, Pennsylvania 19122, U.S.A.

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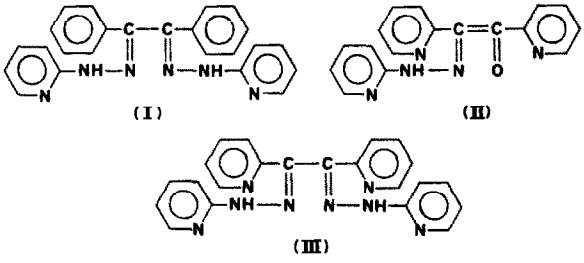
In recent years a variety of hydrazones have been prepared from 2-pyridylhydrazine, pyridine-2-carboxaldehyde, and related compounds for possible use as complexation reagents.[1–5] Many of these possess the ferroin chromophoric group. Some closely resemble 2,2′-bipyridyl, acting as bidentate ligands and forming coloured complexes in reactions with iron(II), cobalt(II) and nickel(II).[1] Hydrazones with terdentate chelating ability have also been synthesized and studied.[2–4] An especially noteworthy feature of these is that they form much more intensely coloured nickel(II) and cobalt(II) chelates than do any other of the ferroin type chromogens. Even more striking and unexpected is the discovery that certain of the terdentate hydrazone derivatives will form highly coloured zinc(II) chelates.[2,5] No practical application has been made of these for determining zinc, perhaps because they are non-selective. However, sensitive methods have been developed utilizing these hydrazones for the determination of trace amounts of other metals. Ryan and co-workers have described the use of pyridine-2-carboxaldehyde-2-quinolylhydrazone, one of the most sensitive chromogens known of this type, for the determination of palladium,[6] cobalt and nickel,[7] and nickel in sea-water.[8]

With the object of providing additional reagents of the hydrazone type, we have prepared the following new mono- and bishydrazones: benzil di-2-pyridylhydrazone (**I**); 2,2′-pyridil mono-2-pyridyl-hydrazone (**II**); 2,2′-pyridil di-2-pyridylhydrazone (**III**); picolinanilide azine with benzil (**IV**); picolinanilide azine with 2,2′-pyridil (**V**); *N*-2-pyridyl benzamide azine with benzil (**VI**) and with 2,2′-pyridil (**VII**); and *N*-2-pyridylpicolinamide azine with benzil (**VIII**) and with 2,2′-pyridil (**IX**). The preparation of the requisite intermediates is described in a previous communication.[9]

An interesting aspect of some of the compounds prepared for the present study is that in addition to a ferroin group they also possess a carbonyl oxygen atom that is potentially capable of serving as a donor in concert with an imine-nitrogen atom to form a five-membered chelate ring. In this particular regard the compounds are very similar to the α-diketone mono-α-pyridylhydrazone type ligands first prepared and characterized by Chiswell, Lions and Tomlinson,[10] except that the latter compounds do not possess ferroin groups.



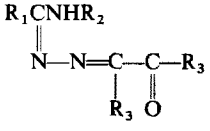
(I) (II) (III)

EXPERIMENTAL

Reagents

Preparation of amide azines with benzil and 2,2′-pyridil. An equimolar mixture of diketone and substituted amidra-

Table 1. Substituted amide azines with benzil and 2,2′-pyridil



	R_1	R_2	R_3	Yield, %	m.p., °C	Crystallization solvent	Formula	Analysis: Calcd., % C	H	N	Found, % C	H	N
IV	2-C_5H_4N	C_6H_5	C_6H_5	63	147–148	C_2H_5OH	$C_{26}H_{20}N_4O$	77·21	4·98	13·85	77·5	4·9	14·1
V	2-C_5H_4N	C_6H_5	2-C_5H_4N	58	173–174	C_2H_5OH	$C_{24}H_{18}N_6O$	70·92	4·46	20·68	70·9	4·6	20·6
VI	C_6H_5	2-C_5H_4N	C_6H_5	37	145	C_2H_5OH	$C_{26}H_{20}N_4O$	77·21	4·98	13·85	77·4	5·1	14·3
VII	C_6H_5	2-C_5H_4N	2-C_5H_4N	58	208	methyl cellosolve	$C_{24}H_{18}N_6O$	70·92	4·46	20·68	71·1	4·5	21·1
VIII	2-C_5H_4N	2-C_5H_4N	C_6H_5	32	154	C_2H_5OH	$C_{25}H_{19}N_5O$	74·06	4·72	17·27	74·0	4·7	17·6
IX	2-C_5H_4N	2-C_5H_4N	2-C_5H_4N	47	173	C_2H_5OH	$C_{23}H_{17}N_7O$	67·80	4·20	24·06	67·5	4·2	24·5

Table 2. Properties of iron(II) chelates

Ligand	Colour	λ_{max} nm	ϵ*	L:Fe ratio	Comments†
I	Yellow	635	$5{\cdot}8 \times 10^3$		*a,b,c,e*
II	Green	621	$1{\cdot}30 \times 10^4$	2:1	*d*
III	Green	595	$8{\cdot}3 \times 10^3$	2:1	
	Yellow-green	573	$1{\cdot}04 \times 10^4$	3:1	
IV	Colourless				
V	Blue	618	$8{\cdot}3 \times 10^3$	3:1	*b,d,e*
VI	Colourless				
VII	Yellow-green	668	$1{\cdot}44 \times 10^4$	3:1	*b,c*
VIII	Colourless				
IX	Green	665	$9{\cdot}8 \times 10^3$		*a,b,d*

* Molar absorptivity ($l.mole^{-1}.cm^{-1}$) at wavelength of maximum absorbance.

† *a*—complex too weak to identify; *b*—weak complex requires large excess of ligand to form completely; *c*—complex insoluble in water; *d*—colour unstable with time; *e*—pH-dependent colour (green for pH > 10).

zone [about 1 g each of the hydrazones of picolinanilide, *N*-2-pyridylbenzamide or *N*-2-pyridylpicolinamide[9]] in 25 ml of ethanol was heated under reflux for 3 hr. After evaporation of the ethanol, the products were crystallized from the solvent mentioned in Table 1.

Preparation of 2,2'-pyridil-2-pyridylhydrazone (**II**). A solution of 1 g of 2-pyridylhydrazine and 2 g of 2,2'-pyridil in 20 ml of ethanol was heated under reflux for 3 hr. Evaporation of the solvent and crystallization of the residue from aqueous methanol yielded 2·3 g (82%) of product melting at 108–109°. Found: C 67·3%, H 4·3%, N 23·3%; $C_{17}H_{13}N_5O$ requires 67·32%, H 4·32%, N 23·09%.

Preparation of benzil-bis-2-pyridylhydrazone (**I**). A mixture of 1·5 g of benzil-2-pyridyl monohydrazone[10] and 0·7 g of 2-pyridylhydrazine was heated for 5 hr at 190–200°. The residue, on crystallization from ethanol, yielded 0·7 g (35%) of product melting at 180° (with sintering). Found: C 73·5%, H 5·2%, N 21·5%; $C_{24}H_{20}N_6$ requires C 73·45%, H 5·14%, N 21·41%.

Preparation of 2,2'-pyridil-bis-2-pyridylhydrazone (**III**). A mixture of 1·5 g each of 2,2'-pyridil and 2-pyridylhydrazine was heated for 5 hr at 190–200°. The resulting product, on crystallization from aqueous ethanol, yielded 0·7 g (26%) of product melting at 222–223°. Found: C 66·5%, H 4·6%, N 28·4%; $C_{22}H_{18}N_8$ requires C 66·74%, H 4·53%, N 28·67%.

Solutions. (0·01 *M*) of the compounds to be tested were prepared by dissolving weighed amounts in ethanol. Standard solutions of metal ions were prepared by dissolving weighed quantities of pure metal in a slight excess of either hydrochloric or nitric acid and diluting to a measured total weight with distilled water.

Iron-free hydroxylamine hydrochloride solution and pH buffer solutions were prepared as described previously.[11]

Apparatus

A Cary Model 14 recording spectrophotometer and Corning Model 7 pH meter with saturated calomel and glass electrodes were used for spectral and pH measurements respectively.

Chelation studies

The pH range over which complexation occurred, as indicated by colour formation, was determined for each metal ion and test compound combination. Absorption spectra in the visible range were recorded for accurately prepared solutions, all buffered at pH 7 (ammonium acetate buffer) to favour more complete complex formation. Ligand to metal ratios for the iron(II) chelates were determined by the mole-ratio method. Details for all three procedures are described elsewhere.[11]

RESULTS AND DISCUSSION

All the coloured metal complexes are at least partially extractable into isoamyl alcohol. Those of **I** and **III** are quantitatively extractable at pH 7 by a volume of isoamyl alcohol equal to one-fourth or less of that of the aqueous phase. Most of the compounds (except **II**, **V**, and **IX**) and their metal complexes are insoluble in water but soluble in ethanol and in ethanol–water mixtures.

Formation of the coloured metal chelates is favoured in ethanol–water solutions of pH 3–12. Maximum colour formation occurs in most cases between pH 6 and 9. All solutions prepared for spectral examination were therefore buffered at pH 7 with ammonium acetate.

The results compiled in Tables 2 and 3 provide a basis for judging the potential analytical utility of the compounds as chromogenic reagents. Of the group studied, compounds **II** and **III** show the most promise as sensitive reagents for cobalt, nickel, zinc, copper and iron. Unfortunately both lack selectivity to the extent that if all five of the foregoing metal ions were present in the same sample, only iron could be determined without appreciable error caused by the presence of any of the others. Compound **VII** also shows promise as a spectrophotometric reagent for iron. It should prove superior to both **II** and **III** with regard to selectivity, becasue it does not form a coloured copper(I) chelate and the molar absorptivities of its cobalt(II), nickel(II) and zinc(II) chelates are considerably less than those of the **II** and **III** complexes. It is also a more sensitive iron chromogen than either **II** or **III**.

Table 3. Absorption properties of chelates*

	Copper(I)		Cobalt(II)		Nickel(II)		Zinc(II)	
Ligand	λ,nm	ϵ	λ,nm	ϵ	λ,nm	ϵ	λ,nm	ϵ
I	430†	$5{\cdot}4 \times 10^3$	531†	$4{\cdot}6 \times 10^3$‡	497	$4{\cdot}9 \times 10^3$	§	§
II	496	$1{\cdot}62 \times 10^4$	489	$2{\cdot}80 \times 10^4$	474	$2{\cdot}80 \times 10^4$	466	$2{\cdot}40 \times 10^4$‡
III	466	$2{\cdot}03 \times 10^4$	480	$2{\cdot}54 \times 10^4$	452	$3{\cdot}20 \times 10^4$	452	$2{\cdot}40 \times 10^4$‡
IV	475	400	§	§	§	§	§	§
V	475†	$3{\cdot}8 \times 10^3$†	475†	$5{\cdot}8 \times 10^3$†	490†	$2{\cdot}6 \times 10^3$†	§	§
VI	§	§	§	§	§	§	§	§
VII	§	§	460†	$1{\cdot}21 \times 10^4$†	475†	$1{\cdot}30 \times 10^4$†	475†	400†
VIII	475†	$1{\cdot}8 \times 10^3$†	§	§	§	§	§	§
IX	§	§	490†	$8{\cdot}9 \times 10^3$†	460†	$1{\cdot}70 \times 10^4$†	475†	$1{\cdot}4 \times 10^3$†

* Measured in the visible region for ethanol–water solutions (all yellow–orange in colour), buffered at pH 7 with ammonium acetate.

† Not a band maximum but at shoulder or side of band just before reagent blank absorbance becomes appreciable.

‡ Weak complex; requires large excess of ligand to form completely.

§ Spectra of metal chelate and of free ligand are very nearly the same.

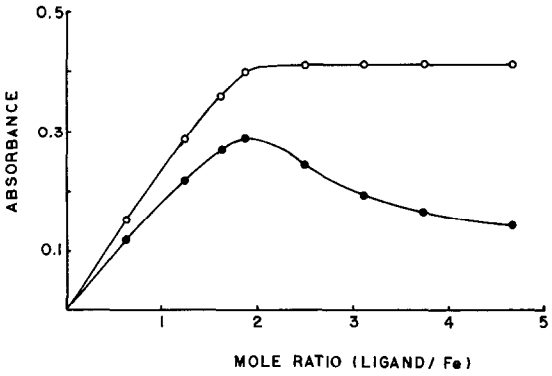


Fig. 1. Mole-ratio plot for the reaction of **III** with iron(II), measured at 598 nm (open circles) and at 640 nm (solid circles).

As expected on the basis of their structural similarities to previously studied hydrazones,[2–5] compounds **II** and **III** form highly coloured chelates with zinc, cobalt and nickel. Neither, however, is superior in chromogenic properties to pyridine-2-carboxaldehyde-2-quinolylhydrazone, which was found by Ryan and co-workers to be so exceptionally sensitive as a nickel and cobalt reagent.[6–8]

Compounds **IV, VI,** and **VIII** do not form coloured complexes with iron(II) or with cobalt(II), nickel(II), and zinc(II). In the case of **VI** this is expected because it does not possess a ferroin group. The other two compounds have such a group, so it is believed that steric effects prevent chelation of iron(II) as well as cobalt(II), nickel(II), and zinc(II), all of which normally form hexaco-ordinate octahedral complexes with ferroin-type ligands. Weakly coloured copper(I) complexes are formed by **VI** and **VIII**, presumably because steric hindrance is absent or less pronounced for tetraco-ordinate copper(I) which normally forms a tetrahedral complex with ferroin-type ligands. All of the other compounds have at least one ferroin group and give coloured iron(II) chelates. Two of these (**II** and **V**), for which reliable mole-ratio data could be obtained, are sufficiently unusual to merit special comment. Compound **II** has one ferroin group and one aza-ferroin group (=N–C–N–N=) which chelate in concert to form a bis-chelate of iron(II), *i.e.*, a complex with ligand to metal ratio of 2:1. Compound **V** has two ferroin groups, but only one is functional (the other is the same as that in **IV** and **VIII** which also failed to function); so **V** acts as a bidentate rather than a terdentate ligand for iron(II), giving rise to a tris-chelate (ligand to metal ratio 3:1).

Remarkable behaviour is shown by **III** in reaction with iron(II). The series of spectra obtained in the mole-ratio study reveals that a bis-chelate forms when the mole ratio of **III** to iron(II) is varied between 0 and 2, and that the bis-chelate is rapidly converted into a tris-chelate when additional amounts of **III** are added. This is clearly indicated by the presence of a well-defined isosbestic point at 598 nm. Mole-ratio plots for data at two distinctive wavelengths are shown in Fig. 1. The unusually high lability of the bis-chelate, enabling rapid conversion into the tris-chelate when excess of **III** is added, is probably a consequence of steric hindrance and weak bonding by the aza-ferroin group. Further study of the chelation properties of **III** should prove rewarding in terms of elucidating relationships among structure, bonding, and kinetics of chelation.

Summary—Preparation of some new mono- and bishydrazones which possess the ferroin chromophoric group is described, together with results of spectrophotometric studies of their chelation reactions with iron(II), copper(I), cobalt(II), nickel(II) and zinc(II). Several of the new compounds show promise as chromogenic reagents for these metals. The results are also of interest with regard to structure–reaction relationships.

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A CHLORATE ION-SELECTIVE ELECTRODE BASED ON A POLY(VINYL CHLORIDE)—MATRIX MEMBRANE

K. HIIRO,* G. J. MOODY and J. D. R. THOMAS
Chemistry Department, UWIST, Cardiff CF1 3NU, Wales

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Commercial nitrate liquid ion-exchangers may be trapped in PVC-matrix membranes to give nitrate ion-selective electrodes with closely similar calibration and selectivity characteristics to those of their liquid-membrane counterparts. Such electrodes have many physical, mechanical and cost advantages.[1]

Chlorate, iodide and perchlorate ions interfere seriously with each type of nitrate ion-selective electrode.[1] However, the interference can be exploited: for example, periodate may be monitored with a perchlorate electrode[2] and tetrafluoroborate with a liquid-membrane electrode based on the tetrafluoroborate form of a liquid nitrate ion-exchanger.[3]

This paper describes a short investigation on the calibration and selectivity parameters of a PVC-matrix membrane chlorate ion-selective electrode made from a nitrate-form liquid ion-exchanger converted into the chlorate form, and compares its behaviour with its nitrate ion counterpart. The nitrate ion-exchanger used was the tridodecylhexadecylammonium nitrate/n-octyl-*o*-nitrophenyl ether sensor/mediator system present in Corning 477316 nitrate liquid ion-exchanger.[1]

EXPERIMENTAL

Preparation of chlorate ion-exchanger

Corning 477316 nitrate liquid ion-exchanger (1·5 g) was converted into the chlorate form by shaking its solution in 15 ml of chloroform with three 15-ml aliquots of 0·5*M* potassium chlorate (analytical reagent grade). The chloroform was removed by evaporation over a period of three days from a beaker covered with a watch-glass.

Construction of the PVC-*matrix membrane electrodes*

Master PVC-matrix membranes were fabricated[4] from solutions of 0·40 g of liquid ion-exchanger and 0·17 g of PVC in 6 ml of tetrahydrofuran. Discs were cut from these membranes for the ion-selective electrode assembly[4] with mixed internal solutions of potassium chloride ($5 \times 10^{-2}M$)/potassium nitrate ($5 \times 10^{-2}M$) and potassium chloride ($5 \times 10^{-2}M$)/potassium chlorate ($5 \times 10^{-2}M$) for the nitrate and chlorate ion-selective electrodes, respectively.

Potentials of the electrodes *vs.* a calomel reference electrode (Corning Cat. No. 476109) were measured with a Beckman Research Model pH-meter for various test solutions maintained at 25 ± 0·1°. The electrodes were blotted with tissue paper between measurements.

Before use, each PVC–nitrate electrode was soaked for at least 1 day in 0·1*M* sodium nitrate for nitrate-ion response, and in 0·1*M* potassium chlorate for chlorate-ion response. The PVC–chlorate electrodes were similarly soaked and stored in 0·1*M* potassium chlorate.

RESULTS AND DISCUSSION

Calibration of the PVC–*nitrate and* PVC–*chlorate electrodes*

The calibration profile of the PVC–nitrate ion-selective electrode in sodium nitrate solutions resembled that previously described.[1] For the chlorate ion-selective electrode, potentials were recorded in standard solutions of both sodium and potassium chlorate, the concentrations of which were first decreased from 10^{-1} to $10^{-6}M$ and then increased from 10^{-6} to $10^{-1}M$ (Fig. 1). All electrodes were free from hysteresis.

General characteristics of the PVC–*chlorate electrode*

Despite frequent exposure to interferents, the electrode showed minimal drift between calibrations and the only deterioration with time was a fall in calibration slope after 16 days. Thus, the response was near-Nernstian, being 60 mV on day 2, 58 mV on days 9–16 with a drop to 52 mV being characteristic of days 18–21. However, in the period between days 16 and 18, the electrode had been exposed to potassium periodate (a serious interferent) during an assessment of selectivity. The detection limit as defined (see Fig. 1) by an e.m.f. difference of 18 mV between the calibration curve and the extrapolated linear section was consistently better than $3 \times 10^{-5}M$. Thus, for the first 16 days the calibrated detection limit was $1{\cdot}5 \times 10^{-5}M$, $3 \times 10^{-5}M$ on day 18 and $1{\cdot}5 \times 10^{-5}M$ on day 21.

While static response times are fast (Fig. 1), the dynamic responses are even faster, with the electrode consistently responding in less than 2 sec and frequently in under 1 second to a halving or doubling of the chlorate ion concentration, such times including injection of diluent or concentrate, mixing time and millivoltmeter/recorder response. For example, injecting 10 ml of water into 10 ml of $10^{-1}M$ potassium chlorate altered a steady e.m.f. reading of +52 mV to a steady +70 mV within 1·5 sec, the 18-mV difference comparing favourably with the expected 17-mV value for the induced change in chlorate ion activity.

Calibration of an electrode fabricated directly from the nitrate form of the Corning 477316 liquid ion-exchanger with standard chlorate solutions gave a detection limit for chlorate of just $5 \times 10^{-4}M$, an order of magnitude poorer than that noted above for the chlorate ion-selective electrode fabricated from the nitrate exchanger previously converted into the chlorate form. Furthermore, response times were of the order of minutes and were not improved by previously soaking the nitrate electrode in 0·1*M* potassium chlorate for a day. Thus, it is essential to first convert the nitrate liquid ion-exchanger into the chlorate form to produce a viable chlorate ion-selective electrode.

* Present address: Government Industrial Research Institute, Osaka, Midorigaoka 1, Ikeda City, Osaka Pref., Japan.

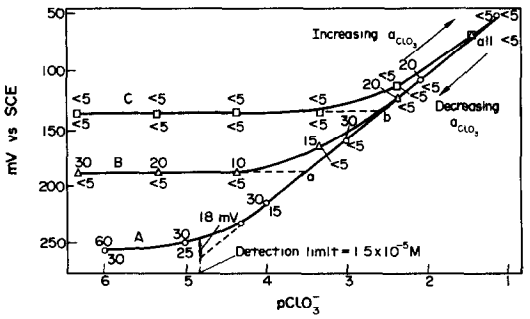

Fig. 1. Response of 9-day-old PVC–chlorate ion-selective electrode in two mixed chlorate–nitrate solutions at 25°. A, sodium or potassium chlorate, nitrate absent, slope = 58 mV per decade; B, $[NO_3^-] = 5 \times 10^{-4}M$; C, $[NO_3^-] = 5 \times 10^{-3}M$. Selectivity coefficients, $K_{ClO_3NO_3}$ at *a*, 0·64; *b*, 0·66. Figures adjacent to the symbols refer to the static response time (seconds) required for steady potentials to be attained.

Selectivity studies

Alkaline conditions are detrimental to the PVC–chlorate ion-selective electrode as they are to the PVC–nitrate electrode:[1] for example, at $10^{-2}M$ there is a fall in e.m.f. above pH 7·5, but steady readings and fast response times (<5 sec) prevail between pH 2 and 7·5.

The electrode responds to various foreign anions, *j*, as well as to chlorate, according to the equation

$$E = \text{Constant} - S\log[a_{ClO_3} + K_{ClO_3j}(a_j)^{1/n}] \quad (1)$$

where n is the charge on the foreign anion, S the calibration slope, and K_{ClO_3j} the selectivity coefficient.[5] The mixed solution approach previously employed in studies of the PVC–nitrate electrode[1] was used for determining selectivity coefficients. These are quoted in Table 1 and illustrated for nitrate interference of the chlorate electrode in Fig. 1 (curves B and C).

In general, K_{ClO_3j} is less than K_{NO_3j} as expected from the value of 1·66 for $K_{NO_3ClO_3}$ with the nitrate ion-selective electrode. Again, the characteristic high values for this tetra-alkylammonium-based ion-exchanger sensor are observed for $K_{ClO_3\,perhalate}$ but, of course, of somewhat smaller magnitude than is the case for the corresponding $K_{NO_3\,perhalate}$. Finally, it is interesting that of the halate ion species, chlorate appears to be the one preferred by this ion-exchanger in both the nitrate and chlorate forms.

Conclusion

Conversion of a nitrate liquid ion-exchanger ion-selective electrode sensor into the chlorate form before fabrication into a PVC-matrix membrane system is clearly beneficial in constructing a chlorate ion-selective electrode of superior character.

Table 1. Selectivity coefficients of nitrate and chlorate PVC–matrix membrane electrodes

Interferent, *j*	Nitrate electrode* K_{NO_3j}	Chlorate electrode† K_{ClO_3j}
F^-	$8{\cdot}7 \times 10^{-4}$	$4{\cdot}7 \times 10^{-4}$
	$(5 \times 10^{-2}M)$§	$(2{\cdot}5 \times 10^{-1}M)$
Cl^-	$9{\cdot}5 \times 10^{-3}$†	$2{\cdot}5 \times 10^{-3}$
	$(5 \times 10^{-1}M)$	$(5 \times 10^{-3}M)$
Br^-	0·16†	$8{\cdot}9 \times 10^{-2}$
	$(5 \times 10^{-4}M)$	$(5 \times 10^{-3}M)$
I^-	17	4·2
	$(5 \times 10^{-5}M)$	$(5 \times 10^{-3}M)$
NO_2^-	$6{\cdot}6 \times 10^{-2}$	$3{\cdot}6 \times 10^{-3}$
	$(5 \times 10^{-2}M)$	$(5 \times 10^{-1}M)$
SO_4^{2-}	10^{-5}	$3{\cdot}3 \times 10^{-4}$
	$(5 \times 10^{-1}M)$	$(1{\cdot}0 \times 10^{-1}M)$
ClO_3^-	1·8,†1·66	1·0
	$(5 \times 10^{-4}M)$	
NO_3^-	1·0	0·66
		$(5 \times 10^{-3}M)$
ClO_4^-	800	220
	$(5 \times 10^{-5}M)$	$(5 \times 10^{-3}M)$
IO_3^-	$8{\cdot}2 \times 10^{-2}$†	$7{\cdot}2 \times 10^{-2}$
	$(5 \times 10^{-4}M)$	$(5 \times 10^{-4}M)$
IO_4^-	1500†	370
	$(5 \times 10^{-5}M)$	$(5 \times 10^{-5}M)$
BrO_3^-	0·12†	0·10
	$(5 \times 10^{-4}M)$	$(5 \times 10^{-4}M)$

* Data from Reference 1 unless otherwise stated.
† This work.
§ Values in parentheses are interferent concentrations.

Acknowledgement—One of us (KH) thanks the Government Industrial Research Institute, Osaka, Japan, for financial support.

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Summary—An electrode has been prepared, consisting of a PVC membrane containing Corning 477316 nitrate liquid ion-exchanger in the chlorate form, which responds to chlorate ions. It has a faster response (1–2 sec) and lower limit of detection ($3 \times 10^{-5}M$) than the nitrate electrode for chlorate determination. Selectivity coefficients for the electrode towards several other ions have been measured.

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TITRATION OF THIOL GROUPS IN NON-AQUEOUS SOLVENTS

KRISHNA K. VERMA

Department of Chemistry, Government Science College, Jabalpur 482001, India

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Methods for the determination of thiols, involving oxidation with iodine or reaction with a metal ion, are satisfactory and widely used. The fact that these methods do not differentiate between aromatic and aliphatic thiols makes other procedures desirable. The titration of thiol groups as acids has long been visualized[1,2] and is explored in the present work.

Aromatic thiols are much more acidic than the corresponding phenols. Benzenethiol and its derivatives with electronegative substituents can be titrated in dimethylformamide or acetone with sodium methoxide, with Thymol Blue as indicator. A gradual and premature end-point is obtained in the titration of naphthalenethiol or derivatives of benzenethiol with electropositive substituents in the *ortho* or *para* positions when dimethylformamide is the medium and either Thymol Blue or Azo Violet is employed as indicator. However, such samples can be titrated satisfactorily in acetone, with Thymol Blue as indicator. In acetone, aliphatic thiols are not acidic to Thymol Blue and this permits an accurate titration of aromatic thiols in the presence of aliphatic thiols.

These titrations are convenient and rapid, yielding sharp and stable end-points. Generally, a precipitate is either not formed or is crystalline and does not affect the accuracy.

EXPERIMENTAL

Reagents

Sodium methoxide solution, 0·05 M, in benzene–methanol was prepared as described by Fritz and Lisicki[1] and standardized against benzoic acid in acetone, with Victoria Blue as indicator.

Indicators. Solutions (0·1%) of Thymol Blue, Victoria Blue, and Azo Violet (*p*-nitrophenylazoresorcinol) and a 0·2% solution of *p*-hydroxyazobenzene in acetone were used.

All solvents were of reagent grade.

Procedures

Titration of individual thiols. Dissolve the sample containing 0·1–2·0 meq of thiol in 25 ml of solvent and add 3–5 drops of indicator (Table 1). Titrate with 0·05*M* sodium methoxide to a blue (Azo Violet or Thymol Blue), red (Victoria Blue) or yellow colour (*p*-hydroxyazobenzene).

When dimethylformamide is used as solvent, add 3–5 drops of Azo Violet indicator to 25 ml of solvent and neutralize the acid impurities; add the sample and titrate to a blue colour.

Preferential titration of aromatic thiols. Dissolve the sample containing 0·1–2·0 meq of aromatic thiol in 25 ml of acetone. Add 3–5 drops of Thymol Blue indicator and titrate with 0·05*M* sodium methoxide to a blue colour.

RESULTS AND DISCUSSION

Analytical results for the titration of aromatic thiols are given in Table 1. Except in the titration of β-naphthalenethiol and *o*-mercaptobenzoic acid, no precipitate was

Table 1. Titration of thiols with sodium methoxide

Compound	Solvent and indicator	Purity, %	
		Present method*	Comparison method
Benzenethiol	Acetone–Thymol Blue	99·3	99·2†
p-Chlorobenzenethiol	Acetone–Thymol Blue	99·6	99·7†
2-Mercaptobenzimidazole	Dimethylformamide–Azo Violet	99·2	99·0§
2-Mercaptobenzothiazole	Dimethylformamide–Azo Violet	97·6	97·4†
2-Mercaptobenzoxazole	Dimethylformamide–Azo Violet	98·3	98·1†
o-Mercaptobenzoic acid	Acetone–Azo Violet	99·7‡	99·8†
m-Bromobenzenethiol	Acetone–Thymol Blue	99·1	99·3¶
β-Naphthalenethiol	Acetone–Thymol Blue	97·8	97·9†
p-Biphenylthiol	Acetone–Thymol Blue	98·2	98·1†
p-Toluenethiol	Acetone–Thymol Blue	99·5	99·7†
p-Mercaptobenzamide	Acetone–Thymol Blue	97·8	97·6§
Methyl-*o*-mercaptobenzoate	Acetone–Thymol Blue	98·9	99·2§
p-t-Butylbenzenethiol	Acetone–Thymol Blue	99·2	99·5†
Thioacetic acid	Acetone–*p*-hydroxyazobenzene	97·5	97·8¶
Thiobenzoic acid	Acetone–Victoria Blue	98·9	99·0¶

* Average of 10 determinations; standard deviation in the range 0·1–0·3%.
† Pb(IV) titration.[3]
§ Hg(II) titration.[4]
‡ Compound dibasic, purity on the basis of one acid group.
¶ Iodimetric titration.[5]

Table 2. Titration of aromatic thiols in the presence of aliphatic thiols

Sample	Amount, *mg*	
	Taken	Found
Benzenethiol	80·6	80·8
1-Butanethiol	56·2	—
p-Chlorobenzenethiol	160·9	160·8
1-Dodecanethiol	100·8	—
Benzenethiol	189·7	190·1
Toluene-α-thiol	62·3	—
β-Naphthalenethiol	75·8	75·6
1-Pentanethiol	63·5	—
m-Bromobenzenethiol	65·3	65·4
1-Hexadecanethiol	70·8	—
p-Toluenethiol	90·5	90·4
Cyclohexanethiol	63·2	—
p-Biphenylthiol	102·7	102·9
1-Propanethiol	88·6	—

formed. In Table 2, results for the determination of aromatic thiols in the presence of aliphatic thiols are given. The results are precise to 0·2%.

The titration of *o*-mercaptobenzoic acid is interesting. In acetone, with Azo Violet as indicator, the first sharp colour change is from yellow to red, corresponding to the neutralization of the carboxyl group. A second colour change is from red to blue when the thiol group is neutralized. A mixture of 2-mercaptobenzimidazole with a carboxylic acid could be analysed by this method. All aromatic thiols are of about the same strength as carboxylic acids. This behaviour is also exhibited in the titration of thiol-carboxylic acid mixtures in acetone, with *p*-hydroxyazobenzene as indicator. Therefore preferential titration of carboxylic acids is possible only in the presence of 2-mercaptobenzimidazole and aliphatic thiols. In acetone, only the carboxyl group of *o*-mercaptobenzoic acid is titrated when *p*-hydroxyazobenzene is used as indicator.

Acknowledgement—Thanks are due to Evans Chemetics, New York, U.S.A., for generous gifts of thiol samples.

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Summary—Thiols are titrated in acetone or dimethylformamide with sodium methoxide, employing visual end-point detection with Thymol Blue, Victoria Blue, *p*-hydroxyazobenzene or Azo Violet. Aromatic thiols are titrated in the presence of aliphatic thiols in acetone, with Thymol Blue as indicator.

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AMPEROMETRIC DETERMINATION OF ORGANIC ISOTHIOCYANATES

BALBIR CHAND VERMA* and SWATANTAR KUMAR

Chemistry Department, Punjabi University, Patiala, Punjab, India

(*Received* 23 *January* 1975. *Accepted* 28 *March* 1975)

Amperometric titrations may be used for the determination of many organic compounds and are inherently more accurate and precise than the conventional electrometric titrations. Silver nitrate has frequently been employed in amperometric titrations, especially in precipitation titrations of organic compounds with sulphur-containing functional groups. The products of such reactions depend on experimental conditions such as pH and solvent. Since organic isothiocyanates find extensive use as intermediates in the synthesis of polymers, their determination is of interest and value. Amperometric titration with silver nitrate can be extended to the determination of organic isothiocyanates if these are first converted into the corresponding substituted thioureas. The only attempt in this direction appears to be due to Fürst[1] who determined small amounts of allyl isothiocyanate by heating it with 25% aqueous ammonia for 10 min at 40°, and titrating the allyl thiourea thus formed, with standard silver nitrate solution amperometrically.

Isothiocyanates have been reported to react significantly with water[2] and hence the use of amines[2–6] (in place of ammonia) has been recommended for their conversion into the corresponding thioureas. Organic isothiocyanates are quantitatively converted with n-butylamine in dimethylformamide into the respective *N*,*N*-disubstituted thioureas[5,6] at room temperature.

$$RNCS + C_4H_9NH_2 \rightarrow RNHCSNHC_4H_9.$$

* Present address: Department of Chemistry, Himachal Pradesh University, Simla 171001, India.

Table 2. Titration of aromatic thiols in the presence of aliphatic thiols

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Isothiocyanates have been reported to react significantly with water[2] and hence the use of amines[2–6] (in place of ammonia) has been recommended for their conversion into the corresponding thioureas. Organic isothiocyanates are quantitatively converted with n-butylamine in dimethylformamide into the respective *N*,*N*-disubstituted thioureas[5,6] at room temperature.

$$RNCS + C_4H_9NH_2 \rightarrow RNHCSNHC_4H_9.$$

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Alkyl isothiocyanates require 10 min for the reaction whereas aryl isothiocyanates react immediately. In the present communication, the reaction has been utilized for the amperometric determination of small amounts of organic isothiocyanates. The proposed method involves treating an isothiocyanate with an excess of n-butylamine in dimethylformamide and titrating the resulting disubstituted thiourea argentometrically in an ammonia–ammonium nitrate buffer, with amperometric detection of the end-point.

EXPERIMENTAL

Apparatus

Amperometric titrations were performed with a manual polarograph, a spot galvanometer, and a dropping mercury electrode. A saturated calomel electrode was connected to the polarographic cell through a potassium nitrate–agar salt bridge.

All pH measurements were made with a pH-meter and glass and calomel electrodes.

Reagents

Dimethylformamide. A commercial grade was purified by standing over anhydrous sodium carbonate (analytical grade) for two days. The solvent was decanted off, distilled, and the fraction distilling at 148·5–149·5° was collected in a coloured bottle.

Silver nitrate, 0·04M, standardized.

n-Butylamine. An approximately 0·1*M* solution was prepared by dissolving the desired amount (purified by distilling over barium oxide) in dimethylformamide.

Organic isothiocyanates. Alkyl isothiocyanates were prepared by well-known methods.[7] Phenyl isothiocyanate, commercial grade, was distilled before use.

Buffer solution. Aqueous 1*M* ammonia–1*M* ammonium nitrate.

Gelatine 0·05% aqueous solution.

Procedures

From 2 to 5 ml of a solution of organic isothiocyanate in dimethylformamide were transferred to a glass stoppered titration cell and 3 ml of n-butylamine (approximately 0·1*M* solution in DMF) solution were added. The volume of the solution was made up to 10 ml with the solvent. The flask was stoppered, swirled to mix the reactants, and set aside for 10 min to ensure completion of the reaction. Then 5 ml of aqueous ammonia–ammonium nitrate buffer and 5 ml of gelatine solution were added. The volume of the solution was made up to 50 ml with water, cooled to room temperature (25°), and deaerated by passage of a slow stream of nitrogen. The drop-time was adjusted to 3 sec. A voltage of −0·56 V was applied to the dropping mercury electrode *vs.* the saturated calomel electrode. The initial galvanometer reading was noted and the titration carried out with 0·04*N* silver nitrate. After every addition, the solution in the cell was stirred by a slow stream of nitrogen and the precipitate allowed to stand for a minute, before the current was recorded. The diffusion current remained constant before the end-point but then the current increased rapidly and linearly with each addition of titrant. Some results are recorded in Table 1.

Table 1. Amperometric titrations of organic isothiocyanates

Compound	Amount taken, *mg*	Amount found, *mg*	Deviation %
CH_3NCS	1·390	1·388	0·1
	2·780	2·777	0·1
CH_3CH_2NCS	2·445	2·440	0·2
	3·700	3·695	0·1
$CH_3CH_2CH_2NCS$	1·615	1·618	0·2
	3·890	3·894	0·1
$(CH_3)_2CHNCS$	1·725	1·719	0·3
	3·956	3·965	0·2
$CH_3CH_2CH_2CH_2NCS$	2·160	2·165	0·2
	4·320	4·308	0·3
$(CH_3)_2CHCH_2NCS$	1·270	1·267	0·2
	4·290	4·285	0·1
C_6H_5NCS	1·950	1·946	0·2
	4·290	4·299	0·2

RESULTS AND DISCUSSION

The results recorded in Table 1 show that 1–5 mg of organic isothiocyanates (methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, and phenyl) can be determined successfully by this method. The maximum error was about 0·4%. In all the determinations, the concentration of the titrant was about 20 times that of the solution in the cell in order to minimize the dilution effect. The pH of the solution in the cell varied between 9·4 and 9·6. Under these conditions there was a continuous precipitation of silver sulphide up to the equivalence point as a result of the reaction between silver nitrate and thiourea (in a molar ratio of 2:1).

The proposed method, besides being simple, accurate, and reliable, has the added advantage that no heating of the sample solution is required. Cyanamide, urea, and organic isocyanates, even when present in amounts up to 25 mg, do not cause any interference in the prescribed range of determinations. Organic thiocyanates, sulphides, and mercaptans, however, interfere.

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Summary—An amperometric titration method is described for the determination of 1–5 mg of organic isothiocyanates, based on their quantitative reaction with n-butylamine in dimethylformamide to form *N,N*-disubstituted thioureas which are then titrated amperometrically in aqueous ammonia–ammonium nitrate buffer with silver nitrate (dropping mercury electrode at −0·56 V). The end-point corresponds to a silver:thiourea ratio of 2:1, with precipitation of silver sulphide. The method is simple, accurate, widely applicable, and gives reproducible results.

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ANALYTICAL DATA

DETERMINATION OF STABILITY CONSTANTS OF CADMIUM(II) WITH SOME AMINO-ACIDS BY USE OF AN ION-SELECTIVE ELECTRODE

G. J. M. HEIJNE and W. E. VAN DER LINDEN
Laboratory for Analytical Chemistry, University of Amsterdam, Nieuwe Achtergracht 166, Amsterdam, The Netherlands

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In a study of the behaviour of very low concentrations of metal ions and organic ligands as they appear in the oceanic environment, the need arose for a consistent set of stability constants for complexes of cadmium with some amino-acids. A survey of the existing literature[1] showed that the available data were very inhomogeneous and incomplete. For that reason this investigation has been carried out. The stability constants were determined according to three different methods described in the literature.

THEORY

The three methods used are all based on potentiometry. Since the stability constants of complexes of cadmium with amino-acids are relatively small, it is necessary to introduce some corrections to the simple methods as they were described originally.

The first method is that by Albert,[2] which makes use of the pH-curve for titration of 1:2 mixtures of metal and ligand with a strong base. From the formation curve $\bar{n}$ *vs.* log [L] the stability constants can be derived:

$$\log \beta_{ML} = \log \bar{n} - \log (1 - \bar{n}) - \log [L] \qquad \text{for } 0{\cdot}15 \leqslant \bar{n} \leqslant 0{\cdot}70$$

and

$$\log \beta_{ML_2} = -2 \log [L] \quad \text{for} \quad \bar{n} = 1{\cdot}0$$

The notation is as usual (*e.g.*, Ringbom[3]) and charges are omitted. [L] is the concentration of free ligand; it can be calculated from the total ligand concentration, C_L, the amount of base added, C_{base}, the protonation constants of the ligand, and the pH. This simple method has been used by several workers, also for studies of cadmium complexes; in our case, however, the results were not satisfactory, probably because of the influence of ML_2 in the region of low $\bar{n}$. Therefore an iterative procedure was adopted.

For each pH the first values obtained for β are used to calculate the free metal ion concentration [M]:

$$[M] = \frac{C_M}{\alpha_{M(OH)} + \beta_{ML}[L] + \beta_{ML_2}[L]^2}$$

It is then possible to obtain a corrected value of [L]:

$$[L] = \frac{C_L - C_{base} - [H] + [OH] + \sum_{x=1}^{N} x\beta_{M(OH)_x}[M][OH]^x}{\beta_{HL}[H] + 2\beta_{H_2L}[H]^2}$$

which allows calculation of a corrected value of [M], *etc.* In the case of a dibasic amino-acid, C_L should be doubled. So for aspartic and glutamic acid the formula is written:

$$[L] = \frac{2C_L - C_{base} - [H] + [OH] + \sum_{x=1}^{N} x\beta_{M(OH)_x}[M][OH]^x}{\beta_{HL}[H] + 2\beta_{H_2L}[H]^2 + 3\beta_{H_3L}[H]^3}$$

When these concentration values are constant they are used to recalculate β_{ML} and β_{ML_2} in a different way:

$$\beta_{ML} = \frac{\bar{n} \cdot C_M - 2[ML_2]}{[M][L]} = \frac{C_L - \alpha_{L(H)}[L] - 2\beta_{ML_2}[M][L]^2}{[M][L]}$$

and

$$\beta_{ML_2} = \frac{\bar{n} \cdot C_M - [ML]}{2[M][L]^2} = \frac{C_L - \alpha_{L(H)}[L] - \beta_{ML}[M][L]}{2[M][L]^2}$$

This procedure is repeated until two consecutive values of β are satisfactorily constant.

The second method was described by Hansen and Růžička,[4] based on an idea proposed by Ringbom and Harju.[5] In the present study their general formula

$$\log \beta_{ML_x} = pM + x \log \alpha_{L(H)} - \log \alpha_{ML_x(H,OH)} - \log \frac{[(L)']^x}{[(ML_x)']}$$

was adapted in the following way, where the side-reaction coefficient $\alpha_{ML_x(H,OH)}$ is included in β_{ML_x}:

$$\log \beta_{ML} = pM + \log \alpha_{L(H)} - \log \frac{C_L - C_M + \alpha_{M(OH)}[M] - [(ML_2)']}{C_M - \alpha_{M(OH)}[M] - [(ML_2)']}$$

and

$$\log \beta_{ML_2} = pM + 2 \log \alpha_{L(H)} - \log \frac{\{C_L - 2(C_M - \alpha_{M(OH)}[M]) + [(ML)']\}^2}{C_M - \alpha_{M(OH)}[M] - [(ML)']}$$

The primes denote any side-reaction with protons or hydroxyl ions. The measured quantities are pH and pM. When the stability constants for protonation of the ligand and for hydrolysis of the metal ion as well as the initial concentrations are known, the values of β_{ML} and β_{ML_2} can

be obtained by iterative calculation, starting without interference of $(ML_2)'$ and $(ML)'$ respectively. The constants for side-reactions can be calculated as well.[5]

The third method was the one by van der Linden and Beers,[6] also based on measurement of pH and pM. From the curves of

$$\log \alpha_{M(L)} = \log\left(\frac{C_M}{[M]} - \alpha_{M(OH)} + 1\right)$$

plotted *vs.*

$$\log[L] = \log\left(\frac{C_L}{\alpha_{L(H)}}\right)$$

for different values of $C_L (C_L \gg C_M)$ the nature of the complexes in the solution can be found, *e.g.*, when the curves coincide and show a maximum slope of 2, only ML and ML_2 need be considered. Since this was true for all amino-acids studied, the stability constants could be obtained from the least-squares line for $(\alpha_{M(L)} - 1)/[L]$ *vs.* [L] because in this case $\alpha_{M(L)} = 1 + \beta_{ML}[L] + \beta_{ML_2}[L]^2$. They are obtained as the intercept and slope respectively.

EXPERIMENTAL

Chemicals

The amino-acids used were DL-α-alanine, DL-valine, DL-serine, L-threonine, glycine and L-aspartic and L-glutamic acids. Most of these were chromatographically pure. Stock solutions were prepared (0·1*M*), except for glutamic and aspartic acid for which 0·01*M* solutions were used because of their low solubility.

A 0·1*M* cadmium(II) solution was prepared from the nitrate and standardized with TRIEN.

In all cases potassium nitrate was used to adjust the ionic strength to 0·1. Protonation constants were also determined at ionic strength 0·5.

The titrations were done with 1·5*M* potassium hydroxide, which was daily checked with 0·1*M* potassium hydrogen phthalate. All reagents were of the purest grade obtainable.

Apparatus

Measurements were carried out with a glass electrode (Electrofact 7G111) and an Orion 94-48 A cadmium(II) ion-selective electrode (ISE), both versus SCE (Metrohm EA402). The pH was read on a Radiometer PHM 26 (expanded scale); the potentials of the ISE were read on a Radiometer PHM 4c compensation meter within 0·2 mV. The titration vessel was thermostatically controlled at 25 ± 0·1°. An air-driven magnetic stirrer was used. The titrant was added from a Metrohm microburette.

Procedure

First the protonation constants of the ligand were determined by titrating a 0·033*M* solution of the ligand. Then the following systems were examined:

(*a*) $3{\cdot}0 \times 10^{-3}M$ cadmium + $6{\cdot}0 \times 10^{-3}M$ ligand for method 1

(*b*) $1{\cdot}0 \times 10^{-3}M$ cadmium + $2{\cdot}0 \times 10^{-3}M$ ligand for method 2

(*c*) $1{\cdot}0 \times 10^{-4}M$ cadmium + $2{\cdot}0 \times 10^{-3}M$ ligand for method 3

(*d*) $1{\cdot}0 \times 10^{-4}M$ cadmium + $1{\cdot}0 \times 10^{-2}M$ ligand for methods 2 and 3.

For aspartic and glutamic acids system (*d*) contained only one third of these concentrations, and the determination of the protonation constants was done with a $6{\cdot}7 \times 10^{-3}M$ solution of the acid.

The cadmium ion selective electrode

The potentials of the ISE *vs.* SCE were converted into pCd values by means of calibration graphs obtained in 0·02*M* acetic acid–acetate (1:1) buffer, at ionic strength 0·1*M*, by addition of cadmium nitrate from a burette. The concentration of cadmium was varied from 5×10^{-7} to $5 \times 10^{-3}M$. Preliminary experiments with the rather time-consuming calibration according to Růžička and Hansen[7] showed that in cadmium buffers a linear response of *E vs.* pCd was found between 10^{-2} and 3×10^{-8} or $3 \times 10^{-9}M$ in acetate (pH 4·5) and borate (pH 9·1) buffers respectively.

The electrode potential is given by $E = E' + S \log a_{Cd^{2+}}$ where S is the linear response (mV/decade), E' the intercept of the line at $a_{Cd^{2+}} = 1$, and $a_{Cd^{2+}}$ is the activity of the cadmium ion. The value of the activity coefficient is calculated according to Kielland [8] to be $-\log \gamma = 0{\cdot}42$ for ionic strength 0·1. During the main part of this study 40 calibration graphs were made. Values of S varied from 28·3 to 31·6 mV/decade and values of E' from −67·4 to −53·4 mV. About 60% of the calibration curves had a response slope between 30·0 and 31·0 mV/decade and a value of E' between −63·0 and −56·0 mV. These results are comparable with those given by Gardiner.[9] Because of this variation every series of measurements was accompanied by at least three calibrations: one before system (*a*) and after system (*d*) and one between systems (*b*) and (*c*).

Regular polishing of the electrode surface was necessary for proper functioning of the ISE. Perspex A2 polishing fluid (ICI) was used for that purpose.

RESULTS AND DISCUSSION

In the calculation of the stability constants the value $\log K_w = \log([H^+][OH^-]) = -13{\cdot}96$ was used, as determined by Anderegg[10] for the same circumstances. The constants for the complexation of cadmium with hydroxyl ions were determined with the cadmium ISE in 0·1*M* potassium nitrate medium, and found to be $\log \beta_{CdOH} = 4{\cdot}3$ and $\log \beta_{Cd(OH)_2} = 8{\cdot}3$. The method used was that of Leden.[11] These values agree reasonably with the literature.[1,3,9]

In Table 1 the measured protonation constants are given. These all agree very well with the literature.[1] The stability constants of the cadmium complexes are summarized in Table 2. The values given in "*Stability Constants*"[1] show differences ranging over more than one order of magnitude. After 1968 (the last year covered by this compilation so far) only few papers on this subject have been published, the most important being that by Münze *et al.*[12] Their values for glycine, aspartic acid, glutamic acid and some others are rather lower, possibly because of the chloride medium used. For these reasons it is hard to make a valid comparison with the literature, but one can say that there is no major disagreement.

When the results of the present study are considered, we see that the values of β_{ML} for the methods involving

Table 1. Protonation constants of amino-acids at 25°C

Amino-acid	$\log \beta_{HL}$ $I = 0{\cdot}1$	$\log \beta_{HL}$ $I = 0{\cdot}5$	$\log \beta_{H_2L}$ $I = 0{\cdot}1$	$\log \beta_{H_2L}$ $I = 0{\cdot}5$
DL-α-alanine	9·80	9·75		
L-aspartic acid	9·72	9·61	13·53	13·40
L-glutamic acid	9·62	9·52	13·86	13·74
glycine	9·69	9·69		
DL-serine	9·14	9·06		
L-threonine	9·00	8·98		
DL-valine	9·61	9·54		

Maximum values of standard deviations are 0·01 at I = 0·1 (KNO_3) and 0·03 at I = 0·5 (KNO_3).

Table 2. Logarithmic values of stability constants of cadmium complexes with amino-acids [ionic strength 0·1 (KNO_3), temperature 25°C]

Method	Albert[2]		Hansen[4]		v.d. Linden[6]	
Amino-acid	β_{ML}	β_{ML_2}	β_{ML}	β_{ML_2}	β_{ML}	β_{ML_2}
DL-α-alanine	4·0	7·4	4·4	7·2	4·1	7·3
L-aspartic acid	4·7	8·1	4·9	8·2	4·8	8·2
L-glutamic acid	4·0	7·1	4·3	7·0	4·1	7·1
glycine	4·5	8·0	4·4	8·0	4·5	8·0
DL-serine	3·8	7·2	4·2	7·2	4·1	7·4
L-threonine	3·9	7·2	4·0	7·0	3·9	7·0
DL-valine	3·7	6·9	4·2	6·8	3·7	7·0

measurement of free cadmium ion tend to be somewhat higher than for the method of Albert. This is probably caused by a difference between the expected electrode potential and the measured one, the latter being 3–9 mV more negative. There is some indication that this effect is most pronounced for the range of pH up to 7·5, which is of relatively small interest in the present case. A study is in progress to find the cause of this phenomenon. The β-values calculated cover the experimental results from pH 7·5 up to pH 9–9·5, where the measurements were ended. The results for β_{ML_2} correspond reasonably for all methods.

For the iterative calculation according to the method of Hansen and Růžička a computer program was developed, which excluded those values that showed irregularities caused by the phenomenon mentioned above.

Acknowledgement—The authors thank Mr. J. C. Smit for writing the computer program.

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Summary—Three different methods were used to obtain the stability constants of the complexes of cadmium with several mino-acids. Two made use of an ion-selective electrode; the third was based on pH-measurement only. Values of β_{ML} and β_{ML_2} obtained in 0·1*M* KNO_3 at 25° corresponded reasonably for most amino-acids examined and accorded with the values given in the literature, as far as comparison was possible.

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SPECTROPHOTOMETRIC INVESTIGATION OF THE REACTION OF ERIOCHROME CYANIN RC AND MAGNESIUM AND ALUMINIUM

N. G. ELENKOVA and EK. POPOVA

Higher Institute of Chemical Technology, Sofia 56, Bulgaria

(*Received* 26 *November* 1974. *Accepted* 19 *March* 1975)

Eriochrome Cyanin RC (ERCR) has been used both as a chromogenic reagent and as a metallochromic indicator for determination of many metal ions.[1–5] So far, however, there is no consensus about the nature of its complexes with magnesium or aluminium. It has been assumed that it forms a lake with magnesium, similar to those formed with quinalizarin and curcumin,[4] and that with aluminium it forms complexes such as $Al(ERCR)_3$, Al(ERCR) *etc.*[3,5–7] or that lakes[9–10] or undefined compounds[11,12] are formed.

In the present work we have made a systematic study of the magnesium and aluminium complexes of ERCR and find that 1:1 complexes are formed, which may be protonated in the case of aluminium; the magnesium complex is a mixed hydroxo-complex.

THEORETICAL

Consider that the complex formation between a metal ion M and the fully dissociated anion of ERCR, L, takes place according to the reaction (charges on the metal ion and L are omitted):

$$mM + jOH^- + iH^+ + nL \rightleftharpoons M_m(OH)_jH_iL_n \qquad (1)$$

so the overall formation constant is

$$\beta_{mni} = \frac{[M_m(OH)_jH_iL_n]}{[M]^m[L]^n K_w^j [H^+]^{(i-j)}} \qquad (2)$$

Table 2. Logarithmic values of stability constants of cadmium complexes with amino-acids [ionic strength 0·1 (KNO_3), temperature 25°C]

Method	Albert[2]		Hansen[4]		v.d. Linden[6]	
Amino-acid	β_{ML}	β_{ML_2}	β_{ML}	β_{ML_2}	β_{ML}	β_{ML_2}
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L-aspartic acid	4·7	8·1	4·9	8·2	4·8	8·2
L-glutamic acid	4·0	7·1	4·3	7·0	4·1	7·1
glycine	4·5	8·0	4·4	8·0	4·5	8·0
DL-serine	3·8	7·2	4·2	7·2	4·1	7·4
L-threonine	3·9	7·2	4·0	7·0	3·9	7·0
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In the present work we have made a systematic study of the magnesium and aluminium complexes of ERCR and find that 1:1 complexes are formed, which may be protonated in the case of aluminium; the magnesium complex is a mixed hydroxo-complex.

THEORETICAL

Consider that the complex formation between a metal ion M and the fully dissociated anion of ERCR, L, takes place according to the reaction (charges on the metal ion and L are omitted):

$$mM + jOH^- + iH^+ + nL \rightleftharpoons M_m(OH)_jH_iL_n \qquad (1)$$

so the overall formation constant is

$$\beta_{mni} = \frac{[M_m(OH)_jH_iL_n]}{[M]^m[L]^n K_w^j [H^+]^{(i-j)}} \qquad (2)$$

where K_w is the ion-product of water. In the calculation of the conditional stability constant

$$\beta'_{mn} = \frac{[M_m(OH)_jH_iL_n]}{C'_M C'_L} = \frac{\beta_{mni} K_w^j [H^+]^{(i-j)}}{\alpha_{L(H)}\alpha_{M(OH)}} \quad (3)$$

$\alpha_{M(OH)}$ is the coefficient for the side-reaction of M with hydroxide ions, and $\alpha_{L(H)}$ that for the reaction between L and protons.[13]

In logarithmic form, equation (3) becomes

$$\log \beta'_{mn}\alpha_{L(H)}\alpha_{M(OH)} = \log \beta_{mni} K_w^j - (i-j)\text{pH} \quad (4)$$

giving the relation between the pH of the solution and the composition of the complex.[14] If only one complex has been formed, a plot of $\log \beta'_{mn}\alpha_{L(H)}\alpha_{M(OH)}$ *vs.* pH should be linear, with a slope of $(j - i)$. The values of m and n can be determined by spectrophotometry at a given pH and various analytical concentrations of M and L. A set of measurements at various pH values gives the influence of the pH on the conditional stability constant β'_{mn}. Thus after all possible side-reactions have been taken into account, the composition of any mixed (protonated or hydroxo) complex can be found from the plot of log $\beta'_{mn}\alpha_{L(H)}\alpha_{M(OH)}$ *vs.* pH. If more than one complex is formed, the slope of the line will not be an integer, but an average "proton number", *e.g.*,

$$\beta'_{mn} = \frac{[M_mH_pL_n] + [M_mH_{(p+1)}L_n]}{C'_M C'_L} \quad (5)$$

The overall stability constants of the two complexes would be

$$\beta_{mpn} = \frac{[M_mH_pL_n]}{[M]^m[H^+]^p[L]^n} \quad (6)$$

and

$$\beta_{m(p+1)n} = \frac{[M_mH_{(p+1)}L_n]}{[M]^m[H^+]^{(p+1)}[L]^n} \quad (7)$$

Combination of equations (5)–(7) gives

$$\frac{\beta'_{mn}\alpha_{L(H)}\alpha_{M(OH)}}{[H^+]^p} = \beta_{mpn} + \beta_{m(p+1)n}[H^+] \quad (8)$$

and a plot of $\beta'_{mn}\alpha_{L(H)}\alpha_{M(OH)}/[H^+]^p$ *vs.* $[H^+]$ would have a slope of $\beta_{m(p+1)n}$ and an intercept of β_{mpn}.

EXPERIMENTAL

All reagents were of analytical grade. The 10^{-3} *M* magnesium chloride was standardized gravimetrically *via* magnesium pyrophosphate. The 10^{-3} *M* aluminium solution was standardized gravimetrically.[15] The 10^{-3} *M* ERCR was prepared fresh daily by dissolving 0·5346 g of reagent in a litre of water, and the 10^{-2} *M* solution by dissolving 5·364 g of ERCR in 10 ml of 8 *M* nitric acid in a 1-litre standard flask, adding 100 ml of water, 8 g of sodium chloride and 8 g of ammonium nitrate and diluting to the mark.[16] Ammonia buffer solutions (0·1 *M*) were obtained by mixing 0·2 *M* ammonia and 0·2 *M* ammonium chloride in appropriate proportions, and the pH-values were measured with a pH-meter. Other pH adjustments were made with perchloric acid or sodium hydroxide solution. The ionic strength was about 0·1.

The magnesium system was found to come to equilibrium in 10 min; the aluminium system took 90 min, and was then stable for at least 3 hr.

RESULTS AND DISCUSSION

Magnesium

Figure 1 shows the absorption spectra of 2×10^{-5} *M* ERCR solutions at various magnesium concentrations. The absorption maxima are at 440 nm for the reagent and 570 nm for the complex. The isosbestic point indicates formation of a single complex. Preliminary investigations by the continuous-variations and mole-ratio methods showed the large effect of the total concentration of magnesium and ERCR (in the region of $1–6 \times 10^{-4}$ *M*) on the curves. To eliminate this effect of reagent self-association,[17] all measurements were made on sufficiently dilute solutions in 30-mm and 50-mm cells. The absorbances of the mixtures with various magnesium concentrations at a given pH and ERCR concentration ($2–20 \times 10^{-5}$ *M* Mg, $C_{ERCR}:C_{Mg} = 4$) were measured, and the measurements repeated for fixed C_{Mg} and pH and varied C_{ERCR}. These experiments were repeated at various pH values between 10 and 11·5. At pH < 10 the absorbances were too small and the equilibrium was unfavourable, whereas at pH > 11·5 the complex was fairly strong. The molar absorptivity was obtained from measurements at a sufficient excess of the reagent as well as over a wide range of con-

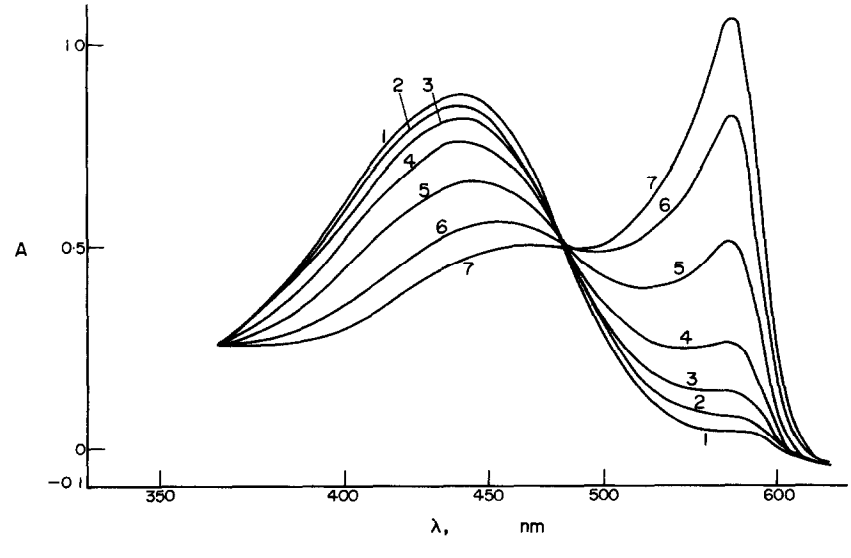

Fig. 1. Absorption spectra of 2×10^{-5} *M* ERCR solutions at various Mg(II) concentrations. C_{Mg}, 10^{-5} *M*: *1*—0; *2*—4; *3*—8; *4*—15; *5*—30; *6*—50; *7*—70.

Table 1. The molar absorptivity of the Mg-ERCR complex at different pH values

pH	10·4	10·7	11·0	11·25	11·5	
ϵ, 10^3 *l. mole*$^{-1}$ *cm*$^{-1}$	1·74 ± 0·3	1·70 ± 0·26	1·90 ± 0·09	2·20 ± 0·75	1·95 ± 0·21	(mean 1·90 ± 0·14)

Table 2. log β'_{11} at different Mg(II) and ERCR concentrations, pH = 11·0

$C_{Mg} = 1 \times 10^{-4}$ *M*			$C_{Mg} = 6 \times 10^{-5}$ *M*			$C_{ERCR} = 1 \times 10^{-4}$ *M*			$C_{ERCR} = 6 \times 10^{-5}$ *M*		
C_{ERCR}, 10^{-5} *M*	ΔA	log β'_{11}	C_{ERCR}, 10^{-6} *M*	ΔA	log β'_{11}	C_{Mg}, 10^{-5} *M*	ΔA	log β'_{11}	C_{Mg}, 10^{-5} *M*	ΔA	log β'_{11}
6	0·086	4·66	5·4	0·199	4·61	5	0·070	4·64	4	0·037	4·57
8	0·103	4·64	6·0	0·218	4·72	6	0·081	4·63	5	0·046	4·54
9	0·116	4·67	9·0	0·304	4·71	8	0·103	4·66	6	0·060	4·94
10	0·125	4·75									
14	0·141	4·73									
18	0·156	4·75									
Mean log β'_{11}		4·70			4·64			4·64			4·69

Table 3. Mean log β'_{11} values at various pH values, magnesium and ERCR concentrations

	C_{Mg}, 10^{-5} *M*			C_{ERCR}, 10^{-5} M			log $\beta'_{11} \pm \Delta$ log β'_{11}	log β'_{11} $\alpha_{L(H)}$ $\alpha_{Mg(OH)}$
pH	2	4	6	2	4	6		
10·4	3·38	3·18	3·15	3·45	3·52	3·25	3·32 ± 0·20	4·83
10·7	4·02	3·95	3·99	3·96	4·18	4·12	4·04 ± 0·17	5·30
11·25	4·85	5·18	5·33	4·80	5·01	5·23	5·07 ± 0·23	6·03
11·50	5·26	5·23	5·57	5·15	5·38	5·64	5·37 ± 0·21	6·25
11·00							4·62 ± 0·15	5·70

centrations, and was calculated by an iteration method[18] (Table 1).

Several methods (continuous variations, mole ratio, Bent and French)[18,19] were used to determine the formula of the complex. It was found that $m = n$, so to distinguish between the 1:1 and 2:2 complexes the method of proportional absorbances[20] was used, and showed that only one complex (mononuclear) was formed. To evaluate the conditional constants β'_{11}, absorbances were measured for given C_{Mg} (2–10 × 10^{-5}*M*) and different C_{ERCR}, and *vice versa*. Then the optimum measurement conditions for obtaining the best values of β'_{11} were chosen, according to Nordheim.[21] This procedure was repeated until the calculations gave an optimal constant β'_{11} value (Table 2). The results clearly show that β'_{11} is constant at given pH and is independent of C_{Mg} and C_{ERCR}, and this was confirmed statistically.[22]

The arithmetic mean of the β'_{11} values and the confidence limits were calculated (Table 3). The values of $\alpha_{Mg(OH)}$ and $\alpha_{L(H)}$ were calculated from the constants[13,21] log $\beta_{Mg(OH)} = 2·6$ and $pK_3 = 11·83 \pm 0·04$. The mean values of log $\beta'_{11}\alpha_{L(H)}\alpha_{Mg(OH)}$, when plotted against pH, gave a straight line with slope 1·30 ± 0·25 evaluated by least squares. Hence if $i = 0, j = 1$, the predominant complex is $MgOHL^{3-}$. The overall stability constant of this complex, β_{111}, was calculated from equation (4), and the individual values are given in Table 4.

Table 4. β_{111} values for the various pH values

pH	log β_{111}
10·4	8·43
10·7	8·60
11·0	8·70
11·25	8·78
11·5	8·75

Aluminium

Figure 2 shows the absorption spectra of the aluminium–ERCR solutions. The absorption maximum is shifted to 555 nm for the complex. The pH-range investi-

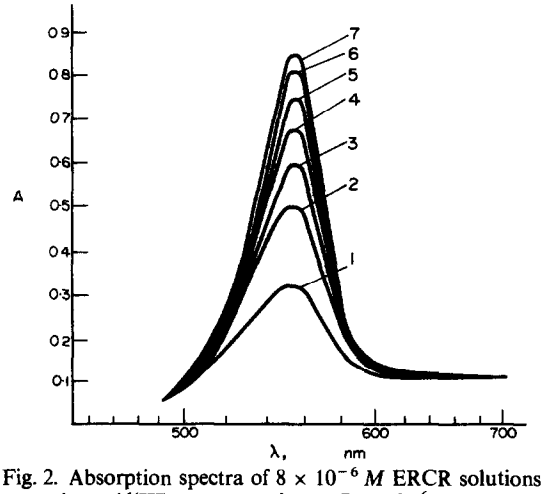

Fig. 2. Absorption spectra of 8 × 10^{-6} *M* ERCR solutions at various Al(III) concentrations. C_{Al}, 10^{-6} *M*: *1*—1·6; *2*—4; *3*—5·6; *4*—8; *5*—12; *6*—20; *7*—24.

Table 5. log β'_{11} values for various aluminium and ERCR concentrations at pH = 4·0

$C_{Al} = 4 \times 10^{-6} M$		$C_{Al} = 5 \times 10^{-6} M$		$C_{Al} = 8 \times 10^{-6} M$		$C_{ERCR} = 4 \times 10^{-6} M$		$C_{ERCR} = 5 \times 10^{-6} M$		$C_{ERCR} = 8 \times 10^{-6} M$	
C_{ERCR}, $10^{-5} M$	log β'_{11}	C_{ERCR}, $10^{-5} M$	log β'_{11}	C_{ERCR}, $10^{-5} M$	log β'_{11}	C_{Al}, $10^{-5} M$	log β'_{11}	C_{Al}, $10^{-5} M$	log β'_{11}	C_{Al}, $10^{-5} M$	log β'_{11}
0·8	4·95	0·75	4·90	1·2	4·84	0·6	5·02	1·0	4·93	1·2	4·86
1·0	4·91	1·0	4·97	1·6	4·81	0·8	4·86	1·2	4·83	1·6	4·74
1·2	4·92	1·25	4·93	2·0	4·86	1·0	4·85	1·5	4·74	2·0	4·78
1·4	5·02	1·5	4·81	2·4	4·74	1·2	4·77	1·75	4·68	2·4	4·73
1·6	5·01	1·75	4·81	2·8	4·83	1·4	4·69	2·0	4·65	2·8	4·78
		2·0	4·80	3·2	5·02	1·6	4·61			3·2	4·73
Mean log β'_{11}	4·96		4·85		4·85		4·80		4·77		4·77

Table 6. log β'_{11} values for various aluminium and ERCR concentrations at different pH values

	C_{Al}, $10^{-6} M$					C_{ERCR}, $10^{-6} M$						
pH	4	5	6	8	10	4	5	6	8	10	log $\beta'_{11} \pm \Delta$ log β'_{11}	log $\beta'_{11}\alpha_{L(H)}\alpha_{Al(OH)}$
3·0	4·73	—	4·74	4·71	—	4·75	—	4·68	4·69	—	4·72 ± 0·05	16·33
3·5	4·92	—	4·93	4·66	—	4·68	—	4·68	4·79	—	4·78 ± 0·05	15·43
4·0	4·96	4·85	—	4·85	—	4·80	4·77	—	4·77	—	4·83 ± 0·02	14·61
4·5	—	4·86	—	4·95	4·82	—	4·88	—	4·95	4·81	4·88 ± 0·02	13·97
5·0	4·88	—	4·92	4·87	—	4·95	—	4·99	4·89	—	4·92 ± 0·02	13·66
5·5	4·85	—	4·79	4·77	—	4·81	—	4·77	4·81	—	4·80 ± 0·01	13·58
6·0	4·38	—	4·38	4·41	—	4·37	—	4·29	4·30	—	4·36 ± 0·02	13·60

Table 7. log β_{101} values calculated at different pH values

pH = 5·0	pH = 5·5	pH = 6·0
13·62	13·63	13·62
13·66	13·57	13·65
13·61	13·55	13·61
13·69	13·59	13·53
13·73	13·55	13·62
13·63	13·59	13·54

gated was 3·0–6·0 at intervals of 0·5. The molar absorptivity was calculated by an iteration method,[18] and found to be $3{\cdot}87 \pm 0{\cdot}04 \times 10^4$ l.mole^{-1}.cm^{-1}. The values of m and n were again equal and the method of proportional absorbances showed $m = n = 1$. The conditional stability constants are shown in Tables 5 and 6, and were calculated as before. β'_{11} is independent of C_{Al} and C_{ERCR}.

The formation of soluble polynuclear aluminium hydroxo-complexes depends on pH as well as the aluminium concentration.[12] According to Kragten,[23] polynuclear aluminium complexes do not exist in dilute solutions ($< 10^{-3} M$), and for all calculations of $\alpha_{Al(OH)}$ we used Kragten's values for $\beta_i = [Al(OH)_i][H^+]^i/[Al^{3+}]$, namely log $\beta_1 = -4{\cdot}3$, log $\beta_2 = -9{\cdot}3$, log $\beta_3 = -15$, log $\beta_4 = -22$. The $\alpha_{L(H)}$ values were calculated from the constants $pK_1 = 1{\cdot}83 \pm 0{\cdot}02$, $pK_2 = 5{\cdot}74 \pm 0{\cdot}04$, $pK_3 = 11{\cdot}83 \pm 0{\cdot}04$.[12]

The mean values of log $\beta'_{11}\alpha_{L(H)}\alpha_{Al(OH)}$, when plotted against pH, gave a straight line with slope of $-1{\cdot}60$ over the pH range from 3·0 to 4·5, and a straight line with zero slope at pH > 5·0. These results suggest that two protonated complexes may be formed at pH < 4·5 (AlH_2L and AlHL) and that AlL ($i = j$) predominates at pH > 4·5. A plot of $\beta'_{11}\alpha_{L(OH)}\alpha_{Al(OH)}/[H^+]$ *vs.* $[H^+]$ and regression analysis both showed that β_{111} was $2{\cdot}58 \pm 1{\cdot}3 \times 10^{18}$ and β_{121} was $1{\cdot}96 \pm 0{\cdot}24 \times 10^{22}$. The overall stability constant for AlL was $\beta_{101} = 4{\cdot}57 \pm 0{\cdot}11 \times 10^{13}$ (Table 7). From these stability constants we calculated the distribution diagram for Al^{3+}, AlL, AlHL and AlH_2L as a function of pH for $C_L = 10^{-3} M$ (Fig. 3).

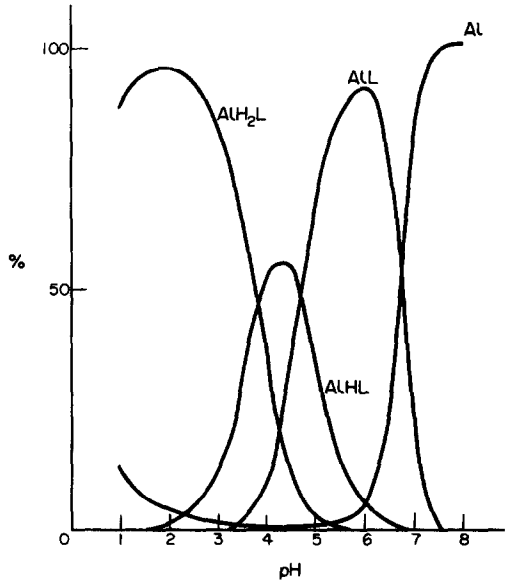

Fig. 3. Distribution of Al(III) and complexes AlH_2L, AlHL and AlL as a function of pH for a given value of C_L ($10^{-3} M$).

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STABILITY CONSTANTS OF SOME BIVALENT FIRST ROW TRANSITION METAL CHELATES OF DICARBOXYLIC ACIDS CONTAINING ETHER LINKAGES

M. MIYAZAKI and K. TÔEI

Department of Chemistry, Faculty of Science, Okayama University, 3-1-1, Tsushimanaka, Okayama-shi, 700 Japan

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The mixed stability constants of the Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+} and Zn^{2+} chelates of four dicarboxylic acids (**I**, $n = 0$; **II**, $n = 1$; **III**, $n = 2$; **IV**, $n = 3$) containing ether linkages, $HOOCCH_2O(CH_2CH_2O)_nCH_2COOH$ ($n = 0$–3), have been determined by the procedure described earlier.[1] The concentration of the metal ion was generally kept higher than that of the dicarboxylic acid to prevent the formation of chelates other than that having a metal to ligand ratio of 1:1.

Table 1. Chelate stability constants at an ionic strength of $\mu = 0{\cdot}10$ (KNO_3) and at $25{\cdot}0 \pm 0{\cdot}1$°C

	log K_1					
Reagent	Mn^{2+}	Fe^{2+}	Co^{2+}	Ni^{2+}	Cu^{2+}	Zn^{2+}
I	$2{\cdot}5_2$	$2{\cdot}6_3$	$2{\cdot}6_5$	$2{\cdot}7_8$	$3{\cdot}9_3$	$3{\cdot}5_8$
II	$2{\cdot}7_9$	$2{\cdot}3_5$	$1{\cdot}6_9$	$1{\cdot}7_9$	$3{\cdot}3_9$	$2{\cdot}6_5$
III	$2{\cdot}9_0$	$2{\cdot}7_1$	$2{\cdot}2_9$	$2{\cdot}3_9$	$2{\cdot}8_5$	$2{\cdot}6_0$
IV	$2{\cdot}1_8$	$2{\cdot}4_6$	$1{\cdot}9_2$	$1{\cdot}9_4$	$2{\cdot}6_5$	$2{\cdot}1_8$

The results are tabulated in Table 1. The stability constants of the reagents with each metal ion are not so large as those with the corresponding amines, $H_2N(CH_2CH_2NH)_nCH_2CH_2NH_2$ ($n = 1$–3).[2–6] The log K_1 values for reagent **I** are in the Irving-Williams[7] order, but those for reagents **II**, **III** and **IV** are not.

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M. MIYAZAKI and K. TÔEI

Department of Chemistry, Faculty of Science, Okayama University, 3-1-1, Tsushimanaka, Okayama-shi, 700 Japan

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Table 1. Chelate stability constants at an ionic strength of $\mu = 0{\cdot}10$ (KNO_3) and at $25{\cdot}0 \pm 0{\cdot}1$°C

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II	$2{\cdot}7_9$	$2{\cdot}3_5$	$1{\cdot}6_9$	$1{\cdot}7_9$	$3{\cdot}3_9$	$2{\cdot}6_5$
III	$2{\cdot}9_0$	$2{\cdot}7_1$	$2{\cdot}2_9$	$2{\cdot}3_9$	$2{\cdot}8_5$	$2{\cdot}6_0$
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The results are tabulated in Table 1. The stability constants of the reagents with each metal ion are not so large as those with the corresponding amines, $H_2N(CH_2CH_2NH)_nCH_2CH_2NH_2$ ($n = 1$–3).[2–6] The log K_1 values for reagent **I** are in the Irving-Williams[7] order, but those for reagents **II**, **III** and **IV** are not.

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LIGAND EXCHANGE REACTION BETWEEN EDTA AND IRON(III)–INDICATOR COMPLEXES SALICYLIC ACID AND 1,2-DIHYDROXY-3,5-BENZENEDISULPHONIC ACID

E. MENTASTI and E. PELIZZETTI

Istituto di Chimica Analitica, Università di Torino, Torino, Italy

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Previous kinetic investigations[1] on the rate of formation of the Fe(III)-chelate of EDTA showed that the main reaction pathways in acidic media ($[H^+] = 0{\cdot}01M$) are given by:

$$FeOH^{2+} + H_4EDTA \rightarrow FeEDTA^- + 3H^+ + H_2O \quad (1)$$

$$FeOH^{2+} + H_3EDTA^- \rightarrow FeEDTA^- + 2H^+ + H_2O \quad (2)$$

Pathways 1 and 2 fit the experimental reaction rate dependences on acidity; however, it should be noted that because of a "proton ambiguity" the possibility of a fast protolytic reaction before the rate-determining step (the first substitution of entering EDTA species for water), such as

$$Fe^{3+} + H_nEDTA^{(4-n)-} \rightleftharpoons FeOH^{2+} + H_{n+1}EDTA^{(3-n)-}$$

cannot be ruled out, so paths 1 and 2 are kinetically indistinguishable from the reactions $Fe^{3+} + H_3EDTA^-$ and $Fe^{3+} + H_2EDTA^{2-}$ respectively. In such circumstances, it is nevertheless possible to assign pathways 1 and 2 as the reaction mechanism by examining the reasonableness of the rate constants obtained, taking into account that $FeOH^{2+}$ has a higher reactivity (by a factor of $\sim 10^3$) than Fe^{3+}.[3,4]

On the basis of these findings, we have undertaken a kinetic investigation of the displacement by EDTA of metal indicators complexed with Fe(III):

$$FeIn + EDTA \rightarrow FeEDTA + In$$

where In = salicylic acid (H_2Sal) or Tiron (1,2-dihydroxybenzenedisulphonic acid, H_2T). The reactions were found to be first-order with respect to both reactants (FeIn and EDTA) and to be unaffected by reverse reactions; the dependence of the reaction rates on acidity enable us to state that for both reactions the pathways involved are:

$$(FeT^+)\,FeSal^+ + H_4EDTA \xrightarrow{k} FeEDTA^- + H_2Sal\,(H_2T) + 2H^+$$

$$(FeT^+)\,FeSal^+ + H_3EDTA^- \xrightarrow{k'} FeEDTA + H_2Sal\,(H_2T) + H^+$$

and that these displacements, still involving a substitution-controlled mechanism, are slower than direct attack of EDTA on Fe(III) (see Table 1).

These systems are concerned in the end-point detection for chelometric titrations of Fe(III); in particular Schwarzenbach and Flaschka[5] pointed out that the high stability of the Fe(III)–EDTA complex permits a relatively selective determination of Fe in strongly acidic medium; the lower the pH, the more selective the titration.

The present data yield quantitative information on the suggestion that such titrations should be performed with a moderately warm titration solution. In fact, assuming titration of 100 ml of Fe(III) at 18° and at pH = 2, with a titrant concentration of $5 \times 10^{-2}M$, one drop of EDTA (about 5×10^{-2} ml) will produce at the end-point complete disappearance of the $FeIn^+$ colour with a pseudo first-order rate of $\sim 0{\cdot}07\ sec^{-1}$ which corresponds to a time of half-reaction of ~ 10 sec both for Tiron and salicylic acid, and the displacement, *i.e.*, the end-point detection, becomes slower with increasing acidity.

Table 1. Rate constants and activation parameters for the reactions of Fe(III) and FeIn with EDTA (t = 25·0°C, ionic strength = 1·0M, $NaClO_4$)

Reaction	k, $10^3\,l.mole^{-1}.sec^{-1}$	$\Delta H^{\ddagger}$, *kcal/mole*	$\Delta S^{\ddagger}$, $cal.mole^{-1}.deg^{-1}$
$FeOH^{2+} + H_4EDTA$	30 ± 3	7 ± 1	−15 ± 3
$FeOH^{2+} + H_3EDTA^-$	110 ± 10	6 ± 1	−15 ± 3
$FeSal^+ + H_4EDTA$	0·84 ± 0·10	17 ± 2	+8 ± 6
$FeSal^+ + H_3EDTA^-$	14 ± 1	15 ± 1	+7 ± 4
$FeT^+ + H_4EDTA$	0·58 ± 0·10	17 ± 2	+8 ± 6
$FeT^+ + H_3EDTA^-$	17 ± 1	15 ± 1	+9 ± 4

Summary—Kinetic data on the displacement by EDTA of indicators complexed to Fe(III) (salicylic acid and Tiron) are discussed with reference to end-point detection in chelometric titration of Fe(III).

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ANNOTATION

STUDIES WITH DITHIZONE ANALOGUES—II

PREPARATION AND CHARACTERIZATION OF 2,2′-DICHLORODITHIZONE AND THE INVESTIGATION OF ITS REACTIONS WITH SOME METAL IONS

A. M. KIWAN and A. Y. KASSIM

Department of Chemistry, The University of Kuwait, Kuwait

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2,2′-Dichlorodithizone [1,5-di-(2-chlorophenyl)-3-mercaptoformazan] was first described by Pelkis, Dubenko and Pupko[1] who prepared it by the nitroformazyl method[2] and reported that its electronic absorption spectrum exhibits two characteristic peaks at 645 ($\lambda_{1\,max}$) and 465 ($\lambda_{2\,m}$) nm. More recently, Ramakrishna and Fernandopulle[3] have repeated its preparation by the same method, and reported different wavelengths for the absorption maxima, namely, 670 and 470 nm respectively. They have also given data for the molar absorptivities of 2,2′-dichlorodithizone and some of its metal complexes.

However, during our current studies on dithizone analogues, we have found that Ramakrishna and Fernandopulle's data are radically different from ours and so a reinvestigation seemed desirable.

This paper describes the preparation and characterization of 2,2′dichlorodithizone (abbreviated hereafter as Cl_2H_2Dz) and reports the results of an investigation of its reactions with Ag(I), Hg(II), Cu(II), Bi(III), Zn(II), Cd(II), Co(II), Ni(II) and Pb(II) ions.

EXPERIMENTAL

Reagent

The 2,2′-dichlorodithizone was prepared by the nitroformazyl method.[2] It was purified by dissolving it in dilute isopiestically distilled ammonia solution[4] followed by extraction into analytical-grade chloroform and finally precipitation with 2% isopiestically prepared hydrochloric acid. It was washed free from acid and dried *in vacuo*; m.p. 138–139° (literature values: 112–113°;[1] 138°[3]). Found: C 47·9%, H 3·4%, N 17·2%, Cl 21·7%; $C_{13}H_{10}Cl_2N_4S$ requires C 48·29%, H 3·09%, N 17·33%, Cl 21·98%.

Reagent grade salts were used and the usual precautions were taken with dithizone.

Procedures

The methods used for the determination of the molar absorptivities of 2,2′-dichlorodithizone and its metal complexes, their compositions, and the effect of pH on their extractabilities into CCl_4 were those which were used for dithizone.[5–7]

The acid dissociation constant and the partition coefficient P_t of 2,2′-dichlorodithizone were measured by applying the technique used by Sandell.[8] The average value of pK_a calculated from six determinations was found to be 4·75 ± 0·5. The average value of the partition coefficient between carbon tetrachloride and water was 6·1 ± 1 × 10^4.

The partition coefficients, P_{ML} for copper(II) and zinc(II) complexes between carbon tetrachloride and water were determined by the technique used by Geiger and Sandell.[9] The average values were 3·5 × 10^4 and 1·5 × 10^4 respectively.

The extraction constants K_{ext} for $M(Cl_2HDz)_n$ were determined for the Zn(II), Cd(II) and Pb(II) complexes by performing extractions from 1*M* perchlorate solutions, and calculating the equilibrium concentrations of $M(Cl_2HDz)_n$, M^{n+}, Cl_2H_2Dz and H^+. The concentrations of 2,2′-dichlorodithizone and its metal complex were determined spectrophotometrically, M^{n+} from the degree of extraction, and H^+ from the pH of the aqueous phase.

The extraction constants of $Hg(Cl_2HDz)_2$ and $Cu(Cl_2HDz)_2$ were determined by following the procedures given by Takei and Kato.[10]

RESULTS AND DISCUSSION

Visible absorption spectra of 2,2′-dichlorodithizone and its metal complexes

The introduction of chlorine atoms into the *ortho* positions of the phenyl nuclei of dithizone was found to shift both absorption bands bathochromically to 644 and 462 nm respectively (*vs.* 620 and 450 nm for dithizone). Our values are quite close to those (645 and 465 nm respectively) reported by Pelkis, Dubenko and Pupko,[1] but they are different from the values 670 and 470 nm given by Ramakrishna and Fernandopulle,[3] which for reasons given later, appear to be incorrect. The positions of λ_{max} for the metal complexes were also found to undergo various shifts as shown in Table 1.

The molar absorptivities of 2,2′-dichlorodithizone were also affected (Table 1). $\epsilon_{2\,max}$ for 2,2′-dichlorodithizone has increased to 2·97 × 10^4.mole^{-1}.cm^{-1} whereas $\lambda_{1\,max}$ has decreased to only 3·34 × 10^4. Ramakrishna and Fernandopulle's $\epsilon_{2\,max}$ (3·83 × 10^4 calc. by us from their peak ratio) is too high. Further, the anamolous shape of the shorter wavelength band, the displaced positions of both absorption peaks and the low peak ratio reported by them, cast serious doubts on the purity of their materials and/or the reliability of their data.

The molar absorptivities of the metal complexes undergo analogous changes, compared with the corresponding metal dithizonates.[11]

The spectral data which were given by Ramakrishna and Fernandopulle[3] for the Hg(II), Ag(I), Bi(III), Pb(II), Zn(II), Cu(II), Cd(II), Co(II) and Ni(II) complexes of 2,2′-dichlorodithizone, given in Table 1, appear to be in serious disagreement with ours.

Reaction between 2,2′-dichlorodithizone and metal ions

2,2′-Dichlorodithizone was found to react with various metal ions in a stoichiometrically identical way to dithizone, giving primary and secondary 2,2′-dichlorodithizonates. The former are formed when the reagent is in excess, the latter when the pH and the proportion of metal to ligand are increased.

The extraction data for metal complexes with 2,2′-dichlorodithizone are included in Table 1, inspection of which reveals the following features.

Table 1. Characteristic absorption and extraction data for 2,2'-dichlorothizone and some of its metal complexes. Some values for the corresponding dithizone complexes are included for comparison. Values in parentheses are the molar absorptivities ($l.mole^{-1}.cm^{-1}$) $\times 10^{-3}$

Compound	λ_{max} (ϵ) This work*	Ref. 3	pH for complete extn.	log K_{ext}	P_{ML}	log β_{ML}
2,2-Dichlorodithizone	644 (33·4)	670 (33·1)				
	462 (29·8)	470	—			
$Cu(Cl_2HDz)_2$	541 (65·8)	570 (77·4)	4·3–7	6·88	$3·5 \times 10^4$	21·1
$Cu(HDz)_2$	550 (45)[11]		<10[11]	10·48		22·3[9]
$Zn(Cl_2HDz)_2$	533 (97·2)	560 (105)	7–9	0·4	$1·5 \times 10^4$	14·9
$Zn(HDz)_2$	538 (92)[11]	425 (70)	6–14	2·18[11]		15·05[14]
$Hg(Cl_2HDz)_2$	485 (86·3)	500 (80·9)	<10	26·18		
$Hg(HDz)_2$	485 (71)[11]		<10[11]	26·81[13]		
$Cd(Cl_2HDz)_2$	527 (111·4)	550 (94·6)	6–8	1·47		
$Cd(HDz)_2$	520 (88)[11]		6–8·5[13]	1·88[13]		
$Pb(Cl_2HDz)_2$	514 (70·8)	530 (90·3) 430 sh.	5·5–7·5	1·85		
$Pb(HDz)_2$	520 (69)[11]		7–9	−0·05[13]		
$Ag(Cl_2HDz)$	460 (39)	470 (38·7)				
$Bi(Cl_2HDz)_3$	490 (104·7)	520 (76·1)				
$Co(Cl_2HDz)_2$	539 (55·7)	514 (70·8)				
$Ni(Cl_2HDz)_2$	669 (26·7)	460				
	545 (37·4)					
	428 (41·3)					

* Except where indicated by reference number.

(1) The ranges of pH for the complete extraction of 2,2'-dichlorodithizone complexes with copper(II), zinc(II) and cadmium(II) are relatively narrower than the corresponding values for dithizone complexes.

(2) The range of pH where mercury(II) is completely extracted was practically unaffected by the presence of chlorine atoms in the *ortho* positions of the phenyl nuclei of dithizone. The extraction constant of the mercury(II) complex has barely decreased from that for $Hg(HDz)_2$.[13]

(3) Both the extraction and the stability constants of $Cu(Cl_2HDz)_2$ are lower than those for $Cu(HDz)_2$. The corresponding constants for $Zn(Cl_2HD_z)_2$ are also slightly lower than those of $Zn(HDz)_2$.

That copper(II) is more sensitive than zinc(II) to the substitution by chlorine in the *ortho* positions of the phenyl nuclei of dithizone, may be explained on the assumption that copper(II) complexes are square planar, whereas the zinc(II) complexes are tetrahedral. The metal atom in a square planar environment would be subjected to relatively more steric hindrance from the substituents than in a tetrahedral one, and hence the stability constant of the former complex may be more adversely affected than that of the latter. The centrosymmetric square planar configuration of Cu(II) dithizonate[15] and the tetrahedral configuration of Zn(II) dithizonate[16] which have been established by X-ray structure determination, lend further support to our argument.

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Summary—1,5-Di-(2-chlorophenyl)-3-mercaptoformazan (2,2'-dichlorodithizone) has been synthesized and characterized. Its acid dissociation constant and its partition coefficient between carbon tetrachloride and water have been determined. The introduction of chlorine atoms into the *ortho* positions of the phenyl nuclei of dithizone was found to affect the visible electronic spectra of the reagent and its metal complexes. The ranges of pH for complete extraction, and the extraction constants, for the Hg(II), Cu(II), Zn(II), Cd(II), and Pb(II) complexes have been determined. The stability constants of the Cu(II) and Zn(II) complexes were also determined. Discrepancies between the present extensive data and the corresponding earlier data have been attributed to use of impure materials and/or inaccuracy of measurements in the earlier work.

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LETTER TO THE EDITOR

ION-SELECTIVE ELECTRODES IN ARGENTOMETRIC TITRATIONS

SIR,

The first potentiometric argentometric titration[1] was described over 80 years ago. The procedure, which utilizes a piece of metallic silver as indicator electrode, has proved its worth over the years, and is still used extensively today.

In recent years, several authors[2–6] have suggested that some of the new ion-selective electrodes are suitable for use as indicator electrodes in argentometric titrations, and it has also been suggested[3–5] that a useful application is the titration of halide ions after oxygen-flask decomposition of organic compounds. Two types of electrode mentioned were the sodium-selective glass electrode, present cost about £20, and the solid-state silver halide electrodes, which cost over £100. By comparison, a piece of silver wire of suitable size should cost less than £0·25. Therefore, one would expect that the ion-selective electrodes must offer considerable advantages over the simpler and more robust silver wire.

For titration of halides by utilizing the sodium electrode,[3] satisfactory end-points were obtained only if the silver nitrate titrant was made up in 80% propan-2-ol, and if the solution being titrated contained at least 90% of acetone. Also, sodium ions had to be absent. By comparison, titration of halides, using a silver wire electrode, is carried out here on a routine basis, in 30% aqueous acetone, and with an aqueous titrant.

The use of a solid-state silver chloride or silver bromide electrode in argentometric titrations has also been described,[5] and it was claimed that such electrodes could be used without interference in the presence of oxidizing agents such as hydrogen peroxide, provided that the pH was between 5 and 7. However, some simple tests carried out here showed that titrations using a silver wire electrode are unaffected by peroxide provided that the pH is <7. In more alkaline solutions, peroxide interferes with both the electrodes, the effect being more pronounced with the solid-state type. A further disadvantage of solid-state electrodes is their slow rate of response.

From these two examples, it is apparent that ion-selective electrodes offer disadvantages rather than advantages over the metallic silver electrode in argentometric titrations. It seems a pity that so much effort has been wasted on the application of these powerful new analytical tools in a situation where they are not needed.

MARY R. MASSON

Department of Chemistry
University of Aberdeen
Meston Walk
Old Aberdeen
Scotland
21 *March* 1974

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CORRIGENDA

The paper entitled "Extraction with long chain amines—VIII. Extraction of the chromium–DCTA complex and its colourimetric determination. *Talanta*, 1974, **21**, 1205", should have been Part IX of the series and not Part VIII.

On page 554, column 2 of the July issue (1975), delete lines 31–33 and substitute:

2450 MHz to excite solutions with apparatus similar to that of Gotô, Hirokawa and Suzuki.[48] Applications to the analysis of steel have been reported.[49–52]

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PRELIMINARY COMMUNICATION

AN EVALUATION OF A MACRO-POROUS SILICA GEL AS A REUSABLE CLEAN-UP ADSORBENT FOR PESTICIDE RESIDUES

Melvin E. Getz

Analytical Chemistry Laboratory, Agricultural Environmental Quality Institute, ARS, United States Department of Agriculture, Beltsville, Maryland 20705, U.S.A.

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Even though a high degree of instrumental sophistication has been developed for identifying and determining pesticide residues, the heart of the analytical methodology remains the extraction and clean-up. If an absolute clean-up were available and the identity of the residue known, any method of determination could be used, but this is rarely the case. In general, the analyst attempts to develop a clean-up method that will isolate the residue in a sufficiently pure state so that a particular form of detection and determination can be used without serious interferences.

Adsorption column chromatography has been the choice of many investigators for the isolation step. There has been much discussion as to which adsorbent is the best for the isolation of pesticide residues. Commonly used adsorbents that exhibit high clean-up efficiency are alumina,[1,2] Florisil,[3,4] and activated charcoal.[2,5] General screening procedures for pesticide residues have been developed with all three. However, when alumina and Florisil are used, many of the polar residues are so firmly bound that the column has to be deactivated by treatment with water in order to elute the residue. This deactivation minimizes the clean-up efficiency, so that unwanted interferences are eluted along with the compounds desired. Charcoal has a strong affinity for aromatic compounds and requires a solvent such as benzene to elute residues exhibiting aromaticity. This type of solvent will also elute any pigments that have been adsorbed by the charcoal, which can cause interference with the final analysis. All three adsorbents exhibit chemisorption, and in some cases the adsorption is irreversible, or the compound of interest undergoes undesirable chemical changes.

Recently, this investigator obtained a sample of a new type of silica gel[6] manufactured for gel permeation or molecular-sieve separations as well as for adsorption or partition chromatography. It is macro-porous and crystalline, in contrast to the amorphous character and smaller pore diameter of the conventional gels. The specific surface area is reported to be less than that of conventional gels. Under controlled conditions its separation properties for small molecules have proved to be unique and useful for separating both polar and non-polar residues from interfering substances in extracts. It responds well to stepwise gradient elution by mixtures of organic solvents of increasing polarity. There is a sharp separation of pigments, pesticides, and other components of extracts. When an eluted fraction is chromatographed by TLC, there is little smearing of the background and non-pesticide materials appear as spots or bands. This type of development on a thin-layer plate is ideal for optical scanning.

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The initial investigations showed that it was possible to quantitatively recover DDT, DDE, DDD, methoxychlor, the two isomers of demeton and their sulphone and sulphoxide analogues, and carbofuran, 3-ketocarbofuran, 3-hydroxycarbofuran and their 7-phenols.

EXPERIMENTAL

Apparatus and Reagents

Chromatographic columns, glass, medium-pressure type, 1-cm bore.
Automatic fraction collector with timing and drop-count facilities.
Silica gel, Merck EM-Gel SI200, 0.040-0.063 mm particle size.
Hexane, redistilled quality that does not discolour sulphuric acid.
Acetone and methanol, redistilled quality free from oxidizing or reducing impurities.

Procedure

Dry-pack 5 g of the silica gel into the chromatographic column with the aid of suction, sandwiching the adsorbent between glass-wool plugs. Prewash the column with hexane under 1-2 psig pressure (from a nitrogen cylinder with low-pressure regulator) until the adsorbent is completely wetted with the solvent. Pipette 1 or 2 ml of the sample solution (contained in 20% acetone in hexane) dropwise onto the column. Add 1 ml of hexane and allow to soak into the column under pressure. Add successively 10 ml each of 2, 5, 10, 15 and 20% acetone solutions in hexane to give stepwise gradient elution, and then 50 ml of 30% acetone in hexane. Collect the eluate in 10-ml fractions at the rate of 4 ml/min. Evaporate the fractions to 2 ml or just to dryness. Adjust the solutions to 2 ml in volume and transfer them to an automatic spotter[7] for spotting onto precoated silica gel TLC plates; develop and visualize the plates, and quantify by optical scanning with a fibre-optics reflectance densitometer.[8]

RESULTS

The figure shows the elution curves of the various pesticides tested. The peak heights are pictorial, but the gradients and volumes are factual. The compounds that are eluted together are resolvable on thin-layer silica gel plates.

Pure solvent solutions and alfalfa extracts were spiked at concentrations equivalent to 0.1 μg/g and 1.0 μg/g. The range of recoveries was from 88 to 105% (average of 5 determinations).

The column has been recycled several hundred times and still gives the same relative resolution with no significant loss in clean-up efficiency. Up to 5 g of alfalfa extract was successfully cleaned up with the 5 g of silica gel in the column.

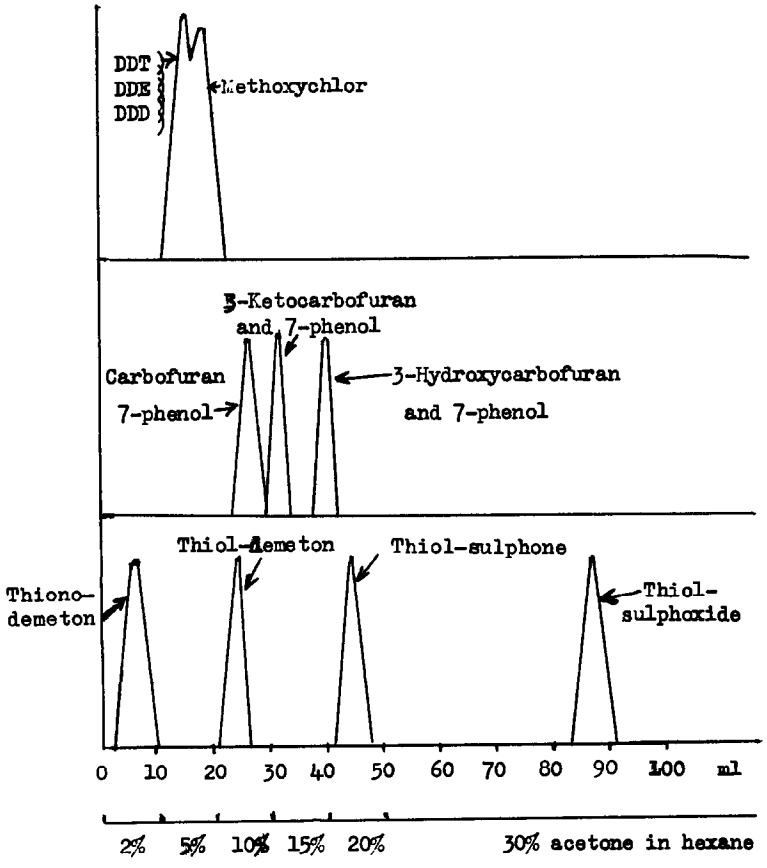
SUMMARY AND CONCLUSIONS

The silica gel used in this investigation is unique in its properties. It has a mean pore diameter of 180 Å, is crystalline in nature, and is homogenous in appearance. This is in sharp contrast to conventional silica gel, which is heterogenous with small pores and has no discernible crystallinity.

Since this silica gel has a crystalline structure, there should be more "free" (and less-reactive) hydroxyl groups exposed. This means that there is very little or no

interaction between adjacent hydroxyl groups. This may account for its unusual separation properties. Ordinarily a large-pore material would be expected to exhibit only molecular-sieve properties. Under the conditions of gradient elution used in this study it appears that the polarity of the molecule or certain substituent groups affects the partitioning between the adsorbent and the mixed solvent system so that the selective adsorption effects predominate.

There is much more to be learned about these types of gel. It is predicted that this gel will have universal application in pesticide residue analysis. Research is going on to utilize this material in a more sophisticated and controlled manner.



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SCANDINAVIAN CONTRIBUTIONS TO ANALYTICAL CHEMISTRY

E. RANCKE-MADSEN
Royal Danish School of Educational Studies, Department of Chemistry, Emdrupvej 115B, DK-2400 Copenhagen NV, Denmark
R. A. CHALMERS
Chemistry Department, University of Aberdeen, Old Aberdeen, Scotland

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Summary – A review is given of the major contributions of Scandinavian chemists to analytical chemistry, illustrating the great importance of their work in development of the science as it is known today.

In this article we aim to present the highlights of Scandinavian work in analytical chemistry, and to indicate the breadth of current interests, and to show how strong are the links between past and present. It seems fair to say that in proportion to their numbers, Scandinavian chemists have played an outstanding part in the development of the theory and practice of analytical chemistry, from its earliest days up to the present time.

THE PERIOD UP TO 1900

No-one is able to say with certainty who carried out the first qualitative or quantitative analysis or when it was made. The answer would also depend on how complete the analysis ought to be in order to deserve to be so named. If we do not demand too much from an analysis, analyses were carried out far back in antiquity at a time when "chemistry" as such hardly existed.

Within historical times we can mention various names in connection with qualitative tests and with more or less imperfect quantitative determinations. First of all, *Robert Boyle*, (1627–91) who described among other things a number of reagents to be used in the examination of mineral waters. From Scandinavia can be mentioned the Dane *Oluf Borch* (1626–90), even though his achievements did not make an essential contribution to further developments. Borch proved that pure silver solutions do not turn blue when ammonia is added, as presumed till then, but that this effect is due to inclusions in the silver. In 1677 he published a guide to analysis of minerals, *Dissertatio de docimastice metallica*, which was translated into German and Swedish.

There is a temptation to say (paraphrasing a well-known chemical saying) "Analytical chemistry is a Swedish science. It was founded by Bergman, of immortal memory." At any rate, this assertion is not far from the truth.

The contributions of Sweden to the development of chemistry in the 18th century were very great, while the other Scandinavian countries made few contributions This outstanding position of Sweden was due to its abundance of minerals and the work which was done in order to extract and utilize them. During this century several Swedes distinguished themselves as chemists; the two most outstanding were undoubtedly *Torbern Bergman* (1735–84) and *Carl Wilhelm Scheele* (1742–86), both of whom carried out analyses – perhaps better than anybody else at that time However, Scheele did not produce any literature on analysis, whereas Bergman treated this subject in several of his papers.

Qualitative analysis may be divided into analysis by dry processes and by processes in solutions (wet methods) The first-mentioned is the older form of analysis, and dates back to times when there was an incipient interest in the metal content of ores and alloys. During the 17th and 18th centuries, analysis by dry processes was worked out with a view to exploring and classifying minerals An obvious method was to heat the minerals, and such heatings were probably made in far-back ages without any special intentions. The minerals were examined more systematically by the Swede *Magnus von Bromell* (1679–1731); he heated them and found whether they were fireproof, fusible, *etc* However, analysis by dry processes was soon to a considerable extent based on the use of the blowpipe.

As far as we know, the blowpipe was mentioned for the first time in 1669 by the Dane *Rasmus Bartholin* (1625–98) in his famous treatise on Iceland spar, but nothing seems to indicate that he is the inventor of the blowpipe. It was, however, in Sweden that the blowpipe was developed and used. About the middle of the 18th century it was used by *Anton von Swab* (1703–68) and *Axel Fredrik Cronstedt* (1722–65). It has been debated which of them first used the blowpipe, but at any rate it was Cronstedt who first examined minerals systematically with it. In 1758 Cronstedt published a Swedish textbook of mineralogy, later translated into English (1770) by *Gustav von Engestrom* (1738–1813) who added detailed instructions on the use of the blowpipe.

The mineral analyses were carried out by heating the mineral on a piece of charcoal; this showed how the mineral behaved at a high temperature. Afterwards the mineral was heated with a flux, three different ones being used – soda, borax, or *sal microcosmicum* ($NaNH_4PO_4$) – and the expert analyst would then be able to draw his conclusions from what he observed.

While Cronstedt analysed minerals, Bergman used the blowpipe for analysing other sorts of substance as well, which meant an extension of the field of application of dry analysis. In 1779 Bergman published a treatise on the use of the blowpipe. The blowpipe was also extensively used by Bergman's pupils. His best pupil was probably *Johan Gottlieb Gahn* (1745–1818), who continued this form of analysis in the 19th century and taught it to *Jons Jacob Berzelius* (1779–1848) It was Gahn who introduced the use of the platinum loop.

Qualitative analysis by wet methods dates from the analysis of mineral water. Thus Boyle used a number of reagents for examination of mineral waters, and in other countries in Europe mineral waters were the object of interest at the end of the 17th century. In Sweden *Urban Hiärne* (1641–1724) began in 1678 to analyse mineral waters, and several other Swedish names can be mentioned, especially that of *Georg Brandt* (1649–1768) who also used wet methods for analysis of ores and minerals.

In 1779 Bergman wrote on mineral water analysis (*De analysi aquarum*) and in 1780 on the general use of wet methods of analysis

Quantitative analysis can also be carried out by both dry and wet methods. That by dry processes is the older; if the metal content of an ore was to be determined, the metal was won from the ore, and weights of the metal and ore were compared. Bergman thought that this method was very uncertain and he saw the importance of the wet methods. He introduced the gravimetric method in which is found the weight of a precipitate isolated from the dissolved sample. In 1780 he wrote on quantitative determinations (*De praecipitatis metallis*). He was aware that the precipitates had a constant composition and stated in a table the weights of the respective precipitates that contained 100 g of metal.

In all, Bergman wrote about 50 chemical treatises and in several of them he gave analytical methods. Quantitative analysis was often very slow, but that did not bother the chemists of the time. For instance, in *De analysi aquarum*, Bergman says of a ferruginous precipitate that for some weeks it must be exposed in an open vessel to the rays of the sun, but such a prolonged drying causes no trouble at all as it is possible to take the precipitate on one's travels!

We should also mention the Finnish chemist *Johan Gadolin* (1760–1852) before we leave the 18th century. Gadolin was born in Åbo, studied under Bergman and later returned to the University of Åbo. His first scientific paper from his time with Bergman was analytical (*De analysi ferri*, 1781) and he continued his interest in analytical determination of iron In 1780 Bergman had proposed a determination of iron by precipitation as Prussian blue, and later on Gadolin went into this subject more closely. He used the precipitated Prussian blue as the weighing form, and also described a titrimetric method in which iron was titrated with potassium ferrocyanide [this was probably inspired by the work of the Irish chemist *Richard Kirwan* (1735–1812)].

Gadolin also devoted some time to the analysis of minerals, and one result of his analysis of a mineral from Ytterby was that in 1794 he was able to publish the discovery of a new and hitherto unknown earth. The mineral was later called gadolinite, and the metal contained in it was called yttrium.

From the first half of the 19th century we can mention many great chemists, but during the period about 1810–1830 the greatest name may well be that of *Berzelius* and in those years he was undoubtedly the leading analyst.

In 1796 Berzelius started his medical studies at the University of Uppsala, and in 1800 he had already obtained a position as doctor at the watering place in Medevi, even though he had not yet graduated. This occupation resulted in a treatise on mineral water analysis (*Nova analysis aquarum Medeviensium*). Berzelius followed with great interest the development of science, and even though it has no analytical relevance it may be mentioned that his dissertation in 1802 was on the use of the galvanic current of the voltaic pile as a cure for various diseases of the patients in Medevi.

During his first years as a graduate Berzelius continued his chemical experiments, partly in cooperation with *Wilhelm Hisinger* (1766–1852). The results were partly electrochemical research achievements and partly the discovery of the element cerium, based on the analysis of a heavy mineral from Bastnäs. In those years Berzelius struggled with heavy economic difficulties, and it was a great disappointment to him that a vacant professorship in 1805 was given to *Conrad Quensel* (1767–1806) and not to himself. For economic reasons Berzelius had to consider giving up chemistry, but the situation changed when Quensel died unexpectedly in 1806, and Berzelius was appointed his successor in 1807. It has rightly been maintained that through his death Quensel had a decisive influence on the development and history of chemistry.

When Berzelius lectured on physiological chemistry to the medical students he discovered that the textbooks from abroad were very brief and often wrong. He therefore plunged into a systematic analysis of animal natural products. His

analyses were amazingly exact, and he became a deserving successor of Scheele, who may be regarded as the founder of organic chemistry. Among other things Berzelius proved that the pigment of the blood was a chemical compound containing 0·5% of iron. He published his results [*Föreläsningar i Djur-Kemien* (Lectures in Animal Chemistry)] in 1806 and 1808.

After 1810 Berzelius was especially interested in inorganic chemistry and mineralogy, and he particularly developed inorganic analysis. In connection with qualitative analysis he specialized in the use of the blowpipe. While Berzelius worked on the first edition of his great textbook of chemistry (*Larbok i Kemien*, published 1808–10) he met the nearly 70-years old J G. Gahn who taught him to analyse minerals by means of the blowpipe. Later Berzelius lauded Gahn for his exceptional ability to carry out these analyses, and he made Gahn contribute to the chapter on the blowpipe. Berzelius too became a virtuoso of this form of analysis and in 1820 wrote a book of 300 pages on it. This book was published in several editions and was translated into German, French, English, Russian and Italian, and as late as 1845 an enlarged and revised edition was published in Boston. When Berzelius was travelling he always took his blowpipe with him, and often impressed the people he visited abroad by the skill with which he used it (among others, *Goethe*, whose private collection of minerals he examined in 1822).

When Berzelius started writing his textbook on chemistry he soon realized that the composition of many of the simplest chemical compounds was uncertain. As the elements of the chemical substances seemed to be combined in constant proportions, an analytical research might result in the determination of the equivalent weights of these elements and hence to the atomic weights. Berzelius needed to make the analytical methods more exact, and he began and finished a gigantic task. In 1810 he published his first results, and in 1818 he was able to state atomic weights for 45 of the 49 elements then known. He determined 39 of these himself, as he usually relied only on his own analytical work. Actually it is remarkable that many of the famous chemists of that time did all the necessary experimental work themselves, even though it was time-consuming and lengthy. The experiments took a lot of time, and generally one had to make one's own apparatus and reagents. Nowadays, when most experimental work is instrumental and quick, most research work is done by teams and more and more seldom by individual workers.

Berzelius's experimental efforts were quite overwhelming during the years 1810–20, but he continued to publish experimental works nearly until his death. To this must be added new editions of his textbooks and the publishing of *Årsberättelser* (Annual Surveys of Progress in Science) 1821–48. The first volumes of these surveys dealt with chemistry, mineralogy, physics, astronomy, zoology, botany and technology, but the later ones only with chemistry and mineralogy, and the 27 volumes comprised about 12000 pages.

Berzelius carried on researches into all the disciplines of chemistry. He mastered not only inorganic analysis but also organic, and made contributions to its development which will be mentioned below.

Organic elemental analysis was introduced by *Antoine Laurent Lavoisier* (1743–94) and improved (*ca* 1810) by *Louis Joseph Gay-Lussac* (1778–1850) and *Louis Jacques Thénard* (1777–1857). In 1814 Berzelius further improved the method Gay-Lussac and Thénard used a vertical combustion tube in which they placed the organic substance mixed with potassium chlorate, whereas Berzelius used a horizontal combustion tube in which he placed the sample mixed with potassium chlorate and sodium chloride. The two French chemists found the hydrogen content by a laborious and not quite correct calculation of the quantity of oxygen used for the formation of water, while Berzelius weighed the water formed, which was partly absorbed in a calcium chloride tube

From now on the Swedes' leading position in analytical chemistry was at an end. As time went on, elemental analysis was improved by chemists of many different nationalities. A special chapter is the determination of nitrogen in organic substances, but before this we should like to mention the determination of sulphur. About 1830 the Dane *William Christopher Zeise* (1789–1847) carried on researches into certain types of organic sulphur compounds. Zeise proved the presence of the sulphur by fusing his sample with metallic potassium, by means of which hydrogen sulphide was given off, and he determined the sulphur by fusing the sample with potassium nitrate, by means of which the sulphur was oxidized to sulphate.

It is also worth mentioning that the Dane *Christen Thomsen Barfoed* (1815–69), after he had written an excellent Danish textbook on the analysis of inorganic substances was inspired to write about organic substances. During the years 1866–77 he worked on a quite original textbook on organic qualitative analysis which attracted so much attention that it was translated into German in 1881. Barfoed's textbook was used for a number of years, but the idea of parallelling the qualitative analyses of both inorganic and organic substances was unable to survive in the long run.

The determination of nitrogen in organic substances had always caused difficulty, but in 1831 *Jean Baptiste Dumas* (1800–84) found out how to determine nitrogen after a suitable combustion whereby free nitrogen was evolved, then was

driven from the combustion tube with carbon dioxide and collected over a solution of potassium hydroxide This method was also difficult, but after various corrections and improvements is still used today, especially in its automated form.

Dumas had also attempted a nitrogen determination by means of a decomposition technique which formed ammonia, and several other chemists worked on the same principle. The decomposition generally took place in basic medium, but generally the methods based on this principle did not yield satisfactory results

Then in 1883 the Dane *Johan Gustav Kristoffer Thorsager Kjeldahl* (1849–1900) published his epoch-making method. On the 7th of March it was submitted to the Danish Chemical Society (Kemisk Forening) and it was described in a Danish and a German periodical. The organic substance containing nitrogen was destroyed by concentrated sulphuric acid, and after heating of the mixture nearly to boiling, potassium permanganate was added. Hereby ammonium ions were formed, and then ammonia was distilled off from alkaline medium and determined titrimetrically. The method has since been modified in various ways but the principle is still the same, and since 1883 many millions of Kjeldahl determinations have been carried out all over the world. As we know, the greatest honour that can be done to a physicist is to name a unit of measurement after him, and normally the greatest honour which can befall a chemist is that his name is attached to a substance, an apparatus, a reaction or a method. However, the most exclusive must be to have one's name made a verb, and any chemist knows what "to kjeldahl" means.

In 1873 Kjeldahl graduated from the Technical University of Copenhagen founded by *H. C. Ørsted.* From the 1st of May 1875 he was employed by *J C Jacobsen,* the brewer who founded the Carlsberg Laboratory. Kjeldahl was appointed principal of the chemical department (and later titular professor). He carried on researches into enzymes and proteins, and it was in connection with this research that he was in need of a quick and reliable method for the determination of nitrogen

However, Kjeldahl soon gave up research on proteins, so after publication of his method it was rather seldom that Kjeldahl himself kjeldahled. He carried on research on starch and types of sugar, and here too was engaged in improving the methods of determination, but his efforts in this direction were not of the same lasting importance. At the end of the nineties Kjeldahl was in bad health; he died on 18 July 1900 while bathing at Tisvildeleje (North Zealand).

No history of Scandinavian analysis before 1900 would be complete without mention of the Norwegians *Guldberg* and *Waage* and the Swede *Arrhenius,* whose theories are fundamental to modern analytical chemistry (and indeed to much of chemistry as a whole) The law of mass action, advanced in 1867 by *Cato Maximillian Guldberg* (1836–1902) and *Peter Waage* (1833–1900) forms the basis of much analytical chemistry. The theory of electrolytic dissociation, advanced in 1884 by *Svante Arrhenius* (1859–1927), directly helped to develop the theoretical foundation of analytical chemistry, as *Wilhelm Ostwald* (1853–1932) at once went to Sweden to see Arrhenius, and thereby Ostwald's own epoch-making work was clearly catalysed and accelerated. Arrhenius was awarded a Nobel Prize in 1903.

THE PERIOD SINCE 1900

Scandinavian contributions to analytical chemistry during the present century show an interesting mingling of development of new ideas and continued application of old ones, and demonstrate very well that chemistry should really be regarded (and taught) as a unified discipline, and not as a group of unconnected sub-disciplines. For example, we can easily link together the idea of *Niels Bohr,* the use of the blowpipe, and *Lundegårdh's* development of the burner that bears his name, to arrive at flame-emission and atomic-absorption spectrophotometry.

Similarly, we can couple another indespensable concept in modern chemistry, that of pH by *Sørensen,* with the *Brønsted-Lowry* theory and acid-base titrimetry. A great deal of developmental work on electrodes and electrochemical methods has been done in Scandinavia, as is demonstrated by some of the contributions to this issue and by the extensive use of potentiometric and coulometric methods both in analysis and in complexation chemistry. The schools of *K. J. Karrman* and *G. Johansson,* for example, are well known, and so is the work of *J. Růžička* and his colleagues in Copenhagen on ion-selective electrodes.

It is, perhaps, only natural that a large body of Scandinavian chemistry should be based on Guldberg and Waage's law. The extensive development of methods of study of co-ordination compounds (which has made complexation chemistry yet another "Swedish science") is associated with the names of *Niels Bjerrum* and his son *Jannik,* of *Leden, Fronaeus, Rydberg* (grandson of the *Rydberg* of "constant" fame), *Dyrssen,* and above all the late *Lars Gunnar Sillén* and his world-famous school at Stockholm.

Sillén's name is associated with the application of the powerful computer techniques now so extensively used for dealing with problems in equilibrium chemistry, and his pit-mapping techniques and other mathematical methods, the programs such as LETAGROP and HALTAFALL, and the massive compilation (along with *A. E.*

Martell and others) of stability constants all serve as a lasting monument to one of the great chemists of our time.

Another outstanding contribution to modern analysis was the development by the late *Anders Ringbom* (Finland) of the concept of conditional constants in calculation of reaction conditions for quantitative analysis The great merit of this was the recognition that logarithmic diagrams greatly simplified the long-known methods of calculation, and that the necessary data could be assembled once and for all, and thus eliminate the tedious arithmetic. His book *Complexation in Analytical Chemistry* is a milestone in the development of analytical theory, but has perhaps overshadowed his many other contributions to analytical chemistry, which include much work on spectrophotometry and indicator theory.

A significant new method for location of the end-point in titrimetry was developed by *Gran* in Stockholm and further developed there by *A. Johansson* and *Ingman* and in Åbo by *Still.* This work may be regarded as in the mainline Scandinavian tradition of potentiometric methods.

The tradition of organic analysis has also been continued, notably by *Kirsten* in Uppsala and *Veibel* in Copenhagen, whose outstanding contribution is the application of simple quantitative determinations in qualitative analysis. Organic analysis is nowadays bound up with chromatographic methods, and here *Arne Tiselius* did pioneering work on the mechanism of separation, establishing the principles of frontal analysis, displacement chromatography and elution chromatrography. His work on electrophoresis gained him a Nobel Prize in 1948. In gel-filtration the pioneering work by *Porath* and *Flodin* and the development of "Sephadex" and its application are well known. *Theodore Svedberg's* work on ultracentrifuges has played a highly significant role in colloid chemistry *etc.* and gained a Nobel Prize in 1926.

Several groups in Scandinavia are engaged in the development of analytical procedures based on high-performance liquid chromatography. In Uppsala, *Schill* and his co-workers are using procedures based on ion-pair extraction systems for the separation and determination of pharmaceuticals and their metabolites in biological samples.

Links between the past and modern analysis have already been mentioned. One of the most striking is the renaissance of the "Berzelius" method of decomposition of silicates with hydrofluoric acid, *Langmyhr* and his fellow Norwegian workers in rock analysis have developed hydrofluoric acid methods extensively and continued the Berzelius tradition of careful and accurate work

Much work has been done on solvent extraction methods, especially in connection with complexation chemistry, and the work of the Goteborg school (*Dyrssen, Rydberg,* and their co-workers) is well known The same school is very active in oceanographic analysis and application of computer techniques to analytical problems. In ion-exchange a leading figure is *Olof Samuelson* (Goteborg).

The mineral wealth of Scandinavia has naturally led to development of metallurgical analysis, and here the powerful tool provided by EDTA has been extensively applied, notably in Finland by *Kinnunen, Wennerstrand* and *Wänninen*

CONCLUSION

In a short survey such as this, it is impossible to be exhaustive in cataloguing contributions to the field, and omission of a name or method is not a mark of disrespect. Quite the contrary in fact, since the very large number of names that have to be left out is itself witness to the wide scope and vigour of Scandinavian analytical chemistry. We have attempted – and, we hope, succeeded in the attempt – to select and present those areas of analytical chemistry where Scandinavian workers have made outstanding contributions in development and exploitation of ideas, and in many cases have led the world

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CHOICE OF CHEMICAL CONDITIONS IN ORDER TO OBTAIN LINEAR TITRATION CURVES IN POTENTIOMETRY

AXEL JOHANSSON

Royal Institute of Technology, Stockholm, Sweden

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Summary – In the titration of an acid HA with a strong base, [HA] diminishes, on the whole, in proportion to the addition of titrant. However, $[HA] = K_{HA}[H][A]$, and if [A] is kept constant [HA] will be proportional to [H]. Therefore if [H] instead of [HA] is plotted against ml of titrant added, one obtains a linear titration curve. [A] is kept constant by addition of NaA before titration in such high concentration that the formation of A can be neglected during the titration. When an acid stronger than acetic acid is titrated, sodium acetate can be used as the added salt. Even mixtures of acids, mono- or polybasic, then yield straight titration curves since one is in fact titrating acetic acid in the presence of excess of acetate. For weaker acids sodium sulphite is used. In the oxidation–reduction titration of, for example, ferrous iron with permanganate, the potential measured is dependent on the ratio $[Fe^{2+}]/[Fe^{3+}]$. If $[Fe^{3+}]$ is kept constant by the addition of ferric chloride before the titration, the potential will be dependent only on $[Fe^{2+}]$. Since this diminishes in proportion to the added volume of titrant, straight titration curves can be obtained in this case also. No correction for dilution should be made

The most widely used method for obtaining linear titration curves in potentiometric titrimetry is the so-called Gran method.[1,2] In principle this method involves plotting the concentration of an appropriate sample species as a function of the volume of titrant added during a titration. One can then assume with good approximation that this concentration falls in proportion to the amount of titrant added before the equivalence point. After the equivalence point the concentration of titrant undergoes a linear rise. For example, in the titration of a strong acid with a strong base the hydrogen-ion concentration decreases proportionally before the equivalence point; the hydroxide-ion concentration increases proportionally after the equivalence point. The simple expressions which Gran has presented are, however, limited in their application. The expressions are not the same for titration of weak acids as for titration of strong acids, neither of these sets of expressions is applicable, therefore, to titration of moderately strong acids. In addition, the expressions for weak acids are only valid for acids with stability constants between 10^3 and 10^7 at normal concentrations ($10^{-2}-10^{-3}M$).

Ingman and Still[3] have developed Gran's method for weak acids to include acids with stability constants up to 10^{10}. Johansson[4] has pointed out that the same expression can be used for strong and moderately strong acids and has described an automatic titration method which is based on the expressions derived. These expressions are rather complex but still useful if one has access to a calculator.

A simpler method will now be described in which no complicated calculations need be performed, not even correction for dilution during titration. The only calculation done is the transformation of, for example, pH into hydrogen-ion concentration, *i.e.*, the calculation of the antilogarithm of the pH. If one has access to an instrument which shows antilog pH, this calculation is also eliminated. Johansson[6] has described such an instrument. The titration curve is here automatically drawn, but of course one can transform measured pH values for a number of points almost as conveniently with the help of a pocket calculator and plot the titration curve by hand.

In principle, the method involves choosing the experimental conditions so that:

(1) the sample concentration is kept proportional to the concentration that can be measured,

(2) the sample concentration diminishes in proportion to the amount of added titrant.

The second condition can also be formulated in this way: the titrant shall chiefly react with a single species in the solution, and this reaction ought to be regarded as complete. If the observed values are plotted *vs.* the volume, a straight line results.

When the method is applied to the titration of an acid HA with a strong base, [HA] is plotted against ml of base solution added before the equivalence point. [HA] is proportional to [H][A] according to the equilibrium equation, and if [A] can be kept constant [HA] will be proportional to [H], which can, of course, be measured. Application of the method to oxidation–reduction involves keeping one of the components in the redox pair at constant concentration. For example, if Fe(II) is titrated with permanganate, the potential that is measured is dependent on the ratio $[Fe^{2+}]/[Fe^{3+}]$. If $[Fe^{3+}]$ is kept constant, then the potential is dependent only on $[Fe^{2+}]$. $[Fe^{2+}]$ or a constant × $[Fe^{2+}]$ can

therefore be measured and plotted against the volume of permanganate, thus resulting in a straight line which intercepts the volume axis at the equivalence volume.

Under the heading of examples, a more detailed account is given of the application of the method to titration of acids or bases and to determination of the sum of several acids. In addition, the determinations of iodine with thiosulphate and Fe^{2+} with permanganate are treated under redox titrations. The expressions given by Gran have shown themselves to be unsuitable for practical application to redox titrations.

The fact that there is a linear relation between the sample concentration and the volume of titrant added makes it also possible to conveniently perform so-called one-point titrations. If one knows the approximate concentration of, for example, an acid in the sample solution, one can with a pipette add base equivalent to approximately 90% of the calculated amount required for reaching the equivalence point. Afterwards, the remaining hydrogen-ion concentration (proportional to the remaining acid concentration) is measured and in this way the total concentration of the acid can easily be determined. In a following article examples of such titrations are given.

EXPERIMENTAL

Potentiometric measurements

Potentiometric titrations are usually carried out by means of the cell shown in Fig. 1.

reference half-cell	sample solution	probe for hydrogen ions, metal ions, electrons *etc.*

Fig. 1.

Many types of electrodes can act as probes. Hydrogen-ion concentrations are usually measured by glass electrodes. The range of probes for metal ions, anions such as fluoride, and molecules such as ammonia, has been extended by the introduction of various ion-selective electrodes. The ratio between different ions or molecules can also be determined by means of redox electrodes, *e.g.*, a platinum wire.

If the cell contains a glass electrode in the right-hand half-cell the emf of the cell may be described by an equation consisting of three terms:

$$E = E'_0 + Q \log[H^+] + E'_j \qquad (1)$$

where Q is $RTF^{-1}\ln 10$. The first term E'_0 depends on the type of cell and includes the standard potential, the potential of the reference electrode, the asymmetry potential of the glass electrode and the invariant part of $Q.\log \gamma_H$ and the liquid-liquid junction potential, where γ_H is the activity coefficient of hydrogen ions. The second term accounts for the variation of the measured potential with the concentration of hydrogen ions according to Nernst's equation if activities are replaced by concentrations. The third quantity E'_j includes the variant part of the potential at the liquid-liquid junction and of $Q.\log \gamma_H$. This division into three terms is perhaps somewhat artificial but nevertheless very practical. The term E'_j varies with changing acidity and ionic medium. Strongly acidic solutions are avoided with the titration method described in this paper and if in addition the ionic strength is kept constant, E'_j will be close to zero. The term can be neglected at pH >4 (see Table 1 in ref. 7). It follows then from (1) that.

$$-\log [H] = \frac{E'}{Q}{}^{0} - \frac{E}{Q} \qquad (2)$$

and that

$$[H] = \text{const} \times \text{antilog}\,(E/Q) \qquad (3)$$

This quantity [H] is recorded by the instrument described in more detail below. Usually it is not necessary to know the value of the constant. It is, however, possible to determine its value by calibration with solutions of known [H]. It should be stressed that although the glass electrode in principle responds to hydrogen *activity* it may nevertheless be calibrated with solutions of known hydrogen-ion concentrations.[7] If the activity factor is constant, this leads only to different values of the constant in formula (3). In order to ensure linear plots it is necessary that the Q-value is not only constant, but also correct. Q is often called the slope. In the case of the glass electrode, it is constant over a large concentration range. The titration methods suggested here assume constant slope only over a few orders of magnitude.

Instrumental

If it will suffice to plot the titration curves by hand, one requires, besides the burette, only a pH-meter. It is most advantageous if the meter has a digital read-out with at least 2 or, even better, 3 decimals. If one wishes to register the titration curves automatically, it may be suitable to use an instrument which transforms pH directly into concentration.[6] Such an instrument works in the following way. For each change of a pH-unit or a log [H]-unit in the sample solution, the voltage of the cell in Fig. 1. is changed by Q mV. At 25°, $Q = 59{\cdot}16$ mV for a glass electrode. This voltage is measured by a pH-meter, which is basically a voltmeter with high input impedance which divides the measured voltage by Q and shows this value on a scale. The pH-meter which was used in the experiments (Orion model 801) also had an output which gave 10 mV for every change of input voltage of Q mV, in other words for every change of one unit in pH. This voltage has then been used to calculate [H], which is the antilog of $-\log$ [H]. The instrument which carries out this operation was made by Optilab AB, Stockholm. The amplification in this antilog apparatus can be adjusted so that one pH unit is equivalent to, for example, 100 mV; 2 pH units are then equivalent to 1000 mV and 3 pH units to 10,000 mV. For every increase of output voltage by 10 mV on the pH-meter, the voltage from the antilog unit is multiplied by 10. In order to cover the entire pH range without the voltage on the antilog unit becoming too great, one can connect an extra voltage source in series with the cell to move the scale's zero point. It is suitable to make the displacement in whole pH-steps (59.16 mV), in other words in whole powers of ten on the antilog scale. A Metrohm pH-simulator E 448 has been used as the extra voltage source. In some cases a combination instrument has been used in which pH-meter, antilog attachment and digital voltmeter are built into one single instrument. This has also been built by Optilab AB and can possibly be called CONC-meter or [ION]-meter since it indicates directly a concentration. In most of the experiments described below, the output from the antilog apparatus has been written on a recorder (Metrohm Potentiograph E 336 A) which simultaneously shows the added volume of titrant. The deflection is first adjusted to zero by short-circuiting of the input. The electrodes are then dipped into the sample solution and amplification on the antilog apparatus is adjusted so that full deflection is

obtained on the recorder. If one wishes to register only the final tenth of the titration curve, the amplification should then be increased tenfold. When the titration has passed the equivalence point, the inverted concentration value is registered, for example 1/[H]. Here it is suitable to adjust the amplification so that the lines before and after the equivalence point form the same angle with the axis. The antilog apparatus then switches automatically from [H] to 1/[H] at the equivalence volume.

EXAMPLES

As stated in the introduction, straight titration curves are obtained if the experimental conditions are chosen so that the demands specified there are met. This is elucidated in the following examples.

A Acid-Base Titrations

We can choose as the first example titration of a weak acid with a strong base. The main reaction during the titration is

$$HA + OH^- = A^- + H_2O \qquad (4)$$

On the whole, HA is consumed in proportion to the hydroxide addition before the equivalence point, and therefore if [HA] is plotted against ml of hydroxide, a straight line is obtained. This would be simple if one had access to an electrode which senses [HA], but since [H] is measured, [HA] must be calculated from the equilibrium condition

$$[HA] = K_{HA}[H][A] \qquad (5)$$

where K_{HA} is the stability constant of the acid.

If one can keep [A] constant, then

$$[HA] \propto [H] \qquad (6)$$

producing straight lines, although with different slopes, if [HA] or [H] is plotted against ml of hydroxide. The easiest way to keep [A] constant is to add a salt NaA at the start of the titration. Since A^- is formed during the titration, enough NaA must be added for the change to be neglected. In the titration of 0·01*M* acetic acid, for example, sodium acetate can be added so that its concentration is 1*M*. Deviations from the straight line then become insignificant. Thus condition 1 (above) is satisfied. At the same time, condition 2, which requires that the hydroxide reacts with only one acid, is also met as is shown by the following.

Usually when a weak acid is titrated, it has partially dissociated into H^+ and A^- and both this H^+ and HA react with OH^-. Through the addition of A^- before titration, the dissociation becomes negligible. If 0·01*M* acetic acid is titrated and acetate is added so that its concentration is 1*M*, −log[H] becomes 6·5, which means that less than one ten-thousandth of the acetic acid has dissociated.

In order for a straight line to be obtained, however, the reaction $HA + OH^- \rightleftharpoons A^- + H_2O$ must be complete. Addition of A^- displaces the equilibrium to the left, meaning that the weakest acids cannot be determined by the method suggested. This will be discussed further in the section *"Treatment as conditional titration"*.

Titration curves

The equation of the titration curve before the equivalence point can be derived as follows. Assume the initial concentration of the acid is C^0_{HA}, that the sample volume is V_0 ml and that V ml of base with concentration C_B are added. Further, we can assume that we add A from the beginning in concentration C^0_A. If it is assumed that A is formed in proportion to addition of hydroxide,

$$(V_0 + V)[A] = V_0C^0_A + VC_B \qquad (7)$$

The combination of (5) and (7) yields

$$[HA] = K_{HA}[H] \times \frac{V_0C^0_A + VC_B}{V_0 + V} \qquad (8)$$

If one takes into consideration that according to definition

$$V_eC_B = V_0C^0_{HA} \qquad (9)$$

where V_e is the equivalence volume, and further assumes that HA is consumed in proportion to addition of hydroxide, then

$$(V_0 + V)[HA] = V_eC_B - VC_B \qquad (10)$$

If (8) and (10) are combined, we obtain

$$V_e - V = \frac{K_{HA}}{C_B}(V_0C^0_A + VC_B)[H] \qquad (11)$$

If $V_0C^0_A >> VC_B$, then (11) can be formulated as

$$V_e - V = \text{constant} \times [H] \qquad (12)$$

or, expressed in words, if [H] is plotted as a function of volume V of titrant added, a straight line is obtained which intersects the volume axis when $V = V_e$, that is, at the equivalence volume. There should be no correction for dilution. This follows since both HA and A are diluted equally during the titration.

In the derivation of the formula, we have made the following assumptions.

(1) That $V_0C^0_A >> VC_B$. This corresponds to our condition 1. So that deviation from the straight line will not be too great, $V_0C^0_A$ should be 50–100 times greater than VC_B. If one wishes one can naturally use formula (11) instead of formula (12) for plotting and obtain a completely straight line. The formula can then be written as

$$V_e - V = \text{constant} \times \left(1 + \frac{VC_B}{V_0C^0_A}\right)[H] \qquad (13)$$

If V_0 = 100 ml, C_B = 0.1*M* and C^0_A = 1*M*, the

second term in parenthesis = $10^{-3}V$. If one uses the simpler formula (11) instead of (13), the deviation will be greatest around the half-neutralization point.

(2) That A is formed and HA consumed in proportion to the addition of base. This corresponds to our second condition and assumes that HA and A do not take part in any secondary reactions and that the equilibrium constant is large enough for the reaction $HA + OH^- \rightarrow A^- + H_2O$.

(3) That [H] is proportional to the antilog of pH. The requirement for this is taken up in the introduction.

In this example, before the titration of an acid HA, a salt of the same acid has been added. This is not necessary. If one wants to titrate hydrochloric acid, for example, one can add sodium acetate in excess. An amount of acetic acid is released equivalent to the amount of hydrochloric acid present; this acetic acid is then titrated. Another advantage in connection with this procedure is that the solution never becomes so acidic that one must take the term E_j' in equation (1) into consideration. When titrating a polybasic acid such as oxalic acid in which both proton complexes are stronger acids than acetic acid, it is suitable to choose sodium acetate as the addition. One obtains then a single straight line since it is actually acetic acid one is titrating. The same thing applies to mixtures of acids, which are stronger than or as strong as acetic acid.

Choice of salt to be added

When choosing which salt is best suited as an addition in the titration of an acid or a mixture of acids, one should above all make sure that condition 2 is met. However, many salts can be considered, and so one should choose a salt which can be obtain analytically pure and which is inexpensive as well. Suppose one wants to determine an acid HB by titration and adds the salt NaA before titration. The acids HA and HB may be identical but need not be. The following reaction must then be taken into consideration.

$$HB + A^- = HA + B^- \qquad (14)$$

with the equilibrium expression

$$\frac{[HA][B]}{[HB][A]} = \frac{K_{HA}}{K_{HB}} \qquad (15)$$

If condition 2 is to be fulfilled, equilibrium (14) has to be displaced far to the right; in other words, only the acid HA should be present in concentration worth mentioning. As a condition one can set $[HA] \geqslant 100[HB]$. [B] will then be nearly equal to C^o_{HB}, *the original concentration of acid HB.* One obtains

$$K_{HA} \geqslant K_{HB}\frac{100C^o_{HB}}{[A]} \qquad (16)$$

If $[A] = 1M$ and $C^o_{HB} = 0{\cdot}01M$ then $K_{HA} \geqslant K_{HB}$

Sodium acetate can be used in the titration of acids having a stability constant less than about 10^5. For weaker acids one can choose, for example, sodium sulphite with $\log K_{HA} = 7{\cdot}0$. The method is not usable for very weak acids (see below).

In the titration of bases, the same rules apply, *mutatis mutandis.* Addition of ammonium chloride is suitable for titration of ammonia and stronger bases

Logarithmic diagrams

For those familiar with them, logarithmic diagrams quickly give information as to whether a certain acid–salt combination is suitable or not. In Fig. 2 the titration of an acid HB is drawn with $\log K_{HB} = 3.0$ and $C^o_{HB} = 0.01M$ after the addition of sodium acetate to a concentration of $0{\cdot}5M$. Log K_{HAc} has been assumed to be 4·50 (concentration constant at ionic strength 0·5).

According to equation (14) [HAc] and [B] are equal at the start. This corresponds to a vertical line through point 1. Here [HAc] is $0{\cdot}01M$, [HB] $10^{-5\cdot3}M$, [H] $10^{-6\ 3}M$ and [Ac] = $0{\cdot}5M$. Thus, HAc is the only acid in appreciable concentration. During the titration HAc is consumed (and the small concentrations of H^+ and HB) and one moves to the right from point 1 in the diagram.

The situation represented by a vertical line through point 2 is that which occurs at the equivalence point. Here the hydroxide-ion concentration is equal to the acetic acid concentration. (Actually it should be equal to the sum of [HAc], [HB] and [H], but the last two concentrations are so low that they can be neglected.) [HAc] = $10^{-4\cdot9}M$, [Ac] = $0{\cdot}5M$, [B] = $0{\cdot}01M$.

Since the lines for [HAc] and [H] in the logarithmic diagram are parallel during the whole titration from point 1 to point 2, [HA] = constant × [H] and thus condition 1 is met.

During the titration the acetic acid concentration drops from $0{\cdot}01M$ at the start to $1{\cdot}3 \times 10^{-5}M$ at the equivalence point. The reaction is therefore as good as complete, and since only HAc is titrated, one obtains a single straight line. Condition 2 is met.

Treatment as conditional titration

The method of conditional constants which Ringbom[8] has so successfully used in many contexts is here also an excellent tool for calculation of the titration curves and for judging which acids can be titrated according to the suggested technique. In order to determine which acids can be titrated with this technique it can be advantageous to regard the method as a conditional titration of H^+ with OH^-, and we assume as

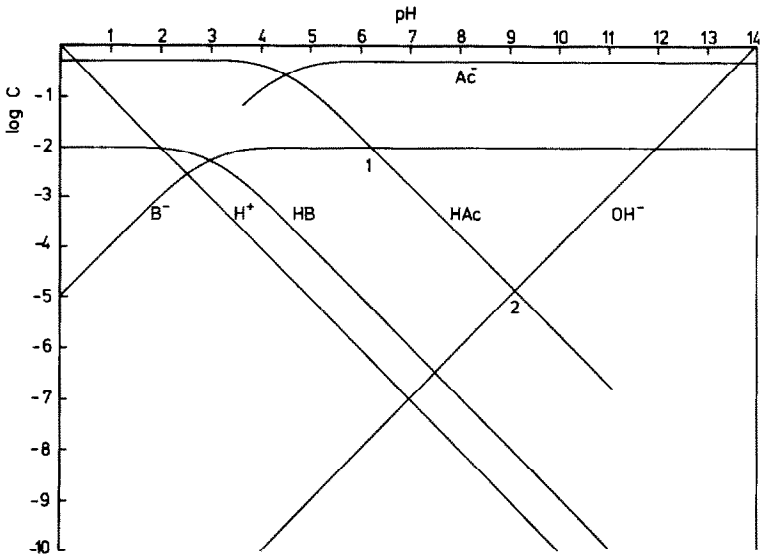

Fig. 2. Logarithmic diagram of log C as a function of pH for the acid–base pair HB – B^- after addition of sodium acetate Ac^-. Total conc. $C_{HB} = 0.01M$; log $K_{HB} = 3.0$, total conc. $C_{Ac^-} = 0.5M$; log $K_{HAc} = 4.5$.

before that an acid HB is to be titrated and that a salt NaA is added.

The main reaction is taken to be

$$H^+ + OH^- = H_2O \qquad (17)$$

and the equilibrium equation

$$[H][OH] = K_W \qquad (18)$$

Formation of HA and HB are regarded as side-reactions, and one takes these into account by introducing the conditional hydrogen-ion concentration [H′] which represents the total concentration of H which is not bound to OH. Thus.

$$[H'] = [H] + [HA] + [HB] \qquad (19)$$

Furthermore, the side-reaction coefficient (see Ringbom[8]) is defined by

$$\alpha_H = [H']/[H] \qquad (20)$$

which can be calculated from

$$\alpha_H = 1 + K_{HA}[A] + K_{HB}[B] \qquad (21)$$

If (18) and (20) are combined, one obtains

$$K_W\alpha_H = K'_W = [H'][OH] \qquad (22)$$

where K'_W is the conditional ion-product of water, which is constant if α_H is constant.

Under these conditions (α_H being constant), a titration of a weak acid can be treated formally as a titration of a strong acid, except that the value of the ion-product is changed. Therefore if [H] or [H′] is plotted as a function of added volume of titrant, straight lines which intercept the volume axis at the equivalence volume, although with different slopes, are obtained in both cases. For α_H to be constant, it is necessary above all for [A] to be constant. The term $K_{HB}[B]$ is so small that it can be neglected [equation (21)]. [A] changes somewhat during the titration since new A is formed, but the requirement for the method is that new A can be neglected in relation to total A.

The value of K'_W can be calculated from (21) and (22). If $K_{HA} = 10^{4.5}$, $K_{HB} = 10^3$, [A] = $0.5M$ and [B] = $0.01M$, then $\alpha_H = 10^{4.2}$ and $K'_W = 10^{-9.8}$ (the same example as demonstrated with the logarithmic diagram). During the titration [H′] changes from $0.01M$ to $10^{-4.9}M$ at the equivalence point. At the half-neutralization point [H′] = $0.005M$. The titration curve is straight almost the whole way and deviation at the equivalence point is negligible. If one does not plot the area near this point but instead extrapolates the straight portion of the curve, one obtains an intercept on the volume axis at the equivalence volume.

Very weak acids, for example the ammonium ion with log $K_{HB} = 9.5$, give rise to very flat titration curves when titrated in the usual manner. Addition of the corresponding base, ammonia, increases the conditional ion-product to $10^{-4.5}$, which means that titration of a $0.01M$ solution of NH_4^+ is not possible. For practical purposes, the line is drawn at acids which have a lower stability constant than 10^8. In one of the examples below, the first two dissociation steps of the phosphoric acid have been utilized for titration after addition of sodium sulphite.

Examples

In Fig. 3 titrations of (*a*) acetic acid, (*b*) hydrochloric acid, (*c*) oxalic acid and (*d*) phosphoric acid are presented. In titrations *a*, *b*, and *c* sodium acetate was added so that the concentration was $0.5M$ and in *d* sodium sulphite so that the concentration was $0.25M$. Acid concentration was $0.01M$ in cases *a* and *b* and approximately $0.005M$ in cases *c* and *d*. The volume in all four instances was 100 ml. Hydrogen-ion concentration

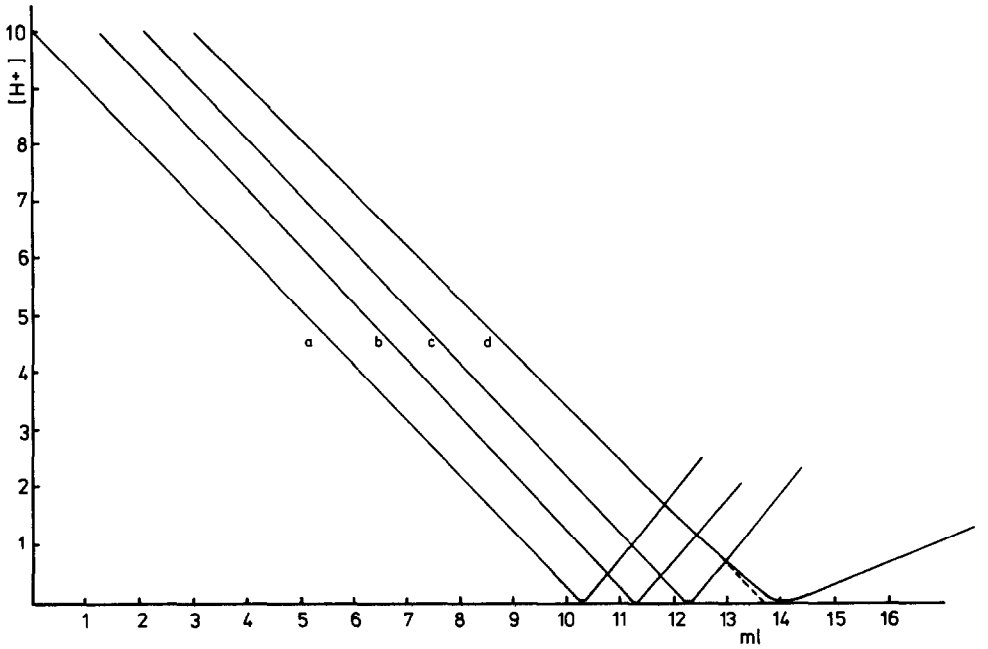

Fig. 3. Titrations with strong base of (*a*) acetic acid, (*b*) hydrochloric acid, (*c*) oxalic acid after addition of sodium acetate (0·5*M*). Curve (*d*) represents a titration with strong base of phosphonic acid after addition of sodium sulphite (0·25*M*). Zero on the volume axis has been displaced 1·00 ml for each titration.

was recorded in arbitrary units against ml of titrant (0.0980*M* NaOH + 0.4*M* NaCl). Zero on the volume axis has been displaced 1 ml for each titration. The curves are practically straight lines. The equivalence volumes read from the curves are 10·22, 10·19, 10·19, and 10·78 ml, and the expected values 10·20, 10·20, 10·20, and 10·82 ml. In titration *d* the graph is curved in the vicinity of the equivalence volume, but the correct value is obtained if the straight part of the graph is extrapolated to the volume axis. In all cases 1/[H] was recorded after the equivalence point.

In Fig. 4 curves have been recorded for the titration of 100 ml of approximately 0·01*M* NH_3 with 0·1*M* HCl (also approximately 0·4*M* with respect to NaCl). Curve *a* represents a normal titration, pH against ml, and curves *b* and *c* titrations in which the sample solution was made 0·5*M* with respect to NH_4Cl. In *c* only the titration curve round the equivalence point was recorded. The expected value was 9·80 ml and the values found 9·80, 9·82 and 9·82 ml.

It is important that the ionic strength is kept constant during the titration and that the right *Q*-value is used, in other words, that the temperature knob on the pH-meter is adjusted to the right value, since *Q* varies with temperature. A deviation of a few degrees makes no difference, however.

B. Oxidation–Reduction Titrations

Iodometric titrations

Titration of iodine with thiosulphate is a typical example of areas in which the expressions stated by Gran[2] cannot be applied. This is because one must add iodide from the beginning in order to keep the iodine in solution, and the Gran functions assume that one is dealing only with iodide which is formed during the titration. However, if the amount of iodide added from the beginning is made so large that the iodide formed during the titration can be neglected, one can apply the same principles as in the previous section on acid–base titrations. Iodine concentration is plotted as a function of added volume of thiosulphate, thus resulting in a straight line which intercepts the volume axis at the equivalence volume. If the titration is carried out potentiometrically, one measures primarily a cell voltage *E* which is dependent upon both iodine concentration and iodide concentration. If the latter is regarded as constant, then *E* will be dependent only upon the former.

Let us assume that V_O ml of an iodine solution with concentration C_A^O is to be titrated with *V* ml of a thiosulphate solution with concentration C_B. Furthermore, the concentration of iodide in the iodine solution has been set at concentration C_I^O.

$$I_3^- + 2S_2O_3^{2-} = 3I^- + S_4O_6^{2-} \qquad (23)$$

If the titration is followed potentiometrically with a cell in which the probe in the right-hand half-cell in Fig. 1 is a platinum wire, one obtains

$$E = E'_O + \frac{Q}{n} \log \frac{[ox]}{[red]} \qquad (24)$$

where E'_O encompasses normal potential, reference potential and expressions for the invariable part of

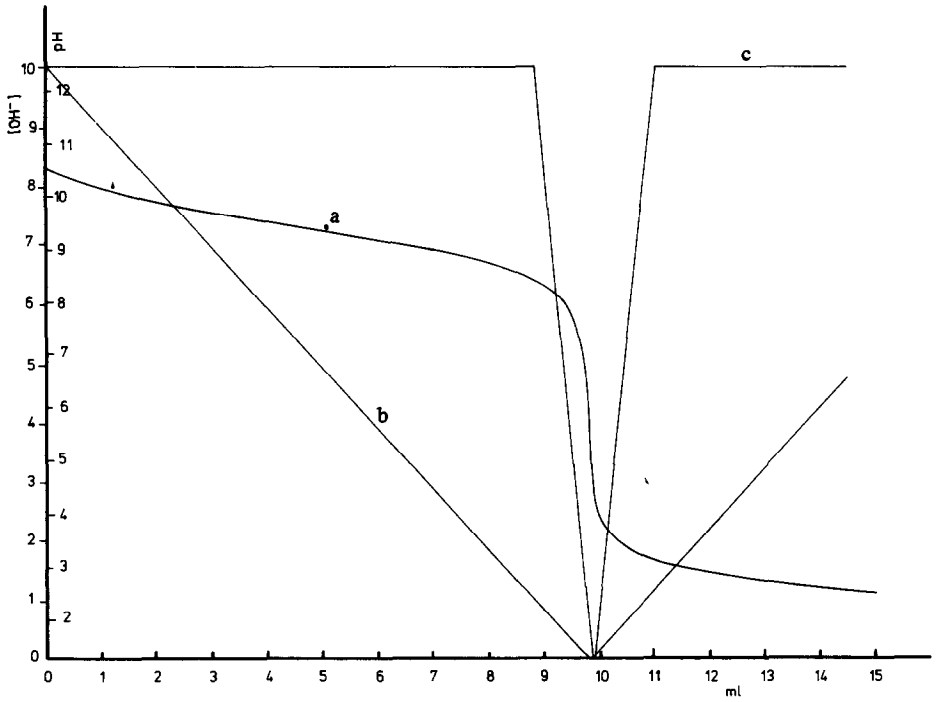

Fig. 4. Titrations of 100 ml of approx. 0·01*M* NH_3 with 0·1*M* HCl. Curve (*a*) represents a normal titration curve, pH against ml; curves (*b*) and (*c*) are titrations in which the sample solution was made 0·5*M* with respect to NH_4Cl. In (*c*) the sensitivity was increased tenfold.

the activity factors and liquid–liquid junction potentials. If the activity factors and liquid–liquid junction potentials can be kept constant, E'_0 will be constant Q, as before, is RTF^{-1} In 10 and n is 2 in this case.

If one assumes complete reaction then

$$[\text{red}] = \frac{V_0 C_I^0}{V_0 + V} + \frac{VC_B}{V_0 + V} \qquad (25)$$

$$[\text{ox}] = \frac{V_0 C_A^0}{V_0 + V} - \frac{VC_B}{2(V_0 + V)} = \frac{C_B}{2(V_0 + V)}(V_e - V) \qquad (26)$$

where V_e = equivalence volume, defined by

$$V_e C_B/2 = V_0 C_A^0 \qquad (26a)$$

(25) and (26) yield

$$\frac{[\text{ox}]}{[\text{red}]} = \frac{C_B (V_e - V)}{2(V_0 C_I^0 + VC_B)} \qquad (27)$$

If $VC_B \ll V_0 C_I^0$ and (27) is substituted into (24), then

$$V_e - V = \frac{2V_0 C_I^0}{C_B} \times 10^{\frac{2}{Q}(E - E'_0)} \qquad (28)$$

or

$$V_e - V = \text{constant} \times 10^{\frac{2E}{Q}} \qquad (29)$$

Thus if antilog $2E/Q$ is plotted as a function of titrant volume V, one obtains a straight line which intercepts the volume axis at $V = V_e$.

In Fig. 5 a titration of 10·00 ml of *ca.* 0·05*M* iodine and 90 ml of water with 0·100*M* thiosulphate is represented. The sample solution was 0·8*M* with respect to KI and the thiosulphate ionic strength was adjusted to 0·8 with KCl. A platinum wire was used as the indicator electrode and an Orion double-junction electrode Model 90-02-00 as reference electrode. The instrument yields a constant × antilog $2E/Q$, and this value has been plotted manually against volume of thiosulphate. The intercept on the volume axis shows V_e = 10·50 ml, which is equal to the true value.

Titration of Fe(II)

If all iron in a sample is in ferrous form, Gran's functions for evaluation of a titration can be applied. If there is ferric ion present the titration curve is not straight and an evaluation according to Gran is difficult to perform. As in the previous section, one can avoid difficulties by adding an excess of ferric iron from the beginning. According to Nernst's formula

$$[Fe^{2+}] = [Fe^{3+}] \text{ antilog } (E'_0 - E)/Q \qquad (30)$$

If $[Fe^{3+}]$ is kept constant, $[Fe^{2+}]$ will be proportional to antilog (constant $-E)/Q$.

Titration of ferrous iron with permanganate or with cerium(IV) yields linear titration curves if

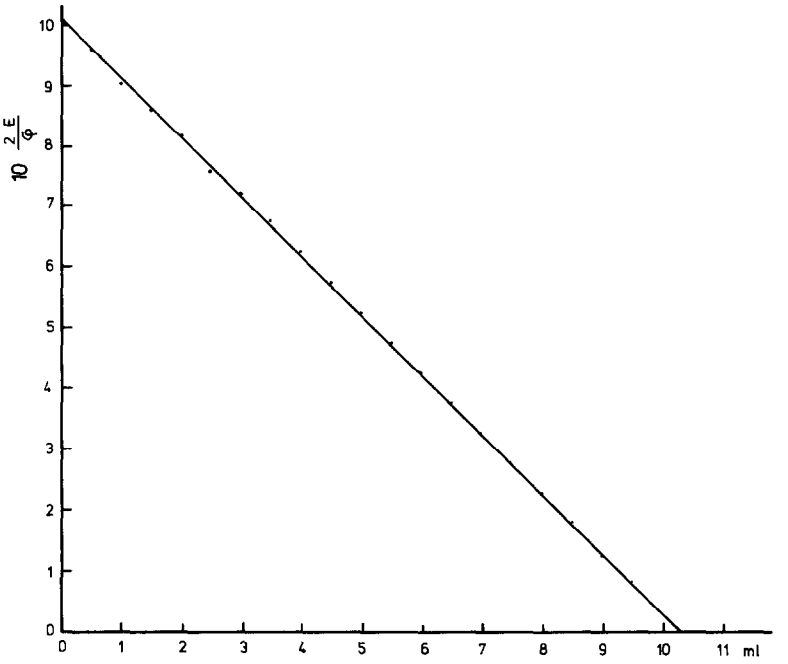

Fig. 5. A titration of 100 ml of approx. 0·005*M* iodine (0·8*M* KI) with 0·1000*M* thiosulphate (0 8*M* KCl).

the solutions are made 0·5*M* with respect to Fe^{3+} before the start It is suitable to use ferric chloride. Titration solutions of Ce(IV) are usually very acidic, and in that case the sample solutions must be adjusted to the same acidity and to the same concentration of complexing agents if the titration curves are to be linear.

Example. About 125 mg of two standard samples of iron oxides were weighed. These were dissolved in acid and the solutions treated according to Zimmerman-Reinhardt in the usual way. Five g of ferric chloride hexahydrate were then added to each sample solution. Each sample was diluted to *ca.* 100 ml and titrated with 0·02*M* permanganate. During the last tenth of the titration, antilog $(-E/Q)$ was registered from full scale on the graph to near zero. The results were·

Samples 1:64.8, 65.0 %Fe (true value 64.9%)
Samples 2:71.1, 71.5 %Fe (true value 71.1%)

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THE HYDROGEN-ION SELECTIVE GLASS ELECTRODE

GILLIS JOHANSSON, BO KARLBERG* and ANDERS WIKBY†

Department of Analytical Chemistry, University of Umeå, S-901 87 Umeå, Sweden

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Summary—The properties and mechanism of operation of hydrogen-ion selective glass electrodes are reviewed and a model using information from recent research is presented In the gel layer of a pH-glass protons or hydronium ions are bound to negative charges in a silicon network cross-linked with bi- or tervalent metal ions The composition of the gel layer is discussed, it is known that the outer part contains water The formation of a gel layer and its destruction in alkaline solutions are discussed Between the gel layer and the dry glass there is a transition layer characterized by a very high resistivity This forms a barrier to ion transport and prevents rapid corrosion of the glass The ionic mobilities of various ions change drastically with distance inwards towards the dry glass The alkaline and acid errors are discussed as well as the asymmetry potential By etching away the gel layers and the transition layers on both sides of the glass and then starting hydration simultaneously on both sides, two symmetric layers can be produced This will result in an almost complete cancellation of the asymmetry potential Some applications to precision measurements and measurement in non-aqueous solvents are discussed

For almost half a century the hydrogen-ion selective glass electrode has been a very important tool in the chemical laboratory A substantial improvement during that time has resulted in much more rugged and convenient electrodes as well as in electrodes with better selectivity and stability The early work was summarized in the classic book "The Glass Electrode" by Dole[1] and further work was surveyed by Kratz[2] The modern view of glass electrodes has been presented by Bates[3] A number of reviews on the hydrogen and alkali-metal ion selective glasses are collected in a book edited by Eisenman[4] The subject has also been reviewed by a number of authors[5–11] Although several treatises are available, fundamental misunderstandings are quite common in general textbooks, as pointed out by Fisher[12] The pH-concept has been thoroughly and critically treated by Feldman,[13] Bates[3] and Mattock[14]

This review will concentrate on the mechanistic aspects of the hydrogen-ion selective glass electrode and an attempt will be made to present a consistent explanation of the electrode behaviour The techniques developed during recent years have provided information which is taken into account in the new model presented here

HISTORICAL

Glass was included in voltaic piles by Ritter as early as 1802 and during the 19th century several researchers studied conduction through glass Thomson[15] was the first to make experiments in which the possibility of surface conduction had been excluded, and he showed that glass behaved as an electrolytic conductor The early work and theories were discussed extensively by Cremer,[16] who developed the technique for potentiometric measurements on cells with high internal resistances In his studies of glass membrane cells he found that the voltage changed when he added acid or base to the physiological salt solutions on either side of a membrane Further research was done by Haber and Klemensiewicz,[17] who did a number of acid–base titrations with the aid of the electrode It was concluded that the phase boundary of the glass behaved as a reversible hydrogen electrode They were mainly interested in the theoretical implications and did not realize the practical importance of the electrode They knew that the glass surface swelled in water and supposed that adsorbed water formed a separate solid water-phase with well-defined hydrogen-ion and hydroxyl-ion concentrations The hydrogen-ion activity in this water-phase remained essentially constant even when that in the surrounding solution was changed These assumptions made a thermodynamic treatment of the potential possible as a special case of Nernst's theory of the electromotive forces It was stated[17] that the glass surfaces worked as hydrogen electrodes with a potential difference of 58 mV at room temperature for each tenfold change in the hydrogen-ion concentration Without the glass membrane between the surfaces only small differences due to differences in ionic mobilities should have appeared

Freundlich and Rona,[18] and Freundlich,[19] clarified the difference between the so-called "Haber-potential", the Nernst (or electrochemical) potential and the electrokinetic (or zeta) potential The ζ-potential could

* Present address Astra Pharmaceuticals AB, S-151 85 Sodertalje

† Present address AB Draco, Fack, S-221 01 Lund

be influenced by ter- or quadrivalent ions and by surface-active substances but the influence on the phase-boundary potential was very small It was concluded that the electrokinetic potential arose between a liquid skin adsorbed on the solid, and the bulk of the liquid The Nernst potential was determined by the potential difference between the interior of the solid phase and the bulk of the liquid

Hughes,[20] in 1922, was the first to turn completely to the practical and experimental aspects of the glass electrode He showed its usefulness by making direct comparisons between a glass electrode and a hydrogen electrode The work of Hughes represented a breakthrough for the glass electrode, and the number of papers increased rapidly in succeeding years A detailed review of the early work is given by Kratz.[2]

Horovitz[21] studied the effect of changes in glass composition on the pH function He assumed that the glass played a more important role than that necessary for Haber's solid water-layer model He also found that glasses could act as metal-ion selective electrodes A phase-boundary potential was supposed to arise as a result of an exchange adsorption The composition and blowing of the glass were of importance for the adsorption ability The conduction through the glass was ascribed to sodium ions, in accordance with the findings of Warburg [22] The work of Horovitz was extended by his student Schiller[23] who investigated sodium- and potassium-ion selective electrodes. He also tried to make zinc-ion selective glass electrodes Michaelis[24] suggested that the glass could be treated as a semipermeable membrane in which the transference number of the hydrogen ion was practically unity Dole could not accept Michaelis's theory as he realized that each surface potential was produced independently. Dole did not, however, express himself very precisely about the mechanism He used a statistical thermodynamic approach[1] and supposed that equilibrium positions existed on the glass surfaces, which could be occupied by hydrogen or alkali-metal ions

The glass-electrode errors have been important in understanding the origin of the glass-electrode response. The alkaline error is a deviation from the ideal pH-response, which manifests itself in the presence of alkali-metal ions, especially sodium and lithium, in the high pH-range This is equivalent to the metal-ion function first noted by Horovitz[21] and Schiller [23] The term alkaline error was introduced by Dole during his systematic studies of deviations [25–28] The etching action of alkaline solutions on the glass electrodes was not known and the response degradation noted [29] after some days could not be explained The appearance of an alkaline error suggested an ion-exchange model, although it was supposed in the beginning that the ions were adsorbed on the glass surface The deviations in acid solutions were first reported by MacInnes and Belcher[30] and by Buchbock [31] In the former work it was suggested that anions might penetrate the glass Dole [32,33] observed similar deviations in non-aqueous solutions and salt solutions He interpreted the deviation in terms of a decreased water activity in the solutions and he concluded that the electrode was in error if a_{H_2O} was different from unity Measurements on magnesium sulphate solutions seemed to confirm the theory [34] It was therefore concluded[1] that "as hydrogen ions migrate from the solution to the glass surface, one water molecule per proton is carried along" Because of the strong impact of Dole's outstanding book the water theory held its position for a long time Beck and Wynne-Jones[35] summed up evidence against it in 1952 Schwabe and Glockner[36] finally showed positively that halogen acids were taken up by the glass The newer lithia glasses also showed much less acid error, which was inconsistent with the water-activity theory

Nicolsky[37] used an ion-exchange model for the interaction between the surface layer and the solution and he derived response equations from thermodynamic arguments Haugaard[38] showed by electrolysis that only sodium ions (in a sodium glass) passed through the electrode These conclusions were confirmed in more accurate experiments by Schwabe and Dahms[39,40] thus disproving Michaelis's theory [24] Tendeloo and Voorspuij[41,42] suggested that the glass contained adsorption sites for ions and they deduced equations which in contrast to Nicolsky's equation predicted anion response Landqvist[43] also used an adsorption model but arrived at equations similar to those of Nicolsky Haugaard[44,45] developed a three-layer electrode model, in which the bulk glass was considered to be covered by a gel layer on each side Hubbard *et al.*[46,47] found that some water was necessary for satisfactory function of the electrode They tried to correlate the electrode behaviour with the solubility of glass in water By using an interferometer method, Hubbard and Hamilton[48] measured the gel-layer swelling and the decrease in thickness after chemical attack in solutions of various pH

In fact, there was much uncertainty about the mechanism for several years A phase-boundary model or a diffusion-potential model was favoured It is the work of Schwabe and co-workers which seems to have resulted in a more general acceptance of the phase-boundary model Eisenman[49] finally advocated a model in which the glass electrode potential was attributed to a mixed origin Both equilibrium ion-exchange at the glass surfaces and diffusion within the glass were supposed to contribute substantially to the observed potential

THE GEL LAYER

The gel-layer concept was developed by Haugaard[38,44,45] and essential information about its properties was provided by Hubbard *et al* [46,47] and by Schwabe *et al* [39,40] When an electrode is immersed in water, a gel layer is formed and sodium or lithium ions in the glass are replaced by hydrogen ions from

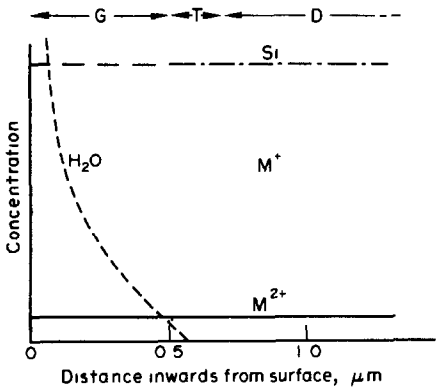

Fig. 1 Concentration profiles inwards from the surface of a pH-electrode G = gel layer, T = transition layer, D = dry glass

the solution The amount of leaching and water uptake was found to depend on the glass composition.[2,50] The gel-layer thickness could be estimated from the ion-exchange.[39,40]

A significant further step towards an understanding of the gel layer was taken by Sendt[51] and by Bouquet, Dobos and Boksay[52] when they etched glasses in hydrofluoric acid. The outermost layer was dissolved and by analysis of the etching solution the composition of the removed layer could be determined. By repeating the procedure on successive layers a concentration profile inwards could be established They also found[53] that the alkali-metal ion concentration was low at the surface but increased inwards in a different way for different glasses Somewhat later, electrical measurements were made by Buck,[54,55] Buck and Krull,[56] Wikby and Johansson,[57] and Brand and Rechnitz[58] It was concluded that there was a surface film on the electrode which had a high impedance which was independent of the pH of the solution An independent method for analysis of the surface composition of glasses was developed by Bach and Baucke[59] They used argon sputtering to excite lithium ions at various depths and measured the luminescence of the removed ions The resolution in the depth co-ordinate is higher than for the etching method

By combining the etching technique with impedance measurements, Wikby[60] was able to show that a layer with high resistivity was interposed between the gel layer and the dry glass. In this region, called the transition layer, the concentration of alkali-metal ions changes abruptly from a low value in the gel layer to a higher value in the dry glass The results were confirmed with the ion-sputtering technique.[61,62]

The results of the investigations mentioned can now be summed up to provide a unified description of the gel layer. When a pH-glass is immersed in water for the first time, alkali-metal ions in the surface move out and hydrogen ions move in. The rate of this process is fast in the beginning but slows down with time.[60] Figure 1 shows the concentration profiles of the surface of a pH-glass electrode hydrated for some days The pattern shown is characteristic for all pH-glasses studied up to now The alkali-metal ion concentration is low in the gel layer even in neutral and acid solution[63,64] It has been shown that isotope exchange is very low in acid solution[39,40,65] Boksay and Lengyel[66] have suggested that the remaining alkali-metal ions in the gel layer are bound within impasses so that they cannot move out The concentration of bivalent alkaline-earth metal ions is essentially unaffected by the hydration The same is true for silicon, the small concentration decrease which occurs is a result of volume expansion[48] The accompanying decrease in density has not been taken into account in Fig 1 The gel layer thus has a roughly constant ionic composition throughout and it forms a well-defined region limited on the inward side by the transition layer By using tritium labelling, Dobos[67,68] was able to measure the distribution of water in very soft pH-glasses The profile in the more durable lithia glasses in not known The water profile drawn in Fig 1 is very uncertain

The concentration profiles change with time as the transition region moves inwards towards the bulk glass For most of the pH-range the rate of movement is independent of the pH of the solution surrounding the electrode. However, the movement is inhibited in non-aqueous solution[69,70] and slows down in strongly alkaline aqueous medium,[71] see Table 1 This shows that both water and hydrogen ions are necessary for the formation of a gel layer The silicon polymer at the outer boundary of the gel layer is also attacked by water The rate of this attack increases rapidly above pH 9[46–48,71,72] It can be measured by analysing the aqueous solution for silicon The gel layer is thus located between two boundaries moving inwards[73] The electrical resistance of the transition region increases when the region moves deeper into the glass and the transport of ions through it becomes more difficult As a consequence, the rate of leaching decreases, see Table 1 The transition region thus prevents rapid corrosion of the glass[62] The lithium flux from an LoT electrode corresponds to 1 nmole cm^{-2} hr^{-1} after 340 hr of hyd-

Table 1 The formation and destruction of a gel layer on an Ingold LoT electrode (25°C) Rate of movement of the boundaries between gel layer/solution = V_1, gel layer/bulk glass = V_2

Time *hr*	Solution	V_2 *nm/hr*	V_1 *nm/hr*	Thickness *nm*
44	Water	1 14	0·10	90
100	Water	0 86	0 08	140
340	Water	0·55	0 05	300
86	Water	—	—	—
186	Isopropyl alcohol	<0 1	<0 1	130
44	Water	—	—	—
54	0 1*M* NaOH	<0 1	1 95	70
88	0 1*M* NaOH	<0 1	1 95	6
101	0 1*M* NaOH	<0 1	1 95	0

ration [60] The reaction responsible for the release of sodium or lithium ions is

$$\equiv SiOLi_{(dry\ bulk\ glass)} + H^+_{(soln)} \rightarrow \equiv SiOH_{(transition\ region)} + Li^+_{(soln)} \quad (1)$$

Transport of protons through the transition region is rate-determining for the reaction.[59,74,75] The highest transport barrier is located in that part of the transition region which is closest to the gel layer

A steady state is approached within weeks or months The two gel-layer boundaries then move with the same rate and the thickness remains constant. The destruction of the gel layer at the outer interface is normally slow but in strongly alkaline solution becomes fast, see Table 1 Since the gel-formation is slow at this pH the whole gel layer may be lost within a short time.

Most of the research work on glass electrodes has been concentrated on the development of suitable glass compositions As only certain combinations of elements give homogeneous glasses the possible variation of major components in the composition has been limited In addition the choice of composition is restricted by the requirement of a low or moderate electrical resistance of the glass. MacInnes and Dole[76] were the first to make a systematic investigation of the glass composition for electrode purposes They developed a glass called Corning 015 (72% SiO_2, 22% Na_2O, 6% CaO) which was shown to represent an optimum in the soda–lime system. Ssokolof and Passynsky[77] found that the glasses containing lithium instead of sodium showed lower alkali error The range of useful glasses increased when pH-meters with lower grid current became available Perley[78–80] studied the effect of additions of small amounts of La_2O_3, Cs_2O, BaO and CaO These multicomponent glasses can give electrodes with properties considerably superior to those of the simple lithia electrodes [78–83]

To-day, sodium glasses are used only for electrode shapes which are difficult to blow (capillary, micro and some flat electrodes) Modern bulb-type pH-electrodes are modifications of the Perley glasses

The glass composition is important for the gel-layer properties, as shown in Table 2 [84 85] The sodium glass, Corning 015, is easily attacked by water and it forms a thick gel layer The multicomponent lithia glasses are more durable, the hydration rate is slower and the gel-layer thickness is smaller The Radiometer B-glass is extremely durable, it acquires a very thin gel layer even after a long time of hydration and the alkaline error is very low

The gel layer contains a high concentration (20*M*) of hydrogen ions, which remains constant, it forms a thin well-defined separate phase containing water at least in the outer part and it therefore corresponds well to the solid water-phase imagined by Haber The silica network serves as a support and provides the co-ions

Table 2 Gel-layer formation on some glass electrodes with different durability

Glass	Hydration time *hr*	Gel-layer thickness *nm*	Type
Corning 015	100	350	Sodium glass
Na_2O CaO SiO_2	190	500	Large alkaline error
Ingold LoT	100	140	Low temperature
Li_2O Cs_2O BaO TiO_2 La_2O_3 SiO_2	190	200	Large alkaline error
Ingold 201	100	15	General purpose
Li_2O, Cs_2O, BaO, CaO, TiO_2, La_2O_3, SiO_2	190	30	Low alkaline error
Radiometer B-glass Li_2O CaO BaO La_2O_3 Cs_2O SiO_2	90	<10	General purpose Very low alkaline error
Radiometer C-glass Li_2O, CeO_2, BaO, La_2O_3 MoO_3, SiO_2	72	60	General purpose Low alkaline error

ELECTRICAL PROPERTIES

The resistivity of dry glasses has been studied by glass scientists for a long time The resistance has been measured as a function of temperature, usually well above room temperature Reviews of this work have been written by Stevels,[86] Mazurin,[87] and Owen.[88]

The temperature-dependence of the glass resistivity follows an equation first given by Rach and Hinrichsen [89]

$$\log \rho = A + B/T \quad (2)$$

where ρ is the resistivity in ohm cm and T the temperature in K The constants A and B usually have values of 1 5–4 5 and 3000–8000 K respectively. The resistances normally given for glass electrodes are those obtained with direct current If a.c. is used for the measurement it is found that the resistance decreases rapidly when the frequency increases. At some frequencies dielectric losses will occur

Univalent alkali-metal ions serve exclusively as current carriers[86–88] in glasses suitable for pH-measurements Transport by hydrogen ions through a dry glass is thus ruled out, but unsupported statements to the contrary are common [90] Prolonged electrolysis with current in one direction will cause depletion of current carriers at the negative side and the resistivity may eventually increase drastically Such a polarization has a non-linear voltage dependence The normal glass resistance follows Ohm's law even for d c

Recent electrical measurements on certain glass electrodes by a c techniques showed that there were two resistive components which could be differentiated by their frequency-dependence [54–58] It was assumed that one was located on the surface or in the gel layer and that the other originated from the glass body By combining etching with resistance measurements, Wikby showed that the surface resistance discovered was located in the transition layer [60] The measurements were made with a pulse technique

Table 3 Transition layer properties

Glass	Hydration time, hr	Durability, hr/mole	Transition layer resistance, MΩ
Corning 015	100	1.1×10^8	0.6
	190	1.5×10^8	0.9
Ingold LoT	100	1.7×10^8	1.2
	190	2.3×10^8	1.5
Ingold 201	100	15.0×10^8	8.6
	190	21.3×10^8	13.2
Radiometer B-glass	90	11.1×10^8	5.8
Radiometer C-glass	72	11.1×10^8	4.7

and the resistive components were displayed as time-constants The time-constant from the glass was in the msec range and that from the transition layer was of the order of tens of seconds The first perturbation thus almost decayed before the second started For some glasses the difference between the time-constants is smaller and for these cases a simple d c technique with simultaneous etching was developed [64] The time-constants discussed here are not observable in true potentiometric, *i e*, zero current, measurements They should not be confused with the time-constants of various electrochemical equilibria However, they may be of importance when an electrode is inserted into an instrument or during switching between different electrodes The equivalent input capacitance of the instrument must be charged to the potential of the electrode. This charging current may be quite large at the moment of connection, as the a c resistance is much lower than the specified d c resistance [91] The current passes through the electrode and the transition layers. The effect of this electrical shock disturbs accurate measurements for several minutes under ordinary laboratory conditions and it may be worse in non-aqueous solvents or at low temperature

The resistance of the transition layer varies with time and glass composition,[74] see Table 3 This table also shows the chemical durability or the reciprocal flux of alkali-metal ions The durability is proportional to the electrical resistance of the transition layer and thus proportional to the inverse rate of movement of the transition layer ($1/V_2$, see Table 1) For a general-purpose electrode the total resistance is around 500 MΩ and the bulk-glass thickness is about 0·2 mm The transition layer thickness is 10 nm or less and its resistance can be seen in Table 3 The resistivity of the transition layer must thus be at least a thousand times that of the glass Both resistances are ohmic at small currents but when the current becomes equivalent to the flux of alkali-metal ions over the transition layer, the transition layer resistance becomes voltage-dependent [60] The resistance of the transition layer increases rapidly in non-aqueous solution and may be ten times higher after a couple of days [69]

It has not been possible to measure the resistivity of the gel layer. It has been estimated[64] that for Corning 015 glass it is less than a fifth of that of the bulk glass Eisenman, Sandblom and Walker[92] studied 1-μm thick glass membranes which were hydrated throughout and found that the resistance varied with the solution composition It was at most 16.5 kΩ The glass composition was different from that of pH-glasses and the water profile is not known Measurements along the surface of some sodium aluminium silicate glasses have been made[75] and this technique may provide more information about the gel layer resistance in the future

Figure 2 sums up the discussion and shows the resistivity of various parts of a pH-glass electrode The gel-layer resistivity may be anywhere within the shaded area The temperature-dependence of a pH-electrode is given by

$$R_{tot} = A_1 \exp\left[\frac{\Delta H_1}{RT}\right] + A_2 \exp\left[\frac{\Delta H_2}{RT}\right] \qquad (3)$$

which is an extension of the Rach–Hinrichsen equation to take the transition resistance into account A_1 and A_2 are constants and ΔH_1 and ΔH_2 are the activation energies for current transport through glass and the transition layer respectively ΔH_1 is around 15 kcal/mole and ΔH_2 20–25 kcal/mole [57] The last term in equation (3) thus becomes more important at low temperatures and may dominate for a low-temperature electrode At higher temperatures, 60–80 , it can normally be neglected

ALKALINE RANGE

Ion-exchange

A glass electrode shows Nernstian response over a large part of the pH-range with high accuracy [93,94] The electrode reaction in this range involves an exchange of hydrogen ions between ≡SiOH sites in the gel-layer and proton acceptors in the solution as has been discussed by Baucke [62] The electrode potential may be written

$$E = E^0 + \frac{RT}{F} \ln \{a_{H^+_{(soln)}}/a_{H^+_{(gel)}}\} \qquad (4)$$

As it is found experimentally that this equation holds it follows that the hydrogen ion activity in the glass remains constant over the range of ideal pH-response.

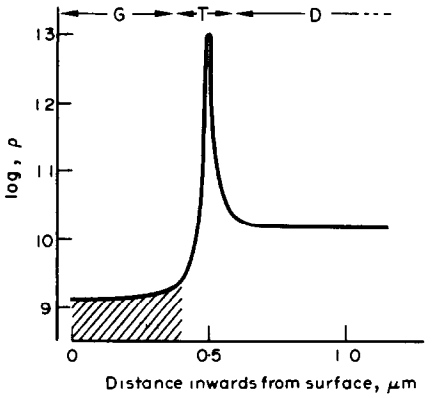

Fig 2 Resistivity as a function of distance inwards from the surface of a pH-electrode G = gel layer T = transition layer D = dry glass

Table 4 Ion-exchange capacity of some glass electrodes hydrated for more than three weeks

Electrode	Type	Ion	Ion-exchange capacity *nmole/cm²*	Total number of sites *nmole/cm²*
Beckman 42	Low temperature	Na^+	12 5	
Ingold LoT	Low temperature	Li^+	5 4	
(specimen No 1)		Na^+	19 6	
Ingold LoT	Low temperature	Li^+	8 3	
(specimen No 2)		Na^+	31 7	800
Ingold 201	General purpose	Li^+	1 5	
(specimen No 1)		Na^+	8 0	100
Ingold 201 (specimen No 2)	General purpose	Na^+	5 0	
Metrohm UX	General purpose	Li^+	7 3	
		Na^+	19 0	
Ingold HA	High temperature	Na^+	2 1	

In a solution with low concentration of hydrogen ions and high concentration of alkali-metal ions there will be an ion-exchange

$$H^+_{(gel)} + M^+_{(soln)} \rightleftharpoons M^+_{(gel)} + H^+_{(soln)} \qquad (5)$$

Consequently the hydrogen-ion activity in the gel layer will decrease and $a_{H+(gel)}$ in equation (4) is no longer a constant

The first measurements of the ion-exchange were made by Schwabe *et al*[39,40,65] with an isotope technique in aqueous solutions Karlberg,[95] and Wikby and Karlberg[84] measured the ion-exchange of a number of glass electrodes If the sodium exchange of a lithia glass electrode is studied, the exchange can be positively differentiated from the flux of ions from the transition layer according to reaction (1) The gel-layer thicknesses were known for the electrodes and the measurements were made in a non-aqueous solvent to prevent alkaline attack on the glass surface The ion-exchange capacity for some electrodes[96] is given in Table 4 The total number of ≡SiOH sites could be calculated from the total amount of lithium ions leached out during the formation of the gel layer, see Table 4 Apparently, only a small fraction of the sites in the gel layer is available for exchange Karlberg's results, which were obtained with non-aqueous solutions, are in qualitative agreement with those estimated from Schwabe and Dahm's measurements in water

The number of sites available for ion-exchange increases only slowly when the gel-layer thickness increases[84,95-97] The exchange capacity during the first hours of hydration is rather low As only a small fraction of the sites is available for exchange and since the total available exchange capacity is almost constant even if the gel layer grows, it can be inferred that the exchange takes place only in the outer part of the gel layer Even if no experimental evidence is available it is reasonable to assume that the concentration of exchangeable sites has a profile similar to that of water, see Fig 1

Mixed response

As a consequence of the partial or complete ion-exchange in the gel layer the electrode will no longer be an ideal hydrogen-ion sensor By taking into account the ion-exchange, equation (5), Nicolsky[37,98] was able to extend equation (4)

$$E = E' + \frac{RT}{F} \ln \{a_{H^+} + K_{HM} a_{M^+}\} \qquad (6)$$

where a_{M+} is the activity of the univalent metal ions in the solution and K_{HM} is the equilibrium constant of the ion-exchange, equation (5) If $a_{H+} \gg K_{HM} a_{M+}$, equation (6) describes an ideal pH-response and if $a_{H+} \ll K_{HM+}$ it describes an ideal cation-response. Between these limits there is a region of mixed response However, equation (6) predicts a sharper bend and a narrower region of mixed response than that found experimentally Therefore several attempts have been made to modify the Nicolsky equation[46,99-113] to account for this. The approaches have included a supposed variation of activity coefficients with concentration, different binding properties and defect equilibria Nicolsky himself tried a model in which the hydrogen ions were bound to sites with different bond strengths By adjustment of the parameters introduced it has in most cases been possible to obtain a reasonably good fit between the derived equations and the experimentally-measured potentials. As satisfactory agreement has been obtained for different models, it is impossible to evaluate their relative merits Unfortunately the different parameters cannot be measured by independent methods When the composition and properties of the gel layer have been elucidated experimentally as described above, the models should be re-evaluated to take this information into account

The theory can be extended to include ionic interdiffusion in the glass[114] and further development was described in a series of papers by Eisenman and coworkers[4,49,115-118] In addition to the phase-boundary potential there will be an electrical potential in the glass due to different mobilities of the interdiffusing ions The diffusion potential is given by the Nernst-Planck equation which can only be solved under certain conditions The most important assumptions made by Eisenman *et al* were that the standard chemical potential and the mobility ratio of the interdiffusing ions were constant and that the current and

solvent flow were zero The diffusion potential, V_D, for two univalent ions, i and j, is then

$$V_D = -\frac{RT}{F}\ln\left[\frac{a_i' + K_{ij}a_j'}{a_i' + \frac{u_j}{u_i}K_{ij}a_j'}\;\frac{a_i'' + \frac{u_j}{u_i}K_{ij}a_j''}{a_i'' + K_{ij}a_j''}\right] \quad (7)$$

where K_{ij} is the ion-exchange equilibrium constant and u_j/u_i is the mobility ratio, and the primes ' and " denote the activities at the two sides of the membrane Equation (7) is a slight simplification of the equation given by Eisenman[49]

The most striking feature of equation (7) is that the potential becomes independent of time once the equilibria are established at the boundaries of the membrane The ionic-concentration profiles and the electrical-potential profile within the membrane are changing with time but this change does not affect the measured potential It can also be seen from equation (7) that the diffusion potential will be zero when the mobilities become equal The derivation was made by supposing that diffusion occurred into a semi-infinite solid phase and it is suggested that the primes ' and " represent respectively the outside and inside of the glass membrane The model then does not explicitly take into account the differences between the gel layer and the bulk glass This point will be discussed later

The introduction of the diffusion potential did not change the form of the bend in the range of mixed response and therefore Karreman and Eisenman[115] introduced an empirical factor, n, relating the activity and concentration

$$a_i = \rho C_i^n \quad (8)$$

The overall equation for the total potential, which is the sum of the phase-boundary potential and the diffusion potential, then becomes

$$V_{tot} = \frac{nRT}{F}\ln\frac{a_i'^{1/n} + \frac{u_j}{u_i}(K_{ij}a_j')^{1/n}}{a_i''^{1/n} + \frac{u_j}{u_i}(K_{ij}a_j'')^{1/n}} \quad (9)$$

which reduces to the Nicolsky equation if $n = 1$ and $u_i = u_j$, see equation (6)

Ion mobility

In the experiments reported by Karlberg,[95] only a small fraction of the sites was exchanged, see Table 4 He showed also[119] that the ion-exchange was apparently complete in about one hour on a general-purpose pH-electrode The electrode potential changed during the ion-exchange and the potentiometric response was faster when the hydrogen ions moved out and sodium ions moved in than when the movement was in the reverse direction, see Fig 3 This difference in rate is to be expected from general theory[120] if the hydrogen ion has a higher mobility than the sodium ion in the gel layer From these measurements it is possible to calculate the ratio of the diffusion coefficients, which at a given temperature

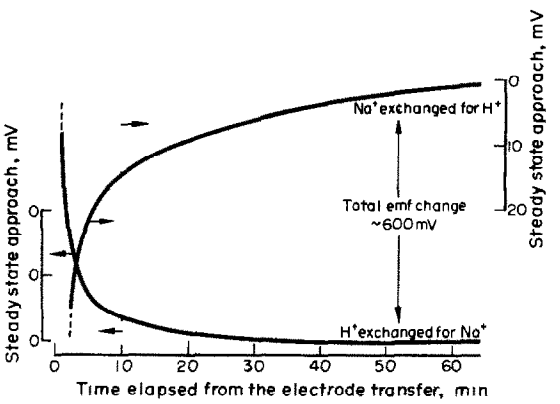

Fig 3 Potential change during ion-exchange in a pH-electrode as a function of time

is equal to the ratio of the mobilities, see Table 5 The data show that the softer glass has a higher ratio than the harder, which contains less water Drying also reduces the ratio From the ion-exchange capacity data it follows that this mobility ratio is valid for an outer part of the gel layer

As discussed above, the hydrogen ion is slower than the sodium ion in the transition layer by a factor of 10^3–10^4, *i.e.*, the ratio D_{H^+}/D_{M^+} is 0·001–0·0001 The mobility ratio thus varies over several orders of magnitude with the distance from the surface to the bulk glass It is very likely that the water plays an important role for this variation In the deeper part the moving species may be the proton and in the outer part it may be a hydronium ion This is supported by the drying experiments[119] in which it was found that the hydrogen-ion mobility decreased much more than the sodium-ion mobility Although not experimentally shown, it may be inferred that the exchange capacity shown in Table 4 relates to sites containing hydroxonium ions rather than protons An exchange with sodium at the hydroxonium sites can then be assumed to be a fast process Further exchange should be a very slow process owing to the low mobility of the protons and in the time scale of the experiments an apparent equilibrium has been reached

The theory of Eisenman and co-workers resulted in equations which were independent of time as discussed above, see equations (7) and (9) Karlberg

Table 5 Ratio between the diffusion coefficient for hydrogen ions and alkali-metal ions at the surface

Electrode	Electrode state	Alkali-metal ion	D_H/D_M
Ingold LoT	hydrated	Na^+	80
Beckman E-2	hydrated	Na^+	64
Ingold 201	hydrated	Na^+	63
Ingold HA	hydrated	Na^+	18
Metrohm UX	hydrated	Na^+	38
Ingold LoT	hydrated	Li^+	102
Ingold LoT	etched	Li^+	123
Ingold LoT	dried	Li^+	28
Ingold 201	hydrated	Li^+	96
Ingold 201	etched	Li^+	70
Ingold 201	dried	Li^+	29

found on the other hand that the potentials changed during ion-exchange, see Fig 3 There is thus a discrepancy between theory and experiment but it can be explained on the basis of the gel layer properties discussed In the derivation it was assumed that the mobility ratio was constant but as discussed above it is in fact varying over several orders of magnitude Thus u_{H^+}/u_{M^+} is almost 10 close to the phase boundary and decreases to 0 001 or less in the transition region A close look at the derivation shows that if the mobility ratio varies with distance inwards, the diffusion potential will become a function of time As the diffusion front moves inwards, the quotient in equation (7) will decrease and the diffusion potential may even change sign The movement will be slower the farther the front moves inwards and therefore an apparently steady-state potential will be approached As the movement inwards will become very slow it should still be permissible to use a semi-infinite space as a diffusion model

It may also be speculated that a model using varying mobility ratio should eventually be able to explain the broadening of the mixed-response region without empirical assumptions about the activity like those of equation (8) Nicolsky[98] assumed ion-exchange sites with different properties, which were evenly distributed in the glass. The model presented here also assumes that the properties of the sites vary, but in a non-uniform way with distance inwards from the surface Structurally the variation depends on the water distribution and its influence on the potential is *via* the variation in transport properties

In addition to the diffusion potential discussed above there will also be a diffusion potential in the transition layer This follows from the difference in mobilities of lithium ions and protons Baucke[61,62] was able to calculate the mobility ratio from the concentration profiles A good agreement was obtained with mobility ratios estimated from the electrical resistance of the transition region [73] A potential jump has also been measured directly in the solid,[64] it was about 90 mV and independent of the hydration time For an electrode hydrated on both sides of the membrane the diffusion potentials in the two transition layers will cancel

The alkaline error of a glass electrode increases with temperature and it is time-dependent [1,93,121] For a number of electrodes kept in sodium hydroxide solution Simon *et al*[93] observed changes between −10 2 and +9 2 mV during 2 hr The time-dependence is most likely a result of the gel-layer destruction and is less for a durable glass [122]

Transient response and response time

Rechnitz and Kugler[123] noted a transient response of cation-selective glass electrodes when the concentration of an auxiliary ion was changed At equilibrium the electrode displayed only slight response but for a short time after the change a considerable transient response was found Karlberg[124] found that pH-electrodes also showed transient response in the range where the alkaline error just starts The slope of the curve was dependent on the relative contributions from the two ions to the potential When the slower sodium ion moved into the gel layer a peaked curve resulted When the sodium-ion concentration in the solution was decreased and the sodium moved out from the gel layer a monotonic curve was recorded The change occurred within one minute for a pH-electrode, *i e*, much more slowly than for the cation-selective electrode

Rechnitz[125] suggested that two effects combine to give the transient response, namely the relative ion-exchange equilibrium constant for the two ions, and their mobility ratio A low mobility ratio for any two ions might more than cancel a favourable ion-exchange constant As discussed above, it has been concluded that for pH-glasses the mobility ratio varies with distance The mobility ratio u_{H^+}/u_{Na^+} is high near the surface and therefore a high diffusion potential will be produced As the diffusion front moves inwards, the mobility ratio decreases and therefore also the diffusion potential decreases This explanation is only qualitative and a full discussion must await the solution of the flux equation for a variable mobility ratio

Distèche and Dubuisson[126,127] studied the response time of Corning 015 glass electrodes and found a time-constant of about 30 msec Perley[80] noted a slow response at high pH The electrode is also slow in poorly buffered solutions [5,80,128] Rechnitz and Hameka[129] measured the time-constant of cation-selective electrodes and found an exponential time-dependence giving a single time-constant, in contrast to some other ion-selective electrodes Buck *et al*[113] noted a slow response at high acidity Rechnitz[130] also reviewed and discussed response characteristics Johansson and Norberg[131] found that a very slow but accurately exponential response was obtained in isopropyl alcohol medium The response time varied with the hydrogen-ion activity of the solution An explanation based on electrode kinetics was forwarded but later in an attempt to extend the investigations, Wikby and Karlberg[132] found that the response time depends on the buffer capacity rather than on the acidity of the solution The ionic strength of the solution may also be important Under most laboratory conditions, mass transfer limits the response time in aqueous solution but in flow kinetics dynamic errors, especially at low ionic strengths, have been observed [133–135] In non-aqueous solvents several minutes may be required for equilibrium[131] and an acceptable quantitative explanation is not available as yet

ACID RANGE

In strongly acid solution, *i e*, at least 1*M*, the pH-glass electrode shows a negative deviation It is largest in solutions of halogen acids and sulphuric acid Schwabe *et al*[36] concluded from electrochemical

experiments that acids penetrate the gel layer As a consequence the hydrogen-ion activity in the gel layer increases and according to equation (4) there will then be a negative deviation. The error increases slowly with time in the acid solution [90] and it was shown[36] that the penetration was a zero-order reaction for the halogen acids With sulphuric and phosphoric acid the rate decreases with time, which suggests a partial dehydration of the gel layer It is much greater in hydrochloric than in sulphuric acid and it is larger the softer the glass [136] Boksay *et al.*[137] found that the rate of penetration was proportional to the hydrogen chloride vapour pressure. It was also suggested that the first step is an adsorption on the glass surface Later Schwabe *et al* [138] showed directly by radiochemical measurements that the halides penetrate into the gel layer and that the amounts are related to the molecular size, Cl > Br > I It has recently been shown by a coulometric technique[139] that the amount that penetrates depends on the glass composition and the gel-layer thickness The penetration of chloride into a hydrated Ingold LoT electrode was 9 nmole/cm^2 and into a hydrated Ingold 201 electrode 1 nmole/cm^2 The former is a low-temperature electrode and the latter a general-purpose electrode The acid error is smaller the smaller the penetration There was much smaller penetration into freshly etched electrodes It was concluded that the penetration involved only an outer part of the gel layer and this has been directly confirmed by Boksay [140] He etched away the outer part of the gel layer and found that the chloride was removed

ASYMMETRY POTENTIAL

If identical solutions are placed inside and outside the bulb of a glass electrode and two identical reference electrodes are immersed in these solutions there will usually be a small potential difference. This potential is called the asymmetry potential

Cremer[16] observed potential differences of about 20 mV, between the inside and outside of his bulb electrodes and sometimes up to 100 mV Hughes[141] realized that the differences varied from one electrode to another as well as with time He also coined the term asymmetry potential MacInnes and Dole,[76] and Zirkler,[142] thought that hard glasses had larger asymmetry potential than soft glasses Theories about the effect of time were also advanced[142–147] and it was observed that the shape of the bulb was important, complicated glass-work resulting in a large asymmetry potential [148] A spiral electrode showed an initial asymmetry potential of 100 mV It was also suggested that the potential reflects the different volumes separated by the membrane and that the leached alkali from the glass was the prime cause [35 147 149–151] The hydrostatic pressure[151] inside the electrode, the film at the electrode stem as well as differences between various parts of the membrane[152] were thought to cause asymmetry Polishing,[149] dehydration[153] or chemical etching on one side[2 3] are all known to produce large potential differences whereas annealing is known to reduce them.[154] Haugaard[38] claimed that the asymmetry potential is a function of pH, which was supported by Aten *et al* [155] and by Kratz.[2] The authors of this paper can add the observation that electrodes blown by untrained glass-blowers show larger asymmetry potential than those blown by professionals from the same melt

Differences in the surface or the hydration between the inside and outside of the membrane are usually supposed to be the main cause of the asymmetry potential The belief that the curvature causes the asymmetry is also common and it seems to be supported even by recent investigations [156]

The increased knowledge about the glass-electrode surface layers forms a basis for a more detailed understanding of the effects causing an asymmetry potential Meyer[157] showed that alkali was lost from glass in a flame and that the leaching was therefore reduced Bach and Baucke[59] have shown that different pretreatments of the dry glass results in different alkali concentration profiles from which it follows that there are structural differences in the surfaces. During normal glass-blowing the inside and the outside are surrounded by different gas mixtures and after blowing the temperature of the external surface will fall more rapidly than that of the internal side Inhomogeneities have also been observed by electron microscopy [158] Hamilton and Hubbard[159] found that between 19 and 36 times as much Victoria Blue B could be adsorbed on the inside as on the outside of an electrode bulb When etching both sides with hydrofluoric acid until the resistance in the surfaces vanished, Wikby[139] found that a much thicker layer must be removed from the inside than from the outside Large differences were found between the surfaces of soft glasses like Corning 015 and Ingold LoT whereas the surfaces of hard glasses were almost the same Wikby and Karlberg[84] found that if hydration of etched surfaces was started simultaneously no asymmetry potential was found If the hydration was started at different times there was a potential difference which varied with time It may take weeks to attain a constant asymmetry potential and still longer for soft glasses An etching will probably also remove the thickness limitation noted earlier [160] Schwabe[161] studied the time-dependence of the asymmetry potential at various temperatures and found that the pH-change in the internal buffer solution was responsible for a large apparent asymmetry potential It was larger for soft glass, in more acid solutions and at higher temperatures These changes were caused by alkali leached from the glass

The most important source of asymmetry potential during normal electrode use is the change in hydrogen-ion activity in the gel layer, see equation (4) The changing hydrogen-ion activity may in turn have

several causes If there is hydrolysis of the silicon network the number of exchange sites will increase with time and consequently the hydrogen-ion concentration will increase This effect should be more pronounced for soft glasses which are less resistant to chemical attack and form a thicker gel layer If the glass compositions on the two sides have become different as a result of flame reactions the gel layers will acquire different amounts of hydrogen ions during hydration There are also large diffusion potentials in the transition layers which are almost independent of the gel layer thickness as discussed above Small differences may exist between these and this should especially be true if the glass compositions are different on the two sides as a result of glass-blowing *etc*

The asymmetry potential can be made very small and almost independent of time if the surface layers formed during blowing are etched away with hydrofluoric acid and the hydration is then started simultaneously at both sides The internal buffer solutions should of course be changed after some time as the pH increases owing to a consumption of protons in the hydration process Under these conditions the change in potential with time at the two surfaces will cancel almost completely

CATION-RESPONSE ELECTRODES

The ion-selectivity between hydrogen and other univalent cations depends strongly on the addition to the glass of some tervalent metal oxides, such as those of aluminium, gallium and boron Small amounts of, *e g*, gadolinium oxide, modify the properties [162,163] The first systematic studies of glass compositions containing these elements were made by Lengyel and Blum[164] who found that there was a shift to an alkali-metal ion-response even in acid solutions Only a few other investigations [165,166] were made until Eisenman and co-workers[118] reported an extensive study which initiated a general interest in cation-selective electrodes Eisenman[167] also examined the atomic basis for selectivity. He calculated the change in free energy of the ion-exchange

$$Cs^+_{(glass)} + M^+_{(soln)} \rightleftharpoons M^+_{(glass)} + Cs^+_{(soln)} \quad (10)$$

for an $\equiv SiO^-$ site or an $(\equiv AlOSi\equiv)^-$ site M^+ is an univalent cation other than Cs^+ The result showed that the selectivity order was $H^+ \gg Li^+ > Na^+ > K^+ > Rb^+ > Cs^+$ for the silicate site and the reverse for an aluminosilicate site The accuracy of the calculations is low and they predict erroneously an ideal H^+-response or an almost ideal Cs^+-response respectively for the two sites Since the negative charge is distributed on four oxygen atoms in the aluminosilicate site the field strength of the anion will be lower than that of a silicate site for which the charge is located on one oxygen atom Nicolsky and Schultz[168] used a model in which $\equiv SiO^-$ was treated as a weak acid site and $(\equiv AlOSi\equiv)^-$ as a strong acid site Using this view it is evident that a strong acid site will form a salt with an alkali-metal ion even in acid media The glasses containing aluminium will therefore be alkali-metal ion-selective

With this discussion as a background, only such investigations on cation-selective glass electrodes as are relevant for a further understanding of the pH-selective electrode will be reviewed A comparison of the surface composition and surface properties might thus give valuable information Savage and Isard[169,170] showed that the addition of aluminium increased the chemical durability substantially An electrode leached at 60° became extremely sluggish, behaviour which was assumed to depend on the formation of a leached layer The drift of the electrodes was ascribed to changes in the degree of hydration of the ion-exchanged layer [150] Eisenman[4] interpreted his tracer-diffusion experiments on NAS 11-18 and NAS 27-4 glasses to mean that the hydration increased with decreasing field strength The conclusion is in contrast to that drawn by Savage and Isard for glasses with similar composition Figure 4 summarizes determinations of the alkali-metal ion profiles of some cation-selective electrodes The measurements were made by Boksay *et al* [171,172] and by Wikby [173] The ion-profile for a pH-selective glass is also included for comparison The results have been obtained by etching away thin layers from the surface and analysing the etching solutions for glass constituents The concentrations are given as a percentage of the concentration in the bulk glass All pH-selective glasses studied form a well-defined gel layer, with a sharp rise in alkali-metal ion concentration at the boundary In this region the alkali-metal ions have been replaced almost completely by hydrogen ions The amount replaced on the cation-selective electrodes varies from one glass to another and varies inversely with the amount of tervalent glass-forming elements There is a gradual leaching and the reaction proceeds at depth rather than as a complete replacement at the surface As much of the glass seems to remain unchanged it might be suggested that the electrode reaction may take place in a solid-state reaction[112,113] between the original glass and the solution in contrast to the case for a pH-electrode in which

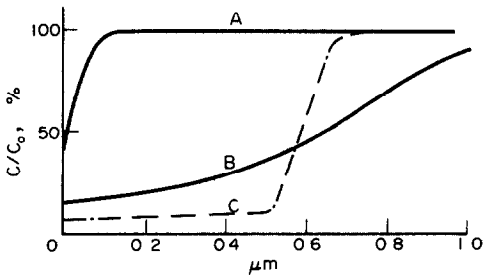

Fig 4 Comparison of concentration profiles inwards from the surface of a pH-electrode (– –) and two cation-selective electrodes (—)
A A sodium-selective glass, Philips G 15-Na
B A soft aluminium silicate glass
C A pH-electrode of lithia glass, Radiometer C-glass

the electrode reaction involves hydronium ions in the gel layer. There is too little information available for any conclusions to be drawn about the need for, or the function of, a hydrated layer on a cation-selective electrode

For a glass in contact with water, several processes may occur simultaneously, *e.g.*, (*i*) an ion-exchange between alkali-metal ions in the glass and hydrogen ions in the solution, (*ii*) a dissolution of the glass surface by the reaction between the network and water, (*iii*) a depolymerization process which occurs by the diffusion of water into the surface layer and its subsequent reaction with the glass structure If process (*iii*) is small in extent an exponential alkali-metal ion concentration-profile may result, as shown by Boksay *et al.*[53,174] If, on the other hand, a glass is strongly influenced by process (*iii*) the alkali-metal ion concentration-profile varies almost stepwise with the distance inwards towards the glass bulk [53] The reason, on a structural basis, for the different concentration profiles between pH-selective and cation-selective glasses should therefore be the relative importance of (*iii*). According to Boksay and Bouquet[175] a quinquecovalent silicon atom must be formed for the reaction to occur and this involves a previous distortion of a tetrahedral unit In a rigid glass containing, *e g*, aluminium, the network is more extensively cross-linked and therefore will be less attacked For each aluminium atom replacing a silicon atom in the network two terminal oxygen atoms will be removed, which increases the rigidity

Eisenman[4,49] determined the tracer self-diffusion coefficients for a number of glasses. He also calculated the self-diffusion coefficients of ions in the dry bulk glasses from available resistivity data He found that the tracer diffusion coefficients were 100–10,000 times as great as the diffusion coefficients in the dry glass and ascribed the difference to a higher mobility in the surface From this he concluded that there should be a hydration of the surface layers There was in fact an initial rapid step which resulted from the high mobility in the surface and later a creep which corresponded to a diffusion coefficient of the same size as that of the dry glass Wikby[173] measured the resistivity of the surface layers of two aluminosilicate glasses He found that the resistivity of the outermost surface layer was higher than that for the bulk glass. In contrast to the pH-glasses the high-resistivity region was distributed over the entire ion-exchanged layer There seems to be no transition region, which is to be expected from the ion-profile curves in Fig 4. Too little is yet known to explain the apparent contradictions between Eisenman's and Wikby's findings

Eisenman[176] studied the ion-exchange on some cation-selective glasses and found exchange capacities varying from that corresponding to a monolayer, to values about 1000 times higher The exchange was in some cases highly non-ideal Karlberg's values for the ion-exchange capacity of pH-electrodes, see Table 4, lie in the middle of the range reported by Eisenman. After comparison with potentiometric selectivity, Eisenman concluded that "there is no correlation whatsoever between surface ion-exchange properties and the (steady-state) electrode potential selectivities." If this is so, the differences in mobilities must account for the observed selectivities, which implies a mobility ratio of up to 7000:1 for sodium and potassium ions.

APPLICATION TO pH-MEASUREMENTS

Numerous research papers report on the application of glass electrodes to measurements of pH under various conditions The early investigations were made with electrodes having compositions that are no longer in use and with instruments and techniques inferior to those common today As the electrode properties were not well understood, the pretreatment may have been questionable It is therefore necessary to make reinvestigations in order to evaluate the limits of performance of modern electrodes, and only a few recent findings will be discussed here.

The most serious source of error for precision pH-measurements in the pH-range 1–9 is presumably changes in asymmetry potential[35] Covington and Prue[177] developed an extrapolation technique for precise measurements when there is a linear drift Various features of the variations of e.m f with time were considered in a subsequent paper [178] A method for electrode-testing over a larger pH-range was also described [179] Karlberg[180] measured the long-term stability of glass electrodes subjected to various pretreatments He found that large maxima, also noted by others,[80,93] could occur when the electrode was transferred from sodium hydroxide solution to hydrochloric acid Even in the reverse direction there was a dependence on the previous storage solution A direct transfer from the acid to the alkali produced larger drift than a transfer *via* dippings in buffer solutions of pH 3, 5, 7 and 9

From what is known today, for precision measurement the electrode should be made from a durable glass, both sides of the membrane should be etched with hydrofluoric acid, and the hydration should be started simultaneously for both sides of the membrane The electrode should not be subjected to rapid pH-variations over a large pH-range and no switching should be performed before measurements.[91] If the electrode is to be transferred into a solution before measurement it should be ascertained that the electrode bulb has precisely the same temperature as the solution,[180] or large transients may appear [181] The input capacitance of the measuring circuit should also be small [91] These precautions should be followed by an evaluation of the electrode performance as described earlier [177,179]

In the alkaline range there will be an attack on the gel layer and it may ultimately be completely removed Besides the alkaline error, which is time-dependent to some degree, there will also be a drift

due to the alkaline attack [180] Not even the most durable electrodes available today are satisfactory in this range, especially at higher temperatures Generally the storage time in alkaline solutions should be kept as short as possible

The introduction of lithia glasses made it possible to use glass electrodes for measurements in non-aqueous solutions [5,161,182-190] Loss of water from the gel layer will cause a slow response, but reimmersion in water will restore the electrode performance [35,108,191] The electrode is subject to alkaline[142] and acid errors which may be so severe that even a titration becomes impossible [193-195] Ivanovskaya *et al.*[196-197] studied the potential-time changes between glass and hydrogen electrodes in going from aqueous to non-aqueous media. The specific influence of organic solvents was also studied [198-200] It was concluded that the changes were due to the presence of a diffusion-potential gradient due to penetration of the solvent and perhaps dehydration of the surface layer For soda glasses the changes were several tens of mV and for lithia glasses an order of magnitude lower. No measurable penetration of isopropyl alcohol could be found by Karlberg *et al.*[70], however. The gel-layer growth is inhibited in isopropyl alcohol[69] and the transition-layer resistance increases subsequently Furthermore, the lithium ion flux is decreased to a tenth of that in water [70] The response time is decreased when the gel layer is etched away with hydrofluoric acid but the selectivity properties change only little.[97] Karlberg has also summed up some precautions for measurements in non-aqueous solvents.[97]

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A THEORETICAL STUDY OF THE INTERFERENCE FROM CHLORINE IN THE OXIDATIVE COULOMETRIC METHOD FOR TRACE DETERMINATION OF SULPHUR IN HYDROCARBONS

ANDERS CEDERGREN

Department of Analytical Chemistry, University of Umeå, 901 87 Umeå, Sweden

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Summary—A theoretical investigation has been made of the interference from chlorine in the oxidative coulometric method for trace sulphur determinations A computer program (SOLGAS), based on the free-energy minimization principle, has been used to predict equilibrium compositions of the products resulting from combustion of a hydrocarbon sample containing sulphur and chlorine The theoretical possibilities of overcoming the interference from chlorine and maintaining a high recovery of sulphur are described

Chlorine and nitrogen are commonly associated with sulphur in petroleum products and chemicals Two of the most generally accepted methods[1] for trace determination of sulphur in hydrocarbons, namely the oxidative and the reductive micro-coulometric methods, suffer from interference from either chlorine or nitrogen Chlorine interferes with the oxidative method, owing to oxidation of iodide to iodine, which causes low results, while nitrogen interferes with the reductive method The interference from nitrogen in the oxidative method can be almost eliminated by addition of sodium azide to the electrolyte [2] Sodium azide has also been reported to be able to suppress the interference from chlorine in the oxidative method[1] but for concentrations of chlorine higher than 0 1% the interference begins to be severe This means that for chlorine concentrations higher than 0 1% the oxidative method cannot be applied to trace sulphur determinations

Another problem associated with the oxidative method is the non-stoichiometric conversion of sulphur into sulphur dioxide High temperature and a low partial pressure of oxygen favour the formation of sulphur dioxide However, in most cases a rather high partial pressure of oxygen is needed to complete the combustion of an organic matrix It should still be possible to obtain a high recovery of sulphur dioxide by raising the temperature but it has been reported that a high temperature produces the opposite effect for organic samples containing more than 0 06% of sulphur [3,4] Various low-temperature combustion methods have therefore been developed

Two different types of oxidative methods have been described The first[5–7] utilizes a temperature in the range 700–900° and recoveries of 65–95% are reported The recovery is higher than that expected from a thermodynamic calculation of the equilibrium between sulphur dioxide, oxygen and sulphur trioxide The reported results indicate that equilibrium has not been obtained The relative standard deviation of more than 2% probably depends on the fact that these methods do not involve equilibrium conditions

The principle of the other approach to the oxidative trace method[4,8] involves dilution of the gas mixture, obtained in a low-temperature combustion, with an inert gas at high temperature (1000°) In this way the partial pressure of oxygen is lowered and equilibrium is obtained because of the high temperature used The recovery of sulphur dioxide is close to 100% and the relative standard deviation for this technique is about 1%

In this work the possibilities of overcoming the interference from chlorine in the oxidative micro-coulometric method have been examined. When an organic sample is burnt in oxygen the main chlorine-containing product is HCl This compound does not interfere with the coulometric titration, in contrast to other chlorine-containing combustion products such as Cl_2 and HClO A theoretical investigation was therefore made in order to find the combustion conditions which give a high recovery of sulphur dioxide without formation of interfering chlorine compounds The traditional hand-calculating method was found to be unsuitable for this rather complex system Calculation of the equilibrium composition of a complex gas mixture can be greatly facilitated by application of the free-energy minimization principle [9,10]

THEORY

For calculating the equilibrium composition, *ie*, the positive set of mole numbers which gives the lowest possible value of the total free energy of the system and which satisfies the mass-balance constraints, a computer program called SOLGAS[11] was used The aim was to predict the equilibrium composition of

the products resulting from combustion of a hydrocarbon sample containing sulphur and chlorine, in an oxygen–argon atmosphere For the sake of simplicity a certain hydrocarbon, cyclohexane, was chosen The system investigated can be illustrated by the following reaction·

$$C_6H_{12} + x\,S_2 + y\,Cl_2 + z\,O_2 + v\,Ar \rightarrow \text{Products} \quad (1)$$

The equilibrium composition of this system was calculated at two temperatures, 1000 and 1300 K The coefficients in equation (1), which are equal to the input number of moles of each substance were varied in the following way $5 \times 10^{-6} < x < 5 \times 10^{-4}$, $5 \times 10^{-5} < y < 0{\cdot}5$, $4{\cdot}5 < z < 18$, $v = 25$ and 250 The total pressure was supposed to be 1 atm. The value $v = 250$ was chosen in order to study the effect of diluting the combustion gas mixture without changing the total pressure The thermodynamic data, *i e*, the values of the free energy for various substances and temperatures, were taken from JANAF [12]

At the beginning of this work about forty different gases, including products of reaction with the quartz tube, such as $SiCl_{2(g)}$, $HSiCl_{3(g)}$, $SiCl_{3(g)}$, $SiO_{(g)}$, $SiS_{(g)}$ and $Si_{(s)}$ were taken into consideration. Most of them could be neglected as they were present in very small amounts. After these initial estimations the following gases were considered to be the main combustion products· CO, CO_2, COS, H_2S, HCl, HClO, ClO, Cl_2, Cl, H_2O, SO_2, SO_3, H_2, O_2 and Ar

RESULTS AND DISCUSSION

The distribution of sulphur species

Figure 1 shows the distribution of the sulphur species COS, H_2S, SO_2 and SO_3 as a function of moles of oxygen added to one mole of cyclohexane containing traces of sulphur The shapes of the curves are practically identical when the sulphur content is

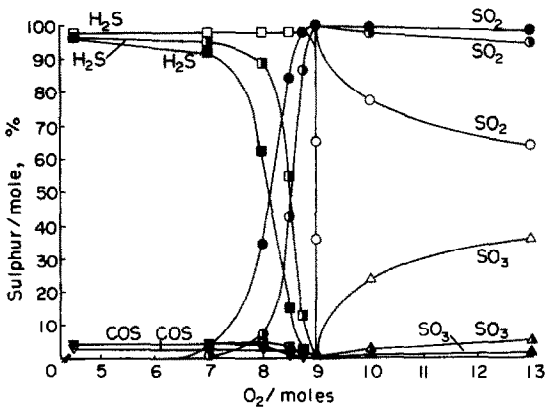

Fig 1 The distribution of the sulphur species COS, H_2S, SO_2 and SO_3 as a function of moles of O_2 added to 1 mole of cyclohexane containing 5×10^{-5} mole of S_2 (○) SO_2, (△) SO_3, (□) H_2S, (▽) COS Unfilled symbols 25 moles of Ar, $T = 1000$ K Partly filled symbols· 25 moles of Ar, $T = 1300$ K Filled symbols 250 moles of Ar, $T = 1300$ K

varied in the range 10^{-5}–10^{-3} mole Therefore the calculations were simplified by selecting a fixed amount of S_2 (5×10^{-5} mole) throughout this study Three different cases are represented in Fig 1 (*i*) addition of 25 moles of argon at 1000 K, (*ii*) 25 moles of argon at 1300 K, (*iii*) 250 moles of argon at 1300 K

Let us first consider case (*i*). The distribution curves show that for $z > 9$ in equation (1) practically all sulphur is present as either SO_2 or SO_3 As expected, the SO_2-fraction decreases with increasing amounts of oxygen For $z < 9$ the main sulphur compounds are H_2S and COS However, equilibrium calculations for this low temperature are probably only of theoretical interest since separate experiments have shown that the equilibrium between SO_2, O_2 and SO_3 is not reached fast enough below 1200 K

In case (*ii*) the system at 1300 K was studied As can be seen in the figure (for $z > 9$) the amount of SO_2 is increased compared with the situation at 1000 K For $z < 9$ it is interesting to notice the relatively high fraction of SO_2 formed For example at $z = 8{\cdot}75$, *i e*, under reducing conditions where H_2S and COS are expected to be the main sulphur-containing components, the equilibrium composition is 86% SO_2, 12% H_2S and 2% COS The reason for this can be understood by considering the water–gas equilibrium

$$CO_{(g)} + H_2O_{(g)} \rightleftharpoons CO_{2(g)} + H_{2(g)} \quad (2)$$

which is displaced to the left at elevated temperature This results in an increasing amount of oxygen available in the system, according to

$$H_2O_{(g)} \rightleftharpoons H_{2(g)} + \tfrac{1}{2}O_{2(g)} \quad (3)$$

In case (*iii*) the gas mixture is diluted at 1300 K This results in an overall increasing recovery of SO_2 The reason for this, when $z > 9$, is that the partial pressure of oxygen is decreased Below $z = 9$ there is a large increase of SO_2 compared with the case with no dilution At $z = 8{\cdot}75$ the composition is 98% SO_2, 2% H_2S and 0% COS The water–gas equilibrium (2) is not affected by changes in pressure However, the equilibrium (3) is pressure-dependent. This means that when the gas mixture is diluted the equilibrium (3) is displaced to the right, which results in more oxygen (and hydrogen) being available in the system This fact evidently favours the formation of SO_2

Interferences from chlorine

Figures 2, 3*a,b,c* and 4*a,b,c* show the distribution of the chlorine-containing compounds HCl, HClO, Cl_2, Cl, ClO for three chlorine concentrations In Fig 2 the amount of chlorine present is equal to the amount of sulphur ($S_2 = 5 \times 10^{-5}$ mole) while in Fig 3 the amount of chlorine is 100 times as large and in Fig 4 10,000 times as large as the amount of sulphur

In Fig. 2, which deals with only case (*ii*), it can be seen that the amount of interfering chlorine com-

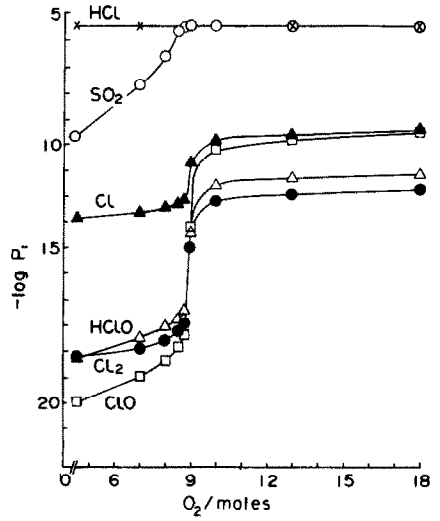

Fig 2 The partial pressures (p_i atm) of chlorine-containing compounds and SO_2 as a function of O_2 added to a sample containing 1 mole of cylcohexane, 5×10^{-5} mol of Cl_2 and 5×10^{-5} mole of S_2 $T = 1300$ K and Ar = 25 moles (×) HCl, (▲) Cl, (△) HClO, (●) Cl_2, (□) ClO, (○) SO_2

pounds is at least four orders of magnitude less than the amount of sulphur dioxide, independent of the amount of O_2 added This means that no interference is expected and this is in agreement with experimental results.[1] Calculations which are not shown in Fig 2 show that there is a decrease in the amount of interfering chlorine compounds when the temperature is raised from 1000 to 1300 K

Figure 3 shows the effect of a 100-fold increase in the input amount of chlorine for the three cases (*i*)–(*iii*) The situation which is represented in these figures corresponds to a cyclohexane sample containing 0·4% chlorine and 0·008% sulphur (w/w). The interference from chlorine in the trace sulphur determination is reported to begin at this chlorine level [1] As can also be seen in the diagram, the interference is significant, especially for the low temperature of 1000 K (Fig. 3*a*) Consequently, it is possible to almost eliminate the interference at this chlorine level by increasing the temperature to 1300 K (Figs. 3*b* and 3*c*). By comparing Figs. 3*b* and 3*c* it can be seen that the amount of interfering chlorine compounds slightly decreases as a result of the dilution of the gas mixture [case (*iii*)]

The effect of a further increase in the input amount of chlorine is demonstrated in Fig 4 For oxidizing conditions (*e.g.*, for $z > 9$) the amount of interfering chlorine compounds is about two orders of magnitude larger than the amount of sulphur dioxide. However, considering the case (*iii*) which is represented in Fig 4*c*, it is interesting to notice the possibility of overcoming the interference from chlorine by using the range $z = 8\,5$–$8\,8$, the recovery of SO_2 being as high as 98–100% The relative amounts of HCl for the three cases (*i*)–(*iii*) are represented in Fig 5 which has a better resolution than Figs 2–4 with respect

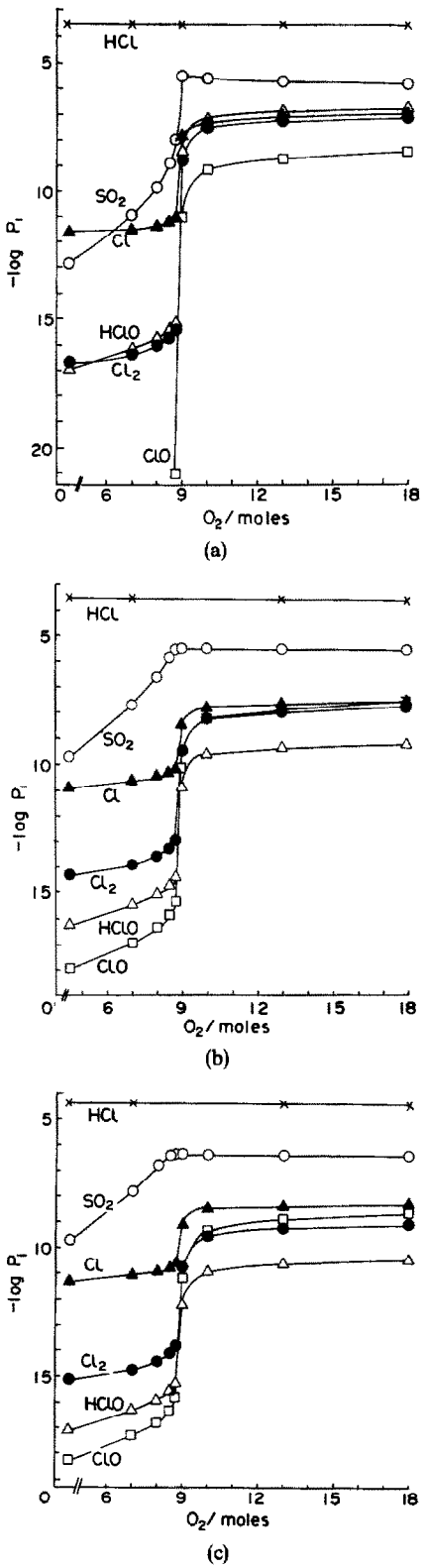

Fig 3 The partial pressures (p_i atm) of chlorine-containing compounds and SO_2 as a function of O_2 added to a sample containing 1 mole of cylcohexane, 5×10^{-3} mole of Cl_2 and 5×10^{-5} mole of S_2 (*a*) 25 moles of Ar, 1000 K, (*b*) 25 moles of Ar, 1300 K, (*c*) 250 moles of Ar, 1300 K (×) HCl, (▲) Cl, (△) HClO, (●) Cl_2, (□) ClO, (○) SO_2

to this compound The conditions for a high recovery of HCl are clearly demonstrated in Fig 5

For the above-mentioned range $z = 8\,5$–$8\,8$, where the recovery of SO_2 is high and the interference from

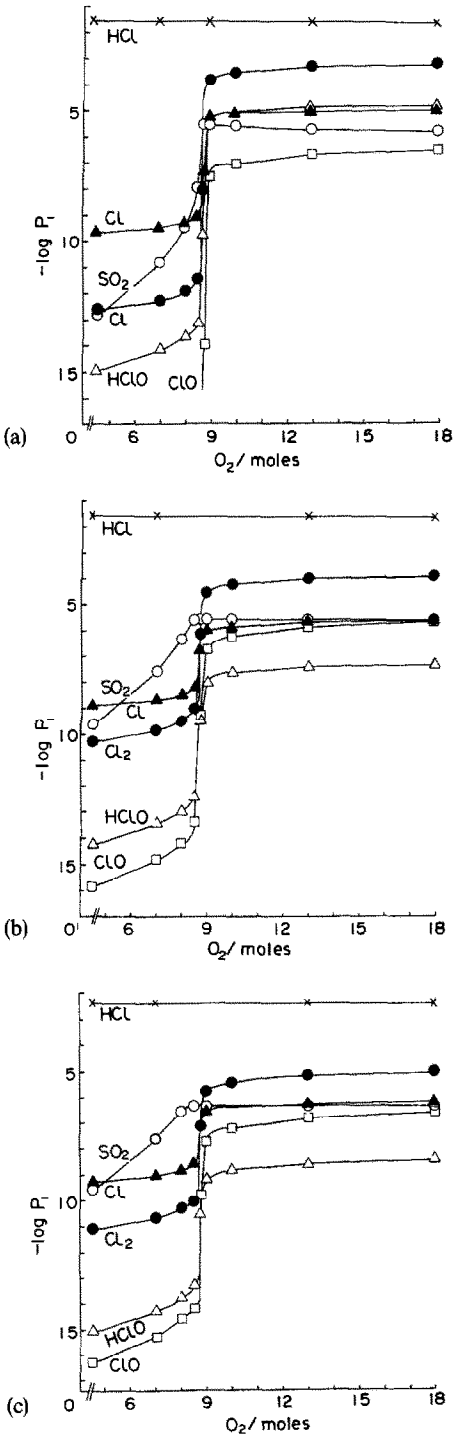

Fig 4 The partial pressures (p, atm) of chlorine-containing compounds and SO_2 as a function of O_2 added to a sample containing 1 mole of cyclohexane, 0·5 mole of Cl_2 and 5×10^{-5} mole of S_2 (*a*) 25 moles of Ar, 1000 K, (*b*) 25 moles of Ar, 1300 K, (*c*) 250 moles of Ar, 1300 K (×) HCl, (▲) Cl, (△) HClO, (●) Cl_2, (□) ClO, (○) SO_2

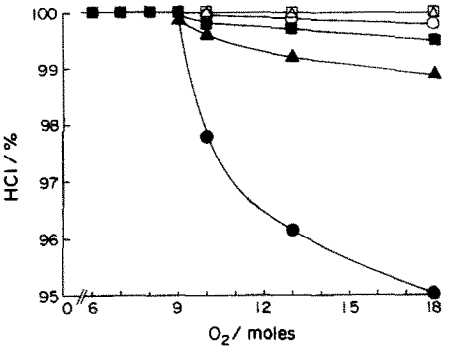

Fig 5 The recovery of HCl as a function of O_2 added to 1 mole of cyclohexane containing either 5×10^{-3} mole (filled symbols) or 5×10^{-5} mole (unfilled symbols) of Cl_2 (○) 25 moles of Ar, 1000 K, (△) 25 moles of Ar, 1300 K, (□) 250 moles of Ar, 1300 K

chlorine compounds is eliminated, the equilibrium value of pO_2 varies between approximately 10^{-11} and 10^{-4} atm By using, for example, the CO/CO_2 couple it would be possible to buffer the gas mixture in order to control pO_2 within these limits

In an acid solution with iodine as reagent, as in the oxidative coulometric method, both H_2S and SO_2 reduce two equivalents of iodine This means that the amount of sulphur in the sample is equal to the sum of H_2S and SO_2 if these are the only sulphur-containing products As can be seen in Table 1 the value of this sum is high (>95%) over a large pO_2 range This means that CO, for example, can be added so that a suitable pO_2 is obtained in the final gas mixture The values presented in the table were obtained at 1300 K for the following input values 1 mole of cyclohexane, 0 5 mole of Cl_2 and $0\,5 \times 10^{-4}$ mol of S_2 One mole of ($\frac{1}{2}Cl + Cl_2 + HClO$) represents two redox equivalents in the titration, which corresponds to a negative error of one mole of sulphur (half the number of moles of Cl gives the equivalent number of moles of Cl_2)

The effect of adding CO to a gas mixture containing an excess of O_2 can be illustrated by the following example Cyclohexane containing a large amount of chlorine and a small amount of sulphur is combusted in an excess of O_2 according to the reaction

$$C_6H_{12} + 0\,5\,Cl_2 + 18O_2 + 5 \times 10^{-5}\,S_2 + 250\,Ar + x\,CO \rightarrow \text{Products}$$

Table 1 The distribution of sulphur and chlorine compounds as a function of pO_2 Input amounts of S and Cl are 10^{-4} and 1 mole respectively ($T = 1300$ K)

pO_2, atm	SO_2, mole %	$SO_2 + H_2S$, mole %	($\frac{1}{2}Cl + Cl_2 + HClO$), mole
$0\,9 \times 10^{-3}$	99 6	99 6	4×10^{-4}
$1\,4 \times 10^{-6}$	99 9	99 9	3×10^{-7}
7×10^{-12}	97 7	99 6	3×10^{-7}
3×10^{-12}	91 8	98 3	2×10^{-7}
1×10^{-12}	79 9	95 3	2×10^{-7}

Table 2 The effect of adding CO to the combustion gas mixture with respect to the recovery of sulphur and to the elimination of interfering chlorine compounds

CO added, *mole*	At equilibrium				
	SO_2, *mole %*	$H_2S + SO_2$, *mole %*	$(\frac{1}{2}Cl + Cl_2 + HClO)$, *mole*	Error,* %	pO_2, *atm*
0	97 8	97 8	$2\,2 \times 10^{-3}$	−2200	3×10^{-2}
15	99 0	99 0	$1\,0 \times 10^{-3}$	−1000	6×10^{-3}
18	99 6	99 6	$3\,8 \times 10^{-4}$	−380	9×10^{-4}
20	97 8	99 4	$3\,1 \times 10^{-7}$	−0 3	8×10^{-12}
22	79 9	95 3	$2\,0 \times 10^{-7}$	−0 2	1×10^{-12}
24	52 1	88 8	$1\,6 \times 10^{-7}$	−0 2	6×10^{-13}

* With respect to the interference from chlorine

Table 2 shows the result at 1300 K As can be seen, the interference from chlorine is eliminated at CO-values larger than 20 moles Above this level the addition of CO must be carefully controlled because both the SO_2 and $H_2S + SO_2$ recoveries decrease with increasing amount of CO because there is then increasing formation of COS

As shown in this paper there are theoretical possibilities for overcoming the interference from chlorine in the oxidative coulometric method However, the calculations are based on the assumption that equilibrium is attained, which of course remains to be proved This assumption is likely to be true at least at such a high temperature as 1300 K The theoretical investigation presented in this paper will soon be followed by an experimental study

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CHROMATOGRAPHY OF AROMATIC COMPOUNDS ON ANION-EXCHANGE RESINS

LUTFUL MAJID JAHANGIR, LENNART OLSSON and OLOF SAMUELSON

Chalmers University of Technology, Department of Engineering Chemistry, Fack, S-402 20 Goteborg 5, Sweden

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Summary—Complex mixtures of aromatic compounds can be rapidly separated on anion-exchangers in the acetate form with acetic acid as eluent and determined automatically by recording the absorbance in the ultraviolet Carboxylates are separated by ion-exchange Hydrogen bonds between non-dissociated acids and the counter-ions influence the distribution coefficients Hydrogen-bonding with the resin has a marked effect on the sorption of solutes containing phenolic protons Intramolecular hydrogen-bonding depresses their sorption Hydrophobic interactions have a predominant influence with hydrocarbons and with phenolic compounds containing non-polar aliphatic substituents The relative importance of these interactions increases with a decreased ion-exchange capacity of the resin

A sharp chromatographic separation of seven phenolic compounds on an anion-exchange resin in 5*M* acetic acid has been previously demonstrated by Halmekoski and Hyle [1] Coarse resin particles were used and about three days were required to effect the separation More recently Rexfelt and Samuelson[2] showed that several aromatic substances could be separated within a few minutes on a pellicular anion-exchanger. Large separation factors were required to achieve good separations.

Chromatography on anion-exchangers in acetic acid is a versatile tool in the analysis of complex mixtures of aliphatic hydroxy-acids but attempts to apply pellicular resins have been unsuccessful The main reason is that satisfactory detectors are not available Moreover, the amounts of separated solutes are so small that their isolation for final identification is difficult. Very often hydrolysates of products of biological origin and waste-waters from various sources contain a complex mixture of aliphatic hydroxy-acids and aromatic compounds It was therefore of interest to study the possibility of separating such mixtures and finding conditions which permit a rapid separation of the aromatic compounds on an ordinary resin

EXPERIMENTAL

Most experiments were made in jacketed columns (350 × 1 9 mm) packed with an anion-exchange resin having quaternary ammonium groups The eluate was analysed automatically (Chromatronix Model 220) by determining the absorbance at 280 nm except in the case of benzene which was determined at 254 nm If not otherwise mentioned, the nominal linear flow was 18 0 cm/min (calculated for the empty part of the column) and the amounts of aromatic compounds added were 0 3–3 5 μg.

The volume distribution coefficients (D_v) were calculated from the peak elution volume[3] determined in runs with single solutes and with mixtures No systematic deviations were detected when the nominal linear flow was varied in the range of 1 4–18 0 cm/min The values were reproducible to ±1% over a period of at least one month when the column was used in 3*M* acetic acid or in dilute hydrochloric acid It is noteworthy that the sorption of aromatic compounds increased when the acetate form of the resin had been used in 3*M* acetic acid in 30% ethanol at 70° for about one month For example, it can be mentioned that the D_v value of phenol, benzene and methoxybenzene increased by factors of 1 2, 1 5 and 1 6 respectively

The D_v values of the strongly held solutes were determined on a smaller column (72 5 × 2 5 mm) to obtain sharper elution curves The D_v of phenol determined on this column differed by less than 2% from the value determined on the larger column

RESULTS AND DISCUSSION

Effect of the eluent composition

In agreement with the results reported by previous investigators[1,4] Table 1 shows that D_v decreases rapidly with increasing concentration of acetic acid in the eluent For comparison, D_v was also determined on the same resin converted into the chloride form These determinations were restricted to low hydrochloric acid concentration to avoid corrosion of the pump. In experiments with pure water the reproducibility was unsatisfactory with both resin forms This can be ascribed to Donnan-hydrolysis

Only the benzoic acids are dissociated to an appreciable extent in the media applied and only with these species can ion-exchange be of importance Increasing the hydrochloric acid concentration from 0·0074 to 0 074*M* resulted in a slight increase in D_v (about 2%) for phenol, 1,2-dihydroxybenzene and 2,6-dimethoxyphenol The effect recorded with benzaldehyde was insignificant With benzoic acid the D_v dropped from 31 at the lower hydrochloric acid concentration to 23 at the higher level Similarly, the D_v value of 4-

Table 1 Volume distribution coefficients (D_v) at various concentrations of acetic acid (acetate resin) and in 0·0074*M* hydrochloric acid in water (chloride resin) and 3*M* acetic acid (mixed resin) Dowex 1-X8, 17–20 μm, 70°

	0·001*M* HAc	0·1*M* HAc	1*M* HAc	3*M* HAc	5*M* HAc	7*M* HAc	HCl in water	HCl in HAc
Benzene	6·71	6·10	5·05	3·15	1·94	1·00	11·0	4·42
Naphthalene	115	97	54	20·6	8·19	3·61	>150	34
Phenol	18·7	15·5	9·24	4·89	3·04	2·04	18·8	6·10
1,3-Dihydroxybenzene	48·5	38	18·1	8·76	5·31	3·73	29·2	8·83
1,4-Dihydroxybenzene	23·8	19·1	9·84	5·10	3·22	2·32	17·0	5·60
2-Methoxyphenol	12·7	9·79	5·53	2·85	1·59	1·01	15·4	4·06
2,6-Dimethoxyphenol	8·53	6·52	3·43	1·65	0·91	0·54	12·9	
Methoxybenzene	9·72	8·32	5·84	3·05	1·63	1·26	17·7	4·78
Benzoic acid			61	14·6	5·73	3·10	31·0	7·14
2-Hydroxybenzoic acid				>150		79	>150	
3-Hydroxybenzoic acid			>150	33	13·6	7·54	70	13·6
4-Hydroxybenzoic acid			96	23	10·0	5·50	64	12·5
2,5-Dihydroxybenzoic acid				>150		127	>150	
Benzaldehyde	5·41	4·09	2·70	1·48	0·85	0·54	8·44	2·42
3-Hydroxybenzaldehyde	28·5	19·8	9·30	3·83	2·10	1·32	24·9	5·1
1,3-Dihydroxynaphthalene				105	46	21·7		
2,7-Dihydroxynaphthalene				62	25·2	12·9		

hydroxybenzoic acid decreased from 64 to 61 for this change in eluent concentration These results show that ion-exchange contributes to the sorption of benzoic acids but is of little or no importance with the other solutes

With the acetate form of the resin the largest concentration dependence was observed with the carboxylic acids In addition to the factors of general importance for non-electrolytes, the decreased dissociation and hence decreased contributions from ion-exchange affect their D_v. The 2-hydroxybenzoic acids which are dissociated to an appreciable extent even at a high acetic acid concentration were not eluted with a reasonable volume of 3*M* acetic acid but were well resolved by the 7*M* acid Even some phenolic compounds, *e.g.*, dihydroxynaphthalenes, were held very strongly in 3*M* acetic acid but were easily eluted as well-separated peaks at the highest acid concentration

In addition to the decreased contributions from ion-exchange, the decrease in D_v with increased acetic acid concentration can be attributed both to factors which increase the solubility of the aromatic solutes in the external solution (including formation of association compounds with acetic acid) and to factors which change the properties of the solution inside the resin phase *e.g.*, by blockage of sorption sites

As previously shown,[5,6] acetate ions (Ac^-) present as counter-ions in the resin have the ability to associate with carboxylic acids (HA) by hydrogen-bonding and give counter-ions of the type $HAAc^-$ This sorption mechanism must contribute to the D_v of the aromatic carboxylic acids With increasing acetic acid concentration the importance of this sorption mechanism decreases, owing to competition with acetic acid for the proton-accepting carbonyl group in the acetate counter-ions This explains why the acetic acid concentration had such a marked influence on the D_v of the aromatic carboxylic acids under conditions where these were virtually non-dissociated

To elucidate the influence of this sorption mechanism further, experiments were made with benzoic acid, 3-hydroxybenzoic acid and 4-hydroxybenzoic acid in a mixed eluent which was 3*M* with respect to acetic acid and 0·0074*M* with respect to hydrochloric acid These aromatic acids are virtually non-dissociated both in this eluent and in 3*M* acetic acid This means that the species present in the external solution will be virtually the same in both media On the other hand the composition of the resin phase is drastically changed In the mixed eluent, the chloride, which has a higher ion-exchange affinity than acetate, is the dominant counter-ion. Separate experiments in which the resin was equilibrated with the mixed eluent, centrifuged and rinsed with water, showed that chloride constituted 95% of the counter-

Table 2 Volume distribution coefficients (D_v) in 3*M* acetic acid and 0·0074*M* hydrochloric acid Dowex 1-X8, 17-20 μm, 70°

	Acetic acid, D_v	Hydrochloric acid, D_v
1,2-Dihydroxybenzene	6·50	19·3
1,3,5-Trihydroxybenzene	16·9	42
2-Hydroxytoluene	6·67	40
3-Hydroxytoluene	6·99	39
4-Hydroxytoluene	6·73	38
2,4-Dimethyl-1-hydroxybenzene	9·60	85
1,2-Dimethyl-4-hydroxybenzene	8·87	66
1,3-Dimethyl-2-hydroxybenzene	6·25	48
1-Hydroxy-2,4,5-trimethylbenzene	12·3	33
3-Methoxyphenol	5·20	35
4-Methoxyphenol	3·69	23·6
2-Methoxy-4-propylphenol	8·55	133
4-Allyl-2-methoxyphenol	6·41	84
1,2-Dimethoxybenzene	1·44	12·1
1,3-Dimethoxybenzene	3·05	32
1,4-Dimethoxybenzene	2·43	24·4
1,2,3-Trimethoxybenzene	1·12	10·8
1,3,5-Trimethoxybenzene	3·38	33
4-Hydroxy-3-methoxybenzoic acid	12·6	50
3,5-Di-tert-butyl-4-hydroxybenzoic acid	>150	>150
2-Hydroxybenzaldehyde	2·58	17·2
4-Hydroxybenzaldehyde	4·47	27·7
2,4-Dihydroxybenzaldehyde	9·38	66
4-Hydroxy-3-methoxybenzaldehyde	2·84	21·0
Benzoquinone	0·39	1·28

ions in the washed resin Only a small amount of hydrochloric acid (0 1 mmole per g of dry resin) was present in the washings. The results given in Table 1 show that the aromatic acids were held much more strongly by the acetate resin than by the resin which was mainly in the chloride form, while the solutes lacking carboxylic acid groups were held less strongly by the acetate resin These results support the conclusion that association with counter-ions contributes markedly to the sorption of the carboxylic acids.

Since hydrogen-bonding of a phenolic proton to proton-accepting groups in other stationary phases is of great importance even in aqueous solution,[7,8] the question arises whether the formation of similar associated species between phenols and the acetate counter-ions contributes significantly to the sorption of phenolic compounds The fact that the D_v values of 1,3-dihydroxybenzene and 1,4-dihydroxybenzene were only slightly higher on the mixed resin than on the acetate resin, while the other compounds lacking carboxylic acid groups were held much more strongly by the mixed resin, suggests that this mechanism has a significant influence

Relationships between the structure of the non-electrolytes and their retention data

Many mechanisms have been suggested for the sorption of aromatic compounds onto ion-exchange resins.[9,10] No doubt various types of interactions co-operate and it is often difficult, if not impossible, to distinguish between, for instance, hydrophobic interactions (sorption enforced by water-structure)[11] and interactions between π-electrons in the aromatic solutes and the stationary phase Conclusions concerning the influence of different types of interactions are complicated by the presence of acetic acid in the eluent, but this is necessary for efficient separations for analytical purposes Despite these complications there exist relationships between the structure of the solutes and their distribution coefficients, which permit prediction of the elution order

For many aromatic solutes there exist great similarities between the elution order in aqueous media on cation-exchangers and anion-exchangers as well as on other polymeric stationary phases Naphthalene and its derivatives are held more firmly than benzene and the corresponding derivatives on all the ion-exchangers so far studied[2,9] including the acetate and chloride forms of the anion-exchanger studied in the present work (Table 1) The same holds true when polyvinylpyrrolidone[7] or polyamides[8] are used as stationary phases Theoretically, the interactions between π-electrons in the aromatic solutes and the stationary phase will increase with increasing number of aromatic nuclei Cyclohexane is, however, held much more strongly than benzene on the resins studied in the present work Since it is known that the decrease in free energy for the transfer from an aqueous solution to an organic solvent is larger for cyclohexane than for benzene[12] this observation strongly indicates that π-electron interactions with the stationary phase are less important than the hydrophobic interactions.

The effect of hydrophobic interactions is reflected in the D_v of the aromatic compounds containing non-polar aliphatic side-chains As expected, the introduction of methyl groups resulted in a significant increase in D_v (Table 2) The larger contributions of ethyl and propyl groups[1] strongly indicate that the hydrophobic interactions are very important even in acetic acid medium The decrease in free energy for the transfer of alkenes from aqueous solution to the pure liquid hydrocarbon is less than that observed for alkanes [12] This permits us to predict the following order of increasing D_v 2-methoxyphenol < 4-allyl-2-methoxyphenol < 2-methoxy-4-propylphenol. This elution order was found to be valid also for pellicular anion-exchangers [2]

The much larger D_v of benzene and naphthalene at low eluent concentrations on the chloride form than on the acetate form shows that non-polar interactions (including water-structure enforced sorption) are strongly affected by the counter-ions Similarly, benzaldehyde and methoxybenzene lacking hydroxyl groups, and the phenolic compounds with the hydroxyl group involved in intramolecular hydrogen bonding (2-methoxyphenol and 2,6-dimethoxyphenol) were held much more strongly by the chloride form, whereas the D_v of phenol was the same on both resin forms The D_v of 3-hydroxybenzaldehyde was higher for the acetate form than for the chloride form Likewise, 1,3-dihydroxybenzene and 1,4-dihydroxybenzene, which are lacking intramolecular hydrogen bonds, exhibited larger D_v on the acetate resin in dilute acetic acid The results indicate that the relative importance of the non-polar interactions is less for the acetate resin than for the chloride resin, while the contributions to D_v from interactions with the phenolic groups are more important for the acetate form

To elucidate the influence of the ions present in the resin phase, experiments were made with a macroreticular styrene–divinylbenzene resin lacking exchange groups (Amberlite XAD-2) [13] In 1m*M* acetic-acid benzene was held much more strongly than phenol Both solutes exhibited much higher D_v than with the anion-exchangers, whereas the opposite was found for 1,3-dihydroxybenzene The distribution coefficients decreased markedly in 3*M* acetic acid but the elution order was the same as at the lower concentration Hence, the order was the reverse of that for both forms of the anion-exchanger, independent of the eluent concentration On cation-exchange resins of sulphonic acid type (H^+ and Na^+ forms) with the same polymer matrix as that of the anion-exchangers studied, these compounds were eluted in the order 1,3-dihydroxybenzene, phenol, benzene, *i e*, in reversed order compared to the anion-exchange, Moreover, the sorption was much less than that on the anion-exchanger [4] A decreased sorption of non-

Table 3 Volume distribution coefficients (D_v) at 70° in 3*M* acetic acid on Aminex A-28 (8–12 μm) and Dowex 1-X8 (17–20 μm)

	Aminex A-28, D_v	Dowex 1-X8, D_v	$\Delta \ln D_v$
Benzene	9 11	3 13	1 07
1,3-Dihydroxybenzene	9 50	8 65	0 09
1,4-Dihydroxybenzene	5 03	5 05	0 00
2-Hydroxytoluene	14 4	6 67	0 77
2,4-Dimethyl-1-hydroxybenzene	25 7	9 60	0·98
1-Hydroxy-2,4,5-trimethylbenzene	38 9	12 3	1 15
2-Methoxyphenol	5 88	2 90	0 71
4-Methoxyphenol	7 03	3 69	0 64
2,6-Dimethoxyphenol	3 98	1 64	0 89
Benzoic acid	18 9	14 5	0 27
Benzaldehyde	3 75	1 49	0·92

polar non-electrolytes with an increased ion-exchange capacity has also been demonstrated.[14,15] Evidently salting-out effects due to the ions present in the resins have a great influence on the distribution coefficients The results reported in the present work show that the counter-ions have a great influence, but most likely the ions fixed to the resin matrix are also of great importance

In this connection it is worth mentioning that quaternary ammonium salts exert a pronounced salting-in effect on both benzene[16,17] and benzene derivatives[18] The larger distribution coefficients for the anion-exchanger compared to the cation-exchanger can therefore in part be ascribed to the fixed quaternary ammonium ions in the anion-exchanger

Tables 1 and 2 show that for comparable compounds lacking intramolecular hydrogen bonds the sorption on both forms of the anion-exchanger increases for increasing number of phenolic groups These results indicate that there are specific interactions between free phenolic protons and the anion-exchanger. The observations that 2-methoxyphenol and 2-hydroxybenzaldehyde with intramolecular hydrogen bonds were held less strongly than the isomeric species and that 2,6-dimethoxyphenol had an extremely low D_v which could be ascribed to steric hindrance and intramolecular hydrogen bonds, support this conclusion. The reversed elution order of benzene, phenol and 1,3-dihydroxybenzene compared to that on the non-ionic resin and on the cation-exchanger strongly indicates that these specific interactions are due to the ions within the anion-exchanger. This conclusion is further supported by the observation[4] that intramolecular hydrogen-bonding increases the sorption onto cation-exchange resins and by the experiments with the anion-exchanger in the mixed eluent The results indicate that hydrogen-bonding in which the phenolic proton is involved contributes significantly to sorption onto the acetate form of the anion-exchanger but that this type of interaction is also of importance for the chloride form. The observations[9] that in ethanol and butanol, compounds containing phenolic hydroxyl groups are retained effectively by the chloride form, while the distribution coefficients of aromatic hydrocarbons are very low, support this conclusion In this connection it is worth mentioning that hydrogen-bonding between chloride ions and hydroxyl groups in non-aqueous media has been demonstrated.[19]

Influence of the exchange capacity

The co-operation between non-polar interactions and hydrogen-bonding of the phenolic proton to the anion-exchanger can also explain the effect of the number of fixed ionic groups in the resin phase on D_v, observed in the experiments referred to in Table 3 Both anion-exchangers were styrene–divinylbenzene resins of the benzyltrimethylammonium type and the exchange capacities determined per ml of bed

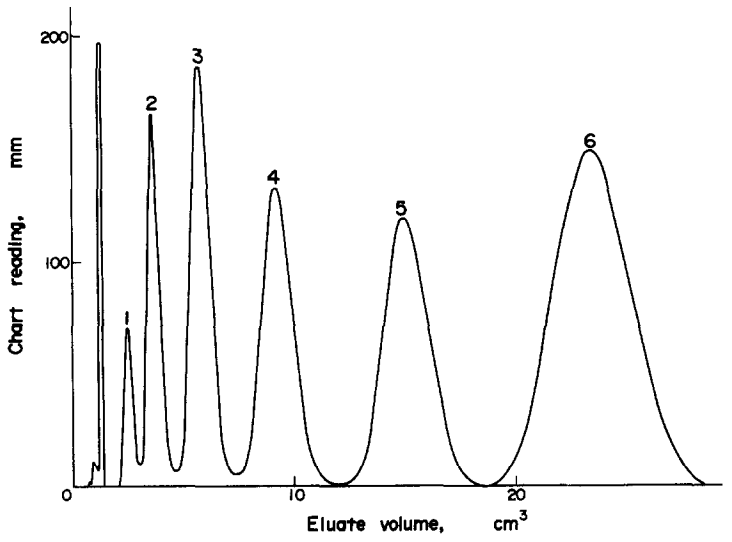

Fig. 1 Separation of (1) 2,6-dimethoxyphenol, (2) 2-methoxyphenol, (3) 1,4-dihydroxybenzene, (4) 1,3-dihydroxybenzene, (5) benzoic acid and (6) 4-hydroxybenzoic acid in 3*M* acetic acid at 70° Column 350 × 1 9 mm, Dowex 1-X8, 17–20 μm Nominal linear flow 18 0 cm/min

volume were very similar (Dowex 1-X8, 1·11 mmole/ml, Ammex A-28, 1·23 mmole/ml). On the other hand the exchange capacity per unit weight of the resin (determined for the dried chloride form) was much higher for Dowex 1-X8 (3·13 mmole/g) than for Aminex A-28 (2·21 mmole/g). As expected with regard to the larger concentration of non-substituted aromatic rings in Aminex, benzene was held much more strongly on this resin than on Dowex 1. The difference in ln D_v was even larger for 1-hydroxy-2,4,5-trimethylbenzene and is ascribed to increased non-polar interactions due to the methyl groups and to the shielding of the hydroxyl group. On the other hand 1,4-dihydroxybenzene exhibited the same D_v on both resins This is explained by increased contributions of hydrogen-bonding to the resin and decreased non-polar interactions. As expected, $\Delta \ln D_v$ was also small for the other two solutes which had a pronounced ability to participate in hydrogen-bonding (1,3-dihydroxybenzene and benzoic acid) whereas $\Delta \ln D_v$ was very large for benzaldehyde, which lacks proton-donating groups, and 2,6-dimethoxyphenol (intramolecular hydrogen-bonding and steric hindrance) Intramolecular hydrogen-bonding explains the larger $\Delta \ln D_v$ of 2-methoxyphenol compared to its isomer

The results presented above show that a co-operation between non-polar interactions and hydrogen-bonding can explain not only the elution order on a given resin but also the differences between resins of different exchange capacities The fact that the D_v values and the elution order are affected not only by the counter-ions but also by the exchange capacity lends great versatility to the separation method For some solutes the separation factors are much more favourable with a resin of high capacity, whereas with others the opposite is true

PRACTICAL APPLICATIONS

The distribution coefficients presented above show that most of the compounds studied can be well separated on anion-exchangers in both ionic forms. Since standard pumps made of stainless steel can be used at high concentrations of acetic acid, and in addition the elution positions can be controlled by proper choice of eluent concentration, a resin in the acetate form is preferred With solutes such as dihydroxynaphthalenes and benzoic acids it is recommended to choose a high acetic acid concentration (*e.g.*, 7*M*) whereas with other solutes a lower concentration (*e.g.*, 3*M*) is preferred A chromatogram recorded in this medium, using a resin with a relatively large bead diameter (Dowex 1-X8, 17–20 μm), is given in Fig 1 The six solutes were separated within 55 min The peak areas were reproducible within ± 1·5% or better

The distribution coefficients given in Table 1 show that a mixture containing benzene, phenol, 2-methoxyphenol and methoxybenzene cannot be separated in

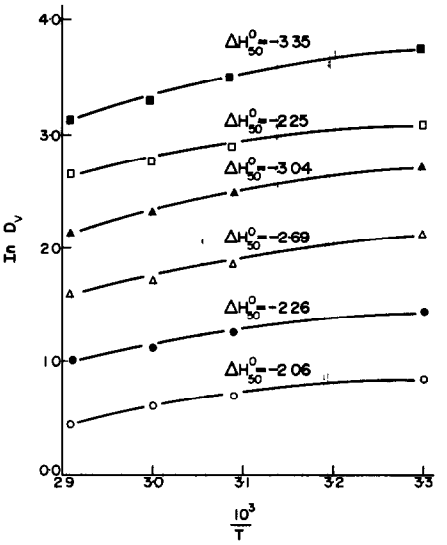

Fig 2 Influence of the absolute temperature (°K) on the volume distribution coefficients in 3*M* acetic acid Column 350 × 9 mm, Dowex 1-X8, 17–20 μm Nominal linear flow 18·0 cm/min ○ 2,6-Dimethoxyphenol, ● 2-methoxyphenol, △ 1,4-dihydroxybenzene; ▲ 1,3-dihydroxybenzene, □ benzoic acid, ■ 4-hydroxybenzoic acid

these media but that the conditions are favourable for a quantitative separation in 0·1*M* acetic acid and even at lower concentration.

The temperature greatly influences the distribution coefficients. For this reason reproducible results are obtained only with thermostated columns. With all solutes studied (Fig 2) the distribution coefficients in 3*M* acetic acid decreased with increasing temperature In some systems the separation factors were lower at a higher temperature However, since at the

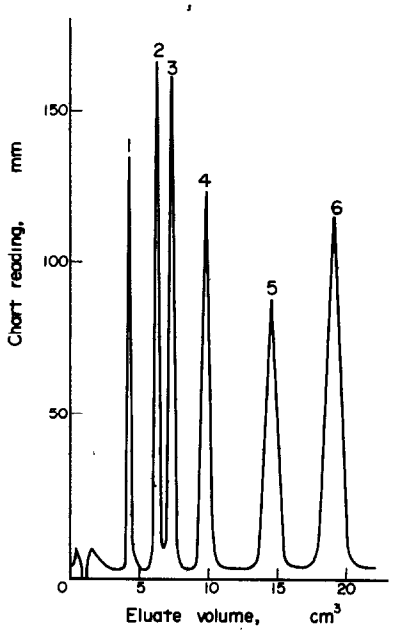

Fig 3 Separation of (1) benzaldehyde, (2) 2-methoxyphenol, (3) 4-methoxyphenol, (4) 1,3-dihydroxybenzene, (5) 2-hydroxytoluene and (6) benzoic acid in 3*M* acetic acid at 70°. Column 350 × 1·9 mm, Aminex A-28, 8–12 μm. Nominal linear flow 7·7 cm/min

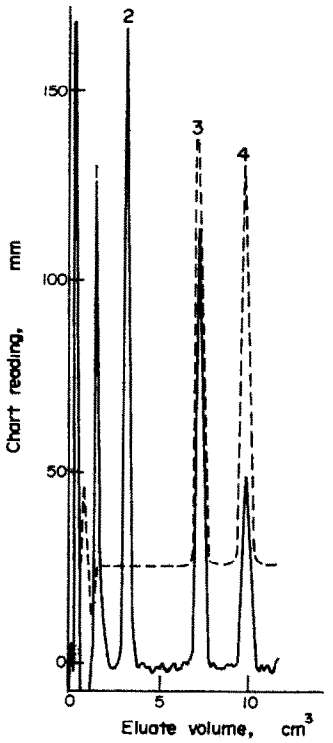

Fig 4 Separation of (1) gluconic acid, (2) glucuronic acid, (3) 4-methoxyphenol and (4) 1,3-dihydroxybenzene in 3*M* acetic acid at 70° Column 350 × 1 9 mm, Aminex A-28, 8–12 μm Nominal linear flow' 7 7 cm/min Broken line ultraviolet-monitor, 254 nm (0 64 absorbance = 250 mm) Full line differential refractometer, Laboratory Data Control Model 1107 L

same nominal flow, broader peaks and higher pressure drop are obtained at low temperature, it is recommended to run the separations at elevated temperature As an example of the effect of the temperature on the broadening of the elution curves it can be mentioned that the height of a theoretical plate (calculated for 1,3-dihydroxybenzene) was 3 4 mm at 30°, 2 3 mm at 50°, 1·9 mm at 60° and 1 5 mm at 70° The values refer to experiments at a nominal linear flow of 18 0 cm/min With regard to the instability of the resin, 70° was chosen as the highest temperature in this investigation Likewise the flow-rate has great effect on the peak broadening At 70° the plate-height decreased to 0 7 mm at a linear flow of 4 cm/min and to 0 4 mm at 2 cm/min

Like other separations on ion-exchange resins, those of aromatic compounds can be improved markedly by decreasing the particle size of the resin beads This is illustrated by the chromatogram (Fig 3) recorded in an experiment with Aminex A-28, 8–12 μm, at 70° and a nominal linear flow of 7 7 cm/min Slight overlapping occurred between 2-methoxyphenol and 4-methoxyphenol (separation factor 1 18) whereas the other solutes were completely separated The last compound was eluted within 95 min The height of a theoretical plate calculated for 1,3-dihydroxybenzene was 0 14 mm The results show that sorption equilibrium is established very rapidly and that the rate-determining step is the diffusion inside the resin particles.

In practice, many types of aqueous solutions containing both strongly polar aliphatic hydroxy acids and aromatic compounds have to be analysed Since the aliphatic acids give no significant response in the ultraviolet-monitor these do not interfere with the chromatographic analysis, but if it is desired to isolate the aromatic solutes for additional identification or preparative purposes, advantage can often be taken of the fact that many aliphatic acids appear earlier on the chromatogram than the aromatic compounds. Figure 4 illustrates the separation of two aromatic compounds in a solution containing gluconic and glucuronic acids. It is seen that at the acetic acid concentration used, the aliphatic acids appeared early on the chromatogram as well-separated peaks recorded by a differential refractometer These acids were well separated from the aromatic compounds, which appeared as discrete peaks Under the conditions used, the last peak was completely eluted within 50 min

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A GENERAL METHOD FOR COULOMETRIC TITRATION OF ALKYLPHENOLS WITH BROMINE

B KINBERGER, L. E EDHOLM, O NILSSON and B E F SMITH®

Department of Technical Analytical Chemistry, Chemical Center, Lund, Sweden

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Summary—A general method for coulometric titration of alkylphenols with anodically generated bromine is described The reaction is carried out in a water–acetic acid medium and the reactivity is governed by varying the water content and the concentration of bromide ion and by the addition of pyridine In that way all types of alkylphenols can be titrated quantitatively For phenols containing more than one free *ortho* and *para* position, the titration can also be carried out either to the monobromination stage or to the full bromination stage The mean relative error is ±1 2% for monobromination and ±1 5% for full bromination A method for rapid determination of the number of free *ortho* and *para* positions in alkylphenols by using two coulometric titrations is also described

Bromination has historically been an important method for the quantitative determination of phenols The phenol bromination method was introduced by Koppeschaar[1] as early as the previous century and it has, with certain modifications, been in frequent use since then [2–7] The first more general quantitative phenol bromination method was described by Smith in 1956 [8] Instead of free bromine, as used in the Koppeschaar method, an aqueous solution of potassium bromide and potassium bromate was added in slight excess to a solution of the phenol in acetic acid which had been further acidified with hydrochloric acid Potassium iodide solution was then added and the iodine formed was immediately titrated with thiosulphate, starch being used as indicator. For slowly reacting phenols a larger excess of bromide–bromate and longer reaction time was employed Only full bromination took place, *i.e.*, hydrogen at all free positions *ortho* and *para* to the phenolic hydroxyl group was replaced by bromine

Coulometric bromination methods for phenols, in which bromine is anodically generated from bromide ion by using a constant current and the amount of bromine consumed by the phenol is calculated from the magnitude of the current and the time of reaction, are of fairly recent date Carson[9] seems to have been the first to utilize a coulometric bromometric titration for the determination of a phenol He determined 8-hydroxyquinoline in an aqueous solution which was 0·2*M* with respect to sodium bromide and 0·001*M* with respect to hydrochloric acid The fact that the fully brominated phenol was partly precipitated made the method somewhat unreliable

The most comprehensive investigation in this field is due to Lichtenstein[10] who brominated phenol and nine methylphenols in aqueous solution which was 0·2*M* with respect to potassium bromide and 1*M* with respect to sulphuric acid In all cases monobromination took place except for 3,5-dimethylphenol which was dibrominated The errors varied between 1 and 5% The dependence of the apparent bromine consumption on the pH of the titration medium was first pointed out by van Zyl and Murray[11] and was later more closely studied by Čůta and Kučera [12] It was found that the reactivity of the phenol towards bromine increased with increasing pH. Thus, at pH 3, *o*-cresol apparently consumed three moles of bromine per mole and at pH 5 *m*-cresol consumed four. As these phenols have only two and three vacant *ortho* and *para* positions, respectively, bromine must be used up in connection with other reactions than substitution at free *ortho* and *para* positions and/or electrons are transferred at the anode in reactions other than bromine formation

In previous coulometric bromometric titrations of alkylphenols[9–14] water was used as titration medium throughout and the pH ranged from −0·3 to 8 The lowest value used for the constant generating current was 0 3 mA and the highest 15 mA The titrations were generally followed biamperometrically with two platinum electrodes, and the indicator currents plotted manually against time

INFLUENCE OF VARIOUS FACTORS ON THE BROMINATION REACTION AND TITRATION CURVE

Among the investigations discussed above, only one seems to offer a more general method for monobromination without side-reactions [10] However, only a limited number of phenols was titrated, and it is questionable whether the titration medium used (water) is suitable as a solvent for alkylphenols with larger alkyl groups As it was judged desirable to develop a general coulometric bromination method which could be applied to all types of alkylphenols, a systematic study of several factors affecting the bromination reaction and the shape of the titration curve was undertaken

Titration medium

The composition of the titration medium has a decisive influence on the bromination reaction As mentioned above, previous investigations of coulometric bromometric titrations of alkylphenols were made with water as titration medium, often resulting in higher values than would be expected for regular nuclear bromination Water also appears to be unsuitable as a solvent for both alkylphenols and their bromination products Because of good experience with acetic acid as medium in bromide–bromate titrations of phenols,[8] it was decided to try mixtures of acetic acid and water as media for the coulometric titrations.

Acetic acid–water mixtures turned out to function excellently in that no uncontrollable overbromination occurred and the reactivity of bromine towards phenol was a function of the ratio of acetic acid to water, increasing with the water content At the highest water content used—40% v/v (60 40 medium)—the solvent properties of the medium are still satisfactory Nearly all of the phenols tested can be quantitatively monobrominated either in this medium or, for more reactive phenols, in a medium containing 10% v/v water (90 10 medium)

Only one very reactive phenol was fully brominated in the 60 40 medium and none in the 90 10 medium In order to bring about replacement of hydrogen by bromine at all free *ortho* and *para* positions, 5% v/v of the acetic acid was exchanged for pyridine in the 60 40 medium, giving a 55.40 5 medium A still faster medium (55·35 10) contains 10% v/v pyridine The accelerating effect of pyridine on the bromination of phenols was pointed out by Ingberman[15] and seems to be rather specific for this base[16] The active brominating reagent is believed to be a pyridine–bromine complex One of several possible structures is pyridinium bromide perbromide (PyH^+Br^-,Br_2) which was used by Williams *et al*[17] for the bromination of phenols in the presence of 1,1,3,3-tetramethylguanidine.

Three main solvent compositions with varying content of acetic acid, water and pyridine were utilized in this work (see Table 1) However, in order for bromine to be generated, the solution must contain bromide ion, which also influences the bromination reaction Although the effect of bromide concentration on the rate of bromination has been studied in connection with the coulometric bromination of tyrosine,[18] the bromide concentration does not seem to have been used for modifying reactivity In this work it was found that, within each solvent group, the reactivity could be graded by varying the bromide concentration, the reactivity decreasing as the concentration increased Thus, each solvent group could be divided into several subgroups as shown in Table 1

Table 1 Composition of media used for bromination of phenols

Medium	Acetic acid, % v/v	Water, % v/v	Pyridine, % v/v	$[Br^-]$, M
I-1	55	35	10	0 1
II-1	55	40	5	0 1
II-2	55	40	5	0 4
II-3	55	40	5	1 2
III-1	60	40	—	0 1
III-2	60	40	—	0·4
III-3	60	40	—	1 2
IV-1	90	10	—	0 1*
IV-3	90	10	—	1 2*

* In these cases lithium bromide was used instead of sodium bromide because of the low solubility of the latter in 90% v/v acetic acid

In a solution containing both bromine and bromide ion the reaction

$$Br_2 + Br^- \rightleftharpoons Br_3^-$$

takes place Bromine has been shown to be the active reagent when tyrosine is brominated in acid solution[18] and also for the monobromination of 8-hydroxyquinoline in the 5-position However, on further bromination to the 5,7-dibromo-8-hydroxyquinoline, tribromide ion as well as bromine takes part in the reaction.[19,20] We are not aware of any similar kinetic investigations of the bromination of alkylphenols but, as the bromination-promoting properties of the titration medium decrease with increasing bromide concentration, it may be assumed that tribromide ion is not the main brominating reagent

As mentioned previously, the pH of the titration medium is also significant for the bromination result As there is a decrease in pH from medium I to medium IV, the difference in the reactivity of a phenol might be due partly to the pH-change It should, however, be pointed out that the reactivity-increasing effect of pyridine is not due to the pH-change. This could be shown by addition of sodium acetate instead of pyridine to medium III, until the pH of medium II was attained, and then titrating phenols in this medium No full bromination resulted (see also ref. 16) As in the present work it was found possible to arrive at the desired variation in reactivity by changing the contents of acetic acid, water and pyridine and the bromide concentration, no attempt to regulate the pH has been made

Generating current

It is evident that the generating current should ideally have such a value that bromine is formed with the same speed as it is consumed in the electrophilic nuclear substitution reaction If the current is too high, a certain bromine excess will exist with accompanying risk of side-reactions such as oxidation and bromine substitution in side-chains If the current is too low, the analysis time will be long and unavoidable side-reactions of unknown nature can exert a dominating influence, causing erroneous results A current of 3 mA was found to be suitable when determining phenols in amounts ranging from about 300

to about 2000 μg, depending on the molecular weight and the number of entering bromine atoms (see the following section).

Amount of phenol

The amount of phenol titrated is not insignificant There is in fact a lower as well as an upper limit for a titratable phenol The lower limit is set partly by the fact that a certain minimum distance is needed on the recorder chart in order to get an accurate measure of the time (see Fig 1) Another factor which influences the lower limit is the correspondence between the rates of bromine generation and consumption The electrolysis time, measured on the recorder chart, gives the generated amount of bromine, which agrees more or less exactly with the amount consumed in the nuclear substitution reaction However, there will always exist a certain error which becomes relatively more significant when smaller amounts of phenols are titrated

The upper limit for the amount of phenol which can be titrated with good accuracy, is partly determined by certain side-reactions at the generator anode and partly by a contamination of the indicating electrode (see experimental section). These reactions seem to occur after a certain time of electrolysis and cause a relative error which increases with the amount of phenol

In the present work an amount of phenol has been used which consumes 10 or 20 μeq of bromine in the monobromination and 20 μeq in the full bromination As each μmole of phenol consumes 2 μeq of bromine in the monobromination, 5 or 10 μmole is the amount of phenol used In the full bromination two or three bromine atoms enter the aromatic ring of a mononuclear phenol, depending on the number of free *ortho* and *para* positions, Accordingly each μmole of phenol consumes either 4 or 6 μeq of bromine and the amount of phenol weighed is 5 or 3 33 μmole respectively

When 10 μeq of bromine are generated, a 161-mm long trace on the recorder chart is obtained at a generating current of 3 mA and a chart-speed of 30 mm/min As this distance can be measured to within ±3 mm (depending on the curve shape) the measurement error amounts to less than ±2% Ten μeq of bromine does not necessarily represent the lower usable limit, nor does 20 μeq represent the upper limit, but we have found that these amounts result in both complete reaction and low interference from side-reactions

Polarizing resistance

The magnitude of the polarizing resistance present in the indication circuit has a decisive influence on the appearance of the titration curve (see Fig 1) As seen, a resistance of 100 kΩ gives the most rapid depolarization in the case indicated, permitting an accurate evaluation of the end-point The steepness of the titration curve after the end-point is a measure

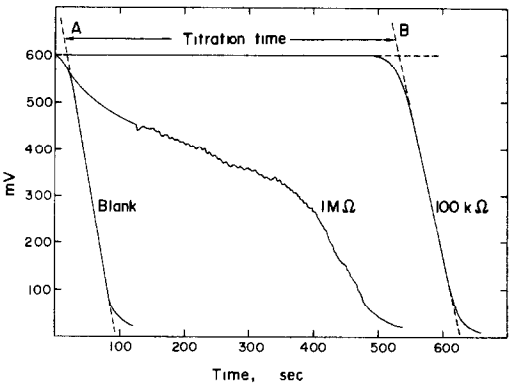

Fig 1 Method of evaluating the end-point, and the dependence of the shape of titration curve on the size of the polarizing resistance

of the indication sensitivity A relatively steep curve is formed with rapid detection of excess of bromine by the double platinum electrode, resulting in a small discrepancy between the real and constructed end-points

It should be emphasized that for each recorder speed, the size of the polarizing resistance must be adapted to the magnitude of the bromine generating current and sometimes to the type of phenol titrated Thus, it was found, when using a current of 4 mA, that a 1-MΩ resistance was best for easily-reacting phenols while 100 kΩ was preferable for more sluggish ones However, at a chart-speed of 30 mm/min the combination of a 100-kΩ polarizing resistance with a bromine generating current of 3 mA could be used for all types of alkylphenols titrated in this work

EXPERIMENTAL

Apparatus

In order that the present titration method be generally accessible, inexpensive standard pieces of apparatus have been used throughout The constant current generator used was a Knick "Prazisions Stromgeber" The titration was performed in a Metrohm titration vessel EA 875–20 equipped with a generating platinum electrode (Metrohm EA 247) with an area of about 2 cm^2, an indicating double platinum point electrode (Metrohm EA 235) and a magnetic stirrer (see Fig 2) The indicating electrode was connected to the polarizing voltage terminal of a Radiometer pH-meter 28 through a 100-kΩ polarizing resistance (Radiometer adapter L 409) The polarizing voltage was 630 mV and the pH-meter output was connected to a Servogor recorder

Reagents

Phenols All phenols were of the best grade commercially available In dubious cases, their purity was ascertained by gas chromatography and, if necessary, the phenols were purified by distillation or recrystallization

Acetic acid Merck 99–100%

Sodium and lithium bromide Sodium bromide, 99%, BDH Lithium bromide, 97%, BDH

Pyridine Mallinckrodt, AnalaR

Titration procedure

The phenol was weighed and transferred to a 50-ml volumetric flask and dissolved in acetic acid An exact

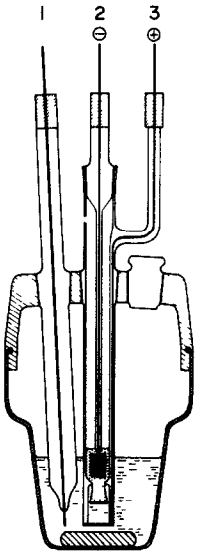

Fig 2 Cell for coulometric titration 1—indicating electrode, 2—cathode containing 2*M* sulphuric acid, 3—generating electrode (anode)

volume of this solution, containing an amount of phenol calculated to consume about 10 or 20 μeq of bromine, was dispensed into the titration vessel by means of an Agla micrometer syringe, 20 ml of the titration medium were then added and the electrodes inserted and connected to their electric circuits The magnetic stirrer was set at a relatively high speed and the pH-meter set to READ The generator current was adjusted to 3 000 mA, the recorder speed to 30 mm/min and the measuring range set to 1 V

The bromine generation was initiated simultaneously as the recorder pen crossed a vertical line on the chart after a stable base-line had been achieved The generation of bromine was continued until depolarization of the indicator electrode was complete The progress of the titration as well as the method for determining the equivalence point are shown in Fig 1 A blank was titrated in the same way and the amount of bromine consumed by the phenol is equivalent to the distance A–B in Fig 1 The indicator electrode should be washed with demineralized water after each titration and in case of contamination it should also be wiped with wet filter paper

The amount of phenol (μg) is calculated from equation (1)

$$m = \frac{t.I.\mathbf{E}.1000}{F} \qquad (1)$$

where t = the time in sec (= twice the distance A–B), I = generating current in mA, F = Faraday's constant = 96487 C/eq, and **E** = equivalent weight of phenol

If a phenol contains one hydroxyl group and its molecular weight is **M**, its equivalent weight is equal to **M**/2, **M**/4 or **M**/6 depending on whether 1, 2 or 3 bromine atoms enter the aromatic ring Some binuclear phenols which contain two hydroxyl groups, one in each ring, have also been titrated (see Table 4) In this case **E** is equal to **M**/4 or **M**/8, depending on whether 2 or 4 bromine atoms enter each ring For 2,7-dihydroxynaphthalene, bromine (1 atom) enters only one of the rings and accordingly **E** = **M**/2

RESULTS AND DISCUSSION

Fifty phenols have been determined by the coulometric bromine titration method Of these, 41 are mononuclear alkylphenols while the remainder are mainly binuclear phenols which from the point of view of reactivity are related to the alkylphenols The titration results for the former are summarized in Table 2 and for the latter in Table 4. Two headings appear in the tables, *viz* monobromination and full bromination Monobromination refers to titrations where one bromine atom enters each aromatic ring containing a phenolic hydroxyl group while full bromination means that hydrogen in all vacant positions (at least two), *ortho* and *para* to a phenolic hydroxyl group, is exchanged for bromine

Table 2 Results of monobromination and full bromination of alkylphenols

	Monobromination					Full bromination				
Phenol	Titr medium	Weight, μg Calc	Found	Bromine consumed, μeq	Error, %	Titr medium	Weight, μg Calc	Found	Bromine consumed, μeq	Error, %
C_6H_5OH	III-2	646 3	645	14	−0 2	II-2	315 4	322	20	+2 1
		969 5	977	21	+0 8			324		+2 7
2-Me	III-2	534 0	531	10	−0 6	II-2	543 5	537	20	−1 2
		1068	1088	20	+1 9			540		−0 6
2-Et	III-2	610 7	610	10	−0 1	II-1	610 7	605	20	−0 9
		1222	1227	20	+0 4			605		−0 9
2-Pr	III-2	714 0	712	10	−0 3	II-2	714 0	690	20	−3 4
		1419	1430	20	+0 8			686		−3 9
2-isoPr	III-2	681 0	679	10	−0 3	II-1	681 0	676	20	−0 7
		1362	1382	20	+1 5			675		−0 9
2-tert-Bu	III-2	750 6	756	10	+0 7	II-1	750 6	734	20	−2 2
		1501	1508	20	+0 5			733		−2 3
3-Me	IV-3	503 3	506	9	+0 5	II-2	362 3	369	20	+1 8
		1354	1333	25	−1 6			373		+3 0
3-Et	IV-1	610 5	598	10	−2 0	II-2	406 8	399	20	−1 9
		1221	1221	20	±0 0			398		−2 3
3-tert-Bu	III-2	733 0	710	10	−3 2	*	—	—	—	—
		1464	1444	20	−1 4					
4-Me	III-2	580 3	560	11	−3 5	II-2	543 5	537	20	−1 2
		1209	1195	22	−1 2			544		+0 1

Table 2 Results of monobromination and full bromination of alkylphenols (*continued*)

Phenol	Monobromination					Full bromination				
	Titr medium	Weight, μg		Bromine consumed, μeq	Error, %	Titr medium	Weight, μg		Bromine consumed, μeq	Error, %
		Calc	Found				Calc	Found		
4-Et	III-1	610·4	604	10	−1·1	II-2	610·7	593	20	−2·9
		1221	1250	20	+2·4			591		−3·2
4-Pr	III-1	684·9	661	10	−3·5	II-2	650·0	642	20	−1·2
		1370	1352	20	−1·3			638		−1·8
4-sec-Bu	III-2	750·6	742	10	−1·1	II-2	750·6	749	20	−0·2
		1501	1492	20	−0·6			749		−0·2
4-tert-Bu	III-1	754·8	757	10	+0·3	II-2	750·6	735	20	−2·1
		1510	1532	20	+1·5			735		−2·1
4-tert-Pe	III-2	821·0	814	10	−0·9	II-2	821·0	818	20	−0·4
		1642	1669	20	+1·6			820		−0·1
4-Oct	III-2	1031	1023	10	−0·8	II-2	1031	1044	20	+1·3
		2062	2090	20	+1·4			1050		+1·8
4-cycloHex	III-2	881·0	868	10	−1·5	II-2	881·0	872	20	−1·0
		1762	1797	20	+2·0			871		−1·1
2,3-diMe	IV-3	503·6	501	8	−0·5	II-2	613·9	613	20	−0·1
		1025	1020	17	−0·5			610		−0·6
2,4-diMe	III-1	609·9	600·2	10	−1·6	—	—	—	—	—
		1220	1219	20	−0·1					
2-Me-4-tert-Bu	III-2	822·2	822	10	±0·0	—	—	—	—	—
		1642	1638	20	−0·2					
2-Me-4-tert-Hex	III-2	967·7	962·3	10	−0·6	—	—	—	—	—
		1922	1907	20	−0·8	—	—	—	—	—
2-tert-Bu-4-Me	III-2	824·9	819·5	10	−0·7	—	—	—	—	—
		1643	1645	20	+0·1					
2,5-diMe	IV-3	502·9	505	8	+0·4	II-2	613·9	611	20	−0·5
		976·3	965	16	−1·2			611		−0·5
2-isoPr-5-Me	IV-3	585·9	595	8	+1·6	II-2	751·0	754	20	+0·4
		1172	1179	16	+0·6			756		+0·7
2-tert-Bu-5-Me	IV-3	821·0	806	10	−1·8	II-2	821·0	804	20	−2·1
		1642	1618	20	−1·5			799		−2·7
2,5-ditert-Bu	III-1	1175	1171	10	−0·3	I-1	1175	1155	20	−1·7
		2264	2255	20	−0·4			1179		+0·3
2,6-diMe	II-2	614·9	617	10	+0·3	—	—	—	—	—
		1228	1238	20	+0·8					
2-Me-6-Pr	III-1	750·1	724	10	−3·5	—	—	—	—	—
		1500	1457	20	−2·9					
2-Me-6-tert-Bu	III-2	812·3	802	10	−1·3	—	—	—	—	—
		2063	2014	20	−2·4					
2,6-diisoPr	III-2	894·9	881	10	−1·5	—	—	—	—	—
		1781	1756	20	−1·4					
2,6-disec-Bu	III-2	1054	1030	10	−2·3	—	—	—	—	—
		1988	1942	20	−2·3					
2,6-ditert-Bu	III-2	1026	981	10	−4·4	—	—	—	—	—
		1878	1839	20	−2·1					
3,4-diMe	IV-1	611·0	619	10	+1·3	II-3	610·7	589	20	−3·6
		1221	1219	20	−0·2			592		−3·1
3,5-diMe†	IV-3	501·8	499	8	−0·6	II-2	409·3	406	20	−0·8
		1004	1020	16	+1·5			408		−0·3
3-Me-5-Et	IV-3	681·0	682	10	+0·1	11-2	456·2	457	20	+0·2
		1362	1367	20	+0·4			459		+0·6
3,5-ditert-Bu	III-1	1228	1192	10	−2·9	*—	—	—	—	—
		1640	1576	16	−3·9					
2,3,5-triMe	IV-3	681·0	688	10	+1·0	II-3	680·8	678	20	−0·4
		1362	1350	20	−0·9			675		−0·9
2,4,5-triMe	III-2	683·5	681·8	10	−0·2	—	—	—	—	—
		1367	1368	20	+0·1					
2,4,6-triMe	II-2	685·8	686·0	10	±0·0	—	—	—	—	—
		1369	1376	20	+0·5					
3,4,5-triMe	IV-3	903·0	902	13	−0·1	III-3	680·8	670	20	−1·6
		1362	1380	20	+1·3			668		−1·9
2,3,5,6-tetraMe	IV-3	750·1	747·3	10	−0·4	—	—	—	—	—
		1502	1492	20	−0·7					

* Cannot be quantitatively fully brominated

† Can also be quantitatively dibrominated in medium III-2 Calculated 308·0 μg (10 μeq) Found 303·9 μg Error = −1·3%

Table 3 Media for monobromination and full bromination of various types of alkylphenols

Number of alkyl groups	Position of alkyl groups in relation to the phenolic hydroxyl group	Medium for monobromination*	Medium for full bromination*	Number of hydrogen atoms exchanged for bromine at full bromination	Group notations for the determination of the number of free ortho and para positions
0	—	III-2 (1)	II-2 (1)	3	A_0
	2	III-2 (5)	II-2 (2) II-1 (3)	2	B_0
1	4	III-2 (5) III-1 (3)	II-2 (8)	2	B_0
	3	IV-3 (1) IV-1 (1) III-2 (1)	II-2 (2)	3	A_1
	2,4	III-2 (3) III-1 (1)	—	—	C_0
	2,6	III-2 (4) II-2 (1) III-1 (1)	—	—	C_0
2	2,3	IV-3 (1)	II-2 (1)	2	B_1
	2,5	IV-3 (3) III-1 (1)	II-2 (3) I-1 (1)	2	B_1
	3,4	IV-1 (1)	II-3 (1)	2	B_1
	3,5	IV-3 (2) III-1 (1)	II-2 (2)	3	A_2
	2,4,6	II-2 (1)	—	—†	D_0
3	2,4,5	III-2 (1)	—	—	C_1
	2,3,5	IV-3 (1)	II-3 (1)	2	B_2
	3,4,5	IV-3 (1)	III-3 (1)	2	B_2
4	2,3,5,6	IV-3 (1)	—	—	C_2

* The number within parentheses denotes the number of phenols titrated
† For type of reaction see text

Monobromination of alkylphenols

Table 3 lists the various media used With two exceptions, monobromination takes place in media III and IV, containing 40 and 10% water, respectively, and without pyridine The exceptions are 2,6-dimethylphenol and 2,4,6-trimethylphenol, which require the pyridine-containing medium II for quantitative bromination The other 2,6-dialkylsubstituted phenols investigated are brominated in medium III With the exceptions mentioned, phenol and alkylphenols with alkyl groups in one or two of the *ortho* and *para* positions, but without alkyl groups in the *meta* positions, are monobrominated in medium III Of the 23 phenols titrated, 12 could be brominated in medium III-2

Alkylphenols which also have alkyl groups in one or both of the *meta* positions are on the whole more reactive with bromine than the above-mentioned types of phenols Accordingly, a less bromination-promoting medium must generally be used for their monobromination Of 16 phenols investigated, 10 had to be titrated in medium IV-3, 2 in medium IV-2, 1 in medium III-3, 1 in medium III-2 and 2 in medium III-1 Of the 4 phenols which could not be titrated in medium IV, but for which a faster medium had to be used, 3 had tert butyl groups in one or both of the *meta* positions Thus, it appears that phenols with tert butyl groups in the *meta* positions are less reactive towards bromine than comparable phenols with for example methyl groups in these positions This fact is most likely associated with the steric requirements of the tert-butyl groups

One of the monobrominated phenol types, *viz* 2,4,6-trialkylphenols, consumes bromine in spite of the fact that no free *ortho* and *para* positions are present in the aromatic ring This is because this type of phenol forms paraquinoid bromocyclohexadienones on reaction with bromine in acetic acid–water medium [21] It is noteworthy that 2,4,6-tritert butylphenol did not react with bromine 2,6-Ditert butyl-4-methylphenol did react but not quantitatively We have here another example of a decreased reactivity caused by the presence of tert butyl groups

Full bromination of alkylphenols

In the full bromination of alkylphenols 2 or 3 hydrogen atoms in the aromatic ring are exchanged for bromine As seen from Table 3, a more bromination-promoting medium is necessary for full bromination than for monobromination. This is because the first entering bromine atom has a deactivating influence and makes the resulting bromophenol less reactive in the following electrophilic substitution reaction Accordingly, a pyridine-containing titration medium is nearly always necessary The only phenol which could be fully brominated in the pyridine-free medium III-3 was 3,4,5-trimethylphenol.

The reaction-inhibiting effect of tert butyl groups is also manifested in the full bromination of alkylphenols Thus, 3-tert butylphenol and 3,5-ditert butylphenol could not be quantitatively brominated in any of the titration media used in this work For 2,5-ditert butylphenol the most active medium (I) was required

Not all alkyl substitution patterns are represented in the material investigated However, it is believed that for alkylphenol types other than those in Table 2 a suitable titration medium can be selected with reasonable certainty on the basis of the information given

Table 4. Results of monobromination and full bromination of some activated phenols related to alkylphenols

Phenol	Monobromination: Titr medium	Weight (μg) Calc	Found	Bromine consumed, μeq	Error, %	Full bromination: Titr medium	Weight (μg) Calc.	Found	Bromine consumed, μeq	Error, %
2,2'-Bis(*p*-hydroxyphenyl) propane	III-2	570 7	547	10	−4 2	II-2	570 7	575	20	+0 7
		1141	1111	20	−2 7			569		−0 3
2-Hydroxybiphenyl	III-2	850 7	841	10	−1 1	II-2	850·7	862	20	+1 3
		1701	1698	20	−0 2			866		+1 8
4-Hydroxybiphenyl	*	—	—	—	—	II-2	850 7	828	20	−2 7
								823		−3 3
2,2'-Dihydroxybiphenyl	III-1	465 5	463	10	−0 5	II-2	465 5	476	20	+2·3
		931 0	950	20	+2 0			472		+1 4
4-Benzylphenol	*	—	—	—	—	II-2	920·8	902	20	−2 0
								903		−1 9
2,6-Dialkylphenol	†	—	—	—	—	§II-2	583 9	604	20	+3 4
								606		+3 8
2-Hydroxynaphthalene	III-2	720 3	721	10	+0·1	‡—	—	—	—	—
		1441	1433	20	−0 6					
2,7-Dihydroxynaphthalene	¶IV-3	800·3	826	10	+3 1	‡—	—	—	—	—
		1601	1615	20	+0 9					
8-Hydroxyquinoline	*—	—	—	—	—	II-2	725 3	728	20	+0 4
								724		+0 2

* Cannot be quantitatively monobrominated
† In medium III-2 approximately 2 moles of Br_2 are consumed per mol
§ Three moles of Br_2 are consumed per mole
‡ Cannot be quantitatively fully brominated
¶ One mole of Br_2 is consumed per mole

Bromination of some activated phenols related to alkylphenols

In Table 4 the titration results for some activated phenols have been summarized These results are not as uniform as for the alkylphenols in Table 2, where all the phenols tested could be titrated by the monobromination method and only 2 phenols out of 27 failed to respond to the full bromination method The phenols listed in Table 4 are more irregular in their reaction with bromine Thus, one third could not be monobrominated and the two hydroxynaphthalenes could not be fully brominated However, in every case either the monobromination or the full bromination method could be applied, which demonstrates the usefulness of having two bromination methods available.

Monobromination means in this instance that one bromine atom enters each ring containing a phenolic hydroxyl group, and full bromination that bromine enters all free positions (at least two) *ortho* and *para* to a phenolic hydroxyl group Exceptions to these rules are 2,7-dihydroxynaphthalene for which monobromination means that bromine enters only one of the rings, and 2,6-diallylphenol where a combination of substitution and addition takes place on full bromination

As for the alkylphenols, monobromination takes place in the pyridine-free media III and IV In the case of 2,7-dihydroxynaphthalene the values in the table refer to exchange of only one hydrogen atom for bromine It is possible to bring about an exchange of two hydrogen atoms by using the faster medium III-2 However, the results are not reported as they are only approximate

Several phenols cannot be quantitatively monobrominated, as mentioned previously In the case of 8-hydroxyquinoline this is probably due to the great reactivity of this phenol, which exerts an auto-catalytic effect on the bromination because of the presence of the pyridine ring Even in the slowest medium (IV-3) the bromine consumption exceeds that calculated for monobromination The monobromination of 4-hydroxybiphenyl fails because of the low reactivity of this compound in pyridine-free media 4-Benzylphenol has an approximate consumption of two equivalents of bromine per mole, but the results are somewhat low

2,6-Diallylphenol is in a unique position in that it contains two unsaturated alkyl groups to which bromine is added. In medium III-2 approximately 2 moles of bromine are consumed per mole We believe that this consumption is due to addition

For full bromination the pyridine-containing medium II-2 was used throughout From a substitution point of view 2,6-diallylphenol is monobrominated as it contains only one free ring position The results have nevertheless been put in the full bromination column since they correspond to a total consumption of 3 moles of bromine per mole The two hydroxynaphthalenes cannot be quantitatively fully brominated This is because the 3(6)-position is less reactive towards attack by electrophilic reagents [22]

DETERMINATION OF THE NUMBER OF FREE *ortho* AND *para* POSITIONS IN ALKYLPHENOLS

As shown by Table 3, monobromination takes place predominantly in pyridine-free media and full bromination in pyridine-containing media This makes it possible to estimate the number of free *ortho* and *para* positions on the basis of two coulometric bromination titrations Certain conclusions concerning the number of *meta* alkyl groups may also sometimes be drawn from the titration curves The new method constitutes a considerable simplification in comparison with existing methods[23] for the determination of the number of free *ortho* and *para* positions in phenols on the basis of a bromination titration Thus, about 500 μg of a phenol is monobrominated in medium III-2 and the same amount fully brominated in medium II-2 according to the procedure described in the experimental part The resulting titration curves are then inspected

Interpretation of the titration curves

The alkylphenols studied have been divided into four groups, denoted by A, B, C and D The division is made according to the number of free *ortho* and *para* positions Thus group A has 3, group B has 2, group C has 1 and group D has no free *ortho* and *para* positions Within each group a subdivision is made according to the number of *meta* positions occupied by alkyl groups The figure after the letter denotes this number Thus to group A_1 belong phenols with 3 free *ortho* and *para* positions and 1 *meta* alkyl group and to group C_2 belong phenols with 1 free *ortho* or *para* position and 2 *meta* alkyl groups The discussion of the test results will now be subdivided according to groups of alkylphenols (see also Table 3)

Group A The ratio of the titration times is 3 1, indicating that the phenol has 3 free *ortho* and *para* positions However, for *meta*-substituted phenols heavy tailing occurs and the ratio can be nearer to 3 2 This is because medium III-2 is too fast for the monobromination of this type of phenol If an additional titration in medium IV-3 is done, the correct number of free *ortho* and *para* positions can be ascertained From the appearance of the curve for titration in medium III-2, conclusions can thus be drawn concerning the presence (tailing) or absence of *meta*-alkyl groups, except for tert butyl groups

Group B For this group the ratio of the titration times is 2 1 which shows that two vacant *ortho* and *para* positions are present An exception is constituted by certain reactive B_2-phenols, for example those with an occupied *para* position In this case the titration curves tend to become distorted in both of the standard titration media as these are faster than those used for quantitative determination of these phenols Accordingly, the curves cannot always be interpreted and complementary titrations in media III-3 and IV-3, respectively, are necessary With medium III-2 it should be possible to discriminate between B_0-phenols on one hand and most B_1- and B_2-phenols on the other, on the basis of the titration curves

Group C There is no difficulty in the case of this group of phenols in confirming that only one of the *ortho* and *para* positions is vacant It is generally not possible to distinguish between the three subgroups as the appearance of the titration curves is rather similar However, certain possibilities seem to exist for identifying a C_2-phenol If the monobromination is performed in medium IV-3 instead of in III-2, the titration curves for C_0- and C_1-phenols are similar to the titration curve for the blank, while the only available C_2-phenol gives a normal titration curve

Group D Only type D_0 has been investigated, *i e*, phenols with all *ortho* and *para* positions occupied by alkyl groups but without alkyl groups in the *meta* positions In the standard media this type of phenol gives titration curves which cannot be distinguished from those given by certain C_0-phenols The erroneous conclusion that one vacant *ortho* or *para* position is present would accordingly be drawn However, for 2,4,6-tritert butylphenol correct information is obtained, as it does not consume bromine in either of the standard media

For those phenols which consume bromine in the standard media, an additional titration should be performed in medium III-3 We have found that reactive D_0-phenols give a curve with a gradual slope in the normally horizontal portion in this medium while interfering C_0-phenols generally give a normal titration curve

CONCLUSIONS

The coulometric bromination method described in this paper could be used for the quantitative determination of any of the alkylphenols in Table 2 Monobromination is always possible, and full bromination of phenols containing more than one free *ortho* and *para* position can generally also be achieved The only exception found is that of phenols with tert butyl groups in one or both of the *meta* positions, which are not quantitatively fully-brominated in any of the titration media used in this work. One alkylphenol with three vacant *ortho* and *para* positions can also be dibrominated, *viz* 3,5-dimethylphenol which contains two *meta*-alkyl groups and is monobrominated in a type IV medium For this type of phenol there exist accordingly three separate bromination methods for quantitative analysis

Some types of activated phenols other than those in Table 2, and mainly binuclear, showed a less regular reaction with bromine than the real alkylphenols Thus, in some cases either the monobromination or the full bromination failed However, in every instance one of the methods succeeded, thus permitting the quantitative determination of all the phenols investigated

The rapid method proposed for the determination of the number of free *ortho* and *para* positions in

alkylphenols should become a useful addition to existing methods for the structural investigation of phenols It gives a correct answer in most cases and also permits certain conclusions to be drawn concerning the number of *meta*-alkyl groups present

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IODOMETRIC DETERMINATION OF ASCORBIC ACID BY CONTROLLED POTENTIAL COULOMETRY

RONALD KARLSSON
Department of Analytical Chemistry, Chemical Center, University of Lund, S-220 07 Lund 7, Sweden

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Summary—An iodometric method for the determination of ascorbic acid has been devised The method is based on previously developed coulometric instrumentation The stability of different ascorbic acid solutions has been studied and the best conditions have been established Ascorbic acid has been determined in different kinds of samples but with the main interest on pharmaceutical preparations Special regard has also been paid to the other constituents in such samples, with respect to possible interferences The error of the coulometric method is about 0 1% and the time of an analysis is in the range 2–6 min

A large number of methods are proposed in the current literature for the determination of ascorbic acid (Vitamin C). Most are based on modifications of the method proposed by Tillmans *et al*,[1] where the ascorbic acid is allowed to react with 2,6-dichlorophenolindophenol in a slightly acid solution. This procedure is the official method in several countries for the determination of ascorbic acid in fruit and vegetable juices[2] and in pharmaceutical products.[3] Although it is an official method, it is not applicable to many pharmaceutical preparations, owing to interfering ions generally present in such products One of the more widely used colorimetric methods was developed by Roe and Kuether,[4] who oxidized ascorbic acid to dehydroascorbic acid and let the latter react with 2,4-dinitrophenylhydrazine to give a red colour, which was measured photometrically However, some other substances, such as 2,3-diketogulonic acid, react similarly. Schmall and co-workers[5,6] reacted ascorbic acid with diazotized 4-methoxy-2-nitroaniline in acid medium and measured the intense blue colour developed after addition of alkali Among other authors using diazotized compounds can be mentioned Wecks and Deutsch,[7] who used diazotized *p*-nitroaniline, and Hashmi *et al*,[8] who used diazotized *p*-aminobenzoic acid The latter method was specially worked out for pharmaceutical products

In general, the colorimetric methods suggested for the assay of ascorbic acid are rather time-consuming and many of them suffer from lack of colour stability and are applicable only in rather narrow ranges of concentration Together with the method of Tillmans, the methods involving iodine[9] have received the greatest attention. In the latter methods the following reaction between ascorbic acid and iodine is exploited

$$C_6H_8O_6 + I_2 \rightarrow C_6H_6O_6 + 2H^+ + 2I^-$$

Starch is generally used as indicator According to Stevens[10] the use of iodine has many advantages over other methods proposed The analysis is rapid and high accuracy is obtained The estimation of ascorbic acid by titration with iodine is in many countries an official method[11] for many pharmaceutical preparations. Rather serious drawbacks are that the titrations with iodine are restricted to use in relatively strongly acid solutions and the iodine reagent needs frequent standardization

In our laboratory we have already developed very accurate analytical methods using the iodide–iodine system and controlled-potential coulometry,[12–14] and an electroanalytical approach to the determination of ascorbic acid with iodine as an intermediate seemed interesting The use of controlled-potential coulometry for the determination of ascorbic acid has been proposed earlier by Santhanam and Krishnan,[15] who oxidized ascorbic acid directly at a platinum anode with a potential of 1 090 V *vs.* SCE The high oxidation potential used made the method unselective for ascorbic acid The times of analysis were up to one hour and the error in the range 15–100 mg was not better than ±0 7 mg

In the coulometric method presented in this paper, based on the controlled-potential apparatus developed earlier, iodine in a slight excess over the amount of ascorbic acid to be determined is generated at +300 mV *vs* SCE and after addition of the sample the remainder of the iodine is reduced at 0 mV *vs* SCE and the result is directly obtained on an electronic integrator The times of analysis lie in the range 2–6 min and the error is about ±0·1%

EXPERIMENTAL

Apparatus

The controlled-potential coulometric circuit and the electrolysis cell have been described in detail earlier[13,16] The electrolyte in the counter-electrode compartment and bridge compartment of the electrolysis cell was 2*M* sodium sulphate and in the working electrode compartment 1*M* sodium sulphate/1*M* sodium iodide The pH in the working-electrode compartment was adjusted with acetic acid

Reagents

Extraction solution An 8% solution of glacial acetic acid was prepared for extraction of ascorbic acid from the samples to be analysed

Standard ascorbic acid solutions Prepared from *pro analysi* quality ascorbic acid (E Merck, Darmstadt) The solutions were prepared immediately before use either with doubly-distilled and oxygen-free water or with an oxygen-free solution of 8% acetic acid

Preparation of samples

(*a*) Samples from the standard ascorbic acid solutions were transferred directly to the cell with an Agla micrometer syringe

(*b*) Samples from juices, pharmaceutical solutions and other liquids were either transferred directly to the cell or diluted with the acetic acid extraction solution in carefully calibrated standard flasks Homogeneous and not too viscous samples were generally analysed directly without dilution, to avoid air-contamination

(*c*) Samples from solid products, such as tablets, were first powdered in a mortar, then shaken with the acetic acid extraction solution, filtered, transferred to a standard flask and made up to the mark

Procedure

The compartments of the electrolysis cell were filled with the appropriate electrolytes The solution in the working compartment was continuously deaerated with nitrogen at a flow-rate of 10–20 ml/min Any iodine present in the compartment was reduced at ± 0 mV *vs* SCE until a stable residual current was reached, generally not exceeding 5 μA Then iodine in excess relative to the amount of ascorbic acid to be determined was generated at 300 mV *vs* SCE and the sample was added Then the iodine not consumed in the reaction with ascorbic acid was reduced until the earlier residual current value was reached

RESULTS AND DISCUSSION

The redox potential values for a solution containing ascorbic acid and dehydroascorbic acid have been calculated by many authors[17] and there are rather large discrepancies in the literature According to Rao and Rao[18] the potential varies from -0.012 to 0.326 V with variation of pH from 8.67 to 1.05, and our own determinations give a value of about 0.25 V at pH 3 This high reducing power makes ascorbic acid suitable for reduction of a weak oxidizing agent, such as iodine The redox potential for a solution containing the iodine–iodide couple is about 0.54 V, calculated for the reaction

$$I_3^- + 2e \rightarrow 3I^-$$

The reaction between ascorbic acid and iodine is practically instantaneous and only a very slight excess of iodine needs to be generated, the remainder can be reduced at once In Table 1 some of the results of these measurements are collected As it takes only a few seconds to generate the amount of iodine required, an excess of about 25% is generally produced, avoiding the risk of incomplete reaction

When cloudy or viscous samples are analysed, a relatively large excess of iodine is generated and up to 10 min are allowed to pass before the reduction is started This will eliminate any errors caused by decreased reaction rate between iodine and ascorbic acid. However, a 0.1–0.5% correction must be applied when the excess of iodine is not reduced immediately This is due to small losses of iodine caused by adsorption on the walls and electrodes, by transport through the filter and by volatilization. Figure 1 shows the results from a series of measurements when 5.00 μmole of iodine were generated in each determination and 1, 2, 3, 4, 5 and 10 min were allowed to elapse before the start of reduction The measurements were repeated three times and the results agreed within a few per cent The linearity is rather good and the losses are very small, which facilitates the corrections It also appears that the total time of an analysis increases by more than the waiting period. This is due to the fact that some of the adsorbed iodine slowly goes back into solution and then can be reduced, resulting in a prolonged electrolysis time The time for a complete analysis was measured from the start of oxidation until a residual current of 5 μA was reached

Table 1 Recovery of ascorbic acid, with different excesses of iodine added

Amount of iodine generated, μmole	Amount of ascorbic acid, μmole	
	added	found
4.00	2.07	2.07
3.00	2.07	2.07
2.50	2.07	2.07
2.15	2.07	2.07
2.10	2.07	2.04
2.10*	2.07	2.07

* Allowed to stand for 15 sec before reduction

Solutions of ascorbic acid suffer from a lack of stability,[18] and in earlier investigations it was difficult to monitor this instability and control it during a longer period, owing to the need for extensive standardization of the titration agents and calibration solutions, especially with titration methods employing iodine In the present iodometric investigation, however, this problem is overcome by the *in situ* generation and back-reduction procedures used for the iodine

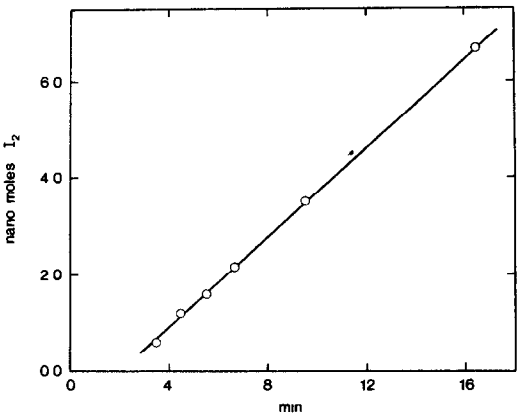

Fig 1 Loss of iodine from the electrolysis compartment of the cell as a function of the total time of analysis

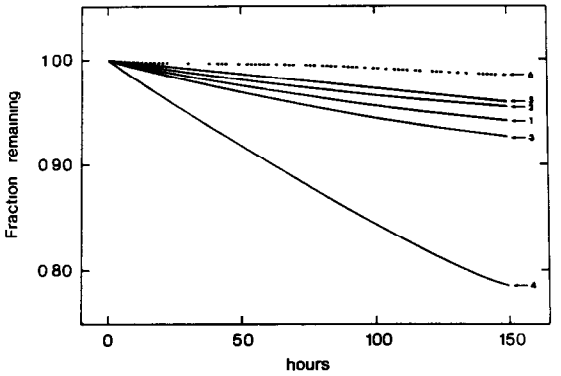

Fig 2 Stability of ascorbic acid in different aqueous solutions (1) 0·1*M* ascorbic acid in 0·05*M* oxalic acid (2) 0·1*M* ascorbic acid in 0·05*M* sulphuric acid (3) 0·1*M* ascorbic acid (4) 0·01*M* ascorbic acid (5) 0·1*M* ascorbic acid in an oxygen-free solution (6) 0·1*M* ascorbic acid in 0·05*M* oxalic acid/0·05*M* sulphuric acid, oxygen-free

Five different ascorbic acid solutions were prepared and transferred to 25-ml standard flasks, two flasks of each solution being made up All solutions were prepared with doubly-distilled water but, except for one of the solutions, which was deaerated with nitrogen, no precautions for excluding air were taken in the preparation During the experiment all the solutions were allowed to stand on the laboratory bench, exposed to light Samples were taken from each flask at intervals of 10–15 hr The results are collected in Fig 2 The curves are based on a least-squares treatment of the values obtained It is clearly shown (curves 1–5) that the deaerated solution (No 5) kept its stability best and that the deterioration is also much diminished by addition of sulphuric acid (No 2)

The use of oxalic acid, which is often recommended[19] for protecting ascorbic acid against oxidation, also shows a slight improvement of stability (No 1) in comparison with the untreated solutions (Nos 3 and 4) On the whole the results show good agreement with the results obtained in similar experiments by Rao and Rao [18] The conclusions are that oxygen-free solutions are a necessity and that the solutions should be acidic and concentrated Figure 2 also shows a curve (6) for the stability of an ascorbic acid solution prepared in accordance with these conclusions, fully confirming their validity

To test the coulometric method with respect to time of analysis, working range and accuracy, a series of standard solutions of ascorbic acid was prepared. Table 2 gives a schematic representation of the results All samples were added with an Agla micrometer syringe and were in the range 0·010–0·500 ml The working range can be expanded in both directions but at the price of increased time of analysis or lower accuracy, as the case may be

Table 2 Determination of ascorbic acid in pure standard solutions

Added amount of ascorbic acid, *μmole*	Error, %	Approx times of analyses,* *min*
5–50	0·1–0·05	5–6
0·5–5	0·2–0·1	4–5
0·1–0·5	0·3–0·2	3·5–4
0·01–0·1	2–0·3	2·0–3

* The times may vary somewhat depending on the excess of iodine generated

Table 3 Determination of ascorbic acid in some citrus fruit juices

Kind of juice	Min amounts of ascorbic acid* *mg/100 ml*	Added amounts of ascorbic acid *mg/100 ml*	Found *mg/100ml*	
			filtered	unfiltered
Orange I	32	–	36·0	36·1
Orange II	35	–	44·2	44·0
	35	–	40·9	–
Orange III	35	19·7	61·0	–
	35	39·5	80·2	81·0
Grapefruit	50	–	55·4	55·2
	25	–	31·1	–
Lemon	25	39·5	70·9	–

* According to the manufacturers

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An iodometric determination of ascorbic acid in citrus fruit juices has been shown to be the most reliable method, since these contain, according to Tauber and Kleiner,[20] no substance which will interfere in such an analysis Hence it seemed attractive to apply the present method to some commercially available juices Samples (0·1–1·0 ml) were taken both directly from the packs and after filtration of the juices The results agreed well, as can be seen from Table 3 The blank values and the times of analysis tended to increase continually when the samples were unfiltered The cell solution must then be changed after a certain number of determinations if uncertain results are to be avoided

If possible, the juices were not diluted, in order to avoid exposure to air The results had an average deviation of about 0·1% from the mean of three values

The determination of ascorbic acid in pharmaceutical preparations has without doubt received most attention Although there are several official methods available, most of them are not applicable to many pharmaceutical products, owing to presence of different kinds of interfering substances Therefore we considered it of interest to test our method on some pharmaceutical products, and chose a group of common multivitamin preparations

Table 4 gives the values for the determination of ascorbic acid in six different preparations Except for the preparation "ABCDin" which is a syrup and was analysed directly, the other preparations were treated according to method (*c*) (see *Preparation of samples*) We always used at least 5–10 tablets of each sample preparation in order to obtain relatively good sampling as individual tablets vary in weight by several per cent

From Table 4 it can be seen that there is good agreement between the results obtained by the official methods of analysis[21,22] and by our method No notable interferences were observed, but some investigation was made of the best method for analysis of

Table 4 Determination of ascorbic acid in some pharmaceutical vitamin preparations

Type*	Number of tablets prepared for each detn	Ascorbic acid found, *mg/tablet*	
		by official methods	by present method
IDO-C(1)	5	516	522 5
Bascoplex(2)	5	301	300·6
Minorplex N(3)	10	43 3	42 8
Multiplex(4)	5	64 1	63 6
Multiplex Comp N(5)	5	62 4	62 6
ABCDin(6)	syrup	573†	574 3†

* All preparations from Ferrosan AB, Sweden
† mg/100 ml
(1) Vitamin C
(2) Vitamins B($B_1B_2B_6$), C. Ca-panthothenate and nicotinamide
(3) Vitamins A, B($B_1B_2B_6$), C and D, Ca-panthothenate and nicotinamide
(4) Vitamins A, B($B_1B_2B_6$), C, D and E, Ca-panthothenate and nicotinamide
(5) Vitamins A, B($B_1B_2B_6$), C, D and E, Ca-panthothenate, nicotinamide and Fe^{2+} (ferrofumarate)
(6) Vitamins A, B(B_1B_2), C, D and nicotinamide

"IDO-C" The only active ingredient in this product is the ascorbic acid, but this is present in such a large amount as about 500 mg in each tablet The samples must generally be diluted in analysis of these tablets, whichever method is to be used Because of the sensitivity of ascorbic acid solutions to oxygen, erroneous results can be obtained, owing to oxygen in the dilution medium. The use of acetic acid solution for dilution preserves the ascorbic acid concentration somewhat, but according to Ponting[23] a loss of more than 30% in concentration is observed within 24 hr In an oxalic acid solution, however, the concentration decreased by only 2 8% during the same time

We made three different sample preparations from IDO-C, which together with the results obtained are shown in Table 5 The effect of oxygen is again confirmed No effect of the oxalic acid was observed, because of the short time allowed to elapse before the analysis was done

Much effort has been made in the pharmaceutical industry to prepare stable ascorbic acid syrups, and a comprehensive review has been given by Hashmi [22] We decided to study the stability of the syrup "ABC-Din" From two identical well-filled flasks of the syrup, samples were taken every fifth day during a period of 35 days One sample was placed in a refrigerator at 3°, while the other was allowed to stay on the laboratory bench, exposed to light No special

Table 5 Effect of different solutions on the recovery of ascorbic acid from a vitamin preparation (IDO-C)

Vitamin sample	Sample solution	Stored before analysis, *hr*	Ascorbic acid found, *mg/tablet*
I	8% acetic acid, oxygen-free + 0 5% oxalic acid	1 0	522
II	8% acetic acid, oxygen-free	1 0	522
III	8% acetic acid	1 0	490

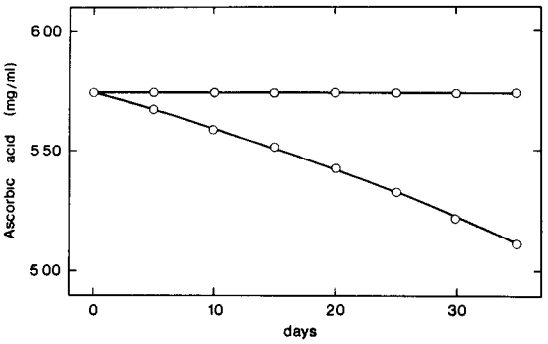

Fig 3 Stability of ascorbic acid in a pharmaceutical syrup (ABCDin) Upper curve stored in a refrigerator at 3°C Lower curve stored on a laboratory bench at room temperature

precautions to exclude air were taken for any of the samples The results are collected in Fig 3

In most of the existing methods for the assay of ascorbic acid in pharmaceutical products, special time-consuming procedures must be undertaken to allow for each kind of substance which can interfere The results in Table 4 indicated that no components of these samples would interfere but in order to be quite sure we made a critical study of nearly all the constituents present in these preparations which could possibly interfere, and which have caused trouble for many other investigators

The experiments were divided into two parts. In the first set the constituents were analysed alone and in the second together with a known amount of ascorbic acid None of the constituents tested caused any observable interference. The lower limit for the amount of added substance in each analysis was set at about 1 mg The following substances were studied raffinose, lactose, maltose, sucrose, fructose, galactose, mannose, xylose, mannitol, nicotinamide, calcium panthothenate, retinol, thiamine, riboflavin, pyridoxine, cyanocobalamin, calciferol, tocopherol, folic acid and biotine There are also some other constituents in the preparations which we have not extensively tested However, analyses on the whole preparations but with ascorbic acid removed did not indicate any interferences

Several ways have been outlined for the determination of ascorbic acid in the presence of copper and iron salts Chapman and co-workers[24] have examined the influence of copper and iron salts in eight different frequently used methods and only one proved to be quite satisfactory As some salts of copper and iron may also be expected to interfere with our method it was necessary to find ways to prevent interference from these salts According to Hume and Kolthoff[25] sodium citrate forms a stable complex with copper We performed some experiments in which a citrate solution was added to the cell just before the analysis of a sample containing ascorbic acid and cupric sulphate, and for small amounts of copper the method worked well However, the use of EDTA instead of citrate as a complexing agent was found to work excellently in all tests performed Ferrous iron, which

occurs in many pharmaceutical preparations, does not interfere at all, which can be seen from the analysis of the preparation "Multiplex Comp N", which contains about 15 mg of Fe^{2+} in each tablet Ferrous iron is, however, easily oxidized to ferric iron which reacts with iodide and also, more seriously, with ascorbic acid In order to prevent these reactions the addition of fluoride or EDTA for complexation of the ferric ions has proved satisfactory

CONCLUSION

A rapid and very accurate method has been devised for the assay of ascorbic acid The method can be used either in routine analyses or for the analysis of completely unknown samples without any special preparations, because the analysis current can be reversed during a determination and an additional amount of iodine generated if a sample contains more ascorbic acid than expected Coloured or cloudy samples present no problems We have not found any interfering substance, in the different samples analysed, of which the effect could not easily be eliminated

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ANALYSIS OF A MIXTURE OF A KNOWN AND AN UNKNOWN WEAK ACID BY TITRATION TO A PRESET pH

ARI IVASKA
Department of Analytical Chemistry Åbo Akademi Abo 50, Finland

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Summary—The preset-pH titration method has been used to indicate the presence of a second acid when the titration curve (pH *vs* volume of added titrant) seems to indicate only one acid By use of the method even small amounts of propionic acid can be detected in an acetic acid solution despite the small value of $\Delta \log K^{H}_{HA} = 0.18$ Binary mixtures of acids may be analysed when one acid is known, and $\log K^{H}_{HA}$ for the unknown acid may be found Acetic acid, as the known acid, has been determined together with hydrochloric, mandelic, hydroxyacetic or boric acid or ammonium ion, with an error of about 1% The method can be used in some cases for titration of ternary mixtures of one known and two unknown acids Only the sum of the unknown acids can then be determined together with the known acid

A common method of analysing aqueous solutions of acids is to titrate them potentiometrically with a strong base The usual titration curve, pH *vs* volume of added base, is then used to determine the number of the acids and their concentrations A solution containing only one acid gives a titration curve with one potential jump. It should be sufficiently high to be used for accurate determination of the concentration of the acid If several acids are present and the differences of their stability constants are larger than four orders of magnitude separate potential jumps for the acids can be obtained. In that case the determination of the composition of the mixture is a simple task When the dissociation stages of moderately strong acids overlap each other, only one potential jump corresponding to the total sum of the acids can be obtained and the evaluation of the concentrations of the different acids is difficult If the difference in the stability constants of two acids is less than one log unit the curve closely resembles the curve for only one acid In that case it is impossible to tell from the course of the titration curve (pH *vs* added volume of titrant) whether the solution contains only one acid or several of almost equal strength

Frisque and Meloche[1] give a method for potentiometric analysis of mixtures of two acids with overlapping dissociation steps Their paper, published in 1954, has unfortunately received too little attention Recently new methods have been developed by Purdie *et al*,[2] Ingman *et al*,[3] Kankare[4] and Ivaska[5] These papers deal with solutions containing two known weak acids The mixtures titrated by Kankare[4] are rather complicated He has for example, achieved reasonable accuracy when determining the composition of a mixture of tartaric and citric acid, a mixture containing five dissociation steps In all five methods mentioned, the acids to be determined are assumed to be known and their stability constants should be known quite accurately In one of his methods Kankare[4] uses the degree of deprotonation instead of the stability constant Frisque and Meloche,[1] Purdie *et al*,[2] Kankare[4] and Ivaska[5] have determined the stability constants from pure solutions of the acids Ingman *et al*[3] have titrated a known mixture of the acids to be analysed and determined the stability constants from these titration data

An analyst, however, quite often has to determine the composition of a mixture of unknown acids He does not know the number of acids or he might know that the solution contains one known and one or several unknown acids and he has to make a quantitative analysis for the known acid in the presence of the other acids This problem arises when he has to test the purity or make an analysis of an industrial product which can contain other acids as by-products from the manufacturing chemical process

The purpose of this paper is to show how the presence of a second acid can be detected though the form of the usual titration curve indicates only one acid The determination of the composition of a binary mixture of weak acids when one of them is known is also discussed

INDICATING THE PRESENCE OF A SECOND ACID

The theory for the method described in this paper has been derived assuming one acid to be known The preset-pH titration method[6] is used in the formulation of the theory

A weak acid HA with initial volume V_0 and mixed stability constant K^{H}_{HA} is titrated with a strong base of concentration C_{OH} The volume of base added to give the preset pH is V and its consumption at the

equivalence point V_{eq} The following equation is valid if the titration is performed to a preset pH [6]

$$V_{eq} = B\ V + A \quad (1)$$

where

$$B = \{H\}K^{H}_{HA} + \frac{1}{C_{OH}}([H] - [OH])(1 + \{H\}K^{H}_{HA}) + 1 \quad (2)$$

$$A = \frac{V_0}{C_{OH}}([H] - [OH])(1 + \{H\}K^{H}_{HA}) \quad (3)$$

The constants B and A can be calculated in advance for any pH

If the solution contains only one, known, acid the value of V_{eq} calculated from different pH values should be constant. Different values of V_{eq} for different pH values indicate the presence of one or more other acids.

Let us consider the case with only one unknown acid *If the unknown acid is stronger than the known one the calculated value of V_{eq} decreases with increasing preset pH and a weaker unknown acid results in increasing values of V_{eq} with increasing preset pH* With the stronger unknown acid V is larger than it would be for only one acid because part of the titrant has been consumed by the stronger acid When the titration is performed to a higher pH the value of V is again larger than it should be but now the proportion of the stronger acid is less than at the lower pH, thus resulting in a decrease in V_{eq} It should be noted that the proportion of V consumed by the known acid always gives constant V_{eq}. With a weaker unknown acid V is again larger than it should be but with increasing pH the proportion of the unknown acid in V increases, resulting in an increase in V_{eq}. This deduction is verified by the following example. Data from a titration of a mixture of acetic acid (HAc) and hydroxyacetic acid (HOHAc) are given in Table 1 The titration is performed to pH 4 200, 4 600 and 5 200 These values have been arbitrarily chosen to cover a major part of the acetic acid titration In the first case (*a*) in Table 1 acetic acid is regarded as the known acid The constants B and A are calculated for log $K^{H}_{HA} = 4\,649$ [5] In the second case (*b*) it is assumed that hydroxyacetic acid is known The values of B and A are calculated for log $K^{H}_{HA} = 3\,719$.[5] In Table 1 titrations of mixtures of acetic acid and propionic acid (HPr), (*c*) and (*d*), are included in order to demonstrate that the method can also be used to indicate the presence of an acid with almost equal strength, Δ log $K^{H}_{HA} = 0{\cdot}180$ [3] In these two titrations (*c*) and (*d*) it is assumed that acetic acid is known

Table 1 Titration of binary mixtures of acids with a strong base Temperature = 25° and μ = 0 1 (KCl)

Acetic and hydroxyacetic acids
V_0 = 52 0 *ml* C_{OH} = 0·09821*M*
Theoretical $V_{eq_{HAc}}$ = 2 66 *ml* $V_{eq_{HOHAc}}$ = 9 37 *ml*

	(*a*) HAc known log K^{H}_{HA} = 4 649				(*b*) HOHAc known log K^{H}_{HA} = 3 719		
pH	V, *ml*	B	A, *ml*	V_{eq}, *ml*	B	A, *ml*	V_{eq}, *ml*
4 200	7 685	3 815	0 159	29 477	1 331	0 056	10·285
4 600	9 505	2 120	0 035	20·186	1 132	0 019	10·777
5 200	11 125	1 281	0 005	14 256	1 033	0 004	11 496

Acetic and propionic acids, acetic known

	(*c*) V_0 = 60·0 *ml* C_{OH} = 0 09960*M*				(*d*) 61 0 *ml* 0 09960*M*		
Theoretical	$V_{eq_{HAc}}$ = 4 39 *ml* $V_{eq_{HPr}}$ = 6 30 *ml*				10·98 *ml* 1 05 *ml*		
pH	V, *ml*	B	A, *ml*	V_{eq}, *ml*	V, *ml*	A, *ml*	V_{eq}, *ml*
4 200	2 465	3 815	0 181	9 585	3 03	0 184	11 743
4 600	4 67	2 120	0·040	9 940	5 525	0 041	11 754
5 200	8 02	1 281	0·006	10 280	9 225	0 006	11 823

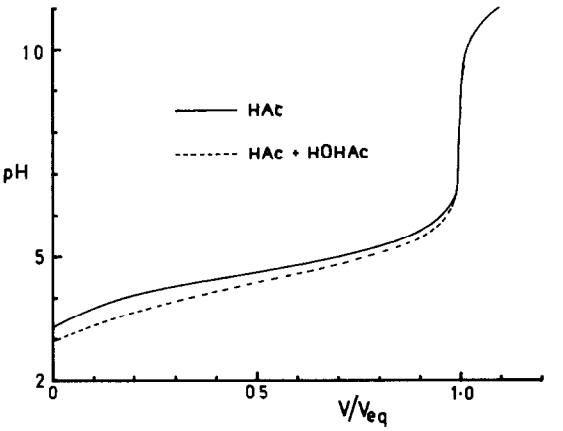

Fig 1 The curve of pH as a function of the titration ratio, V/V_{eq}, for titrations of acetic acid (HAc) and a mixture of acetic acid and hydroxyacetic acid (HOHAc)

As can be seen from Table 1 the presence of a second acid can be indicated by using the method of preset pH titration. Even in case (*d*) the presence of a small amount of propionic acid could be verified The usefulness of the method is obvious when studying the whole titration curves plotted in Fig. 1. These curves are of the HOHAc–HAc titration given in Table 1 and of a titration of HAc alone The curves for the HAc–HPr titrations given in Table 1 coincide with the HAc curve with the scale used On the basis of these curves it is quite difficult to tell whether the solutions contain several acids or acetic acid alone. These curves have been normalized so that the pH is plotted as a function of the titration ratio, V/V_{eq}

A constant value of V_{eq}, or only small variations in it, may be obtained if a ternary mixture of weak acids is titrated, with one unknown acid stronger and one weaker than the known acid, but the unknown acids must have suitable values of stability constants and concentrations in order to give a constant V_{eq} This is possible in theory but quite rare in practice

DETERMINATION OF THE COMPOSITION OF BINARY MIXTURES OF WEAK ACIDS AND OF log K^{H}_{HA} OF THE SECOND ACID

A weak acid HA_I is titrated with a strong base in the presence of an unknown weak acid HA_{II}. The

equivalence volumes are denoted by V_{eq_I} and $V_{eq_{II}}$. The volume of added base V can be considered as the sum of two volumes, V_I and V_{II}, where V_I denotes the volume of added base consumed by the known acid HA_I and V_{II} that consumed by the unknown acid HA_{II}. If the stability constants of the acids do not differ greatly from each other, only the sum of the acids, denoted by $V_{eq_{tot}}$, can be obtained from the titration curve. When the titration is performed to a preset pH, denoted by $(pH)_a$, V_a is the volume giving it, the following equations can be written:

$$V_{eq_I} = B_{Ia}\ V_{Ia} + A_{Ia} \quad (4)$$

$$V_{eq_{II}} = B_{IIa}\ V_{IIa} \quad (5)$$

$$V_{eq_{tot}} = V_{eq_I} + V_{eq_{II}} \quad (6)$$

$$V_a = V_{Ia} + V_{IIa} \quad (7)$$

It should be noted that equation (5) does not have the term A [see equation (3)]. This is because it includes V_0, which has already been taken into account in equation (4) in the term A_{Ia}.

Equations (4), (5) and (7) can be rewritten for other pH values, *e.g.* $(pH)_b$ and $(pH)_c$. The difference between the two V_{eq} values calculated according to equation (1) at $(pH)_a$ and $(pH)_b$ by assuming the presence of only HA_I is denoted by C_{a-b} and can be expressed as follows:

$$C_{a-b} = B_{Ia}\ V_a + A_{Ia} - (B_{Ib}\ V_b + A_{Ib}) \quad (8)$$

By inserting equation (7) into (8) and using equation (4) [which gives the same V_{eq_I} at $(pH)_a$ and $(pH)_b$] equation (8) is reduced to:

$$C_{a-b} = B_{Ia}\ V_{IIa} - B_{Ib}\ V_{IIb} \quad (9)$$

V_{IIa} and V_{IIb} can be solved from equation (5) written for $(pH)_a$ and $(pH)_b$. After insertion of these terms into equation (9), $V_{eq_{II}}$ can be calculated:

$$V_{eq_{II}} = \frac{C_{a-b}}{\frac{B_{Ia}}{B_{IIa}} - \frac{B_{Ib}}{B_{IIb}}} \quad (10)$$

With this $V_{eq_{II}}$ the value of V_{IIc} at another preset $(pH)_c$ can be calculated from equation (5) and V_{Ic} and V_{eq_I} are then obtained by using equations (7) and (4). By assuming different values for $K^H_{HA_{II}}$, different values of $V_{eq_{II}}$, V_{IIc}, V_{Ic} and V_{eq_I} are obtained. The correct value of $K^H_{HA_{II}}$ gives the sum $(V_{eq_I} + V_{eq_{II}})$ equal to the value obtained for $V_{eq_{tot}}$, which can be determined directly from the potential jump or, with the Gran method,[7] from points after the total equivalence point. The Ingman and Still method[8] can also be used by applying it to the points in the vicinity of the potential jump and assuming the presence of only the known acid. The value of V_{eq_I} can naturally also be calculated either at $(pH)_a$ or $(pH)_b$. By use of a third preset pH value $(pH)_c$ more points on the titration curve can be used to evaluate the result.

The method is demonstrated in Table 2, using the HOHAc–HAc titration from Table 1. It is first assumed that acetic acid is known. When different values are assigned to $K^H_{HA_{II}}$, different values for $V_{eq_{II}}$ and V_{eq_I} are obtained. The term $(V_{eq_I} + V_{eq_{II}})$ is then plotted as a function of $\log K^H_{HA_{II}}$ in Fig. 2. A line corresponding to the value of $V_{eq_{tot}}$, determined with points near the potential jump using the method of Ingman and Still,[8] is also drawn in Fig. 2. The point of intersection of these lines gives the correct value for $\log K^H_{HA_{II}}$. The equivalence volumes V_{eq_I} and $V_{eq_{II}}$ are then calculated with this value, $\log K^H_{HA_{II}} = 3.718$, which can be used as an aid when identifying the unknown acid. A similar procedure is used when hydroxyacetic acid is assumed to be the known acid. The value obtained, $\log K^H_{HA_{II}} = 4.650$, can be used as an aid to identify the unknown acid as acetic acid. In both of these cases the equivalence volume of the known acid as well as of the unknown acid is determined with reasonable accuracy, as can be seen from Table 2.

Table 2. Titration of a mixture of acetic acid (HAc) and hydroxyacetic acid (HOHAc). Evaluation of the titration data given in Table 1.

$V_{eq_{tot}} = 12.014$ ml
$(pH)_a = 4.200$ $(pH)_b = 5.200$ $(pH)_c = 4.600$
$V_a = 7.685$ ml $V_b = 11.125$ ml $V_c = 9.505$ ml
Theoretical $V_{eq_{HAc}} = 2.66$ ml $V_{eq_{HOHAc}} = 9.37$ ml

HAc known
$C_{a-b} = 15.221$ ml

$\log K^H_{HA_{II}}$	V_{eq_I}, ml	$V_{eq_{II}}$, ml	$V_{eq_I} + V_{eq_{II}}$, ml
3.70	9.200	2.868	12.068
3.73	9.464	2.512	11.976
3.75	9.654	2.258	11.912
3.718	9.356	2.658	12.014
Error, %	−0.1	±0.0	

HOHAc known
$C_{a-b} = -1.211$ ml

$\log K^H_{HA_{II}}$	V_{eq_I}, ml	$V_{eq_{II}}$, ml	$V_{eq_I} + V_{eq_{II}}$, ml
4.650	2.648	9.367	12.014
Error, %	−0.4	±0.0	

In the method proposed, the titration of the mixture is divided into a known and an unknown part.

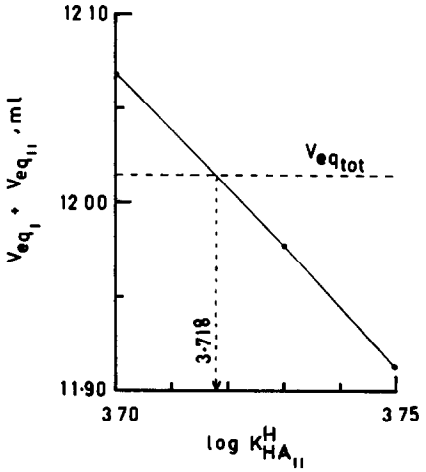

Fig. 2. Graphical determination of $\log K^H_{HA_{II}}$ according to the method presented in Table 2, acetic acid (HAc) being the known acid.

Table 3 Titration of binary mixtures of acids containing acetic acid (HAc) and as the second acid either hydrochloric acid (HCl), mandelic acid (HMa), hydroxyacetic acid (HOHAc), boric acid ($B(OH)_3$) or ammonium ion (NH_4^+) The experimental conditions are similar to those in Table 1 In all titrations acetic acid is the known acid, with equivalence volume V_{eqI}

	Theoretical V_{eqI}, ml	Theoretical V_{eqII}, ml	Found V_{eqI}, ml	Found V_{eqII}, ml	log $K^H_{HA_{II}}$
	$(pH)_a = 4\,200$		$(pH)_b = 5\,200$		$(pH)_c = 4\,600$
HAc + HCl	10 04	0 53	9 96	0 61	0–1
HAc + HMa	3 45	2 53	3 45	2 52	3 307
	0 62	4 44	0 64	4 44	3 305
HAc + HOHAc	9 88	0 95	9 89	0 93	3 684
	7 36	3 32	7 34	3 34	3 740
	$(pH)_a = 9\,100$		$(pH)_b = 9\,500$		$(pH)_c = 9\,300$
HAc + $B(OH)_3$	6 03	3 06	5 99	3 09	9 146
	7 36	5 58	7 38	5 55	9 157
HAc + NH_4^+	6 36	8 28	6 45	8 20	9 416
	5 22	4 38	5 25	4 35	9 407

The unknown part of the titration is described by the dissociation of a second acid The only information received from this part is the stability constant and concentration of the second acid by which the behaviour of the unknown part is described No specific reactions of the unknown anion have been used in determining the composition of the mixture In order to make an absolute identification of the unknown acid qualitative methods should be applied If the solution contains more than one unknown acid the result of an analysis obtained by the method proposed cannot be expected to be good This problem will be discussed later in this paper

The proposed method has been used to analyse mixtures of acetic acid with hydrochloric acid, mandelic acid, hydroxyacetic acid, boric acid or ammonium ion The results are summarized in Table 3 The error obtained is in general about 1% The total equivalence volume $V_{eq_{tot}}$ is determined in the first three cases by using the equation of Ingman and Still [8] In the last two cases the Gran method[7] is applied, using points after the total equivalence point

When the unknown acid is strong, as in the case of HAc + HCl in Table 3, the calculated value of $(V_{eqI} + V_{eqII})$ asymptotically reaches $V_{eq_{tot}}$ with decreasing values of log $K^H_{HA_{II}}$ The individual values of V_{eqI} and V_{eqII} remain almost unchanged at values of log $K^H_{HA_{II}}$ between 0 and 1

In all the cases mentioned so far the mixtures titrated have been binary, containing only one unknown acid An industrial product, however, may contain several acids as by-products In many cases it is not important to know the amounts of the individual by-products but only their total amount The method proposed can be used to solve this kind of problem in certain cases In Table 4 are given data for two titrations of ternary mixtures of acetic, hydroxyacetic and mandelic acids In these titrations it is assumed that acetic acid is known and the solution contains only "one" unknown acid

As can be seen from Table 4 the method is not accurate but can be used in cases where only approximate values are required The change in log $K^H_{HA_{II}}$ with the different molar ratios of mandelic acid and hydroxyacetic acid can also be seen in Table 4 A serious drawback of the method is that it can be used only if the known acid is either stronger or weaker than both the unknown acids One possible explanation for the poor results in Table 4 is that in the titration of the two unknown acids the term B_{IIa} in equation (5) does not follow equation (2)

Table 4 Titration of ternary mixtures of mandelic acid (HMa), hydroxyacetic acid (HOHAc) and acetic acid (HAc) with strong base Temperature 25°, $\mu = 0\,1$ (KCl)

$(pH)_a = 4\,200$ $(pH)_b = 5\,200$ $(pH)_c = 4\,600$

	(a)	(b)
$V_{eq_{HAc}}$	7 97 ml	7 99 ml
$V_{eq_{HOHAc}}$	2 60 ml } 8 95 ml	4 81 ml } 6 60 ml
$V_{eq_{HMa}}$	6 35 ml }	1 79 ml }
V_0	51 5 ml	51 9 ml
C_{OH}	0 09821 M	0 09821 M

Found	$V_{eq_{HAc}}$, ml	Error, %	$V_{eq_{HOHAc}} + V_{eq_{HMa}}$, ml	Error, %	log $K^H_{HA_{II}}$
(a)	8 05	+1 0	8 86	−1 0	3 423
(b)	8 08	+1 1	6 51	−1 4	3 604

DISCUSSION

A proper choice of the preset pH values is difficult In general they can be chosen arbitrarily It is, nevertheless, preferable that they should cover a pH-region where both acids have at least partly dissociated If the pH values are considerably lower than log K^H_{HA} of the known or unknown acid, equation (1) gives quite erroneous results [6] The values of $(pH)_a$ and $(pH)_b$ should not be so close to each other that the value of C_{a-b} is too small Considering the accuracy ($\pm 0\,005$ ml) with which the volume of base added has been measured in this work, a value of about 0 5 ml for C_{a-b} would give an error of 1% in calculating the value of V_{eqII} Greater values of C_{a-b} will decrease this error If for example $(pH)_b$ and $(pH)_c$ were interchanged in the titration in Table 2 where HOHAc is known, a value of $C_{a-b} = -0\,492$ ml would be obtained The optimum choice is for the preset pH values to cover the buffer region of the weaker acid, because both acids can then be determined accurately by means of equation (1) The equivalence volume of the known acid, V_{eqI}, is determined at $(pH)_c$ which should preferably be chosen near log $K^H_{HA_I}$ if the unknown acid is stronger than the known one [6] The values of V_{eqI} and V_{eqII} can even be calculated with a slide-rule but if fast results or more precise values are needed a small programmable calculator should be used

The choice of the preset pH values does influence the result If for example $(pH)_b$ and $(pH)_c$ were interchanged in the titrations given in Table 3, a slight change in the values of V_{eqI}, V_{eqII} and even in log $K^H_{HA_{II}}$ would be obtained Thus the results of an analysis performed by the proposed method should be considered critically This is especially true when acids

with almost equal strength are titrated In that case the value of $V_{eq_{tot}}$ should be determined very accurately because the calculated term $(V_{eqI} + V_{eqII})$ will not change very much with log $K^{H}_{HA_{II}}$ although the individual values of V_{eqI} and V_{eqII} are strongly dependent on it An incorrect $V_{eq_{tot}}$ will give erroneous V_{eqI}, V_{eqII} and log $K^{H}_{HA_{II}}$ When acids with moderately large $\Delta \log K^{H}_{HA}$ are titrated, *e g*, acetic acid and mandelic acid amongst the examples given in Table 3, the individual values of V_{eqI} and V_{eqII} vary slowly with log $K^{H}_{HA_{II}}$ and a very high degree of accuracy in $V_{eq_{tot}}$ is not required

It may be mentioned that when the data of the titrations given in Table 3 were processed by the method given earlier by the present author,[5] using the value obtained for log $K^{H}_{HA_{II}}$, only the result for the titration of acetic acid and hydrochloric acid could be improved, values $V_{eqI} = 10\,03$ *ml* and $V_{eqII} = 0{\cdot}58$ *ml* were obtained. In all other cases the accuracy remained the same or decreased

If the data from the titrations of acetic acid and propionic acid in Table 1 were processed by using the proposed method quite erroneous results would be obtained The titration of acids of almost equal strength requires a high standard of experimental data, as pointed out by Ingman *et al*[3]

It should be emphasized that the calibration of the pH-meter and the electrodes is of importance and should be done in the same way when determining the stability constants[9] or the values of B and A from a calibration titration[6] Even small changes in the stability constant of the known acid will influence the result and cause decreased accuracy

EXPERIMENTAL

A digital pH-meter (Orion Research 801, accurate to $\pm 0{\cdot}001$ pH units) was used with a Beckman glass electrode and a saturated calomel electrode The pH-meter was standardized against 0 05*M* potassium hydrogen phthalate (pH = 4 008 at 25°) Otherwise the experimental conditions and procedures were the same as described in earlier papers[5,6]

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POLAROGRAPHIC DETERMINATION OF CHLORHEXIDINE IN PHARMACEUTICAL PREPARATIONS

EINAR JACOBSEN and BJØRN GLYSETH

Department of Pharmacy, University of Oslo, Blindern, Oslo 3, Norway

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Summary—The electroreduction of chlorhexidine has been studied by d.c, a.c and pulse polarography. Polarograms of the drug recorded from ammonium acetate buffers exhibit a single well-defined wave. The current is diffusion-controlled and proportional to the concentration. The reduction wave is due to an irreversible 8-electron reduction of the four > C=NH groups in the molecule to amino groups. The drug is strongly adsorbed on the electrode surface over a considerable potential range. Hence, the drug can be determined by polarography in the presence of other weaker surfactants often present in pharmaceutical formulations. Procedures have been proposed for pulse-polarographic determination of the drug in antiseptic cream and liquids. The proposed method is simple and accurate and does not involve time-consuming separation of the drug from insoluble constituents present in the sample.

The antiseptic drug chlorhexidine [1-1′-hexamethylenebis(5-*p*-chlorophenylbiguanide)] is strongly bactericidal towards a large number of organisms and is incorporated in several formulations, in a range of concentrations.[1–4] Relatively large amounts of the drug may be determined by titration in non-aqueous medium, but smaller amounts are usually determined spectrophotometrically.[5,6] However, these methods involve time-consuming separations and are inconvenient for routine analysis. The present work was carried out in order to study the electroreduction of chlorhexidine in aqueous solutions and to investigate the application of pulse polarography to rapid determination of the drug in pharmaceuticals.

EXPERIMENTAL

Pharmaceutical-grade chlorhexidine diacetate was obtained from A/S Apothekernes Laboratorium for Specialpraeparater, Oslo. Stock solutions were prepared by dissolving the appropriate amount of the commercial product in distilled water. All other chemicals were reagent grade and were used without further purification. Hibitane antiseptic cream and liquid was obtained from Imperial Chemical Industries Ltd, Cheshire, Great Britain.

Polarograms (a.c. and d.c.) were recorded with a Metrohm/E 261 R Polarecord connected to a Metrohm E 393 a.c. modulator. An Ag/AgCl/saturated KCl electrode served as reference electrode and a tungsten electrode was employed as auxiliary electrode. The capillary characteristics of the dropping mercury electrode, measured in 0·1*M* ammonium acetate buffer at an applied potential of −1·58 V and a corrected mercury height of 48·2 cm, were $m = 1.973$ mg/sec and $t = 3.02$ sec. Dissolved oxygen was removed from the solutions by bubbling oxygen-free nitrogen through the cell for 10 min and passing it over the solution during the electrolysis.

Pulse polarograms were recorded with a PAR polarographic analyser, model 174, in the differential pulse mode. Cyclic voltammetry experiments were performed with a versatile solid-state instrument constructed in this laboratory following the design of Goolsby and Sawyer.[7] A Mosely 7030 AM *X–Y* recorder was used in conjunction with the instrument. A Metrohm E 410 hanging mercury drop was used as working electrode and a platinum coil served as auxiliary electrode. All experiments were performed at 25 ± 0·1°.

RESULTS AND DISCUSSION

Preliminary experiments showed that polarograms of chlorhexidine in acidic solutions exhibit only a poorly-defined wave, with half-wave potential close to the reduction wave of the supporting electrolyte, which is not useful for a polarographic determination of the drug. Better-defined waves were obtained from slightly alkaline media. Experiments showed, though, that the drug is only slightly soluble in ammonia buffers containing chloride and that catalytic waves are obtained with buffers containing nitrate. On the other hand, polarograms recorded for neutral and alkaline ammonium acetate buffers exhibit a single well-defined wave (Fig. 1). Hence, 0·1*M* ammonium acetate/ammonia buffer was chosen as supporting electrolyte.

The effect of pH on the reduction wave was investigated by recording d.c. polarograms of 0·1m*M* chlorhexidine in 0·1*M* ammonium acetate buffers of various pH values. As indicated in Table 1, the limiting current is independent of pH in the range 6·5–8·3 but decreases of higher pH values. The steepest wave was obtained at pH values above 9. Moreover, a better separation of the chlorhexidine wave from that of the supporting electrolyte was obtained at higher pH values. Consequently, 0·1*M* ammonium acetate/0·1*M* ammonia buffer at pH 9·3 was used as supporting electrolyte in the following experiments.

The effect of drop-time was investigated by recording polarograms of 0·1m*M* chlorhexidine in 0·1*M* ammonium acetate buffer at various heights of the mercury column. The constancy of the product $ih^{-1/2}$, where h is the height of the column after correction

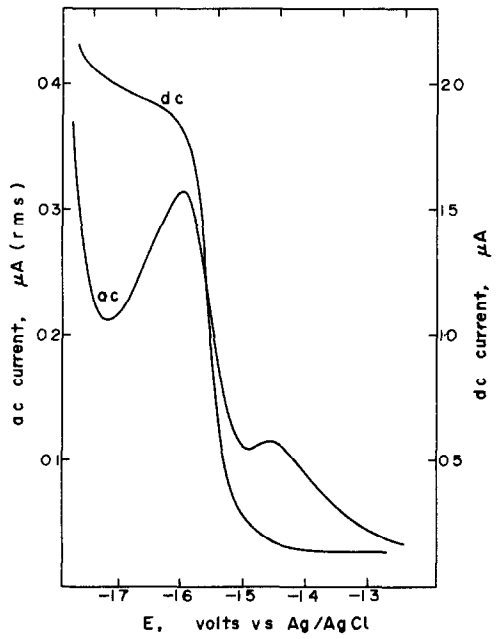


Fig 1 Polarograms (d c and a c) of 0 1 m*M* chlorhexidine in 0 1*M* ammonium acetate/ammonia buffer pH 9 3

for the "back pressure", and the temperature coefficient of 2 1% per degree (over the range 25–45°), indicate that the d c current was diffusion-controlled

The d c polarographic step was followed by an a c polarographic wave (Fig 1) The peak potential E_p, was about 40 mV more negative that the half-wave potential The appearance of an a c polarographic wave indicates that a fast electron-transfer step is involved in the electrode reaction On the other hand, the plots of log $i/(i_d-i)$ *vs* the potential show two almost straight lines with slopes of −45 and −28 mV per log unit, respectively, implying that the electron-transfer occurs in two steps and that the overall electrode reaction is irreversible

The a c polarogram (Fig 1) also exhibits a tensammetric wave with peak potential −1 45 V, indicating that the drug is strongly adsorbed on the electrode surface The adsorption was verified by drop-time measurements As shown in Fig 2 the presence of chlorhexidine causes a large decrease in the drop-time over a considerable potential range The drug is desorbed at −1 45 V (Fig 1) Further experiments showed that chlorhexidine is such a strong surfactant that it may even be used as a maximum suppressor

Table 1 Effect of pH on d c polarograms of 0 1 m*M* chlorhexidine diacetate in 0 1*M* ammonium acetate/ammonia buffers

pH	i_d, μA	$-E_{1/2}$, *V*	$-(E_{3/4}-E_{1/4})$, *V*
6 5	2 16	1 388	0 038
7 2	2 14	1 423	0 037
7 6	2 16	1 445	0 036
8 3	2 14	1 484	0 034
9 0	1 98	1 536	0 032
9 5	1 86	1 586	0 030

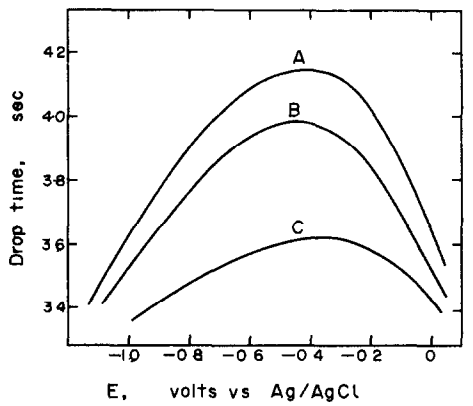


Fig 2 Electrocapillary curves of ammonium acetate buffer in the absence (curve *A*), and in the presence of 2 5 × 10^{-5}*M* chlorhexidine (curve *B*) and 10^{-4}*M* chlorhexidine (curve *C*)

in d c polarography The presence of only 0 0002% chlorhexidine was sufficient to suppress the maximum on the wave for 3 m*M* lead in 0 1*M* potassium chloride, of 0 5m*M* nitrazepam in 0 5*M* sulphuric acid and of 1m*M* nicotinamide in 2*M* sulphuric acid The surface activity of chlorhexidine causes a considerable foaming during deaeration of solutions containing higher concentrations of the drug, but experiments showed that the foaming can be avoided by the presence of a minute amount of n-octyl alcohol

The results in Table 2 indicate that the drug can be determined by d c polarography with a linear calibration over the concentration range from 5 × 10^{-6} to 2 × 10^{-4}*M* which corresponds to 3–125 μg/ml As the a c polarographic peak current is very small (Fig 1) it is not suitable for a practical determination of small amounts of the drug, but the differential pulse polarogram of the drug is very well

Table 2 Polarographic data for the reduction of various amounts of chlorhexidine in 0 1*M* ammonium acetate/ammonia buffer, pH 9 3

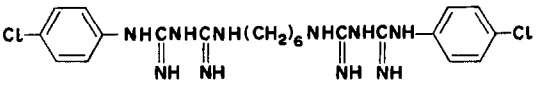
Direct current polarography Conc, *mM*	i_d, μA	$-E_{1/2}$, *V*	i_d/C, μA/*mM*
0 200	3 65	1 640	18 3
0 150	2 81	1 610	18 7
0 100	1 84	1 578	18 4
0 075	1 39	1 564	18 6
0 050	0 92	1 544	18 4
0 025	0 455	1 531	18 2
0 010	0 188	1 523	18 8
0 005	0 092	1 513	18 4
Differential pulse polarography (drop time 0 5 sec, pulse amplitude 50 mV and scan-rate 2 mV/sec)			
Conc, *mM*	i_p, μA	$-E_p$, *V*	i_p/C, μA/*mM*
0 0050	1 200	1 57	240
0 0025	0 590	1 58	236
0 0010	0 243	1 58	243
0 00075	0 185	1 57	247
0 00050	0 127	1 57	254

defined even at low concentrations and by this method the concentration range can be extended down to $5 \times 10^{-7} M$ (0 3 μg/ml)

As indicated in Table 2, the half-wave potential is shifted to more negative potentials with increasing concentration of the drug, whereas the pulse polarographic peak potential (which was obtained with a drop time of 0 5 sec) is independent of the concentration This effect is probably due to a slow adsorption of the reduction product on the electrode surface

Cyclic voltammetry experiments were performed at a hanging mercury drop electrode Reproducible results were obtained provided that the mercury drop was changed between each experiment No anodic peak resulting from reoxidation of the reduction product was observed at any scan-rate or any switching potential, indicating that the overall electrode reaction is irreversible As shown in Fig 3, the cathodic peak has the characteristic symmetrical shape of an adsorption wave If the cyclic sweep is repeated on the same drop the cathodic peak current decreases to a very small value, indicating that the reduction product is adsorbed on the electrode surface and that the adsorbed layer inhibits further electrode reaction Further experiments showed that the current function $i_p/Cv^{1/2}$ increased with increasing scan-rate and decreasing concentration, confirming that adsorption is involved in the electrode reaction [8]

Coulometric reductions of chlorhexidine at controlled potential were performed to determine the number of electrons involved in the overall electron-transfer reaction The experiments were carried out in the absence of air in a small electrolysis cell with a mercury pool as working electrode However, these experiments did not give reliable results, because the reduction potential of the drug is too close to that of the supporting electrolyte Hence, the drug could not be completely reduced without also reducing some of the supporting electrolyte The diffusion current constant, calculated from the d c current in the pH range 6 5–8, was $I = 11\,5$ μA l mmole^{-1} mg$^{-3/2}$ sec$^{1/2}$ Comparison of this value with that of other depolarizers with approximately the same molecular size indicates that 8 electrons are involved in the overall electron-transfer reaction The shift of the half-wave potential to more negative values with increasing pH (Table 1) suggests that hydrogen ions are consumed in the electrode reaction The structure of chlorhexidine is



Hence, the reduction wave of chlorhexidine is probably due to reduction of the four > C=NH groups to amino groups

$$> C{=}NH + 2H^+ + 2e \rightarrow > CH.NH_2$$

As stated above, the electron-transfer occurs in two steps, probably a slow one-electron step followed by a fast one-electron step giving rise to the a.c wave The four > C=NH groups are probably energetically equivalent and hence they are reduced at the same potential and only one polarographic wave is observed

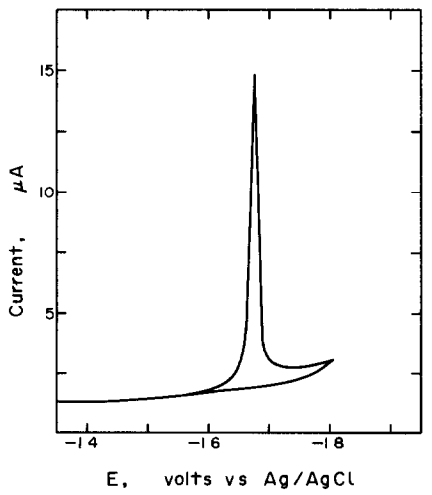


Fig 3 Cyclic voltammogram of 0 05mM chlorhexidine in ammonium acetate buffer, pH 9 3 Scan-rate 0 05 V/sec

ANALYTICAL APPLICATIONS

Because chlorhexidine is reduced at highly negative potentials, differential pulse polarography is the most useful method for the determination of the drug in the presence of other polarographically active substances It is also the most sensitive method

Experiments showed that the antiseptic liquid Hibitane, containing 5% chlorhexidine digluconate, can easily be determined by differential pulse polarography by simply diluting the sample with ammonium-acetate/ammonia buffer and recording the polarogram The commercial antiseptic liquid also contains, in addition to chlorhexidine, certain other surfactants which interfere at high concentrations of the liquid Hence, the sample must be diluted with buffer to give a final concentration below $10^{-4} M$

Recommended procedure

Transfer an aliquot of the sample, equivalent to 1–10 mg of chlorhexidine digluconate, to a 100-ml volumetric flask and add 25 ml of 0·4M ammonium acetate/ammonia buffer (pH 9 3) and one drop of n-octyl alcohol, and dilute to the mark with distilled water Shake the flask and transfer a suitable amount to a polarographic cell Displace dissolved oxygen with pure nitrogen and record a differential pulse polarogram with drop-time 0 5 sec, pulse amplitude 50 mV and scan-rate 2 mV/sec at a starting potential of −1 3 V Measure the peak-current and determine the amount of chlorhexidine by the standard addition method

The amount of chlorhexidine digluconate in Hibitane antiseptic liquid (declared amount 5%) was determined by the procedure above Four determinations gave the results 4 98, 4 94, 4 98 and 5 14%

Further experiments showed that chlorhexidine can be determined in antiseptic cream by almost the same procedure and without any time-consuming separation from the fatty constituents A polarogram of

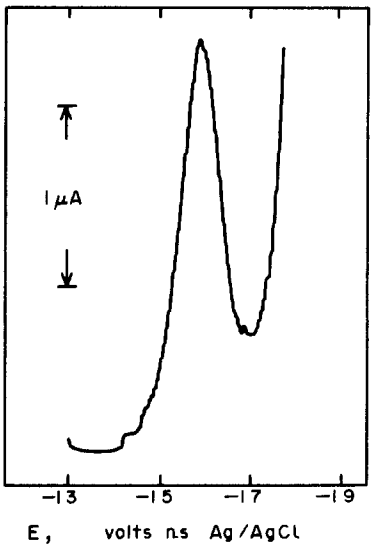


Fig 4 Differential pulse polarogram of a suspension of Hibitane antiseptic cream in 0·1*M* ammonium acetate/ammonia buffer, pH 9·3 Drop time 0·5 sec, pulse amplitude 50 mV and scan-rate 10 mV/sec

Hibitane antiseptic cream suspension in 0·1*M* ammonium acetate buffer (pH 9·3) is given in Fig 4 Experiments showed that the peak current is proportional to the concentration in the range from 3×10^{-6} to 3×10^{-5}*M*. Hence, the suspension must be diluted with buffer to give a final chlorhexidine concentration of less than 1 μg/ml before the polarogram is recorded. On the basis of these experiments the following procedure was outlined for Hibitane antiseptic cream (declared amount 1 g of chlorhexidine digluconate per 100 g of cream).

Recommended procedure

Transfer 0·5 g of antiseptic cream to a 100-ml volumetric flask, dilute to the mark with distilled water and shake well for a few minutes Transfer 10·00 ml of the suspension to a 100-ml flask, add 25 ml of 0·4*M* ammonium acetate/ammonia buffer at pH 9·3, one drop of n-octyl alcohol, and dilute to the mark with distilled water Transfer a suitable volume to a polarographic cell and follow the polarographic procedure above In order to reduce the noise it is advantageous to increase the scan-rate to 10 mV/sec

Several determinations of chlorhexidine in 1% Hibitane antiseptic cream gave the result 1·11–1·13 g of chlorhexidine digluconate per 100 g of cream

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AN ALGEBRAIC APPROACH TO THE STUDY OF THE TITRATION CURVES OF WEAK ACIDS AND THEIR MIXTURES

JOUKO J KANKARE

Department of Chemistry, University of Turku, 20500 Turku 50, Finland

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Summary—It is shown that the titration curves of weak acids and their mixtures which have rational mole-fractions of the components can be transformed into polynomials These protonation polynomials are called normal or abnormal according to whether their coefficients do or do not satisfy certain inequalities derived from statistical considerations The normality of a second-degree polynomial is shown to be a characteristic equivalent to the reality of its zeros Protonation polynomials with real zeros are shown to be normal, but the converse of this statement is not necessarily true The titration curve of a polyfunctional acid is identical with that of an equimolar mixture of monofunctional acids if and only if the protonation polynomial has real zeros A method for determining the functionality of an acid from its titration curve by using protonation polynomials is outlined

Non-linear model-fitting techniques have achieved widespread applications in the problems of analytical and physical chemistry A good example of these applications is the program package developed by Sillén and his co-workers [1,2] These programs may yet be the most common tools of an analytical chemist interested in problems concerning the estimation of equilibrium constants in multicomponent systems Non-linear parameter-estimation methods have also had a profound influence on the work of the experimentalist His most important goal in planning the experimental arrangement is no longer simplicity in the subsequent treatment of the data. He may concentrate instead on the accuracy and precision of the measurements, recording automatically the large amount of data required by the huge computer programs for precise parameter estimation The easy availability of high-speed computers and pertinent software have not, however, been without unfavourable consequences A modern research worker may not feel as much inclined as before towards the deeper mathematical study of his model, because the "brute force" of the computer will deliver the results he needs in a much shorter time However, a more rigorous mathematical treatment may reveal valuable results concerning, *e.g.*, the precision and single-valuedness of the parameter estimates In many cases, also, more efficient parameter-estimation methods may result from these studies

The research field concerning neutralization titrations may seem to be completely exhausted. Indeed, the basic principle of this work, *i.e.*, the integral representation of titration curves was reported as early as 27 years ago by Fronaeus [3,4] However, it seems that the full potentiality of this method has not been exploited, at least in the treatment of the theory of acid–base titrations

Recently Meites[5,6] has revived the old problem of the distinguishability of the potentiometric titration curves of mono- and poly-basic acids In the first publication[5] he derives the general conditions the dissociation constants must fulfil for the titration curve of a polybasic acid to be indistinguishable from that of a monobasic acid In the second publication[6] the same problem is treated with numerical computer methods The characteristic deviation pattern obtained by fitting the titration curve of a monobasic acid to that of the unknown acid reveals the number of removable protons in the acid. In this work these problems and their generalizations are approached from an entirely different standpoint

BASIC EQUATION

To give continuity to the presentation, some equations presented previously[7] will be derived again Let the mixture contain n acids denoted by $H_{m_i}A_{(i)}$ The following equilibria are assumed to prevail in the solution·

$$H_{m_i}A_{(i)} \rightleftharpoons H_{m_i-j}A_{(i)}^{j-} + jH^+, \quad i = 1, \quad , n, j = 1, \quad , m_i \qquad (1)$$

$$H^+ + OH^- \rightleftharpoons H_2O$$

The total mole-fraction of an m_i-basic acid $H_{m_i}A_{(i)}$ is denoted by x_i, and its cumulative acidity constants by β_{ij}, $j = 1, \quad , m_i$ The total molar concentration of the acids in the mixture is A and the mixture is assumed to be titrated with a solution of a strong base, the total concentration of which in the mixture is B.

Assuming that the activity coefficients of the species are constant we get the following set of equations

$$\begin{aligned}\sum_{i=1}^{m_1} \beta_{1i}[H_{m_1}A_{(1)}][H^+]^{-i} + [H_{m_1}A_{(1)}] &= x_1 A \\ \sum_{i=1}^{m_n} \beta_{ni}[H_{m_n}A_{(n)}][H^+]^{-i} + [H_{m_n}A_{(n)}] &= x_n A\end{aligned} \tag{2}$$

$$\sum_{j=1}^{n}\sum_{i=1}^{m_j} i\beta_{ji}[H_{m_j}A_{(j)}][H^+]^{-i} - [H^+] + [OH^-] = B \tag{3}$$

Introducing a quantity

$$Z = \frac{B + [H^+] - [OH^-]}{A} \tag{4}$$

gives from equation (3)

$$Z = \sum_{j=1}^{n} \frac{[H_{m_j}A_{(j)}]}{A} \sum_{i=1}^{m_j} i\beta_{ji}[H^+]^{-i} \tag{5}$$

Equations (2) give

$$\frac{[H_{m_j}A_{(j)}]}{A} = \frac{x_j}{1 + \sum_{i=1}^{m_j} \beta_{ji}[H^+]^{-i}} \tag{6}$$

Substitution into equation (5) gives a simple linear relation

$$Z = \sum_{i=1}^{n} x_i Z_i \tag{7}$$

where the Z_i's are the degrees of deprotonation of the individual acids

$$Z_j = \frac{\sum_{i=1}^{m_j} i\beta_{ji}[H^+]^{-i}}{1 + \sum_{i=1}^{m_j} \beta_{ji}[H^+]^{-i}} \tag{8}$$

In the case of polybasic acids the total concentration of acids is not a directly measurable quantity Titration to the (last) inflection point yields the total normality $\bar{A}$ The following equation is easily seen to be valid

$$\bar{A} = A \sum_{i=1}^{n} m_i x_i \tag{9}$$

Substitution into equation (4) gives

$$Z = \frac{B + [H^+] - [OH^-]}{\bar{A}} \sum_{i=1}^{n} m_i x_i = \bar{Z} \sum_{i=1}^{n} m_i x_i \tag{10}$$

Equation (7) now becomes

$$\bar{Z} \sum_{i=1}^{n} m_i x_i = \sum_{i=1}^{n} x_i Z_i \tag{11}$$

This equation has been previously used for evaluating the mole-fractions from the experimental values of $\bar{Z}$ and Z_i [7]

In the following we shall use a shorthand notation $h = [H^+]$ Inspection of equation (8) reveals that

$$hZ_j = \frac{\sum_{i=1}^{m_j} i\beta_{ji}h^{-i+1}}{1 + \sum_{i=1}^{m_j} \beta_{ji}h^{-i}} = \frac{d}{dh^{-1}} \ln\left(1 + \sum_{i=1}^{m_j} \beta_{ji}h^{-i}\right) \tag{12}$$

Integration gives

$$C' + \int_{h_0^{-1}}^{h^{-1}} Z_j h \, dh^{-1} = C' - \int_{-\ln h_0}^{-\ln h} Z_j \, d\ln h = \ln\left(1 + \sum_{i=1}^{m_j} \beta_{ji}h^{-i}\right) \tag{13}$$

Here C' is an integration constant By use of this equation, equation (11) becomes

$$C'' - \sum_{i=1}^{n} m_i x_i \int_{-\ln h_0}^{-\ln h} \bar{Z} \, d\ln h = \sum_{i=1}^{n} x_i \ln\left(1 + \sum_{j=1}^{m_i} \beta_{ij}h^{-j}\right) \tag{14}$$

We introduce now a function Φ

$$\Phi = \exp\left[-\int_{-\ln h_0}^{-\ln h} \bar{Z} \, d\ln h\right] = 10^{\int_{pH_0}^{pH} \bar{Z} \, dpH} \tag{15}$$

This function has a one-to-one correspondence to the experimental titration curve and it may be called its integral representation With this function, equation (14) becomes

$$(C\Phi)^{\sum_{i=1}^{n} m_i x_i} = \prod_{i=1}^{n} \left(1 + \sum_{j=1}^{m_i} \beta_{ij}h^{-j}\right)^{x_i} \tag{16}$$

This is the equation on which our subsequent mathematical treatment will be based The value of the integration constant C is obtained by allowing h to approach to infinity The right-hand side tends then to 1 and we get

$$C = 10^{\int_{-\infty}^{pH_0} \bar{Z} \, dpH} \tag{17}$$

PROTONATION POLYNOMIALS

For a pure acid the right-hand side of equation (16) is a polynomial In the following this polynomial will be called the "protonation polynomial" The mathematical properties of polynomials have been comprehensively studied for several centuries and it may be expected that some of these properties have applications also in the field of acid–base titrations First we inspect the conditions to be met by the coefficients of the protonation polynomials The first fact is that because these coefficients are equilibrium constants they must be positive Another condition, coming from experimental evidence, is more complicated Let us first derive the result of Meites concerning the titrimetric indistinguishability of mono-

and polyfunctional acids.[5] In the case of a pure monofunctional acid, equation (16) reduces to

$$C\Phi = 1 + \beta h^{-1} \tag{18}$$

This equation is valid if both sides are raised to the mth power

$$C^m\Phi^m = (1 + \beta h^{-1})^m = 1 + \sum_{i=1}^{m} \binom{m}{i} \beta^i h^{-i} \tag{19}$$

This equation is the integral representation of the titration curve of an m-functional acid and thus we are led to the result

Theorem 1 *The titration curve of a monofunctional acid is indistinguishable from that of an* m*-functional acid with cumulative acidity constants* $\beta_i = \binom{m}{i}\beta^i$, *where* β *is the acidity constant of the monofunctional acid*

From this result we can derive Meites's condition for successive acidity constants

$$\frac{K_{i+1}}{K_i} = \frac{\beta_{i+1}\beta_{i-1}}{\beta_i^2} = \frac{\binom{m}{i+1}\beta^{i+1}\binom{m}{i-1}\beta^{i-1}}{\binom{m}{i}^2\beta^{2i}}$$

$$= \frac{i(m-i)}{(i+1)(m-i+1)} \tag{20}$$

As pointed out by Meites,[5] this equation is identical with that obtained by assuming the successive deprotonations of an acid are controlled only by statistical factors It seems that all the reliable experimental results show that for real acids

$$0 < \frac{\beta_{i+1}\beta_{i-1}}{\beta_i^2} \leq \frac{i(m-i)}{(i+1)(m-i+1)} = R(m, i) \tag{21}$$

Here we have introduced a new notation $R(m, i)$ which will be used later The validity of inequality (21) is mainly attributed to electrostatic effects, as already explained by Bjerrum [8] In the following treatment the acids and their protonation polynomials will be called normal or abnormal according to whether the acidity constants are in conformity or not with inequality (21)

Meites[5,6,9] has speculated on the intriguing problem of the existence of abnormal acids The large compilations of dissociation constants[10,11] do not give reliable evidence for their existence, although some examples of doubtful value can be found [5] Meites[5,6] has stated that even if there were no acids having thermodynamic dissociation constants which do not conform with inequality (21), then increase of ionic strength would bring the concentration constants beyond the statistical limit $R(m, i)$ if the thermodynamical constants were sufficiently close in value This statement is based on the supposed validity of the Debye-Huckel limiting law, which in the case of an uncharged difunctional acid H_2A leads to

$$\frac{K_2}{K_1} = \frac{K_2^0}{K_1^0}\frac{f_{HA^-}^2}{f_{H_2A}f_{A^{2-}}} \simeq \frac{K_2^0}{K_1^0}10^{1.02\sqrt{I}} \tag{22}$$

Thus at any finite ionic strength K_2/K_1 will be greater than K_2^0/K_1^0 However, the derivation of the Debye-Hückel law or its well-known extensions rests on the assumption that the ions are point charges or spheres with finite radii According to Bjerrum,[8] the fact that the ratio of the acidity constants is near the statistical limit implies that the distance between the acidic functions is large Hence the ion A^{2-} is far from being a point charge or sphere and we may expect that the activity coefficient $f_{A^{2-}}$ is not correctly estimated by the Debye-Huckel law We may imagine the situation qualitatively by allowing the negatively charged groups to move away from each other They become more and more independent and the activity coefficient $f_{A^{2-}}$ can be substituted by $f_{HA^-}^2$ Substitution into (22) gives the result that the ratio is independent of the ionic strength (assuming the constancy of f_{H_2A}) Quantitatively the problem has been tackled by Scatchard and Kirkwood,[12] who derived the expression for the activity coefficient of a doubly-charged ion by treating the latter as two charged spheres This theory has been applied to the study of the acidity constants of long-chain dicarboxylic acids by Adell [13] From the Scatchard-Kirkwood theory we can calculate that the ratio (22) tends to the statistical limit, but does not exceed it with increasing ionic strength The theory is beautifully supported by the experimental results of Adell [13] A good example is azelaic acid, for which the value for the ratio (22) is 0 134 at zero ionic strength and tends asymptotically to the statistical limit of 0 25, reaching the value 0 243 at ionic strength 2 (NaCl) but does not seem to increase after that The Scatchard-Kirkwood theory is subject to the same limitations as the Debye-Hückel theory, *i e*, it should be valid only for very dilute solutions Hence the excellent agreement between the theory and experiments at high ionic strengths is surprising

From the Scatchard-Kirkwood theory we can only infer the probable non-existence of uncharged difunctional abnormal acids In any case, if abnormal acids do exist, they are exceedingly rare and we have every reason to consider inequality (21) fundamental for polyfunctional acids

The problem which from the mathematical point of view is of fundamental importance in the case of polynomials is the location of the zeros, *i e*, the roots of the polynomial equation

$$1 + \beta_1 u + \beta_2 u^2 + \quad . + \beta_n u^n = 0 \tag{23}$$

In our case the β_i's are all positive and we see immediately that if equation (23) has real roots, they must be negative For the second degree polynomial the roots can be obtained

$$u_{1,2} = \frac{-\beta_1 \pm \sqrt{\beta_1^2 - 4\beta_2}}{2\beta_2} \tag{24}$$

The roots are real if the discriminant is positive But this discriminant criterion is exactly the same as

obtained from inequality (21) and thus we are led to an interesting result·

Theorem 2 *The protonation polynomial of a normal difunctional acid has real negative zeros.*

The normality of the polynomial is not a sufficient condition for the reality of the roots if the polynomial is of higher than the second degree This can be seen by constructing an example

$$S^{(3)}(u) = 1 + 10^{-3}u + 3\,10^{-7}u^2 + 3\,10^{-12}u^3 \qquad (25)$$

Here $u = h^{-1}$, and $S^{(m)}$ is a notation for a protonation polynomial of the mth degree This polynomial corresponds to an acid with successive acidity constants $pK_1 = 3$, $pK_2 = 3\,523$, and $pK_3 = 5$ and is allowable in terms of inequality (21), but it has complex zeros $-1708 \pm 731i$ in addition to the real zero $-9\,66 \times 10^4$ Hence it might be easier to find an acid having a protonation polynomial with complex zeros than an abnormal acid This gives rise to another question does the normality of the protonation polynomial provide a more general rule than the criterion of the realness of its zeros? The answer is given by the following theorem

Theorem 3 *A protonation polynomial which has real zeros is normal*

The proof for this theorem is given in the Appendix This theorem has some consequences in the case of acid mixtures, with which we shall deal later

As stated earlier, the real zeros of a protonation polynomial are negative Example (25) shows that a protonation polynomial may have complex zeros even if it is normal The complex zeros in our example have, however, negative real parts and this leads us to study generally the sign of the real parts of complex zeros The following theorem can be easily proved by using the well-known Hurwitz criterion [14]

Theorem 4 *The normal protonation polynomials up to the fourth degree have zeros with negative real parts*

The proof is given in the Appendix The polynomials of this kind are called Hurwitz polynomials and they play a dominant role in stability theory

DETERMINATION OF FUNCTIONALITY

Sturrock[15] and Meites[5,6] have devised methods for distinguishing monofunctional from polyfunctional acids The form of equation (16) suggests a method which is based on regression of the polynomial For a pure polyfunctional acid, equation (16) becomes

$$(C\Phi)^m = 1 + \sum_{i=1}^{m} \beta_i h^{-i} \qquad (26)$$

Function Φ is calculated from the experimental data Then polynomials are fitted to the powers of this function, beginning with the first degree, *i e*, a straight line. If a polynomial higher than the first degree is required, the acid is not monobasic The same procedure is now applied to the function Φ^2 If the fit is still not satisfactory, the acid is not dibasic, *etc* Generally, if higher than the kth degree polynomial is required to get a satisfactory fit to the points calculated according to the function Φ^k, the acid has more than k removable protons This seemingly simple procedure is not without pitfalls. The solution of the equations resulting from the polynomial regression analysis yields a highly ill-conditioned matrix and any round-off error committed will result in a greatly magnified error in the final solution [16] The situation can be partially mitigated by using proper weighting of the data The weights can be estimated by studying the influence of errors in the pH-measurements on the values of the function Φ^k Differentiation of Φ^k with respect to pH gives

$$\frac{d\Phi^k}{dpH} = k\bar{Z}\Phi^k \ln 10 \qquad (27)$$

Assuming that the errors in the pH-measurements are equal over the whole region, the polynomial regression can be carried out by minimizing the sum of squares

$$F = \sum_{i=1}^{N} w_i[\Phi^k(h_i) - S^{(k)}(h_i^{-1})]^2 \qquad (28)$$

where

$$w_i = [\bar{Z}_i\Phi^k(h_i)]^{-2} \qquad (29)$$

and $S^{(k)}$ is a kth degree polynomial and $\bar{Z}_i$ the degree of total deprotonation calculated at the hydrogen-ion concentration h_i A further remedy for the influence of the round-off errors is the use of orthogonal polynomials. Orthogonal polynomials have achieved widespread application in the physical sciences but their use has been mostly restricted to the least-squares techniques with equally spaced and unweighted data Clearly the reason is that the resulting Gram polynomials are extremely easy to calculate and in many cases there are no difficulties in obtaining equally spaced values for the independent variable In our case the data are weighted, and equally spaced values of h^{-1} would result in the accumulation of values of h at the lower end Experimentally, the data points in the titration curve are most easily obtained at equally spaced additions of base However, only a few points are obtained in the important curved regions and also the numerical calculation of the integrals in equation (15) is cumbersome. Data points at equal pH intervals are almost equally easy to obtain and facilitate the calculation of the integrals by use of, *e.g.*, the Simpson rule Equal pH intervals yield, however, a highly uneven distribution of the values of h^{-1} and necessitate the use of polynomials the orthogonality of which is defined by a weighted scalar product calculated over unequally spaced points The calculational details can be found in most texts on numerical analysis (*e.g*, ref 16)

TITRIMETRIC IDENTITY

Up to this point we have restricted our discussion to the titration curves of pure acids We have found

that on certain conditions the titration curve of a polyfunctional acid is indistinguishable from that of a monofunctional acid, *i e*, the acids are titrimetrically identical The same kind of problem arises in the case of acid mixtures Our unknown acid may be a mixture of acids although the titration curve shows that it is a polyfunctional acid On the basis of equation (16) the following theorem is easily proved

Theorem 5. Let the mixture contain n *acids and the mole fractions of these* m_i*-functional acids be rational numbers* p_i/q_i, $(p_i, q_i) = 1$ *Then the titration curve of this mixture is identical with that of an acid which has*

$$[q_1, q_2, \quad , q_n] \sum_{i=1}^{n} m_i p_i/q_i$$

removable protons

Here (p_i, q_i) is the greatest common divisor of p_i and q_i, and $[q_1, q_2, \quad , q_n]$ is the smallest common dividend of the numbers $q_1, \quad , q_n$ The proof is easily accomplished by raising both sides of equation (16) to the power $[q_1, q_2, \ldots, q_n]$ and inspecting the degree of the polynomial on the right-hand side

In a binary mixture of monofunctional acids we have

$$\frac{p_1}{q_1} = \frac{p}{q}, \frac{p_2}{q_2} = 1 - \frac{p}{q} = \frac{q - p}{q}$$

Substitution into equation (16) and raising to the qth power gives

$$(C\Phi)^q = (1 + \beta_a h^{-1})^p (1 + \beta_b h^{-1})^{q-p} \qquad (30)$$

Thus the mixture behaves in the titration as a q-functional acid, and the apparent acidity constants are obtained by applying binomial expansion to equation (30)

$$(1 + \beta_a h^{-1})^p (1 + \beta_b h^{-1})^{q-p} = 1 + \sum_{k=1}^{q} \sum_{i+j=k} \binom{p}{i}\binom{q-p}{j} \beta_a^i \beta_b^j h^{-k}$$

Hence the apparent constants are

$$\beta_k^{(q)} = \sum_{i=0}^{k} \binom{p}{i}\binom{q-p}{k-i} \beta_a^i \beta_b^{k-i} \qquad (31)$$

With $\beta_a = \beta_b$ this reduces to equation (19) In the applications of equation (31) it is assumed that those binomial coefficients in which the lower number is greater than the upper one are zero

As a numerical example we take a 1 2 mixture of acetic and formic acids and for the acidity constants we take $p\beta_a = 4\,56$ and $p\beta_b = 3\,53$, respectively The mole-fractions are 1/3 and 2/3 which means that the mixture behaves as a trifunctional acid Substitution into equation (31) gives the apparent acidity constants which yield the values for the consecutive constants· $pK_1 = 3\,21$, $pK_2 = 3\,78$, and $pK_3 = 4{\cdot}63$.

The reverse of the theorem can be shown to be valid on certain conditions

Theorem 6 The titration curve of an m*-functional acid is identical with the titration curve of an equimolar mixture of* m *monofunctional acids if and only if the zeros of the protonation polynomial are real.*

The protonation polynomial can be written

$$S^{(m)}(u) = 1 + \sum_{i=1}^{m} \beta_i u^i = \prod_{i=1}^{m} \left(1 - \frac{u}{u_i}\right) \qquad (32)$$

where the u_i's are the zeros of the polynomial We assume first that the zeros are real. They must be negative as shown previously Equation (16) gives

$$(C\Phi)^m = 1 + \sum_{i=1}^{m} \beta_i u^i = \prod_{i=1}^{m} \left(1 - \frac{u}{u_i}\right)$$

which can be written

$$C\Phi = \prod_{i=1}^{m} (1 + \bar{\beta}_i u)^{1/m}$$

where $\bar{\beta}_i = -1/\mu_i$ This is the integral representation of the titration curve of an equimolar mixture of m acids with acidity constants $\bar{\beta}_i$ Obviously this factorization of the polynomial is possible only if the roots are real

This theorem gives the chemical explanation for the zeros of the protonation polynomial As shown previously, the normal second degree protonation polynomial always has real zeros. This gives us the corollary.

Theorem 7 The titration curve of a normal difunctional acid is identical with that of a 1 1 *mixture of monofunctional acids The apparent successive acidity constants of the monofunctional acids are* $-1/u_i$, *where the* u_i*'s are the zeros of the protonation polynomial of the difunctional acid*

As a numerical example we take tartaric acid, for which $p\beta_1 = 2\,82$ and $p\beta_2 = 6\,72$[7] The protonation polynomial is

$$1 + 1\,514 \times 10^{-3} u + 1\,905 \times 10^{-7} u^2$$

The zeros are $-727\,3$ and $-7216{\cdot}0$ which give the apparent acidity constants of the monobasic acids $p\bar{K}_1 = 2\,86$ and $p\bar{K}_2 = 3\,86$ These values can be compared with the successive acidity constants of tartaric acid $pK_1 = 2\,82$ and $pK_2 = 3\,90$ In the case of azelaic acid, for which the successive acidity constants in $2M$ sodium chloride at 18° are 4 432 and 5 047,[13] the apparent acidity constants of the hypothetical monofunctional acids become 4 664 and 4 815, respectively A well-known statement in several textbooks is that the titration curve of any difunctional acid can be approximated by the titration curve of an equimolar mixture of two monofunctional acids having acidity constants which are equal to the successive constants of the difunctional acid We see that this approximation is valid unless the ratio of the successive constants is too close to the statistical limit

A less severe condition for the zeros of the protonation polynomials leads to another theorem

Theorem 8 If the protonation polynomial of a polyfunctional acid is a Hurwitz polynomial, the titration

curve is identical with that of a mixture of mono- and difunctional acids

The proof follows from the previous theorem in the case that all the zeros are real Let us assume that the protonation polynomial has complex conjugate roots $a + bi$ and $a - bi$ The polynomial can then be factorized

$$S^{(m)}(u) = (1 + \bar{\beta}_1 u + \bar{\beta}_2 u^2)S^{(m-2)}(u)$$

where $\bar{\beta}_1 = -2a/(a^2 + b^2)$ and $\bar{\beta}_2 = 1/(a^2 + b^2)$ Because $S^{(m)}(u)$ is a Hurwitz polynomial, a is negative and $\bar{\beta}_1$ and $\bar{\beta}_2$ are positive In this case, however, the hypothetical acid with acidity constants $\bar{\beta}_1$ and $\bar{\beta}_2$ is abnormal

A mixture of monofunctional acids behaves as a polyfunctional acid on certain conditions as we have seen An interesting question is whether this "acid" is normal or abnormal As a direct consequence of theorem 3 we obtain

Theorem 9 A polyfunctional acid, which is titrimetrically identical with a mixture of monofunctional acids, is always normal

CONCLUSIONS

A number of interesting results are seen to arise from the integral representation of titration curves The normality or abnormality of the protonation polynomial plays a fundamental role in the theory of acids, but the question about the existence of abnormal acids remains to be unsettled Although it seems obvious that there are no symmetrical long-chain difunctional acids which become abnormal even on increase in the ionic strength, there are no fundamental reasons to assume their total non-existence Meites[9] has recently discussed a possible structure which might result in the abnormality of the acid A more fruitful subject of study might be to find a normal trifunctional acid with a protonation polynomial which has complex zeros The titration curve of this acid could not be simulated by any mixture of normal acids

Applications of this theory to optimization methods have not been discussed in the present paper The standard methods of polynomial regression may be used for the estimation of the acidity constants [3,4] Equation (30) may be useful for estimating the mole fractions of acids from the titration curves It seems rather tempting in the light of this equation to study the degree and zeros of the experimental protonation polynomial The number and clustering of the zeros would yield valuable information about the number, acidity constants, and mole-fractions of the acids However, the values of the polynomial can be measured only with positive values of h and any effort at reliable estimation of negative zeros will almost certainly end in failure even in the case of rather accurate measurements.

More complex equilibria might be studied by using analogous methods, although the mathematics would certainly be much more involved

APPENDIX

Theorem 3 If the zeros of a protonation polynomial are real, the polynomial is normal

The general form of the protonation polynomial is

$$S^{(m)}(u) = 1 + \sum_{i=1}^{m} \beta_i u^i, \beta_i > 0 \qquad (1')$$

and the condition for normality

$$\frac{\beta_{i+1}\beta_{i-1}}{\beta_i^2} \leq \frac{i(m-i)}{(i+1)(m-i+1)} = R(m,i) \qquad (2')$$

The case of equality is trivial, because then the polynomial can be presented in the form

$$S^{(m)}(u) = (1 + \beta_1 u/m)^m \qquad (3')$$

Thus we can restrict our investigation to the case of inequality in the condition (2')

The proof of the theorem is based on mathematical induction We have previously shown that a second-degree protonation polynomial with real zeros is always normal Let us now assume that all the mth degree polynomials (1') with real zeros are normal Then an arbitrary $(m+1)$th degree polynomial with real zeros and positive coefficients is obtained by

$$S^{(m+1)}(u) = (1 + \bar{\beta}u)S^{(m)}(u) \qquad (4')$$

where $\bar{\beta} > 0$ The coefficients of this polynomial are denoted by γ_i

$$\gamma_1 = \beta_1 + \bar{\beta}, \gamma_{m+1} = \bar{\beta}\beta_m, \gamma_i = \beta_i + \bar{\beta}\beta_{i-1}, i = 2, \ldots, m \qquad (5')$$

The condition for normality becomes

$$\frac{\gamma_{i+1}\gamma_{i-1}}{\gamma_i^2} = \frac{(\beta_{i+1} + \bar{\beta}\beta_i)(\beta_{i-1} + \bar{\beta}\beta_{i-2})}{(\beta_i + \bar{\beta}\beta_{i-1})^2} < \frac{(m+1-i)i}{(m+2-i)(i+1)} = R(m+1,i) \qquad (6')$$

When $i = 1$ the inequality is reduced to

$$\frac{\gamma_2}{\gamma_1^2} = \frac{\beta_2 + \bar{\beta}\beta_1}{(\beta_1 + \bar{\beta})^2} < \frac{1}{2}\frac{m}{m+1} \qquad (7')$$

This can be written

$$\frac{1}{2}\frac{m}{(m+1)}\bar{\beta}^2 - \frac{1}{(m+1)}\beta_1\bar{\beta} + \frac{1}{2}\frac{m}{(m+1)}\beta_1^2 - \beta_2 > 0 \qquad (8')$$

The only region where inequality (8') does not hold, lies between the roots of the corresponding second-degree equation In order that the equation shall have real roots, the discriminant must be positive

$$\beta_1^2\left(\frac{1}{m+1}\right)^2 - \frac{2m}{(m+1)}\left[\frac{1}{2}\frac{m}{(m+1)}\beta_1^2 - \beta_2\right] = \frac{(1-m)}{(1+m)}\beta_1^2 + \frac{2m}{(m+1)}\beta_2 > 0 \qquad (9')$$

This gives

$$\frac{\beta_2}{\beta_1^2} > \frac{1}{2}\frac{(m-1)}{m} = R(m,1) \qquad (10')$$

which is contrary to our assumption In an analogous way we can solve for $i = m$ In the general case $2 \leq i \leq m-1$ the proof is more difficult, but follows the lines presented above Inequality (6') becomes

$$[R(m+1,i)\beta_{i-1}^2 - \beta_i\beta_{i-2}]\bar{\beta}^2 + [2R(m+1,i)\beta_{i-1}\beta_i - \beta_{i-2}\beta_{i+1} - \beta_{i-1}\beta_i]\bar{\beta} + R(m+1,i)\beta_i^2 - \beta_{i-1}\beta_{i+1} > 0 \qquad (11')$$

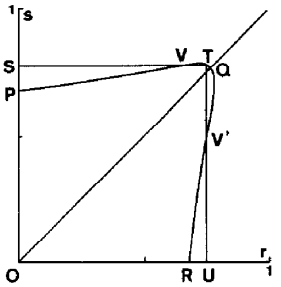

Fig 1 The location of zeros of function $F(r, s) = (1 - rs)^2 - 4R(20,5)(1 - r)(1 - s)$ on the positive quadrant of the rs-plane (curve PQR) and the region of feasible values of r and s (rectangle OSTU)

With the notations

$$r = \frac{\beta_i\beta_{i-2}}{\beta_{i-1}^2}, \quad s = \frac{\beta_{i+1}\beta_{i-1}}{\beta_i^2} \tag{12'}$$

inequality (11') becomes

$$\beta_{i-1}^2[R(m+1,i) - r]\bar{\beta}^2 + \beta_{i-1}\beta_i[2R(m+1,i) - 1 - rs]\bar{\beta} + \beta_i^2[R(m+1,i) - s] > 0 \tag{13'}$$

The allowable values of r and s are

$$0 < r < R(m, i-1), \qquad 0 < s < R(m,i) \tag{14'}$$

occupying the rectangle OSTU in Fig 1 We note that

$$R(m, i-1) < R(m+1, i) \tag{15'}$$

which means that the coefficient of the second-degree term in inequality (13') is positive and the only region where the inequality does not hold with real values of $\bar{\beta}$ lies between the real roots of the corresponding equation In order to have real roots, the discriminant of the equation must be positive After some algebraic manipulations the criterion for positiveness of the discriminant becomes

$$F(r, s) = (1 - rs)^2 - 4R(m+1,i)(1 - r)(1 - s) > 0 \tag{16'}$$

We note that $F(r, s)$ is symmetric with respect to variables r and s and thus the function attains equal values symmetrically at both sides of the line $r = s$ Substitution of $r = s$ into equation (16') gives

$$F(r,r) = (1 - r^2)^2 - 4R(m+1,i)(1 - r)^2 = (1 - r)^2[1 + r + 2[R(m+1,i)]^{1/2}][1 + r - 2[R(m+1,i)]^{1/2}] \tag{17'}$$

Thus the zeros of $R(r,r)$ in decreasing order are 1, $2[R(m+1,i)]^{1/2} - 1$, and $-2[R(m+1,i)]^{1/2} - 1$ The value of $F(r, s)$ at the origin is

$$F(0,0) = 1 - 4R(m+1,i) \tag{18'}$$

The minimum value of $R(m+1,i)$ is attained with $i = 2$ or $m - 1$

$$F(0,0) \leq 1 - \frac{8}{3}\frac{m-1}{m} < 0 \ (m \geq 2) \tag{19'}$$

Accordingly function $F(r, s)$ attains only negative values along the line-segment OQ (Fig 1), where Q is the point $r = s = 2[R(m+1,i)]^{1/2} - 1$ Our next step is to show that $F(r, s)$ has only negative values inside the region OPQR, where the curve PQR is defined by $F(r, s) = 0$ This can be achieved by inspecting the values the function has along the lines $s = a - r$, where $0 \leq a \leq 4[R(m+1,i)]^{1/2} - 2$ Substituting this into $F(r, s)$ and differentiating with respect to r we obtain

$$\frac{dF(r, a-r)}{dr} = 2(2r - a)[r^2 - ar + 2R(m+1,i) + 1] \tag{20'}$$

It can easily be shown that the second-degree factor does not have real zeros, which means that the only extrema are found along the line OQ The second derivative is

$$\left(\frac{d^2F(r, a-r)}{dr^2}\right)_{r=a/2} = 4[2R(m+1,i) + 1 - a^2/4] > 0 \tag{21'}$$

which means that function $F(r, s)$ constrained to lines $s = a - r$ attains minimum values along the line-segment OQ Accordingly, for every interior point of the region OPQR there is at least one point on the boundary of the region, where $F(r, s)$ attains a greater value We note that along the line-segments OP and OR the function has negative values which can be easily verified by substituting $r = 0$ or $s = 0$ into the expression of $F(r, s)$ This proves that $F(r, s)$ is negative in the interior of the region OPQR

The rectangle OSTU may not lie entirely inside the region OPQR First we note by substitution that

$$F[R(m, i-1), R(m,i)] = 0 \tag{22'}$$

Thus the point T lies on the boundary of OPQR If the rectangle OSTU contains points which lie exterior to the region OPQR, there must be other points where the line-segments ST and TU cross the curves PQ and QR These points are denoted by V and V' in Fig 1 Interior to the triangular regions PSV and URV', function $F(r, s)$ attains positive values and thus $\bar{\beta}$ has real values which do not satisfy inequality (13') We shall show that these values of $\bar{\beta}$ are always negative, contradicting our assumption We have already shown that the coefficient of $\bar{\beta}^2$ in inequality (13') is positive It is easily seen that also

$$\beta_i^2[R(m+1,i) - s] > 0 \tag{23'}$$

which implies that the zeros of the polynomial (13') have the same signs Hence, if

$$2R(m+1,i) - 1 - rs > 0 \tag{24'}$$

we can conclude that there are no positive values of $\bar{\beta}$ which do not satisfy inequality (13') The sign of the left-hand side of inequality (24') depends on the maximum value of rs From Fig 1 we see that the maximum values of rs are attained at the points V and V' At the point V the value of s is $R(m,i)$ and the value of r is obtained from $F(r, R(m,i)) = [R(m,i)]^2r^2 + [4R(m+1,i)[1 - R(m,i)] - 2R(m,i)]r + 1 - 4R(m+1,i)[1 - R(m,i)] = 0$ (25')

According to equation (22') one of the roots is $R(m, i-1)$ and thus the other is obtained from

$$r_2 = \frac{1 - 4R(m+1,i)[1 - R(m,i)]}{R(m,i-1)[R(m,i)]^2} \tag{26'}$$

Hence, at the point V

$$rs = \frac{1 - 4R(m+1,i)[1 - R(m,i)]}{R(m,i-1)R(m,i)} \tag{27'}$$

Substituting into (24') and employing the notations $x = R(m, i-1)$ and $y = R(m,i)$, we obtain

$$2R(m+1,i) - 1 - rs = \frac{x(xy - 2y + 1)(xy^2 - 3y + 2)}{2(1 - x)(1 - y)xy} \tag{28'}$$

where we have used equation (22') to obtain the expression for $R(m+1,i)$ in terms of x and y Substitution of the expressions of x and y gives

$$xy - 2y + 1 = \frac{2(m+1)}{(m-i+2)(m-i+1)(i+1)} > 0 \tag{29'}$$

and

$$xy^2 - 3y + 2 = \frac{2(m+1)(m+\imath+2)}{(m-\imath+2)(\imath+1)^2(m-\imath+1)} > 0 \tag{30'}$$

We may infer that inequality (24') is valid at the point V and also in the region PSV Analogous expressions for the point V' can be obtained by interchanging the notations for x and y

$$xy - 2x + 1 = \frac{2(m+1)}{(m-\imath+2)(\imath+1)\imath} > 0 \tag{31'}$$

$$x^2y - 3x + 2 = \frac{2(m+1)(2m+3-\imath)}{\imath(\imath+1)(m-\imath+2)^2} > 0 \tag{32'}$$

Consequently, the real values of $\bar{\beta}$ which do not satisfy inequality (13') are always negative, and the inequality holds for all positive values of $\bar{\beta}$ This completes the proof of the theorem

Theorem 4 *The normal protonation polynomials up to the fourth degree have zeros with negative real parts*

This can be proved by the straightforward application of the Hurwitz criterion,[14] which states that if all the determinants

$$\delta_k^{(m)} = \begin{vmatrix} \beta_1 & \beta_3 & \beta_5 & \beta_{2k-1} \\ 1 & \beta_2 & \beta_4 & \beta_{2k-2} \\ 0 & 1 & \beta_3 & \beta_{2k-3} \\ 0 & 0 & 0 & \beta_k \end{vmatrix} \tag{33'}$$

with $k = 2, 3, \ldots, m$ and $\beta_j = 0$ for $j > m$, are positive, the polynomial $S^{(m)}(u)$ has only zeros with negative real parts Deduction of the sign of the determinants can be simplified by casting the normal protonation polynomial into the form

$$S^{(m)}(u) = 1 + \binom{m}{1}\beta u + \binom{m}{2}Q_1\beta^2u^2 + \binom{m}{3}Q_1^2Q_2\beta^3u^3 + \ldots + \binom{m}{m}Q_1^{m-1}\ldots Q_{m-1}\beta^m u^m \tag{34'}$$

where $0 < Q_i < 1$ It is easily seen that this polynomial is normal and also that any normal protonation polynomial can be represented in this form In our case we can also assume without any loss of generality that $\beta = 1$ For instance,

$$\delta_4^{(4)} = \begin{vmatrix} 4 & 4Q_1^2Q_2 & 0 & 0 \\ 1 & 6Q_1 & Q_1^3Q_2^2Q_3 & 0 \\ 0 & 1 & 4Q_1^2Q_2 & 0 \\ 0 & 0 & 1 & Q_1^3Q_2^2Q_3 \end{vmatrix}$$

$$= 4Q_1^6Q_2^3Q_3(24 - Q_2Q_3 - 4Q_1Q_2) > 1$$

In the same way we can show that all the determinants for $m < 4$ are positive In the case $m = 5$ we obtain

$$\delta_5^{(5)} = 5Q_1^9Q_2^6Q_3^3Q_4(500Q_1 + Q_1^2Q_2^2Q_3^2Q_4 - 100Q_1^2Q_2 - 25Q_1Q_2Q_3 - 10Q_3Q_4 + 2Q_1Q_2Q_3Q_4)$$

Substituting, *e g*, $Q_1 = 0.01$, $Q_2 = 0.1$, $Q_3 = 0.9$, and $Q_4 = 0.8$ we find that $\delta_5^{(5)}$ may attain negative values and the polynomial may have roots with positive real parts

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DETERMINATION OF COPPER AND LEAD IN SCHIST BY ANODIC STRIPPING VOLTAMMETRY

WALTER LUND and MAGNE SALBERG

Department of Chemistry, University of Oslo, Blindern, Oslo 3, Norway

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Summary—Samples were decomposed in $HClO_4$/HF mixture in a Teflon beaker to avoid electrochemical interference from platinum ions The residue remaining after evaporation to dryness was taken up in nitric acid and examined by anodic stripping voltammetry Both the hanging mercury drop electrode and the rotating glassy carbon electrode, mercury-plated *in situ*, were used with success Copper at 120 ppm and lead at 40 ppm were determined with a relative standard deviation of 6% The schist was the Nordic reference sample ASK-2

There appears to be little work published on the analysis of geological samples by anodic stripping voltammetry, but the technique would seem to offer certain advantages over other more frequently used methods, for the determination of low concentrations of lead, for instance Methods such as atomic-absorption spectrometry and neutron-activation analysis are not easily applicable in this case, owing to their relatively poor sensitivity towards lead The use of anodic stripping voltammetry also seems to be advantageous when alternative analytical methods are needed to ascertain the absence of systematic errors in a given procedure.

In this paper the determination of copper and lead in schist is described. The determination of these metals in silicates by anodic stripping voltammetry with medium-exchange has previously been mentioned in a summary by Keren *et al*[1] More recently Khasgiwale *et al*[2] have described the determination of lead in geological samples. In the two investigations mentioned above a hanging mercury drop electrode (HMDE) was used as working electrode In the present paper the determinations are carried out both with this electrode, and with a recently developed mercury film electrode,[3,4] the rotating glassy carbon electrode mercury-plated *in situ*, here called the "Florence" electrode, after the originator.

This work constituted a part of a Nordic methodological correlation project on geological reference materials.[5]

EXPERIMENTAL

Apparatus

A versatile solid-state voltammeter built in this laboratory, and a Hewlett–Packard 7030 AM *XY* recorder were used for the stripping voltammetric experiments The electrolytic cell was a Metrohm EA 880-20 vessel with a thermostated jacket, in which water at 25·0° was circulating When the Metrohm E 410 hanging mercury drop electrode was used the solution was stirred with a three-edged Teflon stirrer connected to a Beckman rotating unit This unit, which consisted of a Variable Speed Drive Unit (188501) and a Rotating Electrode Body (188551), was also used for the rotation of the "Florence" electrode This electrode was made from a 6-mm diameter glassy carbon rod (GC-A grade from Tokai Electrode Mfg Co, Ltd, Tokyo), pressed into Teflon[4] The disc, which had an area of 0·283 cm^2, was polished with fine emery paper, followed by suspensions of aluminium hydroxide with particle size 5 and 0·3 μm The reference electrode, a Metrohm EA 427 saturated Ag/AgCl electrode, was placed inside a salt bridge filled with the solution to be analysed All potentials mentioned in this paper are referred to the Ag/AgCl electrode A platinum spiral served as counter electrode Dissolved oxygen was removed from the solution by passing highly purified nitrogen through the cell The electrolytic cell was treated with a silicone repellent, dimethyldichlorosilane, to prevent adsorption of metals on the glass walls

Reagents and solutions

The acids used for decomposition of the samples were all of Suprapur quality (Merck) A 0·1 *M* mercuric nitrate solution was prepared from highly purified mercury oxidized with nitric acid (Suprapur, Merck). The metal solutions were prepared from analytical grade nitrate or sulphate salts Solutions with a concentration below $10^{-3}M$ were prepared just before use The water used was demineralized with an ion-exchange resin and distilled

Decomposition of the sample

A 0·2-g portion of the Nordic reference sample ASK-2 (a carbonaceous Ordovician schist), was transferred to a Teflon beaker, 5 ml of hydrofluoric acid and 1 ml of perchloric acid were added, and the mixture was heated to dryness on a hot-plate The evaporation was repeated twice, and the residue then dissolved in 1 ml of nitric acid, water was added, and the solution was finally transferred to a volumetric flask and diluted to 500 ml The pH of the final solution was 1·5 Decompositions were also carried out in platinum crucibles, but in these cases the stripping voltammetric experiments were complicated by the presence of dissolved platinum in the solutions, and Teflon beakers were therefore preferred

Procedure—HMDE

A 25-ml portion of the sample solution was deaerated with nitrogen for 15 min, and the deposition was then carried out for 7 min at −0·7 V During the deposition period the solution was stirred by a synchronous motor at a rotation speed of 40 rps After a rest period of 1 min the stripping voltammogram was recorded while the potential was scanned to +0·3 V at a speed of 3 V/min The potential

was kept at +0·3 V for 2 min, and an extra mercury drop was discarded, before a new deposition was carried out on a fresh mercury drop The diameter of the mercury drop was 1·0 mm The concentration of the metals was determined by the standard-addition method, by adding 200 µl of a standard solution to the sample solution The standard solution was $1 \times 10^{-4}M$ in copper and $1{\cdot}5 \times 10^{-5}M$ in lead For the calculation of the concentration (in ppm) of the metals in the schist, the weight of the schist was corrected for the content of hygroscopic water (0·57%)

Procedure—Florence electrode

To 25 ml of the sample solution was added 0·2 ml of $5 \times 10^{-3}M$ mercuric nitrate, and the solution was deaerated with nitrogen for 15 min, while the electrode was rotating to prevent gas bubbles adhering to its surface The electrode was "conditioned" by a 3-min deposition at −0·7 V, followed by a linear sweep to +0·2 V, at which the potential was kept for 5 min The determination was then started by deposition at −0·7 V for 3 min The deposition period was followed by a rest period of 0·5 min, at the end of which the stripping voltammogram was recorded, the potential being scanned to +0·2 V at a speed of 3 V/min The potential was kept at +0·2 V for 5 min, before a new deposition was carried out The electrode was rotated at 70 rps during the deposition step The mercury film was removed with a soft paper tissue only when a new aliquot was to be analysed The concentrations of the metals were determined by the standard-addition method, in the same way as described above for the HMDE

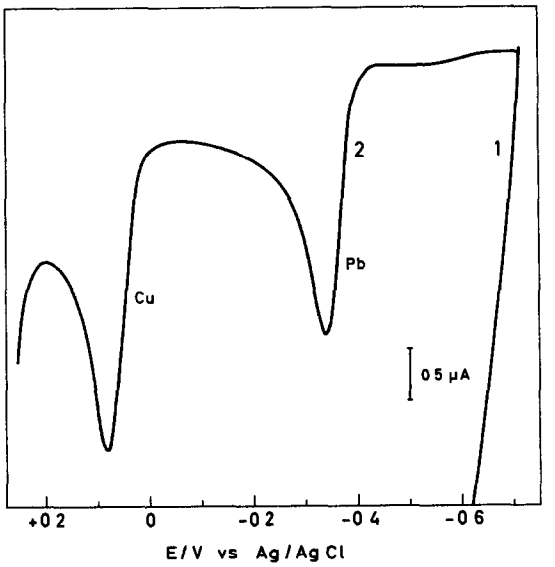

Fig 1 Curve 1, attempt to record a stripping voltammogram (HMDE) of a schist solution—platinum interferes Curve 2, stripping voltammogram (HMDE) of $10^{-6}M$ copper and $10^{-6}M$ lead in 0·15*M* nitric acid Deposition potential −0·7 V, scan-rate 6 V/min, deposition time 6 min

RESULTS AND DISCUSSION

Effect of decomposition procedure

The decomposition of silicates is usually carried out in platinum crucibles Although a small amount of platinum from the crucible is also dissolved during the decomposition, this does not normally cause any difficulties in the subsequent measurements However, for anodic stripping voltammetry the presence of platinum ions in the solution is a great nuisance Dissolved platinum will be reduced to platinum amalgam during the deposition step, causing a marked decrease in the hydrogen over-voltage of the electrode The result is illustrated in Fig 1, curve 1 This curve represents an attempt to record a voltammogram for a schist sample which had been decomposed in a platinum crucible A large oxidation current was observed, which prevented the recording of the voltammogram During the electrochemical deposition, which was carried out at −0·7 V, a marked evolution of hydrogen gas was also observed The same phenomena were observed even at a deposition potential of −0·3 V For comparison an anodic stripping voltammogram was recorded for a pure solution containing only copper and lead in 0·15*M* nitric acid (Fig 1, curve 2) The deposition potential used was −0·7 V, the same as for the schist solution (curve 1) In contrast to curve 1, curve 2 exhibits well-defined peaks for both copper and lead However, when platinum ions [as $(NH_4)_2PtCl_6$] were added to the solution containing copper and lead in nitric acid, the previously mentioned difficulties were once more observed

There are various ways of solving the problems arising from the presence of platinum ions Koster *et al*[6] used an anion-exchange step to remove the platinum, before the voltammetric measurements These authors also suggested the use of Teflon beakers for certain decompositions Khasgiwale *et al*[2] increased the pH of the solution to be analysed, by evaporation of the free acid No doubt the best approach is to avoid the presence of platinum altogether, wherever this is possible When the sample is decomposable in acids, this is easily done by using Teflon beakers for the decomposition of the sample

The voltammograms exhibited well-defined oxidation peaks for both copper and lead, the former being considerably larger than the latter The deposition potential was −0·7 V, and the pH of the solution 1·5 A deposition potential of −0·9 V gave an equally well-defined voltammogram Owing to the relatively large amounts of acids which are needed for the decomposition of the sample, the trace metal content of the acids used must be low, in order to obtain a satisfactory blank value When acids of Suprapur quality (Merck) were used, the blank values were found to be negligible, compared to the concentration of metals in the schist solution

Results obtained with the HMDE

The peak potentials were +0·10 V and −0·32 V for copper and lead, respectively, and the copper peak was particularly well defined

The relationship between peak height and concentration of metal was studied by adding 0·1-ml portions of a standard solution, $1{\cdot}0 \times 10^{-4}M$ in copper and $1{\cdot}5 \times 10^{-5}M$ in lead, to the schist solution Linear calibration curves were obtained for both metals

Table 1 Analytical results for copper and lead, obtained with the HMDE

Sample		Copper			Lead		
No	Weight, *g*	i_1, μA	i_2, μA	Conc, *ppm*	i_1, μA	i_2, μA	Conc, *ppm*
1	0 1987	1 32	2 63	126 9	0 14	0 40	33 3
2	0 1985	1 36	2 76	123 0	0 16	0 43	37 1
3	0 1989	1 25	2 49	126 8	0 15	0 38	39 4
4	0 1984	1 20	2 55	112 4	0 15	0 40	36 3
5	0 1984	1 26	1 52	127 0	0 16	0 40	41 2
6	0 1988	1 40	2 92	116 2	0 18	0 46	39 6
7	0 1995	1 26	2 59	118 6	0 16	0 41	38 7
Mean				121 6			37 9
S_r (%)				5			7
Ref value				120			38–47

i_1 and i_2 represent the peak currents before and after the addition of standard The peak currents given represent the mean of two separate measurements

The results of seven independent determinations are shown in Table 1 The mean values and relative standard deviations obtained are 121 6 ppm (5%) for copper and 37 9 ppm (7%) for lead The "reference" values given in Table 1 were obtained by various other techniques [5] The recommended value for copper, 120 ppm, represents the mean of the results obtained by seven Nordic Laboratories, using atomic-absorption spectrometry and emission spectrography The copper value found by anodic stripping voltammetry agrees quite well with the recommended value for copper, and a *t*-test revealed that there was no significant difference between the two values, even at a probability level of 90%

No recommended value for lead is given in Table 1 The concentration range indicated refers to three results obtained by two laboratories These results were 38, 43 and 47 ppm of lead, all obtained by using emission spectrography The values agree fairly well with the results obtained by anodic stripping voltammetry On the basis of the above-mentioned results, and the results obtained in the present paper, a recommended value of 40 ppm has been chosen for lead

Results obtained with the Florence electrode

The mercury film is here formed *in situ*, by adding mercuric nitrate to the solution The mercury film thickness obtained depends on the concentration of mercuric nitrate, the deposition time, and the rate of rotation of the electrode For the determination of trace metals in sea-water a concentration of mercuric nitrate of $4 \times 10^{-5} M$ has been found advantageous [4] However, the concentration of metals is higher in the schist solution than in sea-water As too high concentrations of metals in the mercury film may result in the formation of intermetallic compounds, it was decided that the use of a thicker film should also be investigated Typical voltammograms obtained with two different film thicknesses are shown in Fig 2 Curve 1 represents the stripping voltammogram of a solution $4 \times 10^{-5} M$ in mercuric nitrate, and curve 2 for ten times that concentration Both voltammograms exhibit very well-defined stripping peaks, for copper and lead The lead peaks in Fig 2 lend themselves more easily to a quantitative determination than do those obtained with an HMDE The peak potential for copper is +0 03 V for both curves, whereas for lead it is slightly different for the two curves, being −0 41 V for curve 1 and −0 38 V for curve 2

As expected, the copper peak is the larger and the peak width narrower for curve 1, which corresponds to the thinnest mercury film This effect is less marked for lead However, for this metal also the peak current for a given deposition time will be greatest for the thinnest film This is not obvious from Fig 2, because of the differences in experimental parameters for the two curves

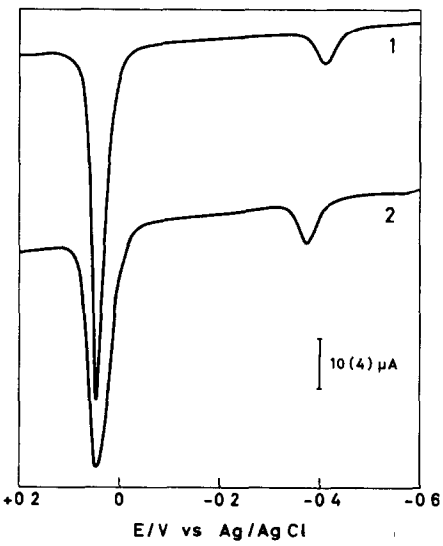

Fig 2 Typical stripping voltammograms obtained with the rotating glassy carbon electrode mercury plated *in situ* The mercuric nitrate was $4 \times 10^{-5} M$ (curve 1) and $4 \times 10^{-4} M$ (curve 2), deposition time 3 min (curve 1) and 1 5 min (curve 2), current sensitivity 5 μA/cm (curve 1) and 2 μA/cm (curve 2) The deposition potential is −0 7 V, and the scan-rate 3 V/min for both curves

Table 2 Analytical results for copper and lead obtained with the mercury film electrode

Sample		Copper			Lead		
No	Weight, *g*	i_1, *μA*	i_2, *μA*	Conc, *ppm*	i_1, *μA*	i_2, *μA*	Conc, *ppm*
1	0 1994	75 3	152 5	123 1	8 1	20 7	39 4
2	0 1989	68 5	143 0	116 2	7 1	18 0	40 1
3	0 1988	69 9	138 0	128 9	7 0	16 7	44 4
4	0 1995	72 9	140 0	136 1	7 2	17 5	42 9
Mean				126 1			41 7
S_r (%)				7			6
Ref value				120			38–47

The concentration of mercuric nitrate is $4 \times 10^{-5}M$ i_1 and i_2 represent the peak currents before and after the addition of standard The peak currents given represent the mean of two separate measurements

The mercury film was not removed between separate measurements carried out on the same aliquot Hence, the film thickness increased when repeated measurements were carried out in the same solution For the first deposition after the "conditioning" of the electrode, the film thickness was calculated to be 0 06 *μm* for the $4 \times 10^{-5}M$ mercuric nitrate solution, and 0 45 *μm* for the higher concentration of mercuric ions. The calculation was based on the reduction current measured during the deposition step

As mentioned above, the largest peak currents are obtained with the thinnest film It was also found, somewhat surprisingly, that the reproducibility was best for this film In spite of the relatively high concentrations of metals in the thinnest film, no serious interference effects were noticed A mercuric nitrate concentration of $4 \times 10^{-5}M$ was therefore used for all the subsequent measurements

The relationship between peak-height and concentration of metal was studied by adding 0 1-ml portions of a standard, $1\ 0 \times 10^{-4}M$ in copper and $1\ 5 \times 10^{-5}M$ in lead, to the schist solution The calibration curve was linear for lead, whereas for copper there was a slight curvature for the highest concentrations, which may be due to approaching saturation of the mercury film It is interesting to note that the slopes of the two calibration curves were almost identical, in contrast to the behaviour of copper and lead in sea-water [4] However, the acidic schist solution is, after all, a simpler matrix than sea-water at pH 8 0

The results of four independent determinations with the film electrode are shown in Table 2 The mean values and relative standard deviations obtained are 126 1 ppm (7%) for copper and 41 7 ppm (6%) for lead, which agree fairly well with the indicated "reference" values A *t*-test revealed that the difference between the copper value found in this work and the recommended value was not significant, even at the 90% level

Comparison between the HMDE and the Florence electrode

An *F*-test indicates that there is no significant difference (at the 95% level) between the standard deviations found for the two electrode systems. When a *t*-test was carried out for the copper results obtained with the two electrodes, it was found that there was no significant difference between these results, even at the 90% level However, when the two lead values were compared in the same way, it turned out that the difference was significant at the 95%, but not at the 99% level

The HMDE and the Florence electrode both have advantages and disadvantages The highest sensitivity and lowest detection limit is obviously attained with the film electrode Thus, for low concentrations this may be the electrode of choice In some ways it is easy to use, as the mercury film is formed *in situ* simply by adding mercuric ions to the solution, but it does require slightly more expensive equipment, involving a synchronous motor and rotating electrode body The glassy carbon electrode may occasionally change its electrochemical behaviour, necessitating a thorough repolishing of the electrode surface Furthermore, it is the authors' experience that the HMDE seems to give more reproducible results than the Florence electrode, in the hands of inexperienced personnel

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SELECTIVE EXTRACTION OF ORGANIC COMPOUNDS AS ION-PAIRS AND ADDUCTS

ROLF MODIN and GORAN SCHILL

Department of Analytical Pharmaceutical Chemistry, Biomedical Center, University of Uppsala, S-751 23 Uppsala, Sweden

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Summary—Selective and easily regulated systems for extraction of organic compounds as ion-pairs and/or adducts are presented The effect of different kinds of hydrophobic agents that give adducts in the organic phase are demonstrated mesitylene for nitrophenols, ethyl acetate and diethyl ether for hexestrol (diphenol), lipophilic alcohols for organic ammonium ion-pairs, dibenzo-18-crown-6 for ion-pairs of primary ammonium ions, HDEHP for hydrophilic aminophenols (adrenaline, isoproterenol, synephrine) It is shown that the extraction selectivity decreases with increasing content of the complexing agent in the adduct The influence of the hydrogen-bonding character of the counter-ion and the organic solvent on the selectivity of ion-pair extractions is demonstrated with ammonium compounds (nortriptyline, amitriptyline and *N*-methylamitriptyline) and inorganic anions Highly hydrophilic anionic compounds (*e.g.*, glucuronides, cholic acid derivatives) can be extracted into chloroform as ion-pairs with large quaternary alkylammonium ions The extraction efficiency of the cation increases with the number of methylene groups to a limit which is due to co-extraction of other sample components (*e.g.*, buffer anions)

In the construction of methods for determination of organic substances such as drugs and drug metabolites in biological and similar complex samples, the main interest is often focused on the development of highly sensitive quantitation techniques, while the preliminary stages of the procedure and particularly the extraction process follow traditional lines

An extraction process that is not adapted to the specific problem may give a yield that is not only low but also varies, owing to lack of control of important conditions. An unsuitable extraction procedure can also decrease the sensitivity of the quantitation step by giving co-extraction of large amounts of interfering sample components

The ideal extraction process gives a yield of more than 99% while only negligible amounts of other sample components are co-extracted This will require a highly selective system, where the differences in the degree of extraction of structurally closely related compounds are large The selectivity can, however, only be fully utilized if the system is also highly flexible and allows adjustment of the degree of extraction to such a level that co-extraction is minimized For example, if the degree of extraction of the substrate increases from 99% to 99.9% the distribution ratio increased by a factor of 10, and the extraction of more polar species may increase to a much greater extent than that of the substrate

EXTRACTION PRINCIPLES

There is wide scope for varying the degree of extraction if the partition process is combined with complexation by a hydrophobic agent in the organic phase, according to the following principles.

An uncharged compound B is extracted by an organic phase that contains a hydrophobic, uncharged complexing agent S If BS_2 is the highest complex (adduct) in the organic phase, the following equilibria are obtained.

$$B_{aq} \rightleftharpoons B_{org}$$
equilibrium constant k_d (1)

$$B_{org} + S_{org} \rightleftharpoons BS_{org}$$
equilibrium constant k_{BS} (2)

$$B_{org} + 2S_{org} \rightleftharpoons BS_{2_{org}}$$
equilibrium constant k_{BS_2} (3)

The distribution ratio D_B is given by

$$D_B = k_d(1 + k_{BS}\,[S]_{org} + k_{BS_2}\,[S]^2_{org}) \quad (4)$$

D_B can be controlled by the nature of the organic solvent and of the complexing agent S (which affect k_d, k_{BS} and k_{BS_2}) and by the concentration of S

If one adduct predominates, equation (4) can be simplified and given the logarithmic form

$$\log D_B = \log(k_d . k_{BS_n}) + n \log [S]_{org} \quad (5)$$

A plot of log D_B *vs.* log $[S]_{org}$ will give a straight line The slope of the line, n, is a formal expression of the number of S-molecules in the adduct. A non-linear relation between log D_B and log $[S]_{org}$ indicates that several adducts of different composition are present

A charged compound X^- can be extracted by an organic phase as a complex (ion-pair) with a counter-ion Q^+ which is added to the aqueous phase.

$$X^-_{aq} + Q^+_{aq} \rightleftharpoons QX_{org}$$
equilibrium constant E_{QX} (6)

The distribution ratio D_X is given by

$$D_X = E_{QX}\,[Q^+] \qquad (7)$$

D_X is controlled by the nature of the organic solvent and of the counter-ion Q^+ (which affect E_{QX}) and by the concentration of Q^+

The two basic procedures can, of course, also be combined A cation Q^+ can be extracted with a counter-ion X^- in the aqueous phase and a complexing agent S in the organic phase Ion-pair adducts will then be formed in the organic phase as illustrated by the equilibrium

$$Q^+_{aq} + X^-_{aq} + nS_{org} \rightleftharpoons QX\,S_{n_{org}} \qquad (8)$$

If ion-pair forms other than $QX.S_n$ are negligible, the distribution ratio D_Q is given by

$$D_Q = E_{QX}\,k_n\,[X^-]\,[S]^n_{org} \qquad (9)$$

where

$$k_n\,[QX\,S_n]_{org}.[QX]^{-1}_{org}\,[S]^{-n}_{org} \qquad (10)$$

D_Q can then be controlled by the nature and concentration of both S and X^-.

The extraction can also be done with a hydrophobic protolytic agent that can act both as counter-ion and as adduct-forming agent in uncharged form An illustration is given by the extraction of Q^+ with a hydrophobic acid HX

$$Q^+_{aq} + nHX_{org} = QX\,(HX)_{n-1\,org} + H^+_{aq} \qquad (11)$$

If one ion-pair adduct predominates in the organic phase, the distribution ratio is given by

$$D_Q = E_{QX}\,k_{n-1}\,[HX]^n_{org}\,K'_{HX}\,k_d^{-1}\,a_{H^+}^{-1} \qquad (12)$$

where k_d is the partition coefficient of HX and K'_{HX} its acid dissociation constant, while k_{n-1} is defined by

$$k_{n-1} = [QX\,(HX)_{n-1}]_{org}\,[QX]^{-1}_{org}\,[HX]^{1-n}_{org} \qquad (13)$$

D_Q can be controlled by the pH and the concentration and nature of HX

Adduct formation

Uncharged compounds of widely different kinds can act as adduct-forming agents in the organic phase The influence of the adduct-formation on the distribution ratio depends on the stability and the composition of the adduct and on the concentration of the adduct-forming agent, as demonstrated in equation (4)

The use of adducts of low stability is demonstrated in Fig 1 which shows the influence of mesitylene on the partition of nitrophenols between ethylene glycol and cyclohexane [1] The non-linearity of the curves indicates that several adducts with different content of mesitylene are formed Stability constants have been determined for the lowest adducts (picric acid $k_{BS} = 7$ and $k_{BS_2} = 10\,5$, dinitrophenol $k_{BS} = 1\,7$ and $k_{BS_2} = 0\,7$), but the tendency to formation of higher

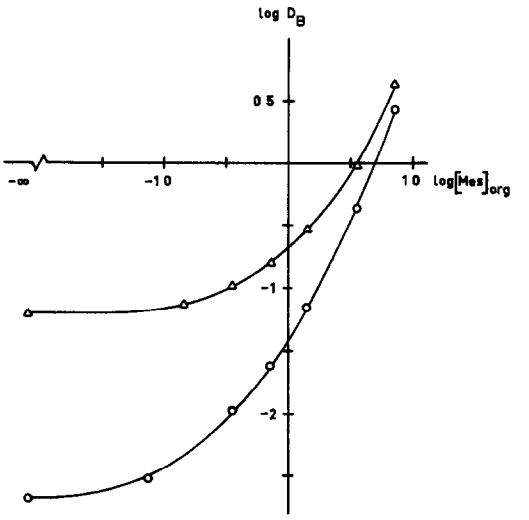

Fig 1 Relation between partition ratios of nitrophenols and the concentration of mesitylene (Mes) in the non-polar phase △, 2,4-dinitrophenol, ○, picric acid Polar phase, ethylene glycol Non-polar phase, cyclohexane (From *Acta Pharm Suecica*, 1974, **11**, 257, by permission)

adducts (BS_3 BS_n) increases with increasing content of mesitylene in the organic phase The figure shows that the extraction selectivity decreases with increasing mesitylene concentration: the higher adducts of picric acid and dinitrophenol have very similar partition properties

Considerably larger effects are obtained when strongly hydrogen-bonded adducts are formed. The influence of the hydrogen-accepting agents ethyl acetate and diethyl ether on the partition of the hydrogen-donating hexestrol [3,4-(4-hydroxyphenyl)hexane] between ethylene glycol and cyclohexane is demonstrated in Fig. 2 [2] The linearity of the curves shows that one adduct predominates in the organic phase The slope is about 2 for both the complexing agents, which indicates that both adducts have the same stoichiometry

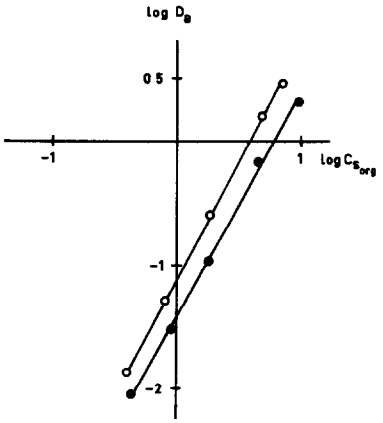

Fig 2 Relation between partition ratio of hexestrol and the concentration of hydrogen-accepting agents (S) in the non-polar phase ○, Ethyl acetate, ●, diethyl ether Polar phase, ethylene glycol, Non-polar phase, cyclohexane (From *Acta Pharm. Suecica*, 1975, **12**, by permission)

Adduct-formation combined with ion-pair extraction [*cf.* equation (8)] has been studied in numerous cases, mainly with lipophilic alcohols as complexing agents [3,4,5] Studies of the adduct-formation can be based on equation (14), obtained by transformation of equation (10) and the definition of E_{QX} [equation (6)]

$$\log E'_{QX} = \log(E_{QX}\ k_n) + n \log [S]_{org} \qquad (14)$$

where

$$E'_{QX} = [QX\ S_n]_{org}\ [Q^+]^{-1}\ [X^-]^{-1} \qquad (15)$$

A constant value of n has been found in most cases

The stoichiometry of the alcohol adducts changes with the hydrogen-bonding ability of the ion-pair An example is given in Fig 3,[6] which shows the extraction of a secondary amine, alprenolol, and its hydroxy-derivative, as perchlorates The slope is 2 for the amine and 3 for the hydroxy-derivative, and the extraction selectivity decreases with increasing alcohol content of the organic phase

The extraction selectivity can also be considerably changed by use of structure-specific adduct-forming agents such as cyclic ethers Dibenzo-18-crown-6 gives highly stable 1.1-complexes with ion-pairs containing primary ammonium ions, while rather small complex constants are obtained when the ammonium ion has a higher degree of substitution.[7] A demonstration of the effect of complexation by the crown ether is given in Fig 4 Two cations, octylammonium and trimethylnonylammonium, are extracted into chloroform as ion-pairs with salicylate (Fig 4A) and naphthalene-2-sulphonate (Fig 4B) Addition of crown ether to the organic phase gives a large increase in the extraction constant of the primary ammonium ion-pair (stability constant of the ion-pair adduct, $k_1 \approx 10^3$) while the extraction constants of

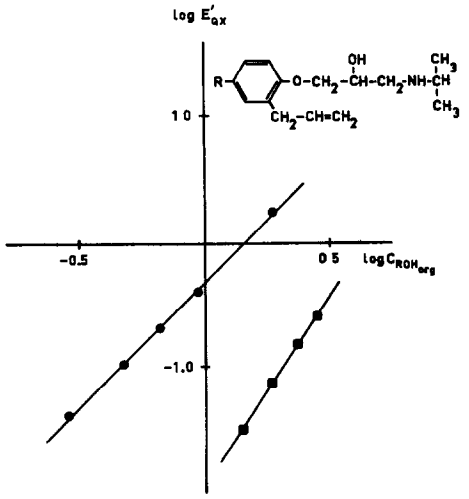

Fig 3 Relation between extraction constant of alprenolol and 4-hydroxyalprenolol and the concentration of pentanol (ROH) in the organic phase, ●, Alprenolol (R=H), ■, 4-hydroxyalprenolol (R=OH) Counter-ion, perchlorate Organic phase, chloroform (From *Acta Pharm Suecica*, 1974, **11**, 313, by permission)

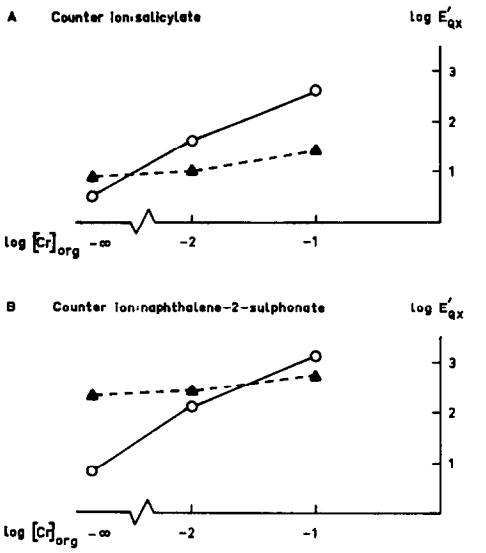

Fig 4 Relation between extraction constants of octylammonium and trimethylnonylammonium and the concentration of dibenzo-18-crown-6 (Cr) in the organic phase ○, Octylammonium, ▲, trimethylnonylammonium, Organic phase, chloroform (From *Acta Pharm Suecica*, 1974, **11**, 541, by permission)

the quaternary ammonium ion-pairs are affected to a much smaller extent ($k_1 \approx 10$)

Organic solvent effects

Organic acids and bases are traditionally extracted in uncharged form from biological material. The partition coefficients are highly dependent on the hydrogen-bonding ability of the organic solvent, as illustrated in Fig 5 with a secondary amine, nortriptyline, and its *N*-methyl-derivative, amitriptyline, as substrates [8] The hydrogen-donating chloroform gives a considerably higher partition coefficient than the hydrogen-accepting solvents (ethyl acetate, methyl isobutyl ketone, diethyl ether), but the selectivity (given by the quotients of the partition coefficients) is fairly independent of the solvent properties

Ion-pair extraction gives considerably better possibilities for variation of both the degree of extraction and the selectivity The extraction constant of an ion-pair depends on the hydration of the ion-pair components in the aqueous phase and on the hydrogen-bonding ability and polarity of the ion-pair in the organic phase The hydrogen-bonding ability of the ion-pair components will not only influence the binding to the solvent but also the polarity of the ion-pair The components of an ion-pair can bind each other by electrostatic forces but hydrogen-bonding will also be of importance, and the stronger the hydrogen-bonding, the lower the polarity of the ion-pair and the higher the extraction constant [7,8]

The influence of the counter-ion and the organic solvent on the extraction of ions with different hydrogen-bonding ability is illustrated in Figs 6 and 7, and the results are summarized in Tables 1 and 2

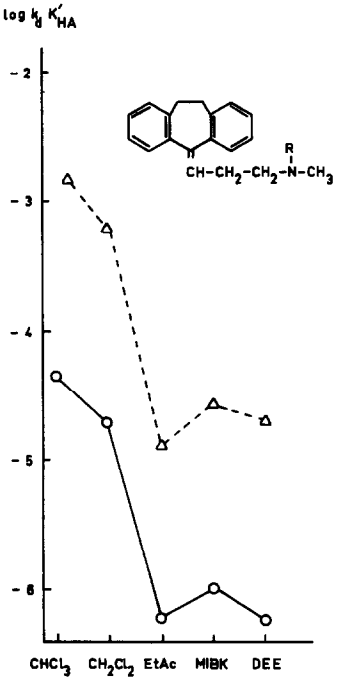

Fig 5 Extraction of nortriptyline and amitriptyline as bases into different organic solvents O, Nortriptyline (R=H), △, amitriptyline (R=CH_3), EtAc = ethyl acetate, MIBK = methyl isobutyl ketone, DEE = diethyl ether, k_d = partition coefficient, K'_{HA} = acid dissociation constant (From *Acta Pharm Suecica*, 1975, **12**, by permission)

A *high extraction constant* is obtained when the hydrogen-bonding is strong between the ion-pair components and between the ion-pair and the solvent A hydrogen-donating substrate should be extracted with a solvent and counter-ion, both of which are hydrogen-accepting; hydrogen-donating solvents and counter-ions should be used when the substrate is hydrogen-accepting (Table 1). The degree of extraction is, in all cases, increased if the counter-ion is large and the solvent rather polar (*cf* ref 9).

High extraction selectivity (*i.e.*, large differences in log E_{QX}) can be obtained by use of a hydrogen-bonding counter-ion and an organic phase that can form hydrogen-bonds with the counter-ion Table 2 gives examples of systems for separation of ammonium ions of different hydrogen-donating ability and for separation of inorganic anions with different hydrogen-accepting properties The ammonium ions should be

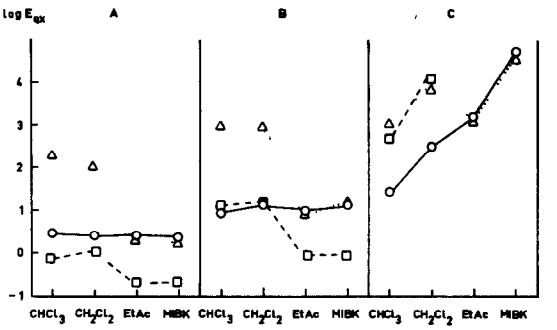

Fig 6 Extraction of nortriptyline, amitriptyline and *N*-methylamitriptyline as ion-pairs into different organic solvents A, Chloride ion-pairs, B, bromide ion-pairs, C, perchlorate ion-pairs, O, nortriptyline, △, amitriptyline, □, *N*-methylamitriptyline (From *Acta Pharm Suecica*, 1975, **12**, by permission)

separated with the hydrogen-accepting chloride ion as counter-ion and hydrogen-donating chloroform as organic phase Good separation of perchlorate, bromide and chloride is obtained with a system containing a hydrogen-donating counter-ion (secondary ammonium ion) and with hydrogen-accepting methyl isobutyl ketone as solvent A non-bonding counter-ion and a weakly hydrogen-donating, rather polar solvent can also be used in the latter case

Extraction of hydrophilic ionized compounds

Ion-pair extraction has particular advantages in the extraction of highly hydrophilic ionized compounds, which can often be extracted even by such weakly

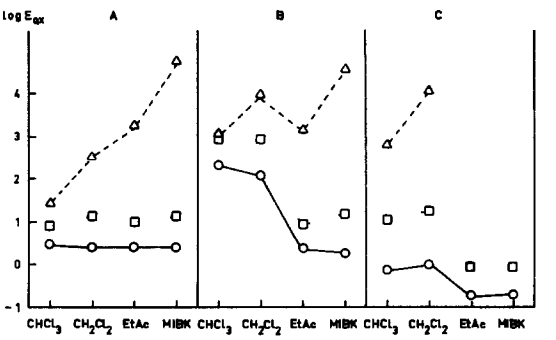

Fig 7 Extraction of inorganic anions as ion-pairs into different organic solvents A, Nortriptyline ion-pairs, B, amitriptyline ion-pairs, C, *N*-methylamitriptyline ion-pairs, O, chloride, □, bromide, △, perchlorate (From *Acta Pharm Suecica*, 1975, **12**, by permission)

Table 1 Counter-ions and solvents for high extraction of ions with different hydrogen-bonding ability

Sample ion	Counter-ion	Solvent
Secondary and tertiary (H-donating) ammonium	ClO_4^- (weakly H-accepting)	MIBK (H-accepting)
Chloride and bromide (H-accepting)	Tertiary (H-donating) ammonium	$CHCl_3$ or (weakly H-donating) CH_2Cl_2
Perchlorate (weakly H-accepting)	Secondary (H-donating) ammonium	MIBK (H-accepting)
Quaternary (non-H-bonding) ammonium	ClO_4^- (weakly H-accepting)	CH_2Cl_2 (weakly H-donating)

Table 2. Counter-ions and solvents for extraction with high selectivity of ions with different hydrogen-bonding ability

Sample ions	Counter-ions	Solvent
Secondary ammonium (H-donating) Tertiary ammonium (H-donating) Quaternary ammonium (non-H-bonding)	Cl^- (H-accepting)	$CHCl_3$ (weakly H-donating)
Chloride (H-accepting) Bromide (H-accepting)	Secondary or (H-donating) tertiary ammonium or	MIBK (H-accepting)
Perchlorate (weakly H-accepting)	Quaternary ammonium (non-H-bonding)	CH_2Cl_2 (weakly H-donating)

solvating organic phases as chloroform or methylene chloride by use of a hydrophobic counter-ion, *i.e*, an ion that contains a high number of alkyl or aryl carbon atoms and no strongly hydrogen-bonding substituents

The size of the counter-ion that will be needed for an extraction can often be estimated on the basis of a few empirical rules for the relation between extraction constant and ion-pair structure [9] Addition of one methylene group will increase log E_{QX} by 0 5–0 6 units, while hydrophilic substituents, *e.g*, hydroxy, carboxylic and amino groups, will decrease the extraction constant by 1–2 logarithmic units, when methylene chloride or chloroform are used as organic solvents Some examples are given in Table 3, which illustrates the extraction of cholic acid derivatives with symmetrical quaternary alkylammonium as counter-ions.[10]

Conjugation of a phenolic hydroxyl group by glucuronic acid decreases the extraction constant by more than three log units, while conjugation with sulphuric acid has only a minor influence on the constant Some examples of extraction constants of glucuronides and sulphates are given in Table 4 [10]

Quaternary alkylammonium ions have several advantages as extracting agents. they are aprotic, which makes their extracting effect independent of pH, and it is also easy to adjust the magnitude of the extraction constant by changing the number of methylene groups

The possibilities for increasing the degree of extraction of a hydrophilic anion by use of a highly hydrophobic counter-ion are, however, limited Large cations will also extract inorganic sample components (*i e*, buffer anions) to a marked extent, as illustrated in Table 5 [11] This will decrease the degree of extraction of the hydrophilic organic substrate since the cation is to some extent used for the extraction of the inorganic anions This is demonstrated by the expression

$$D_X = E_{QX}\,[Q^+].(1 + E_{QY}\,[Y^-])^{-1} \qquad (16)$$

where D_X is the distribution ratio of the organic substrate X^-, and Y^- is the interfering anion The constants E_{QX} and E_{QY} increase to the same degree with increasing size of the cation Q^+, and the partition ratio finally reaches a constant value which is independent of the size of Q^+

An illustration is given in Fig. 8 which shows the extraction of a substrate X^- (log $E_{QX} = -0{\cdot}5$ with tetrabutylammonium) in the presence of HCO_3^- and $H_2PO_4^-$ It shows that extracting agents larger than tetrapentylammonium or tetrahexylammonium are without effect on the distribution ratio when the aqueous phase is 0 1*M* with respect to HCO_3^- or $H_2PO_4^-$

Hydrophilic organic ions can also be extracted with protolytic agents that give ion-pair adducts, as illustrated by equation (11) Alkylphosphoric acids such as bis-(2-ethylhexyl)phosphoric acid (HDEHP) are

Table 3 Extraction constants of cholic acid derivatives (organic phase chloroform)

Anion	R_1	R_2	R_3	R_4	Cation	log E_{QX}
Cholate	OH	OH	OH	O^-	TPeA	2 22
Glycocholate	OH	OH	OH	glyc	TPeA	2 37
Taurocholate	OH	OH	OH	taur	TPeA	3 81
Deoxycholate	OH	H	OH	O^-	TBA	2 23
Glycodeoxycholate	OH	H	OH	glyc	TBA	2 30
Taurodeoxycholate	OH	H	OH	taur	TBA	3 90
Chenodeoxycholate	OH	OH	H	O^-	TBA	2 19
Glycochenodeoxycholate	OH	OH	H	glyc	TBA	2 35
Taurochenodeoxycholate	OH	OH	H	taur	TBA	4 08
Dehydrocholate	=O	=O	=O	O^-	TBA	2 10
Glycodehydrocholate	=O	=O	=O	glyc	TBA	2 33
Taurodehydrocholate	=O	=O	=O	taur	TBA	3·97

glyc = NH CH_2 COO^-
taur = NH $CH_2.CH_2$ SO_3^-
TBA = tetrabutylammonium
TPeA = tetrapentylammonium

Table 4 Extraction constants of glucuronic and sulphuric acid conjugates (organic phase chloroform)

Anion	Cation	log E_{QX}
4-Nitrophenolate	TBA	2 21
4-Nitrophenyl glucuronide	THeA	3 75
	TPeA	1 22
8-Quinolinyl glucuronide	TPeA	1 43
2-Naphthyl glucuronide	TPeA	2 33
2-Naphthyl sulphate	TBA	4 90
	TPrA	2 64
Phenylpropyl sulphate	TBA	4 20
	TPrA	1 95

TPrA = tetrapropylammonium
TBA = tetrabutylammonium
TPeA = tetrapentylammonium
THeA = tetrahexylammonium

Table 5 Extraction constants of inorganic anions (organic phase methylene chloride, counter ion tetrahexylammonium (Q^+)]

Anion	log E_{QY}	log E_{Q_2Z}
HCO_3^-	2 32	—
$H_2PO_4^-$	0 08	—
OH^-	0 98	—
SO_4^{2-}	—	5 54

very powerful extractants for cations, and they have found use in the extraction of amino-alcohols and aminophenols of low molecular weight [12] In the optimum pH-range and with an HDEHP concentration of 0 1*M*, ion-pair adducts containing three molecules of HDEHP are extracted This means that groups containing in all 48 alkyl carbon atoms are coupled to the cation, and this allows quantitative extraction into chloroform of such hydrophilic compounds as adrenaline, synephrine and isoproterenol

An increase of the HDEHP concentration above 0·1*M* in the extracting medium leads to an increase

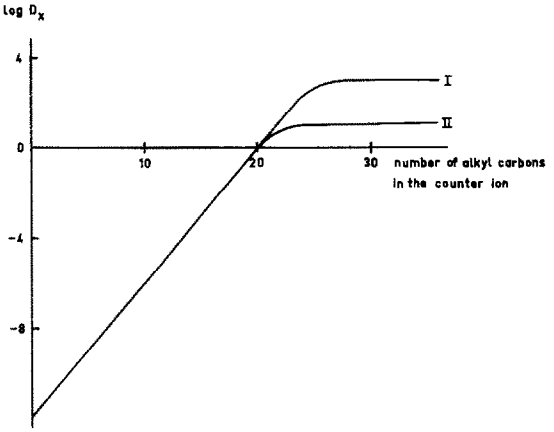

Fig 8 Influence of the size of the counter-ion on the partition ratio of a hydrophilic anion (X^-) in the presence of $H_2PO_4^-$ and HCO_3^- Counter ion symmetrical, quaternary alkalyammonium ion (Q^+) Organic phase methylene chloride Aqueous phase 0·01*M* solution of Q^+ in 0·1*M* $H_2PO_4^-$ (I) or 0 1*M* HCO_3^- (II) (From *Acta Pharm Suecica*, 1975, **12**, by permission)

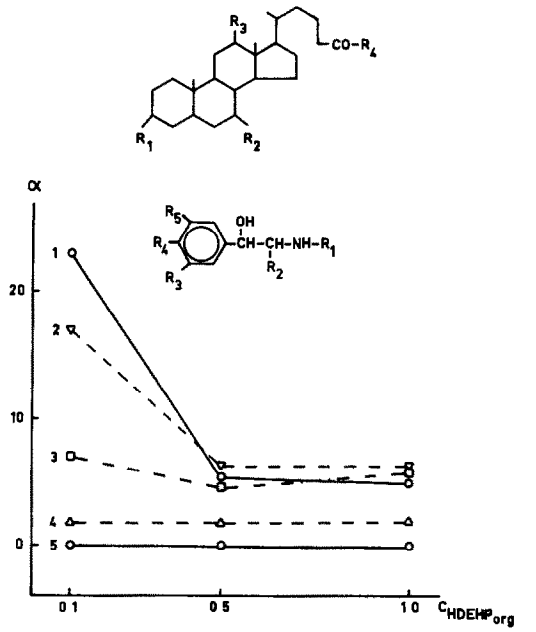

Fig 9 Separation factors (α) in reversed-phase chromatography with HDEHP in the organic phase Aqueous phase phosphate buffer pH 3–5 Organic solvent chloroform

		R_1	R_2	R_3	R_4	R_5
1	Terbutaline	$C(CH_3)_3$	H	OH	H	OH
2	Isoproterenol	$CH(CH_3)_2$	H	OH	OH	H
3	4-hydroxyephedrine	CH_3	CH_3	H	OH	H
4	Synephrine	CH_3	H	H	OH	H
5	Adrenaline	CH_3	H	OH	OH	H

(From *J chromatog*, 1973, **83**, 99, by permission)

of the number of HDEHP-molecules in the adducts This gives a considerable increase in the distribution ratio of the cationic substrate but also a decrease in the extraction selectivity An illustration is given in Fig 9 [13] It shows separation factors obtained by use of the HDEHP extraction system in reversed-phase chromatography The good selectivity obtained with 0 1*M* HDEHP in the stationary chloroform phase is more or less spoiled at an HDEHP concentration of 0 5–1 0*M*

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LONG-TERM STABILITY OF GLASS ELECTRODES IN AQUEOUS MEDIA

BO KARLBERG*
Department of Analytical Chemistry, University of Umeå, S-901 87 Umeå, Sweden

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Summary—The stability of the potential of glass electrodes has been studied The potential changes only slightly during the hydration of freshly etched electrodes With glass electrodes previously used in alkaline solutions, structural transformations within the gel-layer give rise to large potential drifts in neutral or acidic test solutions In alkaline solutions all glass electrodes are attacked, especially the low-temperature type, and the potential changes with time Drying hydrated electrodes affects the stability only slightly Alternating transfers between acidic and basic solutions decrease the stability Recommendations for precise measurements with glass electrodes are given

There are several recommendations in the literature for the care of the glass electrode in order to reduce drift of the potential These recommendations, which involve treatment such as presoaking, conditioning, and bringing the glass electrode to constant temperature, are often contradictory The recommended length of the soaking period, for instance, varies from a few hours to several days The literature has been summarized in treatises on the subject [1,2]

The electrochemical properties of a glass electrode are related to the state of the gel-layer [3] An alteration in the structure of the gel-layer causes an immediate change in potential It is therefore necessary to know the history of a glass electrode exactly, so that the state of the gel-layer can be established Processes which alter the structure of the gel-layer include, among others, hydration and chemical degradation, which can occur simultaneously and which determine the thickness of the gel-layer Hydration continuously renews the gel-layer, the external part of which is subject to some chemical degradation in any solution The degradation is especially rapid in strongly basic solutions In this work, the factors affecting the drift in potential of some commercial glass electrodes have been studied in the light of more recent knowledge about the gel-layer properties [3–9]

EXPERIMENTAL

Electrodes

Only lithia glass electrodes were studied Several specimens of each of the following electrode types were used Ingold LoT low-temperature electrodes, Ingold 201 and Metrohm UX general purpose electrodes, and Ingold HA high-temperature electrodes Etching was performed in 2% hydrofluoric acid for 1–3 min The Ag/AgCl electrode, prepared by Brown's method,[10] was used as reference The potentials of freshly prepared and aged reference electrodes in 0 1*M* hydrochloric acid were compared deviations were very seldom larger than 0 1 mV throughout an observation period of 12 hr At least two reference electrodes were used in each measuring series and these were allowed to equilibrate in the test solution for at least 6 hr before the measurements with the glass electrodes were started All test solutions contained chloride ions, allowing a diffusion-free arrangement for the Ag/AgCl electrode The glass electrodes were always brought to constant temperature before use since even a small temperature difference between the test solution and the glass electrodes resulted in an emf drift of several mV

Solutions

All solutions were prepared from reagent grade chemicals The buffer compositions were as follows

0 1*M* hydrochloric acid—"pH 1"
0 05*M* potassium hydrogen phthalate + 0 10*M* sodium chloride—"pH 4"
0 02*M* "tris" + 0 01*M* hydrochloric acid + 0 10*M* sodium chloride—"pH 8"
0 01*M* borax + 0 02*M* sodium chloride—"pH 9"
ca 0 0025*M* calcium hydroxide + 0 02*M* sodium chloride—"pH 12"

A little silver nitrate solution was added to each buffer and to each of the other solutions to prevent dissolution of silver chloride from the reference electrode and this addition altered the chloride ion content only slightly Nitrogen was used to expel carbon dioxide from the most alkaline solutions

Circuit and emf recording

The electrode vessel was a double-walled titration vessel, Metrohm EA 880, kept at 25 0° and shielded in an earthed metal cage Not more than three glass electrodes were investigated at a time A programmable unit selected and connected the electrodes in selected order to an HP 3460 B voltmeter *via* a follower (Analog Devices Model 302), and the emf was recorded by an IBM typewriter in direct connection The time and order of connection of the electrodes were programmed in advance as were the number of recordings and the time intervals between recordings The typewriter printed both the time and the emf value A reading for each electrode system could be taken about every third minute The electrode was connected to the voltmeter for about 1 min before a reading was made The long-term stability of the voltmeter and follower was investigated separately and the drift was found to be less than 0 1 mV over a period of 24 hr

* Present address Astra Pharmaceuticals AB, Analytical Control, S-151 85 Sodertalje (Sweden)

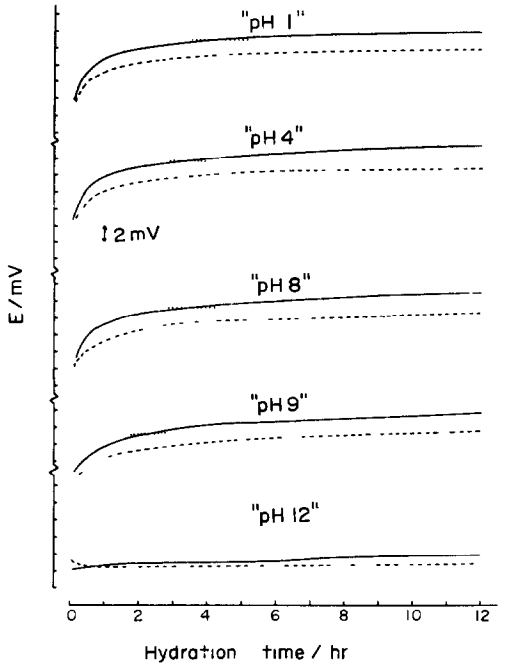

Fig. 1 Emf drift patterns with freshly etched glass electrodes in different buffers Ingold HA (——), Ingold 201 (– – – –), Ingold LoT ( )

RESULTS AND DISCUSSION

Drift pattern of freshly etched electrodes

The potential drifts of three freshly etched electrodes were studied simultaneously in aqueous solutions of various pH The results are summarized in Fig 1 Several interesting conclusions can be drawn from the results The total drift of the electrodes during the gel-layer formation is rather small but is dependent on the glass composition This finding conforms with current knowledge of the rate of gel-layer formation of the different glasses, this rate increases in the order HA < 201 < LoT A fully-developed gel-layer consists of two distinct regions, the external region being thinner than the internal one The LoT glass is readily attacked by water, resulting in rapid growth of the gel-layer The external region is therefore formed rather rapidly Since the response properties of the glass are located in the external part, only small changes of the cell emf are expected once this layer has been established. In fact, the drift curves for the LoT electrode in pH 1, 4, 8, and 9 buffers are almost parallel with the time axis after one hour of hydration On the other hand, the curves for the 201 and HA glasses, which are more resistant to chemical attack by water, require more time to reach a steady value, in accordance with slower formation of the external layer The thickness of the total gel-layer is known to increase for all electrodes even after they have reached a steady potential, but this increase apparently occurs within the internal part of the layer

At higher pH values the probable mechanism of electrode glass attack is neutralization of silicic acid groups [11,12] The hydration process will be retarded by such a reaction and the growth of the gel-layer will consequently be reduced. A different drift pattern is thus expected in alkaline solutions With the HA and 201 electrodes, the drift from lower to higher emf observed at pH 1–9 is compensated at pH 12 With the LoT electrode, the shift towards higher emf values at the very beginning of the curve is compensated to such an extent even at pH 8 and 9 that a drift from higher to lower emf values results

Drift pattern of dried (previously hydrated) electrodes

The three types of glass electrode (LoT, 201, and HA) were hydrated for about one month in distilled water, dried for 2 hr in a warm air stream at 70–80° and allowed to cool in a desiccator They were then brought carefully to constant temperature and immersed in the pH-4 buffer Typical emf values observed at different times are given in Table 1 The immediate conclusion drawn is that drying does not influence the long-term stability The LoT electrode is especially insensitive to drying. It has previously been shown that a similar drying procedure affects the response behaviour in non-aqueous solutions [13,14] Lack of water in the gel-layer hinders proton transfer, which occurs *via* water molecules, and consequently the response becomes slow However, immersion of a glass electrode in an aqueous solution for only 5 min is sufficient to restore the rapid response The redistribution of the water in the gel-layer is so fast that the long-term stability is not affected

Influence of rapid pH changes on the long-term stability

In Table 2, cell emf values are given for the three different Ingold electrodes in going from pH 4 to pH 1 and from pH 4 to pH 9, respectively The change from pH 4 to pH 1 does not seem to have any influence on the long-term stability while, for the Ingold LoT only, the change from pH 4 to pH 9 causes a small but continuous increase of the emf values These results are expected since a soft glass like the LoT glass is more easily attacked in a basic solution than a hard glass, *i e*, the HA glass The degradation of the outermost part of the gel-layer results in a

Table 1 Potentials of "dried" electrodes in pH-4 buffer, *mV*

Electrode	Time, *hr* 0 1	0 3	0 5	1 0	2 0	4 5	10 0	18 0	24 0
LoT	116 8	116 6	116 4	116 7	116 7	116 9	116 7	116 8	116 8
201	107 3	106 9	106 6	106 2	105 9	105 6	106 0	106 5	106 8
HA	106 4	106 0	105 5	105 4	105 1	105 2	105 0	105 4	105 6

Table 2 Emf variation with time following transfer to pH-1 and pH-9 buffers after 24 hr in pH-4 buffer

Electrode	Time, *min* 4	10	20	40	100
		From pH 4 to pH 1			
LoT	308 4	308 4	308 3	308 2	308 1
201	297 8	298 0	298 0	297 9	297 9
HA	296 4	296 5	296·4	296 4	296 4
		From pH 4 to pH 9			
LoT	−206 8	−207 2	−207 4	−207 6	−208 1
201	−218 7	−218 6	−218 5	−218 5	−218 3
HA	−220 2	−220 1	−220 1	−220 1	−220 1

changing potential If the electrodes are subsequently re-immersed in the pH-4 buffer, a similar drift pattern is expected The gel-layer of the LoT electrode, which has been degraded in the basic solution, starts to regenerate and this process causes a drift (Table 3) Stable potentials are obtained for the 201 and the HA electrodes throughout, but slightly different potentials are obtained in the pH-4 buffer, depending on the pH of the solution from which the electrodes have been transferred The shift may be due to changes in the proton activities within the gel-layer This proton activity change may in turn be caused by an altered standard state within the gel-layer, the number of protons may in fact remain constant The results in Tables 2 and 3 indicate that rapid changes within the pH-region 1–9 do not diminish the long-term stability of the 201 and the HA glass electrodes, only the LoT electrode exhibits deviations during and after contact with the pH-9 buffer

The fact that small potential shifts may appear depending on the direction of the pH change in the test solution immediately raises the question of whether an electrode has a Nernstian response over a broad range of pH or not, irrespective of the direction of pH-change Proton activity changes in the gel-layer will occur in basic solutions when protons are exchanged for cations such as sodium, resulting in the well-known alkali error For low-temperature electrodes this deviation occurs even at pH 9–10 However, it is known that by no means all glass electrodes obey Nernst's law in the "ideal" range (pH 1–8) [15] Test procedures with the hydrogen electrode as a reference have been described [16]

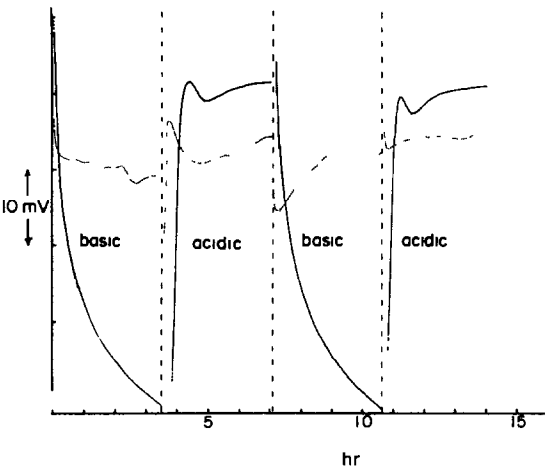

Fig 2 Variations in potential of two hydrated glass electrodes, Ingold LoT (——) and Metrohm UX ( ) in alternating test solutions Basic test solution 0 01*M* NaOH + 0 99*M* NaCl, acidic test solution 0 1*M* HCl + 0 9*M* NaCl The broken vertical lines denote the time of the electrode transfers

Large pH changes (from acidic to basic solutions and *vice versa*) resulted in unexpected behaviour of the low-temperature Ingold LoT electrode, and the general purpose Metrohm UX electrode (Fig 2) In the basic solution (0·01*M* NaOH + 0 99*M* NaCl) the LoT electrode exhibits a strong and regular drift in potential, while the potential of the Metrohm electrode varies rather irregularly After the first transfer to the acidic solution (0 1*M* HCl + 0 9*M* NaCl), both curves show distinct peaks

Table 3 Emf variation with time following transfer to pH-4 buffer after 24 hr in pH-1 or pH-9 buffer

Electrode	Time, *min* 4	10	20	40	100
		From pH 1 to pH 4			
LoT	120 2	120 1	120 0	120 0	120 0
201	110 9	110 7	110 6	110 6	110 5
HA	108 3	108 3	108 3	108 4	108 4
		From pH 9 to pH 4			
LoT	117 7	118 4	118 9	119 3	119 8
201	110 8	111 0	111 0	111 1	110 9
HA	109 4	109 5	109 4	109 4	109 4

Several factors must be taken into account in the interpretation of the drift patterns First, we have the previously mentioned attack on the glass in alkaline solutions Secondly, hydrogen ions in the gel-layer are exchanged for sodium ions in the basic solution, and re-exchange takes place in the acidic solution This ion-exchange process strongly affects the emf in non-aqueous solutions[13] and ought also to be of great importance in aqueous solutions Thirdly, reduction of the gel-layer thickness resulting from the storage in basic solutions causes rehydration to occur in the acidic solution Furthermore, breakdown of the gel-layer structure may occur when traces of acid or base in the surface region of the glass are rapidly neutralized during the transfer of the electrode Other processes may also be involved in determining the emf changes The slow and continuous emf drift observed when the LoT electrode is in basic solution is certainly not due to the ion-exchange process since exchange of hydrogen ions in the gel-layer is fast It is probably the alkaline attack on the electrode glass which causes the emf drift since the LoT glass has a low durability[3] On the other hand, the slow attainment of the peak emf value in acidic solution may be partly caused by the ion-exchange process, since sodium ions within the gel-layer require a considerable time to reach exchange equilibrium

The results presented in Fig 3 support the interpretation that the neutralization reaction may damage the gel-layer An Ingold 201 electrode was transferred to a 0 01*M* sodium hydroxide solution after different pretreatments Curve *a*, showing the emf variation after a direct transfer from 0 1*M* hydrochloric acid, should be compared with curve *c*, which was obtained after electrode transfer *via* short periods of immersion in a series of buffers with successively increasing pH-values The variations in curve *c* are much less than those in curve *a* Even the neutralization of traces of the pH-4 buffer causes a drift in potential (curve *b*), while storage in distilled water seems to be more satisfactory (curve *d*)

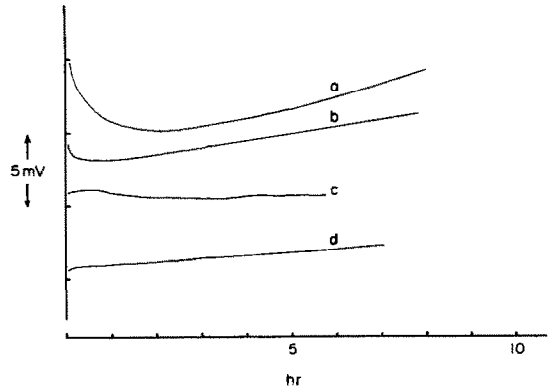

Fig 3 Variation in potential of an Ingold 201 in 0 01*M* NaOH History of the electrode (*a*), 48 hr in 0 1*M* HCl, direct transfer, (*b*), 19 hr in pH-4 buffer, direct transfer, (*c*), 49 hr in 0 1*M* HCl, transfer *via* 10–15-sec dippings in buffers at pH 3, 5, 7 and 9, (*d*), 24 hr in distilled water, direct transfer

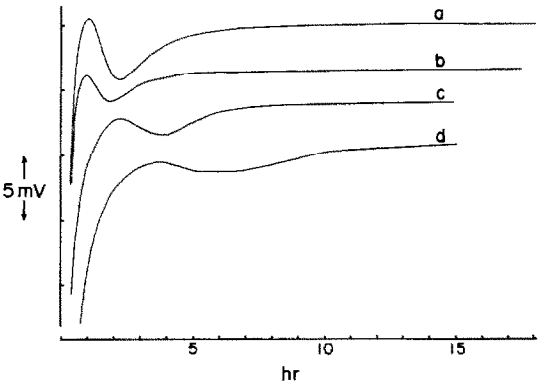

Fig 4 Emf drift with an Ingold LoT electrode (hydrated for several months before the start of the experiment) in 0 1*M* HCl Pretreatments were according to the scheme

Curve	Absolute time, *days*	Time in 0·01*M* KOH, *hr*
a	1	20
b	3	7
c	25	20
d	31	23

The electrode was stored in distilled water between the base–acid test cycles

The "peak phenomenon" appearing in acidic solution (Fig 2) was studied more closely for an Ingold LoT electrode (Fig 4) The alkaline storage solution was 0 01*M* potassium hydroxide and the acidic solution 0 1*M* hydrochloric acid (both aqueous) The electrode had been hydrated for several months before the experiment was started The curves in Fig 4 have been separated from each other for the sake of clarity, in reality, the equilibrium emf values were all very similar It is obvious that the character of the peak changes when the experiment is repeated Additionally, attainment of the peak value is successively slower This last finding can readily be explained Treatment in the alkaline solution causes the external part of the gel-layer to be reduced in thickness,[5] and a further reduction is probably caused by the neutralization The structural rigidity of the gel-layer increases towards the unhydrated glass core, and consequently the diffusion coefficients for the mobile ions in the gel-layer decrease in the same direction Hence, the ion-exchange process slows when the gel-layer structure increases in rigidity owing to the reduction in thickness The hydration process re-opens the structure to some extent, but three weeks of further hydration after test *b* in basic solution is obviously not enough to form a layer similar to that formed after several months of hydration (compare curves *a* and *c* in Fig 4)

CONCLUSIONS

Conclusions and recommendations in this section are based partly on the results presented in this paper and partly on the results of earlier studies

Temperature

For precise measurements, the glass electrode must be brought carefully to constant temperature when

it is in use, since a difference of as little as 2–3° between the electrode and the test solution causes an emf drift of several mV during the first hour It is self-evident that the temperature of the test solution must be thermostatically controlled for precise work

Hydration

Well-hydrated electrodes should be selected for precise measurements in aqueous solutions The hydration process causes the largest initial emf changes when a glass electrode without a gel-layer is immersed in water Electrodes used in solutions with etching properties are subject both to hydration and to other structural transformations of the gel-layer, and these processes together cause a pronounced drift in emf Low-temperature electrodes are especially unstable in basic solutions, errors resulting even when the electrode is used again at a lower pH

Storage

Storage in distilled water, recommended by many manufacturers, is quite adequate Storage in air for short periods is also possible if coatings can be prevented and if the electrode is soaked in water just before use, but it must be emphasized that this is valid only for electrodes that have been completely hydrated New electrodes should be kept in water The pH of the aqueous storage solution is not critical provided too basic or too acidic solutions are avoided

Effect of pH changes

Since small changes in pH do not alter the electrode stability, it is prudent to store the electrode in a solution of similar pH to the test solution If an electrode is used alternatively in acidic and basic solutions, the stability of its potential in any solution decreases rapidly Electrodes used for end-point determination in acid-base titrations should not, therefore, be used for precise pH measurements

Buffer capacity

Emf changes may appear in going from strongly to weakly buffered solutions, even if the solutions have the same pH The opposite transfer is less detrimental Thus, electrodes should be kept in an unbuffered solution before use in a test solution with low buffer capacity The expected emf stability in such test solutions is, however, necessarily lower than in well-buffered solutions

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THE FORMATION OF 2-HYDROXY-1,3-DIAMINOPROPANE-*N,N,N',N'*-TETRA-ACETIC ACID SILVER AND MERCURY(II) CHELATES

LEO HARJU
Department of Analytical Chemistry, Åbo Akademi, 20500 Åbo 50, Finland

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Summary—The stability constants of mononuclear (1 1) and binuclear (2 1) chelates of the Ag–HDPTA and Hg(II)–HDPTA systems (HDPTA = 2-hydroxy-1,3-diaminopropane-*N,N,N',N'*-tetra-acetic acid) were evaluated from pM and pH data, using a method proposed earlier by Ringbom and the author The determinations yielded the following stability constants (concentration)

$$\log K_{AgL}^{Ag,L} = 5\,28, \log K_{AgHL}^{H,AgL} = 7\,60, \log K_{Ag_2L}^{Ag,AgL} = 3\,0,$$

$$\log K_{HgL}^{Hg,L} = 18\,35, \log K_{HgHL}^{H,HgL} = 3\,85, \log K_{Hg_2L}^{Hg,HgL} = 8{\cdot}0$$

The use of the reagent for the analytical determination of silver and mercury(II) ions is also discussed

The formation of chelates of 2-hydroxy-1,3-diaminopropane-*N,N,N',N'*-tetra-acetic acid, HDPTA, has been investigated by several authors during recent years [1–7] The equilibrium data given for the reagent are chiefly for the formation of mononuclear metal chelates. However, the ligand also forms stable binuclear chelates with some metals. As shown earlier[8] the stability constants of both mononuclear and binuclear chelates must be considered, when devising methods of analysis for ligands of this type

Analytically the ligand has been used by Přibil[6] for analysis of multicomponent systems He utilized the fact that lead forms binuclear (2:1) chelates with HDPTA, whereas some other metals react in the molar ratio 1·1.

EXPERIMENTAL

Reagent

HDPTA from La Mont Laboratories, Dallas, Texas, was employed The following logarithmic protonation constants[5] were used in the calculations $\log K_{HL} = 9\,49$, $\log K_{H_2L}^{H} = 6\,96$, $\log K_{H_3L}^{H} = 2\,60$, $\log K_{H_4L}^{H} = 1\,6$

Procedure

Potentiometric measurements were carried out with an Orion Research Model 801 digital pH-meter and an electrode switch The silver and mercury electrodes were standardized against known concentrations of the respective metal ions The glass electrode was calibrated by a titration procedure to give hydrogen concentrations A small amount of a strong acid was titrated with potassium hydroxide solution from a microburette If the pH of 0·05*M* potassium hydrogen phthalate is taken as 4·008, the value $\log f_H = -0\,10$ was obtained All experiments were carried out at 25° and ionic strength 0·1 (KNO_3) in an inert atmosphere The pH was adjusted with potassium hydroxide solution

When a metallic mercury electrode is used, the reduction of mercury(II) can be considered in terms of the side-reaction coefficient

$$\alpha_{Hg^{2+}(Hg)} = \frac{[Hg^{2+}) + [Hg_2^{2+}]}{[Hg^{2+}]} = 1 + K$$

where K is the equilibrium constant for the reaction

$$Hg^{2+} + Hg \rightleftharpoons Hg_2^{2+}$$

A value of 85 given by Schwarzenbach and Anderegg[9] was used for this constant

For mathematical calculations a programmable Monroe 1860 desk calculator was used

DETERMINATION OF STABILITY CONSTANTS

The stability constants of the chelate complexes were determined by a method comprehensively described by Ringbom and Harju in two earlier papers [10] In the following, the method is only shortly reviewed

For the determination of equilibrium constants of mononuclear monoligand chelates, a series of pM and pH measurements is conducted in a solution containing metal and ligand in the molar ratio $C_M.C_L = 0{\cdot}5\ 1$ From the law of mass action and by appropriate use of conditional constants and α-coefficients the following equation can be derived·

$$\log K_{(ML)'}^{M,L} = \log([(ML)']/[L']) + pM_{0\,5} + \log \alpha_{L(H)} \qquad (1)$$

If the mononuclear chelates are quantitatively formed and the ratio $[(ML)']/[L']$ equals unity, the following simplification can be made

$$\log K_{(ML)}^{M,L} = \log 1 + pM_{0\,5} + \log \alpha_{L(H)} \qquad (2)$$

or

$$\log K_{(ML)'}^{M,L} = pM_{0\,5} + \log \alpha_{L(H)} \qquad (3)$$

At the lowest pH values corrections must be applied, because the mononuclear chelate is often dissociated to a considerable degree This can be taken into account by replacing unity in equation (2) by the value

$$\frac{[(ML)']}{[L']} = \frac{C_M - [M']}{C_M + [M']} \qquad (4)$$

Table 1 The determination of the stability constants of mononuclear (1 1) Ag–HDPTA chelates from pAg and pH values C_{Ag} C_L = 0 5 1 C_L = 4 00 × $10^{-3}M$

pH_c = $-\log[H]$	pAg	log $\alpha_{L(H)}$	log $K^{Ag,L}_{(AgL)'}$ pAg + log $\alpha_{L(H)}$	Corrected acc to eqn (5)
5 90	2 92	4 69	7 61	6 98
6 40	3 13	3 76	6 89	6 50
6 90	3 39	2 92	6 31	6 06
7 40	3 66	2 23	5 89	5 71
7 90	3 93	1 65	5 58	5 44
8 40	4 26	1 14	5 40	5 32
8 90	4 62	0 69	5 31	5 27
9 40	4 92	0 35	5 27	5 25
9 90	5 15	0 14	5 29	5 28
10 40	5 26	0 05	5 31	5 30
10 90	5 30	0·02	5 32	5 31

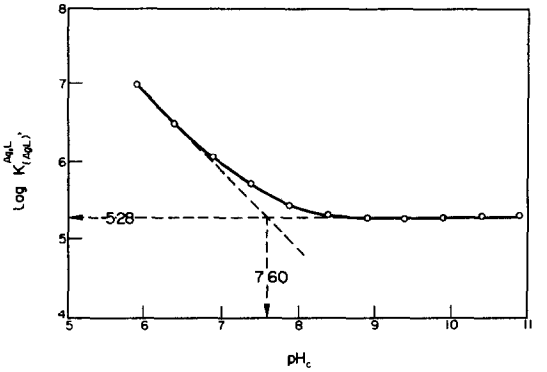

Fig 1 The determination of the stability constants of mononuclear silver–HDPTA chelates

The equilibrium can also be affected to a small degree by the formation of binuclear chelates The following expression for correction can then be derived by considering the dissociation of mononuclear chelate as well as the formation of binuclear chelates

$$\frac{[(ML)']}{[L']} = \frac{C_M - [M']}{C_M\{1 + 3[M']K^{(ML)',M'}_{(M_2L)'}\} + [M']\{1 + [M']K^{(ML),M'}_{(M_2L)'}\}} \quad (5)$$

$K^{M',(ML)'}_{(M_2L)'}$ can independently be determined from a solution containing metal to ligand in a ratio of 1 5 1

For the determination of stability constants of binuclear chelates a solution containing the metal and ligand in the ratio C_M C_L = 1 5 1 is prepared For $\log K^{M,ML}_{(M_2L)'}$ we can write

$$\log K^{M,ML}_{(M_2L)'} = \log([(M_2L)']/[(ML)']) + pM_{1\cdot5} + \log \alpha_{ML(H,OH)} \quad (6)$$

If the 1 1 and 2 1 metal chelates are formed quantitatively, equation (6) can be simplified to

$$\log K^{M,ML}_{(M_2L)'} = pM_{1\cdot5} + \log \alpha_{ML(H,OH)} \quad (7)$$

If the chelate formation is incomplete, $[(M_2L)']$. $[(ML)']$ will differ from unity A correction can be derived from the equations

$$C_M = [M'] + [(ML)'] + 2[(M_2L)'] \quad (8)$$

$$C_L = [L'] + [(ML)'] + [(M_2L)'] \quad (9)$$

$$K^{M'L'}_{(ML)} = \frac{[(ML)']}{[M'][L']} \quad (10)$$

These equations yield the following expression, which can be substituted in equation (6).

$$\frac{[(M_2L)']}{[(ML)']} = \frac{\frac{1}{3}C_M\{3 + [M']K^{M'L'}_{(ML)'}\} - [M']\{1 + [M']K^{M'L'}_{(ML)}\}}{[M']K^{M'L'}_{(ML)}\{\frac{1}{3}C_M + [M']\}} \quad (11)$$

Silver chelates

The results of the determination of equilibrium constants of mononuclear monoligand silver–HDPTA chelates are presented in Table 1 and Figs 1 and 2

Owing to the weak chelate formation, corrections must be applied to the values obtained by the simplified equation (3) (fourth column in Table 1) The corrected values given by equation (5) are presented in the fifth column It should be noted that the correction will cause a decrease in the value of log $K^{Ag,L}_{(AgL)'}$

In Fig 1 log $K^{Ag,L}_{(AgL)'}$ is plotted as a function of pH_c For simplicity the negative logarithm of the hydrogen concentration, $-\log[H]$, is denoted by pH_c in the following text The horizontal course of the log $K_{(AgL)'}$–pH_c curve at pH_c 8 5–11 indicates that the OH-group does not participate in the chelate formation in this system From this section of the curve the value of the non-conditional constant, log $K^{Ag,L}_{AgL}$ = 5 28 is obtained The rise of the left part of the curve indicates the formation of a protonated mononuclear chelate AgHL The stability constant of this protonated chelate can be computed graphically as shown in Fig 1 by the dotted lines The intersection point of the extrapolated tangent of slope −1 and the horizontal line passing through ordinate log K_{AgL} = 5·28 gives log $K^{H,AgL}_{AgHL}$ = 7·60. The same value was obtained algebraically from the data in Table 1

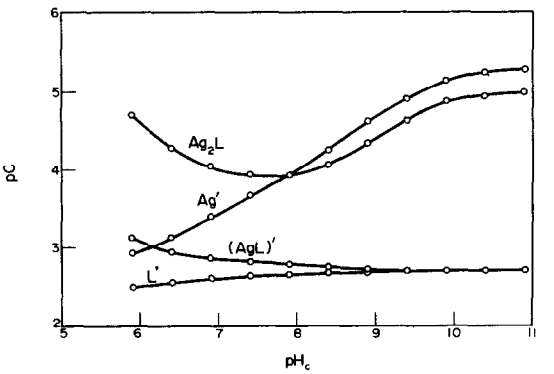

Fig 2 The concentrations of the components (AgL)', L', Ag_2L and Ag' as a function of pH_c for the determination of $K^{Ag,L}_{(AgL)}$ given in Table 1 and Fig 1

Table 2 The determination of the stability constants of mononuclear (1 1) Hg(II)–HDPTA chelates from pHg and pH values C_{Hg} C_L = 0 5 1 C_L = 3 00 × $10^{-3}M$

pH_c = −log [H]	pHg	log $\alpha_{L(H)}$	log $K^{Hg,L}_{(HgL)'}$ pHg + log $\alpha_{L(H)}$	Corrected acc to eqn (5)
2 44	7 84	11 99	19 83	19 77
2 72	8 34	11 26	19 60	19 56
3 04	8 84	10 51	19 35	19 33
3 39	9 33	9 74	19 07	19 06
3 75	9 87	8 98	18 85	18 86
4 17	10 53	8 12	18 64	18 64
4 70	11 44	7 06	18 50	18 50
5 12	12 22	6 22	18 44	18 44
5 96	13 73	4 57	18 30	18 30
6 87	15 33	2 97	18 30	18 30
8 07	16 92	1 47	18 39	18 39
9 00	17 93	0 61	18 54	18 54

In Fig 2 the concentrations of the components L′, (AgL)′, Ag_2L and Ag′ are plotted against pH_c, for the case given in Table 1 This distribution diagram clearly shows the equilibrium situation in the system At pH_c below 4 the 1 1 chelate becomes strongly dissociated and the concentration of Ag and L′ increases From the course of the Ag_2L curve it can be noticed that the formation of 2 1 chelates only slightly affects the ratio [(AgL)′]/[L′] The difference between the lines (AgL)′ and L′ visualizes the correction defined by equation (5).

Silver forms weak binuclear chelates with HDPTA. At pH_c 8 5 a value of log $K^{Ag,AgL}_{Ag_2L}$ = 3 0 (corrected) was obtained

Mercury(II) chelates

Data from experiments for determination of equilibrium constants of mononuclear Hg–HDPTA chelates are given in Table 2 If the corrected values in the fifth column are compared with the constants obtained by the simplified equation (3), they are seen to deviate only in the second decimal at low pH_c values Thus in this case the accuracy obtained by

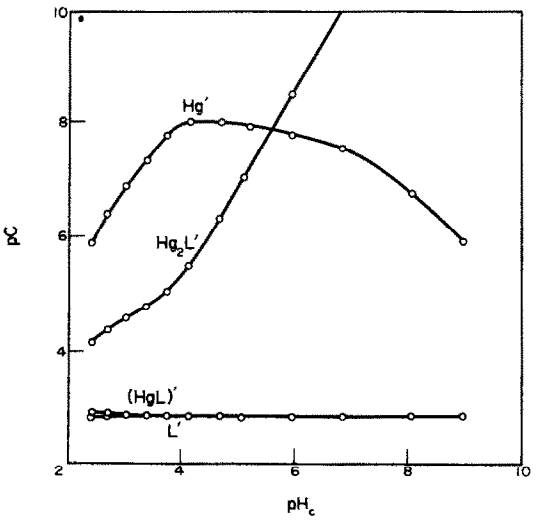

Fig 3 The concentrations of the components (HgL)′, L′, Hg_2L and Hg′ as a function of pH_c for the determination of $K^{Hg,L}_{(HgL)'}$ given in Table 2

Table 3 The determination of the stability constants of binuclear (2 1) Hg(II)–HDPTA chelates from pH and pHg values C_{Hg} C_L = 1 5 1 C_{Hg} = 1 50 × $10^{-3}M$

pH_c = −log [H]	pHg	log $\alpha_{HgL(H)}$	log $K^{Hg,HgL}_{(Hg_2L)'}$ pHg + log $\alpha_{HgL(H)}$	Corrected acc to eqn (11)
2 97	7 12	0 93	8 05	8 08
3 29	7 37	0 66	8 03	8 05
3 87	7 61	0 29	7 90	7 90
4 73	7 95	0 05	8 00	7 94
5 37	8 55	0 01	8 56	8 28
6 54	10 41	0	10 41	8 93

the use of the simplified equation (3) is sufficient for analytical purposes The limiting factor for the attainable accuracy is probably how ideally the mercury electrode follows the Nernst equation at alkaline pH and high pHg values For the 1 1 system the determination yielded the constants log $K^{Hg,L}_{HgL}$ = 18 35 and log $K^{H,HgL}_{HgHL}$ = 3 85

In Fig 3 the concentrations of the components are given as a function of pH_c It can be seen that the formation of 2·1 chelates chiefly affects the ratio [(HgL)′]/[L] At pH_c above 10 the formation of hydroxo-complexes becomes a competitive reaction

Data for the determination of stability constants of 2 1 chelates are presented in Table 3 and Fig 4 At pH_c 5 37 and 6 54 the constants obtained are somewhat higher, which can be due to the formation of binuclear hydroxo-chelates of the type $Hg_2(OH)_nL$ However, as can be seen from the distribution diagram (Fig 4), the 2·1 chelate is dissociated to a considerable degree at these pH_c values, and the constants obtained must be considered uncertain Calculations from experimental points at pH_c below 5 yielded the average value log $K^{Hg,HgL}_{Hg_2L}$ = 8 0

COMPLEXOMETRIC TITRATIONS

A general theory for complexometric titrations of metals as mononuclear (1 1) and binuclear (2 1) chelates has been formulated by the present author and Ringbom in two earlier papers,[8] where a thorough exposition of the principles can be found

In Fig. 5 the conditional constants for 1 1 and 2 1 chelates, as well as pHg at the equivalence points,

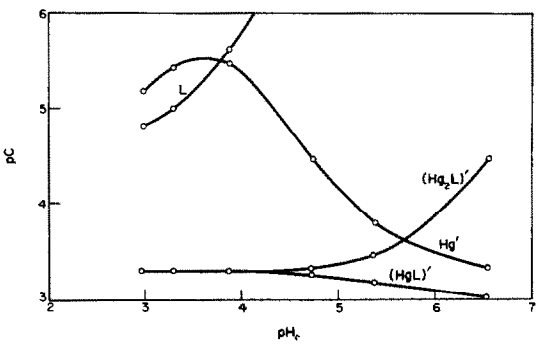

Fig 4 The concentrations of the components $(Hg_2L)'$, (HgL)′, Hg′ and L′ as a function of pH_c for the determination of $K^{Hg,HgL}_{(Hg_2L)'}$ given in Table 3

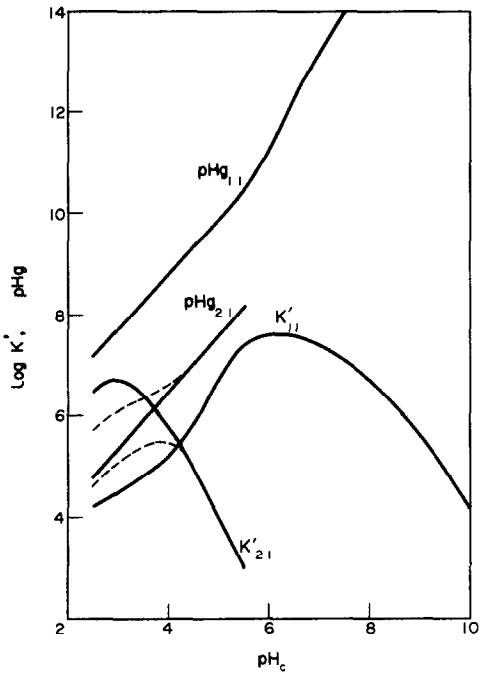

Fig 5 Conditional constants and pHg_{eq} values in titrations of mercury(II) with HDPTA to the 1 1 and 2 1 chelates as a function of pH_c C_{Hg} is assumed equal to $10^{-3}M$

are plotted as a function of pH_c It can be seen that the optimal determination of Hg with HDPTA is obtained by titration to the 1·1 chelate at pH_c about 6, where $K'^{Hg'L'}_{(HgL)'} = 10^{7\cdot6}$. This constant is rather low, but by instrumental methods the titration can be carried out with satisfactory accuracy The conditional 2.1 constant attains its maximum value at pH_c about 3 The dotted lines represent the reduction to mercury(I), when a metallic mercury electrode is used as indicator electrode

Data from a potentiometric titration of Hg at pH_c 5 5, using hexamethylenetetramine as buffer, are plotted in Fig. 6 From the potential jump at the 1·1 equivalence point, the conditional constant can be estimated as *ca.* 10^6 by using the Ringbom error diagram [11] This is in satisfactory agreement with the theoretically calculated value in Fig 6, especially as

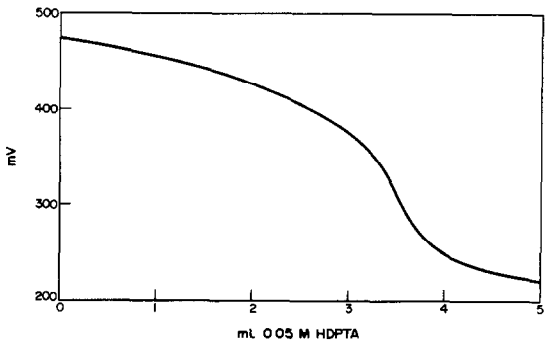

Fig 6 Potentiometric titration of mercury(II) with HDPTA at pH_c 5 50 (hexamine buffer) $V_i = 100$ ml, $\mu \approx 0$ 1 Theoretical equivalence points at 1 76 ml (2 1 chelate) and 3 52 ml (1 1 chelate)

the buffer may affect the equilibrium in the system, *e g.*, by forming mixed-ligand chelates. The 2·1 chelates are not formed to any considerable degree, because the conditional constant is only 10^3 at this pH_c

DISCUSSION

No published values for equilibrium constants of silver–HDPTA chelates could be found The value log $K_{AgHDPTA} = 5\,28$ obtained in this work is surprisingly low when compared with the 1 1 equilibrium constants of other polyaminopolycarboxylic acids. For the corresponding silver–EDTA complex the value 7 3 is reported [12] Owing to the low stability of silver–HDPTA chelates, silver can hardly be determined by titration with the reagent without using some instrumental method for locating the equivalence points The equilibrium constants of the silver–HDPTA system are, however, of importance, for instance, when determining some other metal with the ligand, by use of a silver electrode as indicator electrode

The value log $K_{HgL} = 18\,35$ obtained in this work is in very good agreement with the value 18·4 given by Smith [1] Stankovíansky and Königstein[2] have obtained the value 20 59 by a polarographic method. For 2 1 Hg–HDPTA chelates and for protonated 1.1 chelates no equilibrium constants were found in the literature

If HDPTA is compared with, *e g*, EDTA and TTHA as a chelate-forming reagent, it does not offer any advantages for the analytical determination of silver or mercury The conditional constants of the silver and mercury HDPTA chelates are noticeably low

Acknowledgements—I thank my colleagues for fruitful discussions and Mr M Pickering for revising the English text of this paper

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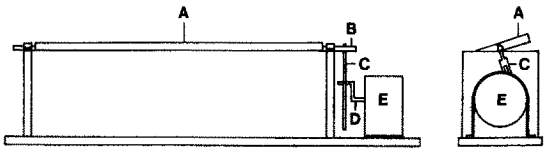

Fig 2 Agitating apparatus A—tray for diffusion dishes, B—axis, C—fork, D—eccentric cam, E—motor

A Metrohm fluoride-sensitive electrode was used with a Metrohm Ag/AgCl electrode with fibre junction as reference electrode The e m f's were measured with the expanded scale of an Orion 701 pH mV-meter

Materials

The fluoride standard solutions were prepared from Merck "Suprapur" sodium fluoride and were made 0 033*M* in both sodium nitrate and hexamethylenetetramine (Merck *p a*), the pH was adjusted to 5·4 with concentrated nitric acid

Perchloric acid (2 7*M*, prepared from the Merck *p a* 60% acid) saturated with hexamethyldisiloxane (HMDS, Fluka AG) was used for the diffusion In some experiments 10% v/v ethanol was added to the perchloric acid before its saturation with HMDS The perchloric acid solution was stored in a separatory-funnel under a layer of HMDS

As trapping solution, 0 1*M* sodium hydroxide was used

Procedure

The diffusion dishes are placed in an inclined position according to Fig 3, three separated compartments are thus formed in each The samples (maximally 10 ml) are pipetted into the left-hand compartments, 5 ml of trapping solution are pipetted into the middle compartments, and 5 ml of HMDS-saturated perchloric acid into the right-hand compartments, after which the lid is immediately replaced and sealed with vaseline This procedure ensures minimal loss of fluoride since the compartments for the sample and the HMDS-saturated perchloric acid are several centimetres apart The immediate replacement and sealing of the lid further reduce the risk of losing fluoride When all the diffusion dishes have been prepared, the sample and the saturated perchloric acid can be mixed by rocking the dish When analysing tooth-paste, *ca* 4 g of a 1 5 w/w mixture of tooth-paste and water is weighed into the diffusion dish For determination of soluble fluoride the mixture is centrifuged at 4000 rpm for 10 min and the supernatant liquid is analysed for fluoride

The diffusion time necessary varies with the composition of the sample but 3 hr is sufficient for most samples When the diffusion is complete the dish is opened and the trapping solution is neutralized and buffered with 5 ml of 0 1*M* nitric acid and 5 ml of hexamethylenetetramine buffer The solution is then analysed for fluoride with a fluoride-sensitive electrode by the method of standard addition

The fluoride concentration C_F in the buffered trapping solution (volume V_0) is calculated from

$$C_F = \frac{V_s C_s}{10^{\Delta E/k}(V_0 + V_s) - V_0}$$

where C_s is the concentration and V_s the volume of the added standard, ΔE the difference in the e m f before and after the addition (mV) and k the Nernstian slope for the electrode

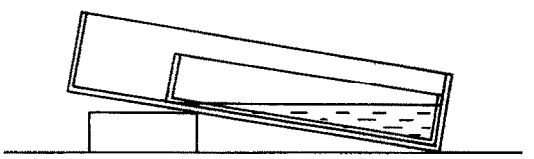

Fig 3 Preparation of the diffusion dish

RESULTS AND DISCUSSION

The first experiments, with 0 1*M* hydrochloric acid used to neutralize the trapping solution, showed that the response time was rather long and dependent on the concentration of the preceding solution measured If the difference in concentration was more than one order of magnitude the response was notably retarded The use of nitric acid for neutralizing shortened the response time by about 50% A typical response time for $10^{-4}M$ fluoride with the nitric acid system was 15 min, but the time could vary between quite wide limits In particular, the first two or three measurements every morning were very slow A recorder connected to the pH-meter was found to be of great help in determining when the potential was stable

The reproducibility of the e m f measurement was found to be reduced because of heating of the solution by the magnetic stirrer motor Attempts to insulate the solution with foam plastic did not give satisfactory results for very dilute fluoride solutions because of the longer response time Much better reproducibility was obtained by using a magnetic stirrer driven by thermostatically-controlled water

The e m f of the measuring cell seemed to change slightly every time the electrodes were lifted out of the solution It was to avoid this that the method of standard addition was used A calibration curve was constructed by adding known amounts of fluoride standard to a buffered sodium fluoride solution of known concentration It was linear over the pF range 2–4. The Nernstian slope for the curve was 57 8 mV at 20° Calculations showed that the e m f's measured did not differ from the calibration curve values by more than 0 1 mV Another advantage of the method of standard addition is that the response time after the addition is much shorter than for a separate solution with the same concentration Also, several additions can be made to give improved accuracy

In the method of Taves, small amounts of 6*M* hydrochloric acid saturated with HMDS are injected into the diffusion dish through a small hole in the lid [8] Since hydrochloric acid often contains small amounts of hydrogen fluoride[8] it has to be purified before use

The Taves[8] and Hall[9] methods were compared experimentally and since HMDS-saturated perchloric acid gave much faster diffusion it was used in all later experiments No loss of fluoride was observed (relative to the injection method) when the diffusion procedure described in the experimental part was used

If larger amounts of fluoride are to be separated it is advantageous to increase the amount of HMDS present, either by using larger volumes of the acid reagent or adding 10% of ethanol to the perchloric acid before saturating it with HMDS and using the normal volume

To determine the effect of agitation on the diffusion time, two series of diffusion dishes were prepared containing the same amount of sodium fluoride One

Table 1 Recovery of sodium fluoride

Sample*	Time, *hr*	Agitation	No of samples	Recovery, %
12 18 μmole NaF + 5 ml 2 7*M* $HClO_4$	3	None	5	98 5 ± 0 6†
12 18 μmole NaF + 5 ml 2 7*M* $HClO_4$	1	Rocking	5	98 7 ± 0 6
12 18 μmole NaF + 5 ml 2 7*M* $HClO_4$ + alcohol‡	1	Rocking	7	99 7 ± 0 9
37 38 μmole NaF + 5 ml 2 7*M* $HClO_4$	3	Rocking	7	98·0 ± 1 0
37 38 μmole NaF + 5 ml 2 7*M* $HClO_4$ + alcohol‡	1	Rocking	7	97 8 ± 1 1

* The perchloric acid solution was saturated with HMDS
† Relative standard deviation
‡ The perchloric acid solution contained 10% v/v ethanol

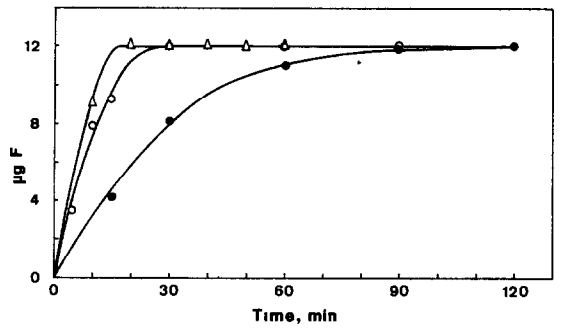

Fig 4 Diffusion time *vs* amount of fluoride found Diffusion of 12 18 μmole of NaF ● No agitation, diffusion using 2 7*M* HMDS-saturated $HClO_4$ ○ Rocking agitation, diffusion using 2 7*M* HMDS-saturated $HClO_4$ △ Rocking agitation, diffusion using 2 7*M* HMDS saturated $HClO_4$ containing 10% ethanol

series was rocked in the agitator and the other was kept static The boxes were opened successively after different times and the trapping solutions were analysed for fluoride The effect of agitation is very clear (Fig 4) The diffusion time for 12 μmole of fluoride was shortened from 2 hr to 30 min The effect of alcohol in the perchloric acid solution was small for this amount of fluoride (Fig 4), but for larger amounts of fluoride the addition of alcohol considerably shortened the diffusion time, *e g*, from over 2 hr to 30 min for 37 μmole of fluoride The reproducibility for samples containing sodium fluoride can be seen in Table 1

Fluoridated teeth have been found to be less susceptible to caries, which is why most tooth-pastes contain fluoride There are reports of methods for determination of fluoride in tooth-pastes by using a fluoride-sensitive electrode[10, 11] but these methods cannot be used for all tooth-pastes because of the differences in composition Many tooth-pastes contain for instance monofluorophosphate (MFP) which is also active against caries Since MFP cannot be determined directly with the fluoride-sensitive electrode the compound must be hydrolysed before analysis These difficulties can be overcome by separating the fluoride from the tooth-paste by diffusion Even samples containing MFP can be analysed, because MFP is hydrolysed by the perchloric acid used in the diffusion Experiments show that the rate of hydrolysis is not a limiting factor for the speed of diffusion Since fluoride even in insoluble salts, such as calcium fluoride, can be separated by diffusion, the method can be used to determine both total and soluble fluoride in the tooth-paste

Tooth-pastes are generally quite thick, which is why they must be diluted with water before analysis A suspension of one part of tooth-paste in five parts of water (w/w) was found to be suitable Such a suspension can easily be centrifuged for the determination of soluble fluoride A sample of the suspension is weighed directly into the diffusion dish for the determination of total fluoride

The diffusion times for tooth-paste (containing solid $CaHPO_4$ $2H_2O$ and 0 100% fluoride as MFP) were determined as for sodium fluoride solutions, 100% recovery being achieved in *ca* $3\frac{1}{2}$ hr with agitation, but no ethanol present, *ca* 2 hr with agitation and with ethanol present, but over 7 hr without agitation or ethanol

Table 2 Recovery of fluoride from tooth-paste containing solid $CaHPO_4$ $2H_2O$ and 0 100% fluoride

Sample*	Time, *hr*	Agitation	No of samples	Recovery, %
4 0 g suspension‡ + 5 ml 2 7*M* $HClO_4$	22	None	5	99 2 ± 0 8†
4 0 g suspension + 5 ml 2 7*M* $HClO_4$	4	Rocking	5	99 3 ± 0 9
4 0 g suspension + 5 ml 2 7*M* $HClO_4$ + alcohol	3	Rocking	5	99 3 ± 0 9

* The perchloric acid solution was saturated with HMDS
† Relative standard deviation
‡ One part of tooth paste and five parts of water (w/w)

The recovery of fluoride when analysing a tooth-paste containing 0·100% fluoride can be seen in Table 2

Tooth-pastes containing the following solid abrasives have been analysed $CaHPO_4$ $2H_2O$, SiO_2, Al_2O_3. The time for complete diffusion was *ca* 2 hr for tooth-pastes containing phosphates or silicon dioxide and *ca* 5 hr for tooth-pastes containing alumina Full advantage of the rapidity of diffusion can be taken only if the diffusion time is determined separately for each type of sample

Analysis of tooth-pastes containing carbonate does not give good results, owing to the formation of carbon dioxide If the absorbing capacity of the alkaline trapping solution is exceeded, there will be overpressure in the diffusion dish, causing leakage of carbon dioxide and trimethylfluorosilane.

The method is also useful for many other types of sample. It has been applied to determine fluoride, often as calcium salts, in such samples as water, foodstuffs and rocks. Fluoride concentrations have been determined in waters with aluminium concentrations up to 1*M* The diffusion time for such samples is, however, considerably longer, around 10 hr

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ANALYSIS OF CHROMITE BY CATION-EXCHANGE USING ETHYLENEDIAMINETETRA-ACETIC ACID

MOHAMMAD JAWAID and FOLKE INGMAN

Department of Analytical Chemistry, The Royal Institute of Technology, Stockholm, Sweden

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Summary—A method for the separation and determination of five major elements in chromite ore (and chrome-bearing refractories), based on complexation of the metals with EDTA is described After removal of silica, the cations are separated into two groups by passing the solution through a cation-exchange resin (Dowex 50W-X8, in Na-form) in the presence of an excess of the complexing agent The optimum conditions for the separation are discussed on the basis of exchange constants that were either known or determined The first group contains Cr and Fe, which emerge in the filtrate at pH between 1 5 and 2 1, whereas Al, Mg and Ca, which are adsorbed on the resin, form another group Complexometric titrations are used for the subsequent determination of the cations in each group The method is simpler and more rapid and accurate for routine analysis than the current methods

The methods available for the analysis of chromite ore and chrome-bearing refractories, are often described as laborious and time-consuming and yet they lack the desired accuracy Consequently, these methods have constantly been subjected to revision and improvement to make them simple, rapid and more accurate

Zagorchev *et al*[1] were probably the first to use an ion-exchange resin to separate chromium from iron in the analysis of ferrochrome alloys Bennet and Marshall[2] employed a liquid ion-exchanger to extract chromium as dichromate in slightly acidic solutions and were able to separate it quantitatively from the rest of the elements present in chromite ore

A complexometric procedure based on the usual analytical separations and complexometric titrations was developed by Sosin and Ztrezeszewska[3] and was modified later by Liteanu and Crişan[4] The methods, although comparatively rapid, had limited accuracy The ion-exchange separation of chromium from iron and aluminium, in the presence of EDTA and DCTA has been reported by Babachev,[5] and in the presence of EDTA by Kratochvil *et al*[6]

In the present method, the separation of cations is carried out by using EDTA as the complexing agent The separations are based on theoretical calculations in accordance with Ringboms' concept of conditional stability constants of metal–EDTA complexes The notation used throughout this work is also that of Ringbom.

The conditional distribution coefficients $D^{M'}$, for Cr, Fe, Al, Mg and Ca on a strongly basic cation-exchange resin (Dowex 50W-X8) in the presence of an excess of the complexing agent (EDTA), may be calculated from known exchange constants and the conditional stability constants of the metal–EDTA complexes and show considerable differences at different pH values These differences in the distribution coefficients can be utilized to choose conditions for separating the cations into some suitable groups, thereby facilitating complexometric titration of one cation without interference from the other cations present in the solution Thus, a direct titration of iron against EDTA can easily be performed in presence of chromium, which, in turn can be back-titrated at a higher pH Similarly, aluminium can be titrated successfully in the presence of magnesium and calcium

EXPERIMENTAL

Apparatus and reagents

Ion-exchange column Conventional ion-exchange columns with a bore of about 1 5 cm were used The resin bed was about 10 cm long The resin, Dowex 50W–X8 (50–100 mesh), was treated with 4–5*M*, hydrochloric acid and washed free from acid with demineralized water It was then rinsed with ethanol and dried overnight at 110° The exchange capacity of the resin was checked by the Fischer and Kunnin[8] method and was found to be 5 1 meq/g of dry resin The resin was converted into the sodium form by agitating it with sodium chloride solution and washing it free from chloride ions

EDTA solution, 0 01*M* Standardized against standard lead nitrate solution with Methylthymol Blue as indicator

Aluminium and iron solutions Prepared from pure metals and standardized against the standard EDTA solution, with Xylenol Orange as indicator

Chromium solution Prepared from potassium dichromate and standardized against EDTA, with Xylenol Orange as indicator

Magnesium and calcium solutions Prepared from analytical grade carbonates and standardized against EDTA, with Eriochrome Black T (EBT) and Murexide respectively as indicators

Choice of conditions for the separation

The formation of metal–EDTA complexes is greatly affected by the hydrogen-ion concentration in the solution

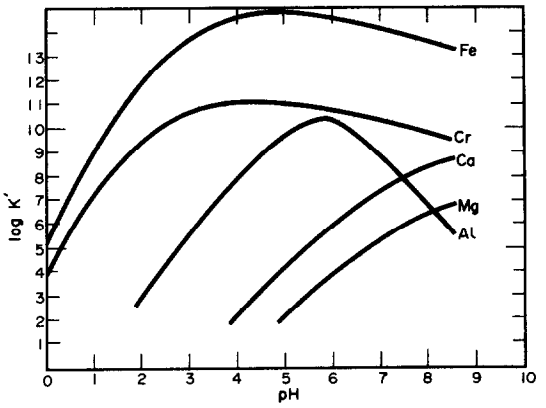

Fig 1 Conditional stability constants of metal–EDTA complexes as a function of hydrogen ion concentration

At higher hydrogen-ion concentrations, a greater proportion of the metal ions is free and consequently more easily adsorbed on a cation-exchanger, whereas in more alkaline solutions most of the metal ions may be bound in neutral or in less positively-charged complexes that are not easily adsorbed

In Fig 1, the conditional stability constants of metal–EDTA complexes of Cr, Fe, Al, Mg and Ca are plotted as a function of hydrogen-ion concentration It can be seen that at higher hydrogen-ion concentrations (pH less than 2 5) Cr and Fe, which have a relatively high complexing ability, are transformed into unadsorbable anionic complexes, whereas Al, Mg and Ca exist predominantly in the cationic form that can be selectively adsorbed on a cation-exchange resin

In Fig 2, the conditional distribution coefficient, D^{M} for Cr, Fe, Al, Mg and Ca in the presence of an excess of EDTA, is plotted as a function of hydrogen-ion concentration The conditional distribution coefficients have been calculated from the stability constants of the metal–EDTA complexes and the exchange constants of the metal ions on the cation-exchange resin The values used for Cr, Mg and Ca are based on the data taken from Bonner *et al*,[9] whereas the exchange constants for Al and Fe were determined by the present workers [10]

The conditional distribution coefficients have been calculated from the expression

$$D^{M'} = \left(\frac{[Na]_r}{[Na]}\right)^n K^{M^{n+}}_{nNa} / \alpha_{M(Y)}$$

where

$[Na]_r$ = concentration of sodium ion in the resin phase = resin capacity

$[Na]$ = concentration of sodium ion in the solution

$K^{M^{n+}}_{nNa}$ = exchange constant of the metal ion on the resin

$$\alpha_{M(Y)} = 1 + \frac{[Y']}{\alpha_{Y(H)}} K_{MY}$$

(K_{MY} is the stability constant of the metal–EDTA complex and $[Y']$ is the excess of complexing agent not bound to the metal ion)

A satisfactory separation of two metals on a cation-exchange resin requires that the conditional distribution coefficient must be greater than $10^{2\cdot5}$ for complete adsorption, and less than $10^{0\cdot5}$ for practically no adsorption [7]

From Fig 2 it can be seen that the conditional distribution coefficient $D^{M'}$ for Al, Mg and Ca is greater than $10^{2\cdot5}$ at pH below about 2 4, whereas for Cr and Fe it is less than $10^{0\cdot5}$ at pH above about 1 4

If we choose to work in the pH range 1 5–2 1, there will be enough margin of safety and the results should be in good agreement with the calculated values

Procedure for the analysis of chromite

Decomposition of chromite sample A mixture of sodium carbonate and borax (3 2) is recommended as a universal flux for the decomposition of chromite ore and chrome-bearing refractories [11] The following procedure has been found suitable by the present workers

Weigh out about 1 g of anhydrous sodium carbonate and about 0 5 g of boric acid in a clean and freshly ignited platinum crucible, and fuse together on a low flame Cool to room temperature and add 0 1 g (accurately weighed) of chromite sample previously ignited at about 650° Heat the contents, first gently with occasional swirling of the crucible, and then place the crucible in an electric furnace at 900–950° for 45 min Allow to cool and extract with dilute hydrochloric acid

The melt cake is taken out in the usual manner The function of very dilute hydrochloric acid is to neutralize the solution and to wash out any solid melt still adhering to the crucible Care should be taken to minimize the contact of melt dissolved in hydrochloric acid with the platinum crucible

If boron is not removed, precipitates will sometimes form during the ion-exchange separation process The removal of boron may be combined with the reduction of Cr(VI) which may be effected by boiling with methanol

Transfer the solution to a conical flask and evaporate it almost to dryness on a water-bath Add a few drops of acetic acid and about 20 ml of methanol to remove boron and reduce Cr(VI) Evaporate to dryness Repeat the procedure twice with further 15–20 ml portions of methanol Dissolve the residue in a minimum quantity of dilute hydrochloric acid, filter off silica and dilute to about 100 ml

Separation of chromium and iron from aluminium, magnesium and calcium To the solution prepared as above add an excess of 0 1*M* EDTA such that the concentration of the *free* complexing agent is about 0 01*M* The excess concentration must not be much higher than 0 01*M* because there is risk of EDTA precipitating Adjust the pH to $1\,8 \pm 0\,3$ (dilute hydrochloric acid or sodium hydroxide) and boil for 20–25 min Cool to room temperature and pass the solution through the column, pretreated with about 50 ml of 0 01*M* EDTA at pH $1\,8 \pm 0\,3$ Adjust the flow-rate to $1\,5 \pm 0\,5$ ml/min Wash the column with 150 ml of 0 01*M* EDTA at the same pH and add the washings to the main filtrate

Determination of Fe and Cr

Heat the filtrate to reduce its volume to about 50 ml Add 15 ml of hydrochloric acid (12*M*) and then in order to destroy EDTA, add cautiously about 2 g of potassium chlorate in tiny portions Evaporate to dryness on a water-bath Repeat the procedure with 10 ml of hydrochloric acid and 1 g of potassium chlorate Take up the solution with a *small* amount of dilute nitric acid while heating on the water-bath, cool to room temperature and make up the volume to 100 ml in a standard flask

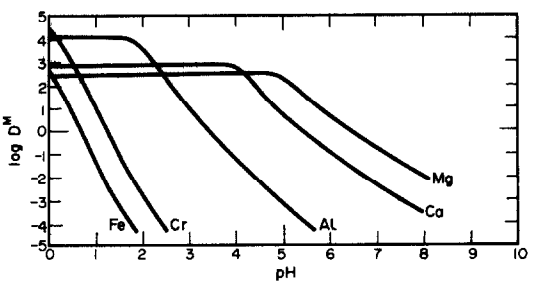

Fig 2. Conditional distribution coefficients of metal ions on Dowex 50W-X8 (sodium form) in the presence of an excess (0 01*M*) of EDTA as a function of hydrogen ion concentration

Determination of Fe To a suitable aliquot (15–20 ml) add about 10 ml of ethanol and heat gently for 5 min Add a drop of nitric acid to oxidize iron Cool to room temperature, dilute to about 100 ml and if necessary adjust the pH to 1 0–1 5 with dilute sodium hydroxide or nitric acid Heat to about 80° and titrate against 0 01*M* EDTA, using Xylenol Orange as indicator

Determination of Cr To the solution after the titration of Fe, add an excess of 0 01*M* EDTA and 10 ml of hexamine buffer at pH 5 Heat to boiling for 20–25 min Cool to room temperature and back-titrate the excess of EDTA with standard lead solution

Elution and determination of Al, Mg and Ca

Elute the sorbed cations with 150 ml of 4–5*M* hydrochloric acid Wash the column with about 50 ml of water and add the washings to the eluate Heat the eluate to reduce its volume to about 50 ml and add cautiously about 2 g of potassium chlorate to destroy EDTA Evaporate to dryness on a water-bath Repeat the procedure with 10 ml of hydrochloric acid and 1 g of potassium chlorate Take up the solution in a small amount of dilute hydrochoric acid and make up the volume to 100 ml in a standard flask

Determination of Al [12] To a suitable aliquot (15–20 ml) of the solution prepared as just described, add an excess of 0 01*M* EDTA and 10 ml of pH 5 5 hexamine buffer Heat to boiling for 5 min, cool and dilute to about 100 ml Check the pH and readjust, if necessary, with solid hexamine and 1*M* hydrochloric acid Back-titrate the excess of EDTA against standard lead solution, using Xylenol Orange as indicator

Determination of Mg and Ca The sum of Mg and Ca is determined in another aliquot (15–20 ml) of the solution by the usual complexometric titration at pH 10 (NH_4Cl–NH_3 buffer) with EBT as indicator Ca is determined in 15–20 ml of the sample solution by titrating complexometrically with EDTA at pH > 13 (sodium hydroxide), with Murexide as indicator Murexide is the only indicator that we have found that will work properly in the presence of a precipitate of magnesium hydroxide Mg is then determined by difference

RESULTS AND DISCUSSION

In Table 1 some results of successive titrations of Fe^{3+} and Cr^{3+} are shown Table 2 shows the results of analysis of a synthetic mixture whereas in Table 3 are presented the results of analysis performed on a standard chromite sample (British Chemical Standards No 308, Grecian chromite ore) The amounts found show a negative error of about 0 5%, which is probably due to losses during the ion-exchange procedure

The present method, in comparison to other methods based on complexometric titrations, posesses certain definite advantages The separation of cations into groups facilitates the complexometric determinations in the same solution by means of one direct and one back-titration This avoids the necessity of masking and demasking, which is often incomplete and thus reduces the accuracy

Iron (III) is titrated at pH 1 0–1 5 in the presence of chromium (III) In this pH range, the conditional stability constant of the Fe–EDTA complex is high enough to permit a direct titration, whereas Cr^{3+} does not enter into reaction since it requires a prolonged heating (more than 10 min)[13] for complex formation However, successive titrations lead to reciprocal errors which may be significant for materials containing large amounts of iron and small amounts of chromium Slight evidence of this is shown in Table 1 Similarly, in the back-titration of Al^{3+} at pH 5 5, Mg^{2+} and Ca^{2+} do not interfere, because of their low conditional stability constants at this pH At higher pH (> 10), the conditional stability constant of the Al–EDTA complex is low enough to permit the direct titration of Mg^{2+} and Ca^{2+}

The method, which is rapid and yields better accuracy than the current methods, will be found useful in the routine analysis of chromite ore (and chrome-bearing refractories), particularly in those laboratories that are poorly equipped

Table 1 Complexometric determination of Fe^{3+} and Cr^{3+} with EDTA, in presence of each other

Amounts added		Amounts found	
Fe^{3+}, *mg*	Cr^{3+}, *mg*	Fe^{3+}, *mg*	Cr^{3+}, *mg*
5 55	5 20	5 53	5 24
11 10	5 20	11 02	5 16
11 10	10 40	11 06	10 34
11 10	15 60	11 08	15 54
16 65	15 60	16 58	15 48

Table 2 Cation-exchange separation of Cr^{3+} and Fe^{3+} from Al^{3+}, Mg^{2+} and Ca^{2+}, in presence of EDTA at pH 1 8 ± 0 3

Cation	Amount added, *mg*	Amount found, *mg* Filtrate (1)	(2)	(3)	Adsorbate (1)	(2)	(3)
Cr^{3+}	25 9	25 2	25 8	25 6	—	—	—
Fe^{3+}	13 9	13 8	13 5	13 5	—	—	—
Al^{3+}	6 8	—	—	—	6 5	6 4	6 7
Mg^{2+}	6 3	—	—	—	6 3	6 1	6 1
Ca^{2+}	6 2	—	—	—	6 2	6 0	6 0

Table 3 Analysis of B C S Sample No 308, Grecian Chromite Ore

No	Cr_2O_3,%	FeO, %	Al_2O_3 %	MgO, %
1	41 26	15 14	19 23	16 27
2	41 17	15 33	19 18	16 35
3	41 32	15 26	19 42	16 41
4	41 24	15 37	19 31	16 25
5	41 38	15 08	19 34	16 21
Range	0 21	0 29	0 24	0 20
Mean	41 27	15 24	19 30	16 30
Reported values	41 5	15 3	19 4	16 4
Mean error	−0 2	−0 1	−0 1	−0 1
Relative error, %	−0 48	−0 65	−0 52	−0 61

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SHORT COMMUNICATIONS

SIMPLE RADIOCHEMICAL NEUTRON-ACTIVATION METHOD FOR THE DETERMINATION OF URANIUM IN ULTRAMAFIC ROCKS

E STEINNES

Institutt for Atomenergi, Isotope Laboratories, Kjeller, Norway

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As ultramafic rocks may be the main constituents of the terrestrial mantle, knowledge of the concentrations of the naturally radioactive elements in them is of importance for heat-flow calculations Even though the concentration of uranium in these rocks is in many cases very low, 1–10 ppM (parts per milliard), the need for reliable data is evident Various modifications of neutron-activation analysis can be used for the determination of uranium in geological matrices Purely instrumental methods based on γ-spectrometry, which may be useful for uranium determination in rocks, especially when using epithermal activation,[1,2] may not be sufficiently sensitive for certain ultramafic rocks Delayed-neutron counting[3,4] may give a slightly higher sensitivity, but would still not be applicable to all ultramafic rocks Fission-track counting[5] is probably still more sensitive, but even that technique may fail in some cases where uranium is present in clusters within the rock.

A number of radiochemical neutron-activation methods for uranium in rocks have been proposed Some of them were based on a fission product of ^{235}U, *e g*, ^{140}Ba–^{140}La [6] Considerably higher sensitivity may be obtained if instead of $^{235}U(n, f)$ the $^{238}U(n, \gamma)$ reaction is employed Furthermore, possible interference due to fission of thorium induced by fast neutrons is avoided in this case The use of 2 35-day ^{239}Np for the uranium determination in ultramafic rocks has been successfully demonstrated,[7,8] but the analysis is complicated by the fact that no neptunium carrier can be used The mother nuclide ^{239}U seems more favourable in this respect, and has been used by Sankar Das,[9] Turkowsky *et al* [10] and Aruscavage and Millard [11] In these cases ^{239}U was measured by β-counting after a sequence of separation steps resulting in a fairly low chemical yield A need for improvement still seemed to be present

Experience in this laboratory[12,13] has shown the solvent extraction of uranium into tri-n-butyl phosphate (TBP) from moderately concentrated nitric acid to be a very efficient means of separating ^{239}U from various types of neutron-activated mixtures, with high and reproducible chemical yield The highest extraction is obtained in the range 7 5–10*M* nitric acid In view of the fact that the heavy rare earths show appreciable extraction at high nitric acid molarity, it was found useful to apply a somewhat lower nitric acid concentration when using this extraction for rock samples, in order to avoid interference from 2 3-hr ^{165}Dy and other short-lived rare-earth nuclides

EXPERIMENTAL

Irradiation

Rock samples (about 200 mg) were weighed into 1-ml polyethylene vials and irradiated for 10 min in the pneumatic-tube facility of the JEEP II reactor with a thermal neutron flux of about $1 5 \times 10^{11}$ n mm^{-2} sec^{-1} and $R_{Cd}^{Au} = 2 8$ The standard used was 1 ml of a 0 1-ppm uranium solution in 0 1*M* nitric acid, from which 0 100 ml was taken for activity measurement Two samples and a standard were irradiated simultaneously The chemical separation was started immediately after the return from the reactor If samples with aluminium contents exceeding 1% are to be analysed, the samples should be left for 5–10 min in order to reduce the radiation level from 2 3-min ^{28}Al

Radiochemical separation

The irradiated sample was transferred to a nickel crucible, containing 5 ml of uranium carrier evaporated to dryness, and fused for 5 min with 1 g of sodium peroxide and 1 g of sodium hydroxide, with an electrothermal burner After cooling, the fusion "cake" was released from the crucible with 20 ml of water and transferred to a beaker Then 20 ml of concentrated nitric acid were carefully added After 1–2 min the mixture was passed through a paper filter into a separatory funnel and subsequently extracted with 20 ml of tri-n-butyl phosphate The aqueous phase was discarded The organic phase was then washed twice with 20 ml of 5*M* nitric acid and transferred to a 100-ml plastic screw-cap bottle for γ-spectrometry The separation procedure took about 20 min

Activity measurement

The γ-activity measurements were performed with a 35-cm^3 Ge(Li) detector connected to a 1700-channel pulse-height analyser based on a small digital computer The counting time was 10 min, and the area of the 74-keV peak of ^{239}U was calculated according to the method of Sterlinski [14]

Chemical yield determination

After the ^{239}U activity of the TBP fractions had decayed to a negligible level, the chemical yield of the radiochemical separation was determined by re-activation The organic phase was diluted to 50 ml with toluene, and 0 100 ml of this solution was sealed in a polyethylene tube and irradiated for 10 sec in the pneumatic-tube facility together with an aliquot of the uranium carrier solution diluted in the same manner with water The γ-activities were measured as described above, with a counting time of 2 min The chemical yield was in most cases 80–90%

RESULTS AND DISCUSSION

The method described in this work was tested on two ultramafic standard rocks issued by the U S Geological Survey, the dunite DTS-1 and the peridotite PCC-1 Results of these analyses are given in Table 1 The two standard rocks have been analysed previously for uranium in several other investigations, the results of which are also listed Data obtained in different investigations, in all cases by some kind of neutron-activation technique, show remarkably good agreement, indicating that DTS-1 and PCC-1 are fairly homogeneous with respect to uranium in spite of the low concentration levels The values of the present

Table 1 Uranium content of two U S Geological Survey standard rocks

Standard rock	Present work: Single values, *ppM*	Present work: Mean value, *ppM*	Literature values, *ppM*
Dunite DTS-1	3 3, 2 8, 2 6, 3 4, 2 8	3 0	3,[3] 4,[4] 3 2,[5] 3 2,[8] 3 8,[11] 4 0,[15] 4 [16]
Peridotite PCC-1	4 6, 4 0, 4 0, 3 3, 3 7	3 9	5,[3] 5,[4] 4 7,[5] 4 1,[8] 4 7,[11] 4 9,[15] 5 [16]

work are in especially good agreement with those of Morgan and Heier,[8] who also used a radiochemical method based on the ^{238}U (n,γ) reaction

The precision of the method appears to be about ±10% when the amount of uranium determined is about 1 ng The radionuclidic purity of the separated sample appeared to be satisfactory, as all the major activities, such as ^{56}Mn and ^{27}Mg, appeared to have been efficiently removed The only foreign activity present in significant amounts appeared to be ^{165}Dy In samples with higher concentrations of the heavy rare-earth fraction or with a more unfavourable U/Dy ratio it is recommended that another 2 or 3 washing steps with 5*M* nitric acid be introduced Each of these steps would reduce the dysprosium concentration by about a factor of 3, while the uranium concentrations would probably not be reduced by more than 2%

The limit of detection of this method with the neutron flux and measurement conditions used in the present work is about 0 2 ng of uranium If necessary, a sample size of 500 mg could be used, thus permitting uranium concconcentrations at the 0 5 ppM level to be determined

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Summary—A radiochemical neutron-activation method for the determination of trace concentrations of uranium in rocks is described The method is based on separation of 23 5-min ^{239}U after alkaline fusion by extraction with tri-n-butyl phosphate from moderately concentrated nitric acid, followed by measurement of the 74-keV γ-ray with a Ge(Li) detector The limit of detection is 0·2 ng of U under the present conditions, and the precision at the 0 005 ppm level is about 10% The method is especially useful for determination of uranium in ultramafic rocks

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COULOMETRIC TITRATION OF DEACTIVATED PHENOLS WITH BROMINE

B KINBERGER, L E EDHOLM and B E F SMITH®

Department of Technical Analytical Chemistry, Chemical Center, Lund, Sweden

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In a previous paper[1] a general method for coulometric titration of alkylphenols with anodically generated bromine was described The present paper deals with coulometric bromination of deactivated phenols The coulometric bromination method has hitherto been applied only to a small number of deactivated phenols Lichtenstein[2] titrated 4-chloro-3,5-dimethylphenol and 2,4-dichloro-3,5-dimethylphenol in aqueous solution which was 0 2*M* with respect to potassium bromide and 1*M* with respect to sulphuric acid One hydrogen atom was exchanged for bromine Delgado[3] titrated salicylic acid and 2- and 4-nitrophenol at pH 3 in aqueous solution which was 0 2*M* with

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Summary—A radiochemical neutron-activation method for the determination of trace concentrations of uranium in rocks is described The method is based on separation of 23 5-min ^{239}U after alkaline fusion by extraction with tri-n-butyl phosphate from moderately concentrated nitric acid, followed by measurement of the 74-keV γ-ray with a Ge(Li) detector The limit of detection is 0·2 ng of U under the present conditions, and the precision at the 0 005 ppm level is about 10% The method is especially useful for determination of uranium in ultramafic rocks

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COULOMETRIC TITRATION OF DEACTIVATED PHENOLS WITH BROMINE

B KINBERGER, L E EDHOLM and B E F SMITH®

Department of Technical Analytical Chemistry, Chemical Center, Lund, Sweden

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In a previous paper[1] a general method for coulometric titration of alkylphenols with anodically generated bromine was described The present paper deals with coulometric bromination of deactivated phenols The coulometric bromination method has hitherto been applied only to a small number of deactivated phenols Lichtenstein[2] titrated 4-chloro-3,5-dimethylphenol and 2,4-dichloro-3,5-dimethylphenol in aqueous solution which was 0 2*M* with respect to potassium bromide and 1*M* with respect to sulphuric acid One hydrogen atom was exchanged for bromine Delgado[3] titrated salicylic acid and 2- and 4-nitrophenol at pH 3 in aqueous solution which was 0 2*M* with

respect to potassium bromide Two hydrogen atoms were exchanged for bromine in this case

Although our previous work[1] in this series dealt with activated phenols, conclusions concerning suitable conditions for the coulometric bromination of deactivated phenols can nevertheless be drawn Monobromination was found to dominate in pyridine-free acetic acid–water media while full bromination mainly occurred in pyridine-containing media As the latter reaction involves bromination of a bromophenol as an intermediate product, *i e*, a deactivated phenol, it can be concluded that brominated phenols require pyridine–acetic acid–water media for quantitative bromination * The same was found to be the case for all fully deactivated phenols titrated in this work

The term "deactivated phenol" is often interpreted as meaning any phenol containing electron-withdrawing groups such as mentioned in the summary A method of determining the relative degree of activation of phenols may be based on reaction with an electrophilic reagent such as bromine A test for this purpose is described later in this paper It should be noted that according to this test, some of the phenols investigated here are activated The effects of various factors on the bromination reaction were reported in the previous paper [1]

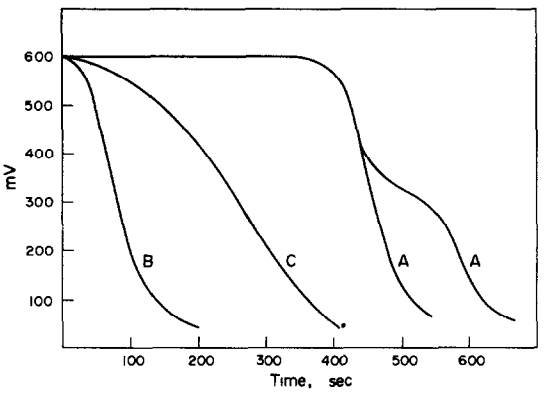

Fig 1 Shape of titration curves obtained in the test for distinguishing activated and deactivated phenols A = activated phenols, B = fully deactivated phenols, C = partly deactivated phenols

EXPERIMENTAL

The apparatus as well as the reagents used were the same as those described earlier [1] All phenols were of the best grade commercially available and they were generally analysed without further purification The standard titration procedure was identical with that used before,[1] *i e*, a generating current of 3 mA at a 2-cm^2 Pt-electrode, and a polarizing voltage of 630 mV through a 100-kΩ resistance were used The chart speed was 30 mm/min The composition of the titration media was shown in Table 1 of the earlier paper [1]

RESULTS AND DISCUSSION

Distinguishing between activated and deactivated phenols

The authors are not aware of any previous method which discriminates between activated and deactivated phenols The test proposed here is based on the reaction between a phenol and bromine in the titration medium III-1 containing 60% v/v acetic acid, 40% v/v water and being 0 1*M* with respect to sodium bromide

If a phenol produces titration curves like those labelled A in Fig 1, when 20 meq are titrated in this medium under standard conditions, it is considered to be activated If the consumption of bromine is small and a titration curve like B in Fig 1 is obtained, the phenol is said to be fully deactivated Naturally not all phenols can be classified as either activated or fully deactivated There are intermediate types which have a certain bromine consumption without giving a usable titration curve (see C in Fig 1) This kind of phenol is considered to be partly deactivated

Of the phenols titrated earlier,[1] all but one turned out to be activated according to the test Only 4-hydroxybiphenyl was partly deactivated Of the phenols titrated in the present work, most were fully deactivated However, those phenols which contained one chlorine atom and one methyl group were partly deactivated and 4-bromo-3,5-dimethylphenol was activated The test fails for 2,4,6-tritert butylphenol which, although activated, gives a type B titration curve It is evident that not only this phenol but all phenols in which all *ortho* and *para* positions are occupied, and which do not form bromocyclohexadienones[1] on reaction with bromine in medium III-1, will give a type B titration curve Accordingly they will be classified as fully deactivated regardless of their activation state

Quantitative bromination of deactivated phenols

As seen from Table 1, pyridine-containing titration media must be used throughout for the quantitative bromination of deactivated phenols No quantitative monobromination is possible for this type of phenol, with the standard media in Table 1 of ref 1 There is nonetheless in Table 1 of the present paper one phenol, 4-bromo-3,5-dimethylphenol, which can be quantitatively monobrominated, but this compound is activated according to the test above In the following, the titration results for various types of deactivated phenols will be discussed in some detail

Halophenols Most of the halophenols without alkyl groups can be titrated in medium II-1 (55% HOAc, 40% H_2O, 5% C_5H_5N and 0 1*M* with respect to NaBr) 3,5-Dichlorophenol, being more reactive, requires a slightly slower medium (II-2, 0 4 *M* with respect to NaBr), presumably because the two *ortho*-directing chlorine atoms are placed *ortho* to the free positions in the phenol The two iodophenols tested, namely 2- and 4-iodophenol, were found to react sluggishly with bromine, even in the fastest medium available (I-1), and the titration curve could not be quantitatively evaluated It was observed that the electrodes were easily contaminated in this case

As expected, the presence of alkyl groups in addition to halogen atoms in the molecule generally makes it more reactive Thus, the three phenols with one chlorine atom and one methyl group were quantitatively brominated in medium II-2 while, for the corresponding chlorophenols without alkyl groups, medium II-1 was required 4-Bromo-3,5-dimethylphenol differs from the other halophenols in Table 1 in that it is an activated phenol Accordingly it can be monobrominated in the pyridine-free medium III-2 For its full bromination, medium II-2 is necessary This fact indicates that 2,4-dibromo-3,5-dimethylphenol is more reactive towards bromine than the corresponding chlorophenol, which had to be titrated in medium II-1 The two trifluoromethylphenols form a special type of halophenol as the halogen atoms are placed in the side-chain instead of in the ring Obviously the deactivating effect of a trifluoromethyl group is greater than that of a fluorine atom, as a faster titration medium had to be used in the former case

Carboxyphenols Of the carboxyphenols tested only *m*- and *p*-hydroxybenzoic acid can be titrated quantitatively

* For exceptions see Table 1

Table 1 Bromination of deactivated phenols

Phenol	Titr medium	Weight*, μg Calc	Found	Error, %	Phenol	Titr medium	Weight*, μg Calc	Found	Error, %
2-Fluoro	II-1	560 5	558	− 0 4	2-Bromo	II-1	911 4	916	+ 0·5
			559	− 0 3				917	+ 0·6
3-Fluoro	II-1	373 6	379	+ 1 4	4-Bromo	II-1	865 1	869	+ 0·5
			379	+ 1 4				859	− 0·7
4-Fluoro	II-1	560 5	563	+ 0 4	4-Bromo-3,5-dimethyl†	II-2	771 0	776	+0 6
			557	− 0 6				779	+ 1 0
2-Trifluoromethyl	I-1	810 6	799	− 1 4	2,4-Dibromo	II-1	2474	2452	− 0·9
			789	− 2 7				2452	− 0·9
3-Trifluoromethyl	I-1	540 3	550	+ 1 8	3-Carboxy	II-1	460 4	464	+ 0·8
			547	+ 1 2				466	+ 1 2
2-Chloro	II-1	679 8	682	+ 0 3	4-Carboxy	II-1	454 2	463	+ 1 9
			684	+ 0 6				462	+ 1 7
2-Chloro-5-methyl	II-2	708 5	713	+ 0 6	2-Formyl	I-1	610 6	622	+ 1 9
			717	+ 1 2				623	+ 2 0
2-Chloro-6-methyl	II-2	1417	1454	+ 2 6	3-Formyl	I-1	406 7	404	− 0 7
			1465	+ 3 4				397	− 2 4
3-Chloro	II-1	428 6	418	− 2 5	4-Formyl	II-1	610 6	624	+ 2 2
			421	− 1 8				630	+ 3 2
4-Chloro	II-1	642 8	648	+ 0 8	4-Acetyl	I-1	681 0	690	+ 1 3
			651	+ 1 3				689	+ 1 2
4-Chloro-3-methyl	II-2	708 5	712	+ 0 5	2-Nitro	I-1	695 6	710	+ 2 1
			709	+ 0 1				708	+ 1 8
2,4-Dichloro	II-1	1630	1657	+ 1 7	3-Nitro	I-1	463 7	461	− 0 6
			1624	− 0 4				466	+ 0 5
2,4-Dichloro-3,5-dimethyl	II-1	1910	1940	+ 1 6	4-Nitro	I-1	695 6	708	+ 1 8
			1949	+ 2 0				709	+ 1 9
2,5-Dichloro	II-1	815 0	829	+ 1 7	2,4-Dinitro	I-1	1841	1854	+ 0 7
			829	+ 1 7				1863	+ 1 2
3,4-Dichloro	II-1	816 8	806	− 1 3	2,6-Dinitro	I-1	1841	1835	− 0 3
			811	− 0 7				1855	+ 0 8
3,5-Dichloro	II-2	632 0	627	− 0 8	Phenolphthalein	II-2	795 3	815	+ 2 5
			627	− 0 8				810	+ 1 8
2,4,5-Trichloro	II-1	1974	2020	+ 0 8					
			2023	+ 0 8					

* This weight consumes about 20 μeq of bromine

† Can also be quantitatively monobrominated in medium III-2 with an error of about 1%

Salicylic acid consumes more than the expected 4 equivalents of bromine per mole, but the result is not reproducible The slight overconsumption is presumably caused by a partial decarboxylation The same reaction, although quantitative, takes place for *p*-hydroxybenzoic acid which consumes 6 equivalents of bromine instead of the expected 4

Decarboxylation has been reported before in connection with phenol bromination [4,5] However, it should be noted that in a previous investigation by one of the present authors,[6] in which salicylic acid was titrated in acidified acetic acid solution with bromide–bromate in aqueous medium, no decarboxylation was observed, the consumption being 4 equivalents of bromine Delgado[3] reported the quantitative determination of salicyclic acid in aqueous medium at pH 3 We have verified this result, using his titration medium and our standard conditions Obviously the composition of the titration medium is of decisive importance for the course of the bromination reaction.

Formylphenols Of the titrated hydroxybenzaldehydes the *ortho* and *meta* isomers require the fastest medium (I-1) with 10% pyridine while *p*-hydroxybenzaldehyde gives high values in this medium and should be determined in medium II-1 The high values might arise from a partial deformylation [4]

Acetylphenols Of the compounds tested *o*-hydroxyacetophenone was found not to react with bromine in any titration medium used in this work This somewhat surprising fact might be attributed to a deactivation due to the hydrogen bond between the phenolic hydroxyl group and the oxygen atom in the acetyl group since the corresponding *para* isomer can be titrated with good accuracy It is noteworthy that the medium used by Delgado[3] also failed for *o*-hydroxyacetophenone, according to our experience

Nitrophenols These are strongly deactivated and accordingly for all nitrophenols the fastest medium (I-1) has to be used

Phenolphthalein This phenol may be expected to be activated but on the basis of a type B titration curve, obtained in medium III-1, was found to be deactivated Consequently quantitative bromination demands a pyridine-containing medium (II-2) Since 8 equivalents of bromine are consumed, it appears that 2 hydrogen atoms in each of the two phenolic rings are exchanged for bromine

CONCLUSIONS

The present work has shown that the coulometric bromination method developed originally for the quantitative determination of alkylphenols is also applicable to the bromination of deactivated phenols containing various electron-withdrawing substituents A fast medium, containing pyridine as a bromination promotor, has to be used throughout

Although the majority of the compounds tested could be determined with good accuracy, difficulty was experi-

enced with certain phenols containing *ortho* substituents capable of forming a hydrogen bond with the phenolic hydroxyl group Thus salicylic acid and *o*-hydroxyacetophenone could not be titrated Although the former reacted, the results were inaccurate owing to incomplete decarboxylation The latter compound totally failed to react. The only two iodophenols tested give another example of a phenolic type which could not be assayed For unknown reasons they reacted sluggishly and gave a sloping titration curve which did not permit any determination of the equivalence point

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1 B Kinberger, L E Edholm, O Nilsson, and B E F Smith, *Talanta*, 1975, **22**, 979
2 H J Lichtenstein, *J Pract Chem*, 1958, **6**, 225
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4 A W Francis and A J Hill, *J Am Chem Soc*, 1924 **46**, 2498
5 A R Day and W T Taggart, *Ind Eng Chem*, 1928, **20**, 545
6 B Smith, *Acta Chem Scand*, 1956, **10**, 1589

Summary—A number of deactivated phenols containing fluorine, chlorine or bromine, formyl, acetyl, carboxyl or nitro groups have been titrated with anodically generated bromine The reaction was carried out in a water–acetic acid–pyridine medium and the reactivity was controlled by varying the water and pyridine content and the concentration of bromide ion Hydrogen in all free positions *ortho* and *para* to the phenolic hydroxyl group is generally exchanged for bromine, but in certain instances a partial bromination is possible The method as developed is widely applicable for deactivated phenols Only certain *ortho*-substituted phenols could not be quantitatively titrated The mean relative error for the phenols titrated was ± 1 2%

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THE TITRATION ERROR IN POTENTIOMETRIC PRECIPITATION TITRATION

P O Kosonen and E J. Hakoila

Department of Chemistry, University of Turku, SF-20500 Turku 50, Finland

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The general theory of potentiometric precipitation titration and the theoretical error in the titration have been discussed by many investigators [1–10]

When the reaction that takes place in a precipitation titration is expressed by

$$mA + nB \rightleftharpoons A_mB_n \quad (1)$$

and the solubility product of the sparingly soluble salt by

$$K_s = [A]^m[B]^n \quad (2)$$

at the inflection point of the titration curve the molar concentrations of the ions are[3,4]

$$[A]_{infl} = \left\{\left(\frac{m}{n}\right)^{3n} K_s\right\}^{1/(m+n)} \quad (3)$$

and

$$[B]_{infl} = \left\{\left(\frac{n}{m}\right)^{3m} K_s\right\}^{1/(m+n)} \quad (4)$$

At the equivalence point of the titration the concentrations are given by[1,3,4]

$$[A]_{ep} = \left\{\left(\frac{m}{n}\right)^{n} K_s\right\}^{1/(m+n)} \quad (5)$$

and

$$[B]_{ep} = \left\{\left(\frac{n}{m}\right)^{m} K_s\right\}^{1/(m+n)} \quad (6)$$

When the concentrations of individual ions are expressed as molarities and the total concentrations of the solutions taking part in the reaction are expressed in normalities the buffer capacity P at the inflection point of the titration is obtained by means of the equation[4]

$$P_{infl} = 2\,303 \times (m+n)\left\{\left(\frac{m}{n}\right)^{2n-m} K_s\right\}^{1/(m+n)} \quad (7)$$

The error of the titration, (molar concentrations only) is given by[6]

$$F = \frac{m^2 - n^2}{m^2}\left\{\left(\frac{m}{n}\right)^{3n} K_s\right\}^{1/(m+n)} \quad (8)$$

The inflection point of the titration curve and the equivalence point of the titration coincide when $m = n$ [3–6]

PRINCIPLES

Let us express the precipitation reaction by equation (1) and the solubility product by equation (2) Let us further assume that the indicator electrode responds to the variation of the concentration of ion A After a permanent precipitate has been formed we have

$$C_A = \frac{m}{n}C_B - \frac{m}{n}K_s^{1/n}[A]^{-m/n} + [A] \quad (9)$$

where the total concentrations of A and B are denoted by C_A and C_B By differentiating this equation with respect to pA we get the buffer index ($\beta_A = -dC_A/dpA = 2\,303\,[A]\,dC_A/d[A]$, for A as titrant), and by differentiating the index with respect to pA and setting the result-

enced with certain phenols containing *ortho* substituents capable of forming a hydrogen bond with the phenolic hydroxyl group Thus salicylic acid and *o*-hydroxyacetophenone could not be titrated Although the former reacted, the results were inaccurate owing to incomplete decarboxylation The latter compound totally failed to react. The only two iodophenols tested give another example of a phenolic type which could not be assayed For unknown reasons they reacted sluggishly and gave a sloping titration curve which did not permit any determination of the equivalence point

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$$[A]_{ep} = \left\{\left(\frac{m}{n}\right)^{n} K_s\right\}^{1/(m+n)} \quad (5)$$

and

$$[B]_{ep} = \left\{\left(\frac{n}{m}\right)^{m} K_s\right\}^{1/(m+n)} \quad (6)$$

When the concentrations of individual ions are expressed as molarities and the total concentrations of the solutions taking part in the reaction are expressed in normalities the buffer capacity P at the inflection point of the titration is obtained by means of the equation[4]

$$P_{infl} = 2\,303 \times (m+n)\left\{\left(\frac{m}{n}\right)^{2n-m} K_s\right\}^{1/(m+n)} \quad (7)$$

The error of the titration, (molar concentrations only) is given by[6]

$$F = \frac{m^2 - n^2}{m^2}\left\{\left(\frac{m}{n}\right)^{3n} K_s\right\}^{1/(m+n)} \quad (8)$$

The inflection point of the titration curve and the equivalence point of the titration coincide when $m = n$ [3–6]

PRINCIPLES

Let us express the precipitation reaction by equation (1) and the solubility product by equation (2) Let us further assume that the indicator electrode responds to the variation of the concentration of ion A After a permanent precipitate has been formed we have

$$C_A = \frac{m}{n}C_B - \frac{m}{n}K_s^{1/n}[A]^{-m/n} + [A] \quad (9)$$

where the total concentrations of A and B are denoted by C_A and C_B By differentiating this equation with respect to pA we get the buffer index ($\beta_A = -dC_A/dpA = 2\,303\,[A]\,dC_A/d[A]$, for A as titrant), and by differentiating the index with respect to pA and setting the result-

ing equation to zero we get for the inflection point of the titration the equation

$$\beta_{A,infl} = 2\,303\,\frac{m+n}{m}\left\{\left(\frac{m}{n}\right)^{3n} K_s\right\}^{1/(m+n)} \quad (10)$$

as well as equations (3) and (4)

Similarly, by differentiating C_B with respect to pA we get the buffer index ($\beta_B = dC_B/dpA$, for A as titrant and an electrode responsive to A, or $\beta_B = -dC_B/dpA$, for B as titrant)

$$\beta_{B,infl} = \frac{n}{m}\beta_{A,infl} \quad (11)$$

At the equivalence point equations (5) and (6) are valid

The absolute titration error F_A in the concentration of ion A is a sum of two terms the difference between the concentrations of A at the inflection and the equivalence points, the "concentration" of A that has been precipitated between the equivalence and the inflection points Thus

$$F_A = [A]_{infl} - [A]_{ep} + \frac{m}{n}([B]_{ep} - [B]_{infl}) \quad (12)$$

When expressions (3)–(6) are substituted in equation (12) we obtain for the error the expression

$$F_A = \left(1 - \left(\frac{n}{m}\right)^2\right)\left\{\left(\frac{m}{n}\right)^{3n} K_s\right\}^{1/(m+n)} \quad (13)$$

This equation is thus the same as equation (8) derived[6] earlier The equation gives the error only with respect to ion A The error with respect to ion B is given by

$$F_B = \frac{n}{m}F_A \quad (14)$$

By combining equations (10) and (13) we get

$$F_A = \frac{m}{m+n}\left[1 - \left(\frac{n}{m}\right)^2\right]\frac{\beta_A}{2\,303} \quad (15)$$

In practical titration we have

$$\beta_{A,infl} = \frac{\Delta V_A c_A}{V_t(\Delta pA)_{max}} \quad (16)$$

where c_A is the molar concentration of the titrant, V_t is the volume of the solution at the inflection point and $(\Delta pA)_{max}$ is the maximum change in pA on addition of ΔV_A of titrant Similarly, if B is the titrant, we have

$$\beta_{B,infl} = \frac{\Delta V_B c_B}{V_t(\Delta pA)_{max}} \quad (17)$$

More generally

$$\beta_{A,infl} = \frac{2\,303RT}{F} \times \frac{|z_{titr}|}{z_{el}^2} \times \frac{\Delta V_{titr} c_{titr}}{V_t \Delta E_{max}} \quad (18)$$

where z_{titr} and z_{el} are the charges of the titrant ion and the electrode (response) ion, ΔE_{max} is the maximum change in the potential on addition of ΔV_{titr} of titrant, and R, T, and F have their usual meanings

When A is the titrant the practical titration errors are

$$F_A = \frac{1}{V_t}\left(V_A c_A - \frac{m}{n} V_B c_B\right) \quad (19)$$

and

$$F_B = \frac{n}{m}F_A \quad (14)$$

When B is the titrant the values of the errors are of opposite sign

EXPERIMENTAL

Reagents and solutions

All the reagents were of reagent grade and the solutions [$CaCl_2$, $Sr(NO_3)_2$, and NaF] were standardized gravimetrically

Procedure

The analyte solution was kept at 25° and was allowed to stand until the potential of the measuring cell became stable After this the titration was started by adding small equal increments of titrant The solution was stirred for 400 sec and the potential was allowed to stabilize for a further 200 sec after every addition of the titrant before the potential was recorded (When strontium fluoride was the precipitate the corresponding times were 600 and 300 sec) The ionic strength of the analyte solution was adjusted with potassium chloride

The titrations were carried out on an automatic titrator described previously[11] The inside of the titration vessel was covered with epoxy resin The indicator electrode was a Philips IS 550 F fluoride electrode and the reference electrode was a Radiometer K 401 saturated calomel electrode

RESULTS AND DISCUSSION

In order to determine the practical titration error and to visualize the principles in precipitation titrations some titrations have been performed The titrations and results are given in Tables 1 and 2, which need some further

Table 1 The titration error and the solubility product when 0 946*M* fluoride is used as titrant

Concentration of analyte, *M*	V_0, ml	I	Error, %: found, eq (19)	Error, %: calculated, eqs (18, 15)	Error, %: predicted, eq (13)	Calculated apparent values of pK_s: from β, eqs (18, 10)	from F_A, eqs (19, 13)	dilution allowed for, *cf* ref 8
Ca^{2+}								
$1\,600 \times 10^{-2}$	12 00	0 112	4 55	4 59	2 63*	9 07	9 08	9 08
$1\,600 \times 10^{-2}$	12 00	0 112	4 37	3 91	2 63*	9 28	9 14	9 13
$1\,600 \times 10^{-2}$	12 00	0 112	4 16	4 31	2 63*	9 14	9 20	9 19
$4\,571 \times 10^{-3}$	21 00	0 104	14 56	15 27	8 98*	9 11	9 17	9 16
$4\,571 \times 10^{-3}$	21 00	0 104	12 87	15 15	8 98*	9 12	9 33	9 33
Sr^{2+}								
$5\,000 \times 10^{-2}$	10 00	0 138	8 04	9 50	3 59†	6 74	6 95	6 91
$5\,000 \times 10^{-2}$	10 00	0 139	11 09	10 13	3 59†	6 66	6 54	6 06

* $pK_s = 9\,8$, ref 13
† $pK_s = 8\,0$, ref 13 ($I = 0\,1$)

Table 2 The titration error and the solubility product when 0 0960*M* calcium is used as titrant

Fluoride concentration of analyte, *M*	V_0, ml	*I*	Error, % found, eq (19)	Error, % calculated, eqs (18, 15)	Error, % predicted, eq (13)*	Calculated apparent values of pK_s from β, eqs (18, 10)	Calculated apparent values of pK_s from F_A, eqs (19, 13)	Calculated apparent values of pK_s dilution allowed for, *cf* ref 8
$2\,755 \times 10^{-2}$	10 30	0 109	−6 77	−5 39	−3 34	9 18	8 88	8 92
$2\,755 \times 10^{-2}$	10 30	0 109	−8 60	−5 52	−3 33	9 14	8 56	8 61
$1\,398 \times 10^{-2}$	10 15	0 105	−9 98	−11 37	−6 19	9 01	9 18	9 21
$1\,398 \times 10^{-2}$	10 15	0 105	−10 31	−10 89	−6 19	9 06	9 13	9 17
$1\,398 \times 10^{-2}$	10 15	0 105	−9 38	−11 79	−6 19	8 96	9 26	9 29

* $pK_s = 9\,8$, ref 13 ($I = 0\,1$)

explanation. The slope of the electrode potential as a function of fluoride ion concentration was found empirically by the titration technique to be 58 7 mV/decade (irrespective of the type of the reference electrode) The maximum potential change (ΔE_{max}) at the inflection point was calculated by Nasanen's method [12] The value of the buffer index at this point was then calculated with the aid of equation (18), and hence the error and the value of the apparent solubility product The pK_s-value was also calculated with the aid of equation (13) from the determined experimental error For comparison, the values of the predicted error and those of the apparent solubility product calculated according to principles previously published[8] (which take into account the dilution of the analyte solution during the titration) are also given

The tables reveal that the observed values of the experimental error and those calculated from the buffer index are in good agreement, but those predicted from the solubility product are always too small

Tables 1 and 2 also reveal that the values of the apparent solubility product calculated from the experimental error and from buffer index values are of the same order of magnitude and larger than the published values This cannot be explained by the dilution of the analyte, it is caused by the method of precipitation When the precipitate is formed during the titration, the particles are small in size, they have not enough time to grow, and thus the solubility (and the ionic product) is larger than under equilibrium conditions When the stirring and stabilization time between increments was increased to 1200 + 600 sec (for CaF_2) the pK_s-values increased by about 0 05–0 1, supporting the explanation given

The difference between the observed and published pK_s-values (and the observed and theoretical error values) might also be due to some side-reaction, *e g*, complex formation However, a side-reaction can always be included in the calculations, and as complex formation is not likely to occur in the titrations performed, it is not considered further

The facts found for the titrations performed can perhaps not be generalized to cover all precipitation titrations but it may be concluded that though in some precipitation titrations the error cannot be predicted from the solubility product, nor can the pK_s-value be calculated from titration data for the inflection point, the error of the titration *can* be estimated from buffer index determinations If the precipitate is formed ideally, the calculation of the solubility product is relevant

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Summary—The titration error can be calculated with the aid of the value of the buffer index determined at the inflection point of the titration curve when a precipitation titration is followed with an ion-selective electrode When the precipitate is not formed ideally in the titration (*i e*, is not formed under equilibrium conditions) the titration error cannot be predicted from the values of the solubility product, nor can the values of the solubility product be calculated from titration data at the inflection point

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ANALYTICAL DATA

THREE TRACE-ELEMENT GEOLOGICAL MATERIALS CERTIFIED AS A RESULT OF A CO-OPERATIVE INVESTIGATION

OLAV H J CHRISTIE

University of Oslo, Laboratory of Mass Spectrometry, P b 1048 Blindern, Oslo 3, Norway

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Since 1968 twenty-two chemical analysts from Nordic countries have participated in a co-operative work for intercalibration of trace-element analytical techniques Three geological materials were selected as working samples

ASK-1, *Larvikite*, from the Tvedalen quarry SW of the town Larvik, Vestfold country, South Norway This is a type locality of the light-coloured variety of larvikite, described by Barth [1]

ASK-2, *Schist*, from the Upper Tremadoc Ceratopyge schist [3b of the Oslo region Arenigan (Lower Ordovician)] in the underground of St Olavs plass, Oslo 1, Norway, described by Bjørlykke [2]

ASK-3, *Sulphide ore*, from the zinc–lead ore-body at Bleikvasli mines, Nordland county, North Norway, described by Vokes [3]

Preparation of samples

Each sample was initially washed in pure water and cut in pieces with a hydraulic rock cutter After the first crushing in a jaw crusher the sample was split into two parts Equal amounts of the two parts were powdered in a steel ring eccentric mill (Labor-Scheibschwingmuhle, Siebtechnik, Germany) The finely crushed sample was split into two parts, and the parts again mixed together in a heavy cardboard container with a 40-kg Turbula mixer (Willy Bachofen, Basel, Switzerland) The cardboard container showed no signs of wear after the homogenization

The homogeneity of the sample materials was checked thus ten independently collected samples of each material were pressed, without binding material and with a backing of poly(vinyl chloride), to form discs of 25 mm diameter suitable for X-ray fluorescence analyses Counts of the *K* line of iron of 64 sec duration were recorded five times for each sample The estimated relative standard deviation of the number of counts per recording of the total number of samples was 0 6‰ whereas 14 recordings of one of the samples over the whole period of analysis gave an estimate of relative standard deviation of 0 4‰, indicative of absence of instrumental drift The 95% confidence interval was $\bar{x}(1 \pm 0.0017)$ for the whole set of observations and $\bar{x}(1 \pm 0.0021)$ for the drift-check parallels

Participants and choice of recommended values

Laboratories and analysts who have supplied concentration data are listed in Table 1 The recommended values in Tables 2 and 3 have been selected in a series of round-table meetings of the participating analysts These values are given as means of values supplied by participants The means are based upon two or more values in good agreement and reported by at least two analysts from

Table 1 Analysts

1	L-H Andersson	FOA, S-104-05 Stockholm 80, Sweden
2	B T Anderassen	Geological Survey of Norway, P b 3006, N-7001 Trondheim, Norway
3	A-L Arnfelt	A B Atomenergi Studsvik, S-611 01 Nykoping 1, Sweden
4	K O Bjørlykke	Institute of Geology, University of Oslo, P b 1047 Blindern, Oslo 3, Norway
5	H J Bollingberg	University of Copenhagen, Mineralogical Museum, Østervoldgade 10, DK-1350 København, Denmark
6	A O Brunfelt	University of Oslo, Mineralogical-Geological Museum, Sars gate 1, Oslo 5, Norway
7	B Bruun	University of Oslo, Mineralogical Geological Museum, Sars gate 1, Oslo 5, Norway
8	O H J Christie	University of Oslo, Laboratory of Mass Spectrometry, P b 1048 Blindern, Oslo 3, Norway
9	L Danielsson	Swedish Institute of Metal Research, Drottning Kristinas vag 48, S-114 28 Stockholm, Sweden
10	G C Faye	Geological Survey of Norway, P b 3006, N-7001 Trondheim, Norway
11	S Fregerslev	University of Aarhus, Department of Geology, DK-8000 Århus C, Denmark
12	F J Langmyhr	(Some data in collaboration with analyst no 15) University of Oslo, Institute of Chemistry, P b 1033, Blindern, Oslo 3, Norway
13	W Lund	University of Oslo, Institute of Chemistry, P b 1033, Blindern, Oslo 3, Norway
14	S Melsom	Institute of Industrial Research, Forskningsveien 1, Blindern, Oslo 3, Norway
15	P E Paus	Institute of Industrial Research, Forskningsveien 1, Blindern, Oslo 3, Norway
16	A R Selmer-Olsen	Norwegian Agriculture University, Laboratory of Chemical Analysis, 1432 Vollebekk, Norway
17	A Simonsen	Technical University of Denmark, Institute of Mineralogy, Bld 204, 2800 Lyngby, Denmark
18	E Steinnes	Institute of Atomic Energy, 2007 Kjeller, Norway
19	G Sundkvist	Boliden AB Ronnskarsverken, Centrallaboratoriet, Skeleftehamn, Sweden
20	I Sørensen	The Geological Survey of Greenland, Østervoldgade 10, DK 1350, København K, Denmark
21	C U Wetlesen	Central Institute of Industrial Research, Forskningsveien 1, Blindern, Oslo 3, Norway
22	H Zachariasen	Falconbridge Nikkelverk A/S, 4600 Kristiansand S, Norway

Table 2 Uncertified concentration values (%) of major and some minor constituents

	ASK-1 Larvikite	ASK-2 Schist	ASK-3 Sulphide ore
SiO_2	59 5	54 2	7 4
TiO_2	1 1	0 92	trace
Al_2O_3	18 6	18 8	0 3
Total Fe as Fe_2O_3	4 6	6 9	—
MnO	0 13	0 03	0 04
MgO	1 1	2 0	0 08
CaO	3 2	0 75	0·05
Na_2O	6 5	0 8	0 018
K_2O	4 2	5 3	0 070
Fe	—	—	35 6
Cu	—	—	0 14
Pb	—	—	2 1
Zn	—	—	9 2
S	—	—	41 50
C	—	8 5	—

different laboratories and using different methods, each analyst having a thorough knowledge of his own method The methods applied are anodic stripping voltammetry, atomic-absorption spectrometry, electrolysis, flame emission methods, gravimetric methods, spectrophotometry, titrimetric methods and X-ray fluorescence

The evaluation of the results has benefited considerably from the extensive methodological discussions in which most of the participants have taken part In several cases the recommended values are different from the arithmetic mean because there has been general agreement on the superiority of given methods or experience of some of the participants Some of the participants have found this type of work so encouraging that it will be continued with other materials

Samples of the present three reference materials are available in 75-g lots, together with a list containing all reported concentration values and covering 41 trace elements Further information is obtainable from the author

Table 3 Recommended trace concentration values (*ppm*) and analytical methods used

	ASK-1	ASK-2	ASK-3	Methods used
Ag	0 05	0 4	19	aa, ms, naa, os
Au	—	—	0 06	naa
As	—	—	630	ms, os, xr
B	—	153	—	os
Ba	1130	—	35	os
Be	4	4	—	os
Bi	—	—	33	aa, ms, xr
Cd	—	—	340	aa, ms, naa, os, xr
Cl	100	14	7	ch, naa
Co	6	27	88	aa, naa, os, xr
Cr	40	90	25	aa, ms, naa, os, xr
Cs	1 5	11	—	naa
Cu	7	120	1450	aa, ch, naa, os, xr
Ga	29	25	6	ms, naa, os, xr
Hg	—	—	7 6	aa, os
In	—	—	17 7	aa, naa
Li	18	30	—	aa, os
Mn	1020	280	260	aa, ms, naa, os, xr
Mo	—	60	45	ms, naa, os, xr
Ni	110	148	37	aa, ms, os, xr
Rb	85	175	—	aa, naa, os, xr
Sc	7	—	—	naa
Sr	680	100	—	naa, os, xr
Ti	main element	main element	33	aa, ch, os
V	49	220	—	ch, ms, os
Zn	105	166	main element	aa, naa, os, xr
Zr	400	168	—	os, xr

aa atomic-absorption methods
ch wet chemical methods, mainly titrimetric
ms spark-source mass-spectrometry
os optical spectrography
xr X-ray fluorescence analysis
naa neutron-activation analysis

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Summary—The results of a Nordic analytical trace-element study of three geological samples are given Recommended concentration values for 27 trace elements and 14 main elements have been arrived at by the analysts in the course of several round-table conferences The samples are now available as reference materials, for other analytical laboratories

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POTENTIOMETRIC AND SPECTROPHOTOMETRIC DETERMINATION OF THE PROTONATION CONSTANT OF HEXAMETHYLENETETRAMINE

ARI IVASKA and LEO HARJU
Department of Analytical Chemistry, Åbo Akademi, Åbo 50, Finland

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Hexamethylenetetramine (urotropine) has found extensive use as a buffer, and is especially suitable for this purpose, because it forms relatively weak complexes with metals In medicine it has long been used in the treatment of urinary tract infections More recently it has been found to have an inhibiting effect on the growth of tumours [1]

Very few equilibrium data can be found in the literature for this reagent [2] Below, both a potentiometric and a spectrophotometric method are utilized for the determination of the stability constant of the reaction

$$H^+ + L \rightleftharpoons HL^+ \qquad K_{HL} = \frac{[HL^+]}{[H^+][L]} \qquad (1)$$

where L denotes the ligand hexamethylenetetramine, and the constant is determined as a concentration constant

EXPERIMENTAL

Reagents

Hexamethylenetetramine and other chemicals were Merck *p a* grade Potassium chloride was used to keep the ionic strength at 0 1 and 0 5 The titrant was potassium hydroxide solution All measurements were made at 25° in an inert atmosphere

Apparatus

The potentials were recorded with an Orion 801 pH/mV meter (precision ± 0 1 mV) using Beckman glass and calomel electrodes The hydrogen-ion concentrations were calculated from the measured potentials by a method slightly modified from the one given by Ingman *et al* [3] The spectrophotometric measurements were performed with a Coleman model 46 UV-VIS Spectrophotometer equipped with a quartz flow-cell The volumes were measured with Metrohm piston and micro burettes

For mathematical calculations a programmable Monroe 1860–44 calculator was used

Procedures

Potentiometric determination A potentiometric method not previously used for determination of stability constants of acids was employed It is due to Ivaska and Wanninen,[4] and uses the equation for titration of weak acids derived by Ingman and Still [5] The data obtained from a potentiometric titration are processed with a desk-calculator The program calculates both the equivalence volume and the stability constant of the acid by an iterative procedure The stability constant is a mean of four values calculated from four points, two on each side of the half-titration point The equivalence volume is determined by the method of Ingman and Still,[5] using titration points near the equivalence point

The titration is started by performing an E'_0-titration[3] and then adding solid hexamethylenetetramine to the solution and hydrochloric acid in excess in order to protonate the reagent The titration is then performed in the ordinary manner, the electrodes remaining in the solution throughout.[3] The titration curve, $-\log[H^+]$ *vs* *V*, the volume of added base, shown in Fig 1a, is the one obtained when protonated hexamethylenetetramine and excess of hydrochloric acid are titrated with potassium hydroxide at μ = 0 5 The excess of hydrochloric acid, *i e*, the starting point for the hexamethylenetetramine titration, can be determined by the Gran method,[6] using points before the first potential jump (Fig 1*a*) The data given in Table 1 represent the titration of hexamethylenetetramine, and the proton stability constant calculated from them is also given The value of the constant at μ = 0 1 is determined in a similar way and is given in Table 3

Spectrophotometric determination Spectrophotometric methods are widely used for the determination of protonation constants [7] However, in this work a less common

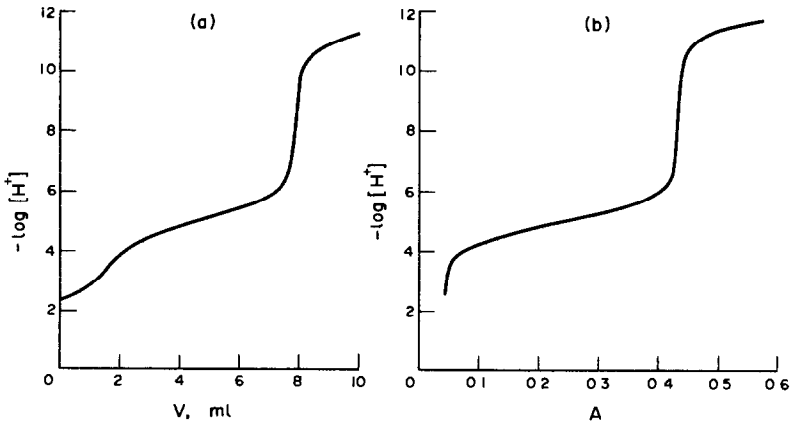

Fig 1 (a) $-\log[H^+]$ as a function of the volume of added potassium hydroxide for a titration of 1 26 × $10^{-2}M$ hexamethylenetetramine containing an excess of hydrochloric acid V_0 = 48 33 ml, μ = 0 5 (KCl), C_{OH} = 0 098 16 *M* (b) $-\log[H^+]$ as a function of absorbance for 5 × 10^{-3} *M* hexamethylenetetramine, which is neutralized by addition of potassium hydroxide V_0 = 100 0 ml, μ = 0·5 (KCl), λ = 215 nm

Table 1 Titration of the proton complex of hexamethylenetramine for determination of its stability constant

V, ml	$-\log[H^+]$	V, ml	$-\log[H^+]$
1 05	4 389	4 05	5 340
1 55	4 590	4 30	5 421
2 05	4 755	4 55	5 511
2 55	4 905	4 80	5 610
2 80	4 977	5 05	5 727
3 05	5 050	5 30	5 864
3 30	5 121	5 55	6 049
3 55	5 190	5 80	6 328
3 80	5 263	6 05	7 075

Found $\log K_{HL} = 5\,04_8$
$C_L = 1\,239 \times 10^{-2} M$

Initial volume $V_0 = 48\,33$ ml, KOH concentration $C_{OH} = 0{\cdot}09816M$, total initial concentration of hexamethylenetetramine $C_L = 0\,0126M$, $T = 25°$ and $\mu = 0\,5$ (KCl)

titration procedure is employed The absorbance and hydrogen-ion concentration of a solution that is gradually neutralized by addition of potassium hydroxide are simultaneously measured The hydrogen-ion concentration is measured as described above The advantages of this procedure are that no buffers are needed and the electrodes need not be removed from the solution during the experiment An absolute necessity for precise spectrophotometric measurements is a fixed cell, *e g*, of flow-through type

A suitable wavelength for the measurement of the absorption by hexamethylenetetramine was 215 nm An example of an absorbance curve plotted as a function of $-\log[H^+]$ is given in Fig 1b The shape of the absorbance curve implies that one proton is liberated at $-\log[H^+]$ about 5 At $-\log[H^+]$ above *ca* 10 there is another rise in the curve, owing to absorption by the hydroxide ion

When only the complex HL^+ is formed, the following equations are valid

$$A = a_{HL}[HL^+] + a_L[L] \quad (2)$$

$$C_L = [HL^+] + [L] \quad (3)$$

A is the measured absorbance and a_{HL} and a_L denote absorptivities, which can be determined from the pH regions where respective species dominate Thus equations (2) and (3) contain only two unknowns and can easily be solved Because a titration is used, the change in volume must be taken into account in calculating C_L, equation (3)

Typical results are given in Table 2 The optimal region for the determination of the ratio $[HL^+]/[L]$ and thus also the protonation constant is at or near the point of

Table 2 Spectrophotometric determination of the protonation constant of hexamethylenetetramine

V, ml	$-\log[H^+]$	A	$\log K_{HL}$	
0 73	4 515	0 1305	5 056	
0 85	4 734	0 1700	5 054	$\log K_{HL} = 5\,05_2$
0 97	4 941	0 2135	5 052	
1 10	5 137	0 2575	5 051	
1 28	5 428	0 3175	5 051	
1 42	5 724	0 3630	5 059	

$V_0 = 100\,0$ ml, $C_{OH} = 0\,5M$, $C_L = 5 \times 10^{-3} M$, $\mu = 0\,5$ (KCl), $T = 25°$ and $\lambda = 215$ nm

Table 3 Summary of the stability constants of the proton complex of hexamethylenetetramine

$\log K_{HL}$	Temp, °C	Ionic strength	Reference
4 92	—	—	Kolthoff[8]
6 30	25	0 5*	Pummerer and Hofmann[9]
4 9	—	—	Evstratova *et al*[11]
4 85	—	—	Reilley and Schmid[12]
$4\,88_6$	25	0 1 (KCl)	This work
$5\,04_8$	25	0 5 (KCl)	(potentiometric method)
$4\,88_7$	25	0 1 (KCl)	This work
$5\,05_2$	25	0 5 (KCl)	(spectrophotometric method)

* 0 5*M* hexamethylenetetramine

half-titration, because small errors in the absorbance measurements then have little effect on the value of $[HL^+]/[L]$ By taking four points around the point of half-titration the mean value $\log K_{HL} = 5\,05_2$ was obtained for the example given in Table 2

DISCUSSION

In Table 3 the protonation constants determined in this work are summarized and compared with published values The values obtained by the potentiometric and spectrophotometric methods are in very good agreement (It is perhaps motivated to give $\log K_{HL}$ to three decimals, especially when the potentials are measured with 0 1 mV and absorbances with 0 001 units accuracy) The difference between a potentiometric and a spectrophotometric method for determination of stability constants can be seen in Fig 1 In potentiometry the amount of added titrant and in spectrophotometry the measured absorbance are used to calculate the mole ratio of $[HL^+]$ to $[L]$ At alkaline pH the two curves are similar, because hydroxide ions absorb at the wavelength used, but in the acid region, the additional HCl affects the shape of the potentiometric curve

The values of the protonation constant of hexamethylenetetramine obtained in this paper are in satisfactory agreement with the values reported by Kolthoff,[8] Evstratova *et al*[11] and Reilley and Schmid[12] although the exact temperature and medium for their experiments are not given The value given in "Stability Constants"[2] could not be found by the present authors in the original paper of Pawelka[10]

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Summary—The protonation constant of hexamethylenetetramine (urotropine) was determined by a potentiometric and a spectrophotometric method. The calculations gave log K_{HL} (concentration constants) 4 89 at $\mu = 0\,1$ and 5 05 at $\mu = 0\,5$ The temperature was 25° and potassium chloride was used to adjust the ionic strength

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ABSORPTION SPECTRA OF CHELATES OF NITROSONAPHTHOLSULPHONIC ACIDS WITH VANADIUM(IV)

O A MAKITIE and K V O LAJUNEN

Division of Analytical Chemistry, Department of Chemistry, University of Helsinki, SF-00100 Helsinki, Finland

(*Received* 4 *April* 1975 *Accepted* 10 *April* 1975)

Ortho-nitrosonaphthols are well-known spectrophotometric reagents in trace analysis of certain metal ions The active chelation grouping also forms coloured complexes with vanadium [1–3] In the present work five sulpho derivatives of *o*-nitrosonaphthols were compared as ligands in complex formation with oxovanadium(IV) in aqueous solution 1-Nitroso-2-naphthol-3,6-disodiumsulphonate (Nitroso-R salt) and 2-nitroso-1-naphthol-4-sodiumsulphonate are known reagents The other ligands, the 5-sulpho, 8-sulpho and 4,6-disulphoderivatives of 2-nitroso-1-naphthol, are new water-soluble reagents of *o*-nitrosonaphthol type

EXPERIMENTAL

Reagents

The disodium salt of 1-nitroso-2-naphthol-3,6-disulphonic acid (Nitroso-R salt), a purissimum grade reagent from Fluka AG, was used after recrystallization from water 2-Nitroso-1-naphthol-4-sulphonic acid (purissimum grade, Fluka AG) was recrystallized as a sodium salt from water The sodium salt of 2-nitroso-1-naphthol-5-sulphonic acid was prepared by a nitrosation reaction from the sodium salt of 1-naphthol-5-sulphonic acid, and the nitroso salt formed was recrystallized twice from water, as the dihydrate [4] The sodium salt of 2-nitroso-1-naphthol-8-sulphonic acid was prepared from 1-aminonaphthalene-8-sulphonic acid through the corresponding diazo-compound, with naphthosultone and naphtholsulphonate as intermediates The product was purified by repeated recrystallization from water [5] The disodium salt of 2-nitroso-1-naphthol-4,6-disulphonic acid was prepared by the method of Saarinen from the bisulphite addition compound of 1-nitroso-2-naphthol-6-sulphonic acid (obtained by nitrosation from 2-naphthol-6-sulphonate, a purified reagent from B D H Ltd) by treating with hydroxylamine hydrochloride in dilute hydrochloric acid and with aqueous sodium chloride solution [6] Vanadium(IV) oxysulphate $VOSO_4\,5H_2O$ (E Merck AG) was used

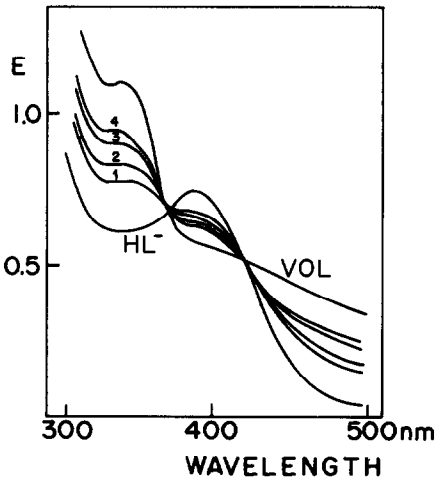

Fig 1 Absorption spectra of 2-nitroso-1-naphthol-5-sulphonate (HL^-) and of its oxovanadium(IV) complex (VOL) in aqueous solution Curves 1–4 refer to solutions where the pH was 3 16, 3 28, 3 43 and 3 55, respectively (c_L = 1 8 × $10^{-4}M$, c_M = 3 3 × $10^{-3}M$)

Apparatus

A Perkin-Elmer Model 402 Ultraviolet Spectrophotometer connected to a Digital Voltmeter Mk III (Weis Electronics, Ltd) was used for the spectral measurements at 25° The pH values were measured with a Radiometer Model PHM4d pH meter connected to a Beckman glass electrode and an open liquid-junction reference calomel electrode containing saturated potassium chloride solution The hydrogen-ion concentrations were calculated by means of the apparent hydrogen-ion activity coefficient values

RESULTS AND DISCUSSION

The formation of the spectrum of the first oxovanadium(IV) complex of 2-nitroso-1-naphthol-5-sulphonic acid, taken as an example,

$$VO^{2+} + HL^- \overset{K_1}{\rightleftharpoons} VOL + H^+ \qquad (1)$$

in solution where metal ions are present in excess relative to the ligand, is illustrated in Fig 1 The absorption spectra of the first complexes of the ligands studied, are reproduced in Fig 2

The vanadium(IV) complexes are all fairly strong, red-brown in colour, and are formed in acid solution The common spectrophotometric method was used for determination of the equilibrium constants of the corresponding reactions (*cf* Table 1)

1-Nitroso-2-naphthol-3,6-disulphonic and 2-nitroso-1-naphthol-5-sulphonic acids were chosen as ligands for experiments on the complex formation in solutions of varying ionic strength (potassium chloride as inert salt) The results in Table 2 show that the Debye-Huckel equation

$$pK_1 = pK_1^0 + Az^2\sqrt{I}/(1 + \alpha\sqrt{I}) - BI \qquad (2)$$

can be fitted to the data (A = 0 509), and the dependence of the pK_1-value on the square root of ionic strength of the solution indicates that the complex species VOL^- and VOL are formed with these ligands, respectively The following values for the constants and parameters in equation (2) were obtained, $pK_1^0 = -0\,45$, $\alpha = 1\,62$, $B = 0{\cdot}03$, and $pK_1^0 = 0\,38$, $\alpha = 2\,66$, $B = 0{\cdot}09$ for complexes of 1-nitroso-2-naphthol-3,6-disulphonic and 2-nitroso-1-naphthol-5-sulphonic acids respectively

At pH 4 4, Job's method of continuous variation gave the molar ratio 1 2 (c_L c_M) for the oxovanadium(IV) complex of 1-nitroso-2-naphthol-3,6-disulphonic acid, and 1 3

Table 1 Determination of the values of pK_1 of the first oxovanadium(IV) complex of 1-nitroso-2-naphthol-3,6-disulphonic acid from absorption spectra of aqueous solutions ($c_L = 1.4 \times 10^{-4} M$, $c_M = 1.8 \times 10^{-3} M$, $I = 0.41$)

$-\log[H^+]$	Absorbance 434 nm	446 nm	454 nm	462 nm	474 nm
(HL^{2-})	0.252	0.160	0.110	0.072	0.024
2.97	0.360	0.296	0.255	0.224	0.143
3.17	0.403	0.345	0.314	0.282	0.187
3.31	0.438	0.397	0.364	0.332	0.227
3.42	0.462	0.425	0.399	0.372	0.255
3.50	0.481	0.451	0.426	0.400	0.279
3.59	0.492	0.467	0.444	0.422	0.294
(VOL^-)	0.647	0.655	0.644	0.620	0.454
pK_1	0.53	0.52	0.52	0.51	0.52

for the complex of 2-nitroso-1-naphthol-5-sulphonic acid, when measured at 470–520 nm in solutions buffered with acetic acid and acetate

The values of the dissociation constants of the ligands studied, and the stability constant values, $\beta_1 = [VOL^{(n-2)-}]/[VO^{2+}][L^{n-}]$, are listed in Table 3

These ligands can be used for spectrophotometric determination of vanadium(IV) In particular the wide absorption band of the chelate of 2-nitroso-1-naphthol-5-sulphonic acid seems to be suitable at about 510 nm, where the spectrum of the ligand does not interfere The details and the spectra of the chelates formed in the presence of excess of ligand were not, however, studied further

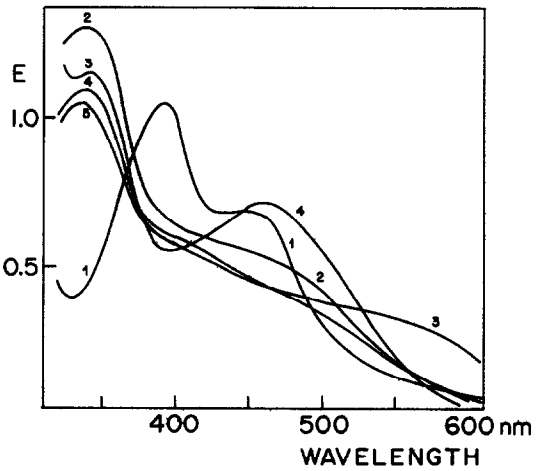

Fig 2 Absorption spectra of oxovanadium(IV) complexes (VOL or VOL^-) in aqueous solution (pH ~ 4) The curves refer to the complexes of 1-nitroso-2-naphthol-3,6-disulphonic acid (1), 2-nitroso-1-naphthol-4-sulphonic acid (2), 2-nitroso-1-naphthol-5-sulphonic acid (3), 2-nitroso-1-naphthol-8-sulphonic acid (4), and 2-nitroso-1-naphthol-4,6-disulphonic acid (5)

Table 2 pK_1 values of oxovanadium(IV) complexes of 1-nitroso-2-naphthol-3,6-disulphonic acid and of 2-nitroso-1-naphthol-5-sulphonic acid at different ionic strengths

1-Nitroso-2-naphthol-3,6-disulphonic acid			2-Nitroso-1-naphthol-5-sulphonic acid		
I	pK_1(obs)	pK_1(calc)	I	pK_1(obs)	pK_1(calc)
0.009	−0.19	−0.20	0.011	0.54	0.55
0.108	0.18	0.21	0.011	0.76	0.75
0.208	0.37	0.36	0.211	0.83	0.82
0.408	0.52	0.52	0.410	0.90	0.90
0.508	0.57	0.57	0.511	0.91	0.93
1.011	0.74	0.74	1.010	1.03	1.03

It is well known that several other metals form coloured chelates with *o*-nitrosonaphtholate ions in acid solution, for instance iron(II),[7] cobalt, palladium and other platinum metals, zirconium,[8] *etc*

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Table 3 Stability constants and some spectral characteristics of the ligands and oxovanadium(IV) complexes

Ligand	pK_a	$\log \beta_1^0$	$\log \beta_1$ ($I = 0.1$)	$10^3 \epsilon_{462(HL)}$ / l mole^{-1} cm^{-1}	$10^3 \epsilon_{462(ML)}$ / l mole^{-1} cm^{-1}
1-Nitroso-2-naphthol-3,6-disulphonic acid	7.51	7.96	6.71	0.56	4.58
2-Nitroso-1-naphthol-4-sulphonic acid	6.63		5.96	0.54	3.29
2-Nitroso-1-naphthol-5-sulphonic acid	7.32	6.94	6.19	0.55	2.23
2-Nitroso-1-naphthol-8-sulphonic acid	8.19		7.19	0.57	1.58
2-Nitroso-1-naphthol-4,6-disulphonic acid	6.51		5.68	0.41	3.97

Summary—The absorption spectra of chelates formed by oxovanadium(IV) with five different *o*-nitrosonaphtholsulphonic acids in aqueous solution are presented All the ligands studied, 1-nitroso-2-naphthol-3,6-disulphonate (Nitroso-R salt), 2-nitroso-1-naphthol-4-sulphonate, 2-nitroso-1-naphthol-5-sulphonate, 2-nitroso-1-naphthol-8-sulphonate and 2-nitroso-1-naphthol-4,6-disulphonate, form red-brown vanadium(IV) chelates in acid solution Values of the first stability constants of the complexes are reported

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EXCHANGE CONSTANTS OF Al(III) AND Fe(III) ON DOWEX 50W-X8

MOHAMMAD JAWAID and FOLKE INGMAN
Department of Analytical Chemistry, The Royal Institute of Technology, Stockholm, Sweden

(*Received* 25 *October* 1974 *Accepted* 16 *January* 1975)

The basic concept involving the adsorption and separation of metallic ions on a cation-exchange resin is that of affinity Argersinger *et al*[1] studied the equilibria between the resin and aqueous phases and developed the concept of an equilibrium constant The work was extended by Bonner[2,3] and his co-workers who determined the "affinities" of a number of metal ions for Dowex-50 resins They arranged the metals in a selectivity scale, based on the numerical values of the equilibrium constants[2,3]

Such data were efficiently used by Ringbom[4] in numerous theoretical calculations of the distribution coefficients of various metals between the resin and solution phases, in the presence of complexing agents, and for predicting the optimum conditions and the extent of separation of different groups of metals Most of these predictions have been confirmed by various workers in the field

Since no such data were available for aluminium and iron, it was decided to determine their exchange constants on Dowex 50W-X8 (50–100 mesh) resin

EXPERIMENTAL

Resin

Dowex 50W-X8 (50–100 mesh) resin was treated with 4–5*M* hydrochloric acid and washed free from acid with demineralized water It was then rinsed with absolute alcohol and dried overnight at 110° The exchange capacity of the resin was determined by the method of Fischer and Kunnin[5] and found to be 5 1 meq per g of dry resin

Procedure

A known amount of the resin with known moisture content was placed in a ground-glass-stoppered flask, and a measured volume of the solution containing a known amount of metal ion and at appropriate hydrogen ion concentration, was added The equilibrium was attained by agitating the mixture for 6 hr at room temperature in a mechanical agitator The distribution of metal ions at equilibrium was determined by analysing the filtrate

Both aluminium and iron were determined titrimetrically with EDTA the former by back-titration with standard lead solution at pH 5 5,[6] the latter by direct titration at pH 1 0–1 5 at *ca* 80°, Xylenol Orange being the indicator

RESULTS AND DISCUSSION

The exchange constants were calculated from the expression

$$K = \frac{[MR_3][H^+]^3}{[M^{3+}][HR]^3}$$

where

$[MR_3]$ = $C_M - [M^{3+}]$ expressed in meq per g of dry resin, C_M being the total concentration of metal ions in the aqueous phase before equilibration,

$[M^{3+}]$ = the concentration of M^{3+} in the aqueous phase at equilibrium (meq/ml),

$[H^+]$ = concentration of H^+ in the aqueous phase at equilibrium,

$[HR]$ = concentration of H^+ in the resin at equilibrium, expressed in mmole per g of dry resin

The results are presented in Tables 1 and 2

Table 1 Exchange constant of Al^{3+} on Dowex 50W-X8 (H^+-form)

Soln vol, *ml*	$[H^+]$, *M*	Resin (dry wt), *g*	Al^{3+} ads, *mg*	Al^{3+} in soln, *mg*	*K*
30 00	1 644	1 325	9 14	7 35	$1\,63_4$
36 00	1 370	1 072	9 21	7 29	$1\,63_0$
42 00	1 174	0 974	9 69	6 80	$1\,66_6$
48 00	1 027	1 121	11 20	5 29	$1\,66_9$
54 00	0 913	1 384	12 85	3 64	$1\,69_6$

Average 1 66, Deviation 0 02, Standard deviation 0 03

Table 2 Exchange constant of Fe^{3+} ion on Dowex 50W-X8 (H^+-form)

Soln vol, *ml*	$[H^+]$, *M*	Resin (dry wt), *g*	Al^{3+} ads, *mg*	Al^{3+} in soln, *mg*	*K*
30 00	1 644	1 274	20 53	13 96	$2\,16_5$
36 00	1 370	1 178	21 92	12 57	$2\,13_4$
42 00	1 174	1 203	24 42	10 17	$2\,27_8$
48 00	1 027	0 841	21 58	12 91	$2\,15_0$
54 00	0 913	1 212	26 95	7 54	$2\,21_9$

Average 2 19, Deviation 0 05, Standard deviation 0 06

The constants above have been determined at room temperature (20 ± 1°) and variable ionic strength However, at the high ionic strengths (0 9–1 7) used, the variations of the activity coefficients are normally small and may be neglected

The choice of nitric acid for adjusting the hydrogen-ion concentration of the solution minimizes the possibility of complex formation of the metal ions with the anion of the acid

Theoretical calculations based on these values were used for predicting the optimum conditions and the extent of separation of these metals from each other and from other metal ions The experimental results agree very well with the predictions[7]

Acknowledgement—The authors wish to express their gratitude to Professor Axel Johansson for interest in their work and for placing facilities at their disposal

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Summary—The exchange constants for Al^{3+} and Fe^{3+} ions on the cation-exchange resin Dowex 50W-X8 (H^+-form) are reported A batch method of equilibrium at room temperature was used to determine these constants, which are

$$Al^{3+} + 3\,HR \rightleftharpoons AlR_3 + 3\,H^+, K = 1\,66$$

$$Fe^{3+} + 3\,HR \rightleftharpoons FeR_3 + 3\,H^+, K = 2\,19$$

R denoting the resin

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LOUIS GORDON MEMORIAL AWARD

Professor Lloyd Smythe (right) presenting the Louis Gordon Memorial Award to J. T. van Gemert during the Third Australian Symposium on Analytical Chemistry.

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SEVENTH TALANTA MEDAL

Dr. M. Williams, Professor Alimarin and Professor Zolotov admire the *Talanta* Gold Medal presented to Professor B. V. L'vov for his work on development of flameless atomic-absorption methods. The medal was formally presented by Professor Alimarin.

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The Editorial Board and Publishers of *Talanta* have pleasure in welcoming Mr. F. C. A. Killer to the Advisory Board. For many years Mr. Killer has supplied the Russian translations of the summaries of papers appearing in *Talanta*.

Mr. Killer was born in 1920 in Eichtal (Austria) and obtained his degree in chemistry from the University of Zagreb, Yugoslavia in 1947. He started work as analyst at the Institute of Petroleum, Zagreb, became head of the Analytical Department. He worked there on problems related to oil production and petroleum processing, in particular desulphurization. After a period in industry in Yugoslavia and Germany he joined the Esso Research Centre at Abingdon in 1961. Where he worked as project leader on chromatographic methods of separation, in particular TLC of petroleum products, and elemental analysis, specializing in microcoulometry of sulphur and sulphur compounds in petroleum. He was also engaged in gas analysis and the prevention of explosions on large oil tankers. He has published *ca.* 20 papers on the analysis of materials related to oil production (characteristics of oil-bearing strata, formation waters, drilling mud), hydrocarbon type analysis, applications of TLC to petroleum products, and microcoulometry.

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Formation of the silver and mercury(II) chelates of 2-hydroxy-1,3-diaminopropane-*N*,*N*,*N*′,*N*′-tetra-acetic acid (HDPTA): LEO HARJU. (10 *January* 1975)

Drying and weighing of standard reference materials for volumetric analysis, and the status of the Faraday constant as an international standard: TAKAYOSHI YOSHIMORI. (14 *January* 1975)

***N*-Hydroxy-*N*,*N*′-diphenylbenzamidine—A new type of analytical reagent: Gravimetric determination of copper(II):** K. SATYANARAYANA and RAJENDRA K. MISHRA. (15 *January* 1975)

Determination of stability constants of cadmium(II) complexes with some amino-acids, by use of an ion-selective electrode: G. J. M. HEIJNE and W. E. VAN DER LINDEN. (17 *January* 1975)

Spectrophotometric determination of silicon in ferrophosphorus: K. A. BROOKING and C. B. BELCHER. (20 *January* 1975)

Electroreduction of uranium(VI) at a platinum electrode, and its analytical applications: P. ZANELLO, G. RASPI and A. CINQUANTINI. (20 *January* 1975)

Interactions of picoline-2-aldehyde thiosemicarbazone with metal ion: D. J. LEGGETT and W. A. E. MCBRYDE. (20 *January* 1975)

Polarographic behaviour of *N*-chlorosuccinimide at a dropping mercury electrode: LALIT NARAIN and C. M. GUPTA. (22 *January* 1975)

Spectrophotometric determination of the aggregation number of Solochrome mordant dyes: WAHID U. MALIK and P. N. GUPTA. (22 *January* 1975)

Ferricyanide as a primary standard for the determination of arsenic(III) and antimony(III) in bicarbonate medium: DEVENDRA MOHAN, P. D. SHARMA and Y. K. GUPTA. (22 *January* 1975)

Amperometric determination of organic isothiocyanates: BALBIR CHAND VERMA and SWATANTAR KUMAR. (23 *January* 1975)

Sequential determination of thorium and rare earths with EDTA and kojic acid: S. Y. SHETTY and R. M. SATHE. (23 *January* 1975)

Anwendbarkeit der flammenlosen Atomabsorption in der messenden Komplexchemie—II. Über Löslichkeit, Stabilität und Verteilung des Cd-Oxinates: B. MAGYAR and P. WECHSLER. (28 *January* 1975)

Talanta. Vol 22, pp I–II Pergamon Press, 1975 Printed in Great Britain

EDITORIAL

Our percipient readers will have noticed that the page size of *Talanta* has been markedly increased, but the full page depth was not always used in the first two issues for the year. The reason for this is the standardization of paper size for Pergamon journals, permitting greater economy in production and hence stabilization of prices. Further economy can be achieved by using double-column type-setting, which allows use of a greater width on the page and saves space by decreasing the size of blank areas around illustrations. We shall be changing to the double-column format in the May issue, and from the beginning of the year we have been using the page size that will be necessary for it, so that the size will be uniform throughout the year. It is hoped that in this way future increases in the cost of paper and printing can be at least partially compensated for. One consequence will be that though we shall publish the usual amount of material, it will occupy fewer pages, and it should be possible to bind *Talanta* in one volume instead of two, giving the subscriber a corresponding saving. We shall therefore revert to the issue of an annual index instead of two 6-monthly ones.

Talanta, Vol 22, p i Pergamon Press, 1975. Printed in Great Britain

PAPERS RECEIVED

Effects of auxiliary complex-forming agents on the rate of metallochromic indicator colour change—II. The mechanisms of the colour change of PAN in copper–EDTA titration: GENKICHI NAKAGAWA and HIROKO WADA. (12 *December* 1974)

Determination of carbon dioxide in coal and minerals: A. C. KNOTT and C. B. BELCHER. (12 *December* 1974)

Iodometric determination of peroxydiphosphate in the presence of copper (II) or iron(II): SURINDER KAPOOR, P. D. SHARMA and Y. K. GUPTA. (13 *December* 1974)

Oxidimetric determination of ascorbic acid in drugs and fruits with thallic perchlorate in acid medium: DINESH GUPTA, P. D. SHARMA and Y. K. GUPTA. (13 *December* 1974)

Plasma emission sources in analytical spectroscopy—II: S. GREENFIELD, H. McD. McGEACHIN and P. B. SMITH. (13 *December* 1974)

Spectrophotometric determination of vanadium and its application to gas turbine fuel oils: SAMARESH BANERJEE, B. P. SINHA and R. K. DUTTA. (17 *December* 1974)

Contributions to the basic problems of complexometry—XXV. Determination of rare earths and phosphates without separation: RUDOLF PRIBIL. (17 *December* 1974)

A rapid and precise method for the estimation of traces of thiol groups: D. SINGH and HARI PRASAD SRIVASTAVA (17 *December* 1974)

The chalcocite copper membrane electrode: A. HULANICKI, M. TROJANOWICZ and M. CICHY. (18 *December* 1974)

Estimation of chromium(II) from the rate of catalysed aquation of potassium hexacyanochromate(III): RAMESH BEMBI and WAHID U. MALIK. (18 *December* 1974)

Gravimetric estimation of manganese(II) with sodium benzilate as precipitating reagent: ASISH KUMAR CHATTERJEE and KALYAN KALI SEN GUPTA. (18 *December* 1974)

Talanta, Vol 22, pp I–II Pergamon Press, 1975 Printed in Great Britain

FOREWORD

The Editorial Board and Publishers of TALANTA take great pleasure in honouring the Scandinavian Schools of Analytical Chemistry by presenting this special issue reflecting their work. They consider it appropriate to link the issue with the name of J. KJELDAHL in this, the year of the 75th anniversary of his death.

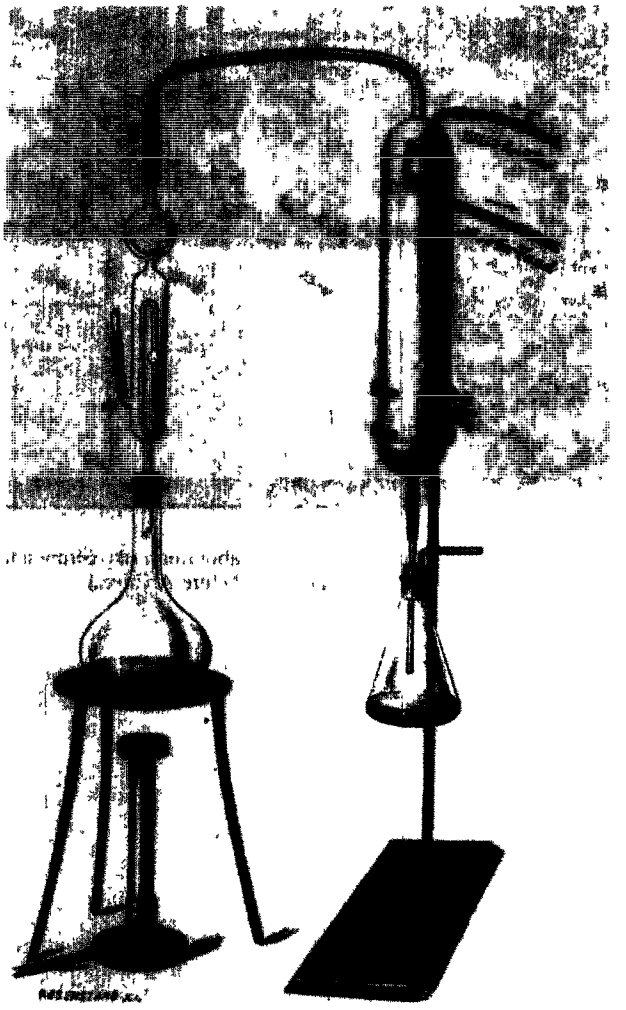

Plate 1 The first published illustration of the Kjeldahl apparatus (1888)

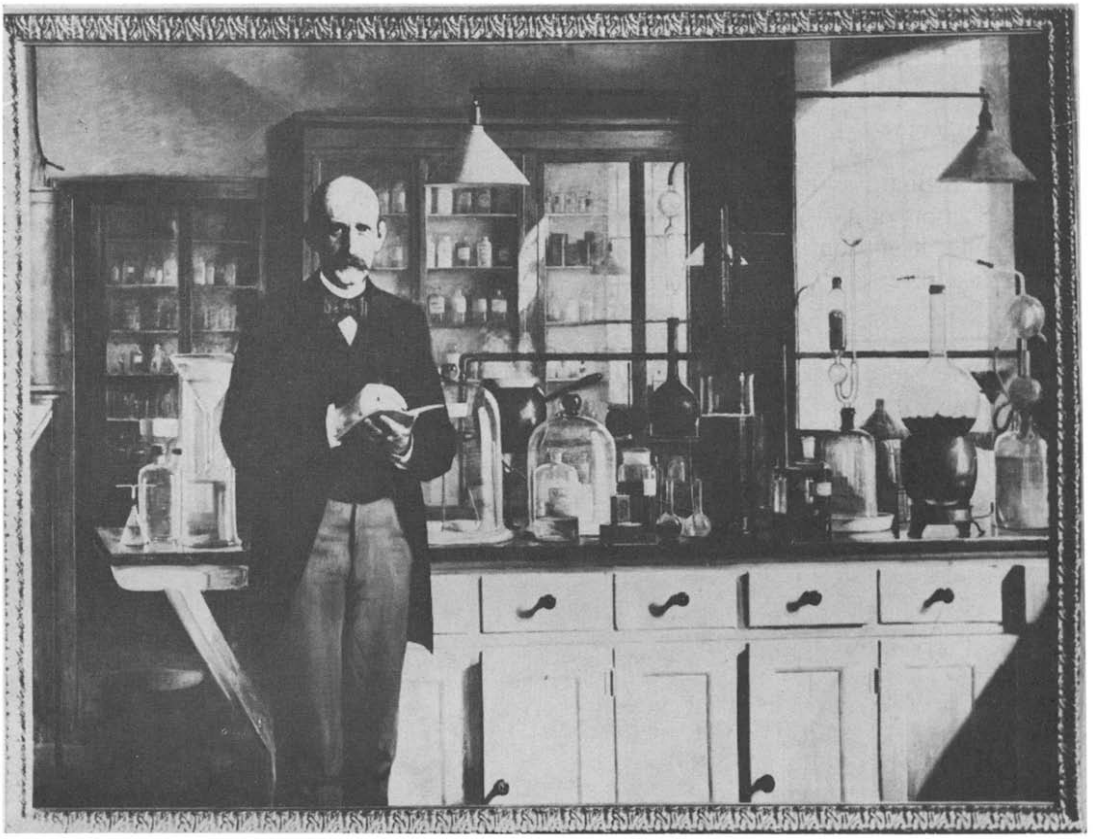

Plate 2 Kjeldahl, at the age of about 47 in the Carlsberg Laboratory (By permission of K M Møller and the Carlsberg Foundation Picture Archives)

Talanta, Vol. 22, pp. i–ii. Pergamon Press, 1975. Printed in Great Britain

PAPERS RECEIVED

Fundamental studies on improvement of precision and accuracy in flameless atomic-absorption spectroscopy with the graphite tube atomizer: Lead in whole blood: V. P. GARNYS and L. E. SMYTHE. (18 *March* 1975)

Emissionsspektrometrische Elementbestimmung im Nano- und Picogramm-Bereich nach Verflüchtigung der Elemente in mit Mikrowellen induzierte Gasplasmen—I. Extrem nachweisstarke Quecksilberbestimmung in wäßrigen Losungen, Luft, organischen und anorganischen Matrices: G. KAISER, D. GÖTZ, P. SCHOCH and G. TÖLG. (18 *March* 1975)

Extraction and spectrophotometric determination of ruthenium and osmium with thiobenzhydrazide: S. C. SHOME, P. K. GANGOPADHYAY and S. GANGOPADHYAY. (19 *March* 1975)

Infrared spectra of *N*-aryl hydroxamic acids: V. K. GUPTA and S. G. TANDON. (21 *March* 1975)

Chromatography of aromatic compounds on anion-exchange resins: LUTFUL MAJID JAHANGIR, LENNART OLSSON and OLOF SAMUELSON. (24 *March* 1975)

An automated submicrogram determination of selenium in vegetation by quartz tube furnace atomic-absorption spectrophotometry: P. N. VIJAN and G. R. WOOD. (24 *March* 1975)

Ion-selective electrodes in argentometric titrations: MARY R. MASSON. (24 *March* 1975)

Formation of isothiocyanatopentaaquochromium(III) polynuclear complexes with mercurous and methylmercuric cations: RICHARD J. BALTISBERGER and RONALD C. SPANGELO. (5 *March* 1975)

Chemical phase analysis of ores and rocks: A review of methods: H. F. STEGER. (25 *March* 1975)

Effect of the nature of organic solvents on their interaction with metal halides—VII. Arsenic trihalides and donor solvents: A. ALIAN, A. BARAKA, S. HAMMOUDA and R. EL-SHEIKH. (26 *March* 1975)

Trace-metal speciation in sea-water—I. Removal of trace metals from sea-water by a chelating resin: T. M. FLORENCE and G. E. BATLEY. (26 *March* 1975)

Iron(III) titration of tungsten reduced with mercury in thiocyanate medium: V. YATIRAJAM and SUDERSHAN DHAMIJA. (26 *March* 1975)

Thiovioluric acid as an analytical reagent—II. Spectrophotometric studies of rhodium(III), osmium(VIII), iridium(IV) and platinum(IV) complexes: R. S. CHAWLA and R. P. SINGH. (26 *March* 1975)

Solvent extraction and spectrophotometric determination of vanadium(V) with *N*-phenyl-n-butyrohydroxamic acid: J. P. SHUKLA and Y. K. AGRAWAL. (26 *March* 1975)

Micro and submicro iodometric determination of arsenite and sulphite ions by amplification reactions: AMIR BESADA, Y. A. GAWARGIOUS and S. Y. KAREEM. (27 *March* 1975)

Determination of low levels of uranium in phosphoric acid solutions obtained by acid attack on phosphate rock: FLORIN T. BUNUS. (31 *March* 1975)

Miniature potassium-sensitive electrode with a neutral carrier in a poly(vinyl chloride) matrix: O. RYBA and J. PETRÁNEK. (31 *March* 1975)

Sensitive tests for nitrite through azo-dye formation: B. S. GARG, Y. L. MEHTA and MOHAN KATYAL. (2 *April* 1975)

The analysis of copper refinery slimes: R. S. YOUNG. (2 *April* 1975)

Zur Problematik der massanalytischen Ammoniakbestimmung: JOSEF MALÝ. (2 *April* 1975)

Fluorescence characteristics of rhodamine complexes with gallium and indium: N. B. ZOROV and J. D. WINEFORDNER. (3 *April* 1975)

Rapid sequential atomic-fluorescence determination of silver and copper with an EIMAC continuum excitation source and a graphite-filament atomizer: F. S. CHUANG and J. D. WINEFORDNER. (3 *April* 1975)

Simultaneous determination of trace niobium, tantalum and tungsten in ferrous and non-ferrous alloys: G. L. VASSILAROS and C. J. BYRNES. (17 *March* 1975)

A thin-layer chromatographic method for separation and estimation of the condensation products of aromatic amines with formaldehyde in acid medium: M. R. G. NAYAR, T. K. RADHAKRISHNAN and D. JOSEPH FRANCIS. (4 *April* 1975)

Absorption spectra of chelates of nitrosonaphtholsulphonic acids with vanadium(IV): O. A. MÄKITIE and K. V. O. LAJUNEN. (4 *April* 1975)

Estimation of short-lived radionuclides in fesh fall-out debris for identification of nuclear weapon tests: S. B. HINGORANI, R. N. KHANDEKAR and S. J. S. ANAND. (7 *April* 1975)

New redox titrants in non-aqueous or partially aqueous media—VI. Potentiometric determinations using dibromamine-T and some further applications of dichloramine-T: C. G. R. NAIR and P. INDRASENAN. (7 *April* 1975)

The determination of traces of cadmium in alloy steels by anodic stripping polarography: KAREL ŠTULÍK and KAREL MAŘÍK. (8 *April* 1975)

Milligram determination of azo compounds: Reaction of azo compounds with *N*-bromosuccinimide in acetic acid medium: UMESH C. PANDE and MADHUBAN GOPAL. (10 *April* 1975)

A novel method of determination of zinc calcium and phosphate: S. V. CHIRANJEEVI RAO. (10 *April* 1975)

The iron(III) derivatives of 4,7-dihydroxy-1,10-phenanthroline: DONALD P. POE and HARVEY DIEHL. (7 *April* 1975)

Tris(4,7-dihydroxy-1,10-phenanthroline)iron(II) as a low-potential oxidation–reduction indicator. Determination of hydrosulphite: DONALD P. POE and HARVEY DIEHL. (7 *April* 1975)

The hydrogen selective glass electrode: GILLIS JOHANSSON, BO KARLBERG and ANDERS WIKBY. (16 *April* 1975)

Selective extraction of organic compounds as ion pairs and adducts: ROLF MODIN and GÖRAN SCHILL. (17 *April* 1975)

Quelques applications de la colorimétrie de précision a la microanalyse élémentaire. Dosages du titane, du platine, du palladium, du molybdène et du phosphore: E. DEBAL, R. CHASSIN and S. PEYNOT. (7 *April* 1975)

Spectrophotometric study of osmium with sulphonated anthranilic acids: D. CHAKRABORTI. (23 *April* 1975)

Conductometric determination of copper with 2′-hydroxychalcone: R. SESHADRI NAIDU and R. RAGHAVA NAIDU. (23 *April* 1975)

A high-precision coulometric method for standardization of vinyl chloride permeation tubes: A. CEDERGREN and S. Å. FREDRIKSSON. (28 *April* 1975)

Analytical properties of 1,3-cyclohexanedione bisthiosemicarbazone monohydrochloride: J. J. BERZAS NEVADO, J. A. MUÑOZ LEYVA and M. ROMÁN CEBA. (28 *April* 1975)

Colorimetric studies on the reaction of U(VI) and Mo(VI) with 3,5-dichloro-2-hydroxyacetophenone and its oxime: KEEMTI LAL and S. P. GUPTA. (29 *April* 1975)

Determination of vicinal hydroxyl groups in poly(vinyl alcohol) (PVA): J. G. PRITCHARD and Y. L. LAN CHUN FUNG. (5 *May* 1975)

Microwave-induced plasma coupled to a tantalum-filament vaporization assembly for trace element analysis: FRED L. FRICKE, OLIVER ROSE, Jr. and JOSEPH A. CARUSO. (6 *May* 1975)

Effects of auxiliary complex-forming agents on the rate of metallochromic indicator colour change—III. Mechanism of the colour change of TAC in nickel–EDTA titrations: GENKICHI NAKAGAWA, HIROKO WADA and OSAMU NAKAZAWA. (14 *May* 1975)

Studies on the molybdenum(VI) chelate with 2-aminobenzenethiol: ANIL K. CHAKRABARTI and SASWATI P. BAG. (14 *May* 1975)

Ion-exchange behaviour of pyridinium tungstoarsenate: W. U. MALIK, S. K. SRIVASTAVA and SATISH KUMAR. (14 *May* 1975)

Studies with inorganic ion-selective membranes—I. Preparation and characterization of membranes: W. U. MALIK, S. K. SRIVASTAVA, V. M. BHANDARI and SATISH KUMAR. (14 *May* 1975)

Development and publication of solvent extraction methods: Y. MARCUS. (14 *May* 1975)

Study of liquid–liquid extraction of perrhenate with cyclohexanone in different media: N. JORDANOV, M. PAVLOVA and D. BOJKOVA. (14 *May* 1975)

Partial masking of copper by cyanide in the formation of copper diethyldithiocarbamate complex: E. O. UMEH. (16 *May* 1975)

Estimation of cyanide via its interference with the formation of copper diethyldithiocarbamate complex, $Cu(DDC)_2$: E. O. UMEH. (16 *May* 1975)

Estimation of glucose and maltose by the two-wavelength method: S. K. MEUR, V. SITAKARA RAO and K. B. DE. (16 *May* 1975)

Extraction and spectrophotometric determination of cobalt(II) with thiobenzoylacetone simultaneous determination of nickel: M. V. R. MURTI and S. M. KHOPKAR. (16 *May* 1975)

Anreicherung von Spuren Au und Pd aus Reinstmetallen Cd, In, Ni, Pb und Zn mit nachfolgender Bestimmung in der Graphitrohr-Küvette: EWALD JACKWERTH and PAUL GÜNTER WILIMER. (16 *May* 1975)

Free energy, enthalpy and entropy changes accompaning the formation of the Ag(I) complexes of ethylenediamine: L. C. VAN POUCKE. (16 *May* 1975)

Plasma emission sources in analytical spectroscopy—III: S. GREENFIELD, H. McD. McGEACHIN and P. B. SMITH. (19 *May* 1975)

Determination of gold in ores by neutron-activation analysis: S. SUKIMAN. (19 *May* 1975)

Quantitative estimations by sodium bisthiosalicylatomercurate: MAHARAJ K. KOUL and KESHAVA P. DUBEY. (20 *May* 1975)

Talanta, Vol. 22, pp. i–ii Pergamon Press, 1975. Printed in Great Britain

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Determination of cadmium by precipitation of cadmium molybdate from homogeneous solution: KAZA SOMASEKHARA RAO and V. G. VAIDYA. (23 *October* 1974)

Mass spectra of metal iodides: KOZO MATSUMOTO, NOBUTOSHI KIBA and TSUGIO TAKEUCHI. (24 *October* 1974)

Potentiometric and spectrophotometric determination of the protonation constant of hexamethylenetetramine: ARI IVASKA and LEO HARJU. (25 *October* 1974)

Polarographic determination of chlorhexidine in pharmaceutical preparations: EINAR JACOBSEN and BJØRN GYLSETH. (25 *October* 1974)

Analysis of chromite by cation-exchange using EDTA as a complexing agent: MOHAMMAD JAWAID and FOLKE INGMAN. (25 *October* 1974)

Exchange constants of Al(III) and Fe(III) on Dowex 50W-X8: MOHAMMAD JAWAID and FOLKE INGMAN. (25 *October* 1974)

Determination of vitamin B_{12} by means of the cyanide group, by thermal decomposition and use of the cyanide-selective electrode: S. GOLDSTEIN and AL. DUCA. (28 *October* 1974)

Equilibrium effects in the determination of tantalum by atomic-absorption spectroscopy: W. F. PICKERING and P. E. THOMAS. (29 *October* 1974)

Automatic classification of chemical behaviour by sequential hypothesization and multiparametric curve-fitting—III. Fully computerized elucidation of polarographic data on stepwise complex formation: LOUIS MEITES. (29 *October* 1974)

Extractive concentration of platinum-group elements and their determination by atomic-absorption techniques: A. A. VASILYEVA, I. G. YUDELEVICH, L. M. GINDIN, T. V. LANBINA, R. S. SHULMAN, I. L. KOTLAREVSKY and V. N. ANDRIEVSKY. (29 *October* 1974)

Spectrophotometric determination of copper(II), zinc(II) and manganese(II): MOHAMED A. ELDAWY, S. R. ELSHABOURI and M. M. ALY. (4 *November* 1974)

Long-term stability of glass electrodes in aqueous media: BO KARLBERG. (4 *November* 1974)

Photometric determination of some aromatic aldehydes with barbituric acid and of barbituric acid with *p*-dimethylaminobenzaldehyde: MOHSIN QURESHI, HAMIR SINGH RATHORE and ALI MOHAMMED. (5 *November* 1974)

Separation and determination of chromium(III) and chromium(VI) by anion-exchange using sodium sulphite: YASUMASA SHIGETOMI, TAKASHI YAMASHIGE and TAKEJI HATAMOTO. (7 *November* 1974)

Cellular and foamed plastics as separation media. A new geometrical form of the solid phase in analytical liquid–solid contact: T. BRAUN and A. B. FARAG. (7 *November* 1974)

A chlorate ion-selective electrode based on a poly(vinyl chloride) matrix membrane: K. HIIRO, G. J. MOODY and J. D. R. THOMAS. (7 *November* 1974)

Studies on inorganic ion-exchangers—I. Synthesis, ion-exchange properties and applications of ferric arsenates: J. P. RAWAT and J. P. SINGH. (12 *November* 1974)

Studies on inorganic ion-exchangers—II. Preparation, properties and applications of ferric phosphates: J. P. RAWAT and PRITAM SINGH. (13 *November* 1974)

Separation of lead sulphate from barium sulphate in their determination in glass: B. C. SINHA and S. K. ROY. (18 *November* 1974)

Computer calculation of distribution diagrams.: RICCARDO MAGGIORE, SALVATORE MUSUMECI and SILVIO SAMMARTANO. (21 *November* 1974)

Phosphorimetry, a spectrochemical method of analysis: J. J. AARON and J. D. WINEFORDNER. (21 *November* 1974)

Spectrophotometric estimation of micro-amounts of ethylene glycol in propylene glycol: M. SRINIVASAN and S. THIAGARAJAN. (25 *November* 1974)

Substoichiometric neutron activation determination of gallium: Extraction from hydrochloric acid with tri-n-octylphosphine oxide in cyclohexane: J. W. MITCHELL and J. E. RILEY, JR. (26 *November* 1974)

Nomenclature in thermal analysis—III: R. C. MACKENZIE (26 *November* 1974)

Spectrophotometric investigation of the reaction between aluminium and Eriochrome Cyanin RC: N. G. ELENKOVA and E. POPOVA. (26 *November* 1974)

Iodometric micro and submicro determination of hydrazines by amplification reactions: Y. A. GAWARGIOUS and AMIR BESADA. (26 *November* 1974)

Studies on amorphous and crystalline thorium tungstate as an ion-exchanger: ANIL K. DE and KAILAS CHOWDHURY. (2 *December* 1974)

2-Methoxyethanol as a solvent for conductometric acid–base titrations: GARY A. SCHWARTZ and BARBARA J. BARKER. (13 *November* 1974)

2-Amino-3-hydroxypyridine as reagent for the spectrophotometric determination of osmium: Y. L. MEHTA, B. S. GARG and R. P. SINGH. (3 *December* 1974)

Chromatography of alkaloids on titanium arsenate papers: Quantitative separation of some alkaloids from nicotine on a titanium arsenate column: MOHSIN QURESHI, SYED ASHFAQ NABI and NIGHAT ZEHRA. (4 *December* 1974)

The determination of lead in carbonate rocks by carbon-furnace atomic-absorption spectrometry after dissolution in nitric acid: W. C. CAMPBELL and J. M. OTTAWAY. (4 *December* 1974)

Use of *p*-diethylaminophenylmercuric acetate for the determination of thiol groups in biological samples: A. J. BUSEV, L. J. TETERNICKOV, M. M. BUZLANOVA, E. D. KASHPAROVA, L. M. ROZDESTVENSKY and P. HENNING. (6 *December* 1974)

Talanta, Vol. 22, pp. III–IV. Pergamon Press, 1975 Printed in Great Britain.

TALANTA ADVISORY BOARD

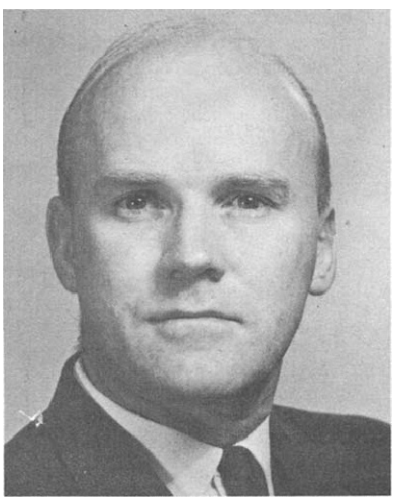
The Editorial Board and Publishers of *Talanta* take pleasure in welcoming the following new members to the Advisory Board of the journal.

C. B. BELCHER
D. M. HERCULES
J. D. R. THOMAS

They also wish to record their sincere thanks for the help given by

J. JORDAN
A. A. SMALES

who retire from the Advisory Board.



C. B. Belcher joined The Central Research Laboratories of The Broken Hill Proprietary Company Limited, Shortland, Australia, in 1956, and is Analytical Sciences and Services Manager. He graduated in Metallurgy from Newcastle Technical College and the N.S.W. University of Technology, in Chemistry from the University of N.S.W., and is a Fellow of The Royal Australian Chemical Institute and The Institution of Metallurgists. Publications include some thirty papers in the fields of atomic absorption, optical emission and X-ray spectrometry, as applied to economic minerals and metals. His present research interest is non-destructive trace element analyses of solid fuels and minerals.

Professor David M. Hercules is 44 years old and graduated in chemistry (B.S.) in 1954, obtaining his Ph.D. in 1957. Since then he has held various academic posts and is now Professor of Chemistry at University of Georgia, Athens, U.S.A. His research interests centre mainly on the application of spectroscopic techniques to the solution of chemical problems. At present he is specially interested in chemiluminescence and electron spectroscopy, but other areas of interest include fluorescence, phosphorescence, electroluminescence, photochemistry and other phenomena involving electronically excited states of molecules. He is already a member of the Editorial or Advisory Boards of *Spectrochimica Acta*, *Journal of Electron Spectroscopy*, *Analytical Chemistry* and *Applied Spectroscopy*, and has been extensively involved with organization of international conferences and with undertaking lecture tours and giving specially invited lectures. He has published nearly 100 research papers and several books.

Following a break in studies through over three years' service in the Royal Army Medical Corps, Dr. J. D. R. Thomas completed his Honours Degree of the University of Wales at University College, Cardiff in 1950. After two years working respectively for Spillers Ltd. and the Public Analyst for Glamorgan, he took a Diploma in Education and became Assistant Lecturer in Inorganic and Physical Chemistry in Cardiff College of Technology and Commerce where with the encouragement of Dr. H. B. Watson he carried out research in physical organic chemistry. In 1956 he moved to the South East Essex Technical College at Barking, Essex, to teach Physical Chemistry and later to the Newport and Monmouthshire College of Technology. He joined the Welsh College of Advanced Technology as Senior Lecturer in Inorganic and Analytical Chemistry in 1961 and is now a Reader at UWIST, Cardiff, where he has established Analytical Chemistry in its own right in the undergraduate curriculum. Dr. Thomas was awarded the D.Sc. degree of the University of Wales in 1972. His current research interests include ion-selective electrodes and separations by ion-exchange and electrophoresis. He has published 5 books and about 100 papers and he directed the IUPAC-sponsored International Symposium on Ion Selective Electrodes held at UWIST, Cardiff, in April 1973. He is a Vice-President of the Society for Analytical Chemistry and of the Analytical Division of the Chemical Society.

Talanta, Vol 22, pp i–iii Pergamon Press, 1975 Printed in Great Britain

PAPERS RECEIVED

The solvent extraction of copper(II) with chlorendic acid SELMAN A BERGER (21 *August* 1975)

Choice of chemical conditions in order to obtain linear titration curves in potentiometry AXEL JOHANSSON (22 *August* 1975)

Raman spectra of phenothiazine and some pharmaceutical derivatives BARBARA KURE and MICHAEL D MORRIS (22 *August* 1975)

Spectrophotometric determination of salicylaldehyde SAIDUL ZAFAR QURESHI, M S RATHI and IZZATULLAH (22 *August* 1975)

Spectrofluorometric determination of thiopurines—I. 6-Thioguanine A D THOMAS (25 *August* 1975)

Hydrogen peroxide determination using luminol and a new catalyst VĚNCESLAV PATROVSKÝ (2 *September* 1975)

Contribution to the determination of lead in propellant samples by atomic-absorption spectrophotometry EDGARDO J WOOD, ROBERTO GONZALEZ, JUAN A BLANCO and ALBERTO O RUCCI (2 *September* 1975)

Recent applications of quantitative nuclear magnetic resonance spectroscopy in pharmaceutical research DAVID M RACKHAM (2 *September* 1975)

The stability of the certified reference ores, MP-1, KC-1 and SU-1 to air oxidation H F STEGER (2 *September* 1975)

Potentiometric determination of *n*-butyl-1-biguanide with a liquid-state Cu^{2+}-sensitive electrode G E BAIULESCU, V V COŞOFREŢ and F G COCU (3 *September* 1975)

Metal oxide electrodes as sensors in complexometric titrations ADAM HULANICKI and MAREK TROJANOWICZ (3 *September* 1975)

Total systematic error in redox titrations with visual indicators—II. Experimental verification ADAM HULANICKI and STANISŁAW GŁAB (3 *September* 1975)

Scandinavian contributions to analytical chemistry E RANCKE-MADSEN and R A CHALMERS (8 *July* 1975)

Potentiometric study of the complexes of copper, nickel, cobalt, cerous and uranyl with 1-hydroxy-2-naphthoic acid S S SANDHU, R S SANDHU and J N KUMARIA (3 *September* 1975)

Rapid spectrophotometric determination of ruthenium with diethazine hydrochloride H SANKE GOWDA and P G RAMAPPA (3 *September* 1975)

Spectrophotometric and fluorometric determination of cobalt P R HADDAD, P W ALEXANDER and L E SMYTHE (3 *September* 1975)

Analytical applications of organic reagents in hydrophobic gel media—II. Selective preconcentration of mercury(II) with dithizone or thiothenoyltrifluoroacetone gel TAIROKU YANO, SHUNSUKE IDE, YOSHIO TOBETA, HIROSHI KOBAYASHI and KEIHEI UENO (3 *September* 1975)

The stoichiometric formation constants of metal complexes with 3-phenylazo-4-hydroxycoumarin, 2-phenylazo-1-naphthol and 1-pyridylazo-2-naphthol (PAN) G S MANKU (4 *September* 1975)

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A sensor for determining hydrogen sulphide NOBUTOSHI KIBA and MOTOHISA FURUSAWA (9 *October* 1975)

Improvement in sample preparation for alpha liquid-scintillation spectroscopy W J MCDOWELL (13 *October* 1975)

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Solvent extraction of metal xanthates ELSIE M DONALDSON (14 *October* 1975)

Schiff's base derived from salicylaldehyde and *o*-aminophenol as a gravimetric reagent for Cu(II) B L WAZIR and C N KACHRU (13 *October* 1975)

The determination of weak acids in aqueous solution by catalytic thermometric titrimetry E J GREENHOW and A A SHAFI (16 *October* 1975)

Thermodynamic examination of pH measurements BJORN BERGTHORSSON (20 *October* 1975)

***N*-*o*-tolylbenzohydroxamic acid as an analytical reagent for tin** M R GHOSH and MRINAL K DAS (13 *October* 1975)

3-Phenyl-5-isoxazolon-4-carbonic acid ethyl ester as a selective reagent for the spectrophotometric determination of iron(III) F CORIGLIANO and S DI PASQUALE (20 *October* 1975)

X-Ray photoelectron spectrometric and X-ray fluorometric studies of sulphur compounds on the surface of copper plates exposed to the atmosphere KATSUO MURAA, SHIGERO IKEDA, TAKAE UTSUNOMIYA and ARATA YASUI (20 *October* 1975)

Selective stripping voltammetric determinations employing cells for electrolysis with simultaneous ion-exchange or solvent extraction KAREL ŠTULÍK and PETR BEDROŠ (20 *October* 1975)

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Determination of cyanide in the ppM range ERVIN JUNGREIS and FANNY AIN (24 *October* 1975)

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Determination of barium and strontium peroxides (active oxygen) in igniters in small arms tracer ammunition GEORGE NORWTIZ and MICHAEL GALAN (27 *October* 1975)

Untersuchunger zur Bildung von *N*-Nitroso-Nornikotin aus Nikotin-*N'*-Oxid H-J KLIMISCH and L STADLER (27 *October* 1975)

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The relationship between the inflection point and equivalence point of a potentiometric titration WALTER LUND (20 *November* 1975)

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Talanta, Vol. 22, p. iii Pergamon Press, 1975 Printed in Great Britain

PUBLICATIONS RECEIVED

Atomic Fluorescence Spectroscopy: V. SYCHRA, V. SVOBODA and I. RUBEŠKA. Van Nostrand Reinhold, London, 1975. Pp. 379. £12.00.

The authors have succeeded in producing a handbook which is comprehensive and at the same time sufficiently brief to be read and not merely consulted. A feature of the theoretical section is the inclusion of many diagrams based on computer calculations of fluorescence growth curves (*vs.* concentration) and line profiles (*vs.* wavelength) for a variety of source types and optical arrangements round the flame. The chapter on instrumentation has been kept brief in those sections dealing with factors common to other modes of flame spectroscopy, but gives particular attention to light sources and to complete instruments for fluorescence studies. Fluorescence characteristics of the elements (39 of them) are reported briefly for each in turn, and the final chapter covers some applications to biological, industrial, and geochemical applications. One of the more exiciting aspects of atomic-fluorescence spectroscopy is that it lends itself more than other flame techniques to simultaneous multi-element determinations, an aspect which is discussed in this book, and which will certainly make it of interest to many analytical chemists. The extensive bibliography covers references up to 1973.

Archeological Chemistry: CURT W. BECK (Ed.). Advances in Chemistry Series, No. 138. American Chemical Society, Washington, D.C., 1974. Pp. ix + 254. $22.50.

It is not often that one finds a chemistry book so fascinating and captivating that one wants to read it through from cover to cover at a sitting, but that is how I reacted to this book. Thirteen papers from a symposium held in Dallas in 1973 are gathered together here, and for most chemists that in itself is a service as accounts of this type of work are usually found not in chemical but in archeological journals. The reason for this becomes clear as one goes through the chapters—the analytical results are only a part of the story, becoming meaningful only when correlated with age, origin, or method of manufacture of the artifacts being studied. The whole book might be described as an essay in sampling. The controversial problem of surface analysis versus bulk analysis is discussed (particularly with reference to early silver articles) and the reliability of the analytical results themselves, on the basis of a round-robin on some bronze samples, comes under fire. There are chapters on lead isotope ratios, silver (3), bronze, ivory, pottery (3), glass, chinese ink, and NMR and Mössbauer spectroscopy. A final tip—read this before you take it home, as the family will all want to have a turn.

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EDITORIAL

One of the most important end-products of analytical research is the established method of analysis, usually laid down on the basis of a collaborative study between laboratories expert in the field and drawn up with the specific intention of serving the purpose of quality control in the broadest sense—quality of iron and steel, bread and butter; ozone in air, collagen in meat products, cholesterol in blood. Such methods (or the results obtained when using them) are not themselves definitive of quality; they are chosen so as to serve as a convenient index of this, on the basis that an acceptable norm can be established by comparison with which quality can be judged. These norms, represented by or perhaps representative of the amount of carbon in steel, moisture in bread, connective tissue in lean meat for example, may vary according to which of a number of standards of excellence or performance is selected to be required of the steel, the bread, the meat.

One of today's problems is not so much the analysis as establishing the norm (which may be a limiting value or a range within two such values) upon which to base the interpretation of the analytical results. The applied analyst today has a choice, at times almost an embarrassing choice, of methods for the estimation or determination of many of these indexes, although he may often need help in evaluating the relative merits of alternative procedures and may need to check the analytical performance for his own substrate of interest. Such matters deserve a fuller attention than perhaps at present they get, not only in collaborative studies but also in the more speculative areas of analytical research. Harmonization of the approach in collaborative studies may be just as important as a further proliferation of the raw material of these, the new or improved method of analysis.

Trace and compositional analyses still go a long way to provide the basis for quality criteria of natural produce when the origin and identity of the produce is known or can be assumed. But identity, and in some cases genuineness, are not always to be taken for granted. In addition, there are often today for very good economic (and sometimes health or safety) reasons, opportunities to substitute, in part or otherwise, natural produce by the products of a well-intentioned technology. Since the aim is usually to simulate, in all its desirable attributes, the natural product itself, the already diffuse analytical criteria may become even less able to deal with such questions as which material is of natural origin and which the product of technology, especially when admixture is the practical answer to the problem of acceptability to the customer. What is then needed is a sounder approach to the problem of relating analytical results to quality. This almost certainly calls for a new and fundamentally different view of trace and compositional analysis as indexes of the quality and identity of natural produce.

A century or so ago saw the establishment of fat, solids-not-fats, and eventually the ratio of various constituent butterfat fatty acids, as a basis for the quality of milk. Nitrogen content and protein (N × 6.25) have long been considered a basis for the evaluation of lean meat in meat products. Sugars, amino-acids, organic acids, trace minerals have similarly been studied as a basis for the quality and content of citrus fruits in soft drinks and similar products and again ratios and similar derived functions based on two or more of such individual parameters have been sought as a sounder basis of such

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evaluations. The philosopher's stone of today—or one of them at least—is the key to the problem of chemical composition and overall acceptability of products such as natural foods and their processed counterparts, not only in terms of such attributes as safety, flavour and aroma, but also in terms of more aesthetic considerations such as the proportion of traditional protein to synthetic or other novel substitutes in a hamburger steak or the proportion of fruit in strawberry jam. Analysis using conventional criteria can still go a long way in providing estimates for such answers; but in recent years the difficulty of doing this and at the same time having a full understanding of the identity of the product has increased. This has led in part to the use of more sophisticated (and more expensive) physical methods of examination and has tended to widen the gap between what is possible and what, from an everyday control point of view, is practicable.

The "applied" analytical method is still one of the most important end-products of analytical research. Selectivity is usually at a premium; but this may not be equally true of sensitivity and how far accuracy and precision are to be taken will depend on the manner of application of the method. These are matters which should be taken into account in selecting methods for designated purposes, and if the methods are not already to hand, these are matters which should for preference be taken into account before the method is developed, not afterwards.

HAROLD EGAN

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NOTICES

1976 PITTSBURGH CONFERENCE

The Twenty-seventh Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy will be held at the Cleveland Convention Center, Cleveland, Ohio, U.S.A., March 1–5, 1976. The theme of the Conference symposia is two-fold: (1) papers on new methods; and (2) papers on methods which are orientated to the practicing chemist to assist him in solving his everyday problems. The symposia have been organized on the following subjects:

1. Gas Chromatography
2. Toxicology
3. Future Trends in Clinical Chemistry
4. Liquid Chromatography
5. Criteria for Method Selection in Pharmaceutical Analysis
6. Recent Advances in Analysis in the Steel Industry in Foreign Countries and in the U.S.A.
7. Coatings in Food and Beverage Can Industry
8. New Trends in Powder Diffractometry
9. Bicentennial Symposium
   (a) History of Chemistry in the U.S.A.
   (b) British Influence on U.S. Chemistry to be presented by British Scientists
10. Energy Dispersive Sources and Systems (ASTM E-2)
11. Awards by Coblentz Society, Society for Analytical Chemists of Pittsburgh, and Spectroscopy Society of Pittsburgh

General papers are *not* restricted to the symposia topics. It is expected that more than 400 submitted papers will cover many aspects of the general fields of Analytical Chemistry and Spectroscopy. Those wishing to present papers in the 1976 Conference Technical Programme should submit three copies of a 300-word abstract (on the special forms provided) to:

Dan P. Manka, Program Chairman 1976,
Jones & Laughlin Steel Corporation,
Graham Research Laboratory,
900 Agnew Road,
Pittsburgh, Pennsylvania 15230, U.S.A.

INTERAN '76

Prague, 23–27 August 1976

This conference will deal with analysis of ores and ore-dressing products, minerals, rocks, and radioactive materials, and with analytical problems in geochemistry, analysis of extraterrestrial materials, and standard samples. New potentialities of chemical and instrumental analysis on the micro and macro scales, new techniques for decomposition of minerals, problems of phase analysis, and statistical evaluation of results will be discussed. Automation will also be an important topic.

All correspondence should be addressed to:

Ing. N. Bajová,
House of Technology,
SVTS, 011 80 Žilina,
Czechoslovakia,

from whom further details may be obtained. Applications should arrive not later than 30 September 1975.

LOUIS GORDON MEMORIAL AWARD

The Editorial Board and Publishers of *Talanta* have great pleasure in announcing that the Louis Gordon Memorial Award for the best-written paper appearing in *Talanta* during 1974 has been awarded to A. L. Wilson, of the Water Research Association, for his paper "Performance characteristics of analytical methods—IV" (November issue, p. 1109).

Talanta, Vol 22, p ii Pergamon Press, 1975 Printed in Great Britain

PUBLICATIONS RECEIVED

Introduction to Organic Electrochemistry: M. R. RIFFI and F. H. COVITZ. Dekker, New York, 1974. Pp. viii + 417.

This is not a book on polarography or on electrode potentials, but on preparative organic chemistry involving electrolysis. The authors stress that though much of the basic information is far from new, it is only more recently that suitable equipment has become commercially available; further, most organic chemists are reluctant to consider electrochemical approaches. It is to these chemists that the book is primarily addressed. Basic principles, approaches and techniques are reviewed briefly, then two chapters deal in more detail with electro-reduction and oxidation of functional groups, and the last two cover electro-initiated polymerization and electro-coating. Those interested in coulometric analysis should find this book interesting and useful.

Modern Quantitative Analysis Experiments for Non-Chemistry Majors: GEORGE G. GUILBAULT. Dekker, New York, 1974. Pp. ix + 243.

I like the "one-book" approach used here—based on the assumption that unless the student has the theory in front of him while he does the experiment he is unlikely to bother looking for it afterwards. This does inevitably result in a book which presents a selection from the field rather than attempting to be comprehensive, but again, particularly for the non-specialist student, this is not a bad thing. The experiments in this book are aimed largely at medical students, but could also be used in courses in many biological sciences. Each experiment is dealt with under seven headings—Purpose, Theory, Apparatus, Reagents, Procedure, Calculations and Questions. The text is concise and clear, and suggestions for further reading are given.

The Chemistry of the Non-Metals: P. POWELL and P. TIMMS. Chapman & Hall, London, 1974. Pp. xii + 281.

The authors call this "a new attempt to interrelate the chemistry of the non-metals". The emphasis is on structure and bonding, and why compounds form (thermodynamics) rather than how they are prepared, although this aspect is not neglected. The authors have succeeded in producing a text which is readable and yet contains a considerable amount of detailed information and comment. The book is intended for advanced students in honours courses.

Volumetric determination of sulphate: C. J. COETZEE. (25 *June* 1975)

Application of ion-exchange separations in organic solvent media to the analysis of inorganic and organic materials—III. Simultaneous isolation and determination of uranium and thorium in natural waters: J. KORKISCH and H. KRIVANEC. (27 *June* 1975)

On the optimum conditions for the reduction of nitrate to nitrite by cadmium: FOLKE NYDAHL. (2 *July* 1975)

Spektralphotometrische Charakterisierung von ternären Komplexen in Lösung durch indirekte Analyse mit Hilfe linearer Transformationen: S. KOCH and G. ACKERMANN. (26 *May* 1975)

Quantitative NMR-spektroskopische Simultananalyse von Mehrkomponentengemischen unter Einsatz eines Rechners im on-line-Betrieb: WERNER STOREK. (9 *June* 1975)

Talanta, Vol. 22, p. iii Pergamon Press, 1975 Printed in Great Britain

PUBLICATIONS RECEIVED

Atomic Fluorescence Spectroscopy: V. SYCHRA, V. SVOBODA and I. RUBEŠKA. Van Nostrand Reinhold, London, 1975. Pp. 379. £12.00.

The authors have succeeded in producing a handbook which is comprehensive and at the same time sufficiently brief to be read and not merely consulted. A feature of the theoretical section is the inclusion of many diagrams based on computer calculations of fluorescence growth curves (*vs.* concentration) and line profiles (*vs.* wavelength) for a variety of source types and optical arrangements round the flame. The chapter on instrumentation has been kept brief in those sections dealing with factors common to other modes of flame spectroscopy, but gives particular attention to light sources and to complete instruments for fluorescence studies. Fluorescence characteristics of the elements (39 of them) are reported briefly for each in turn, and the final chapter covers some applications to biological, industrial, and geochemical applications. One of the more exiciting aspects of atomic-fluorescence spectroscopy is that it lends itself more than other flame techniques to simultaneous multi-element determinations, an aspect which is discussed in this book, and which will certainly make it of interest to many analytical chemists. The extensive bibliography covers references up to 1973.

Archeological Chemistry: CURT W. BECK (Ed.). Advances in Chemistry Series, No. 138. American Chemical Society, Washington, D.C., 1974. Pp. ix + 254. $22.50.

It is not often that one finds a chemistry book so fascinating and captivating that one wants to read it through from cover to cover at a sitting, but that is how I reacted to this book. Thirteen papers from a symposium held in Dallas in 1973 are gathered together here, and for most chemists that in itself is a service as accounts of this type of work are usually found not in chemical but in archeological journals. The reason for this becomes clear as one goes through the chapters—the analytical results are only a part of the story, becoming meaningful only when correlated with age, origin, or method of manufacture of the artifacts being studied. The whole book might be described as an essay in sampling. The controversial problem of surface analysis versus bulk analysis is discussed (particularly with reference to early silver articles) and the reliability of the analytical results themselves, on the basis of a round-robin on some bronze samples, comes under fire. There are chapters on lead isotope ratios, silver (3), bronze, ivory, pottery (3), glass, chinese ink, and NMR and Mössbauer spectroscopy. A final tip—read this before you take it home, as the family will all want to have a turn.

Talanta, Vol. 22, pp. iii–iv. Pergamon Press, 1975. Printed in Great Britain

PUBLICATIONS RECEIVED

Analytical Chemistry of Radium: V. M. VDOVENKO and YU. V. DUBASOV. Wiley, London, and Israel Program for Scientific Translations, Jerusalem, 1975. Pp. VIII + 198. £12.25.

This new addition to the Vernadsky Institute series on the analytical chemistry of the elements follows its predecessors in style. The literature coverage seems to stop at 1970; it is not difficult to update a book like this during translation and even during printing, and at the price the purchaser might well expect this to have been done.

Functional Group Determination of Olefinic and Acetylenic Unsaturation: K. MÜLLER. Academic Press, London, 1975. Pp. xii + 334. £9.20.

This is a very comprehensive and detailed monograph on the analysis of unsaturated compounds. There are three main divisions of the text dealing with olefins, conjugated diolefins and acetylenes. The coverage is restricted to chemical methods of detection and determination, but not all instrumental methods are excluded. Some spectrophotometric techniques are described and there are sections concerned with methods based upon the polarograph. However the analytical chemist will find most useful the extensive experimental details of chemical methods based on addition reactions. These include the addition of halogens, peracids and, more particularly, hydrogen. The separation of mixtures of unsaturated compounds, either directly or in the form of metal complexes, by techniques such as paper or thin-layer chromatography is discussed. References are given at the end of each chapter and an author index is provided. There is no accompanying subject index, although this deficiency is partly remedied by the inclusion of an unusually detailed list of contents.

Determination of Organic Compounds with *N*-Bromosuccinimide and Allied Reagents: N. K. MATHUR and C. K. NARANG. Academic Press, London, 1975. Pp. ix + 166. £5.20.

This is a compact monograph dealing with the synthesis and reactions of *N*-haloamides and imides, in particular the well-known reagent *N*-bromosuccinimide. The authors concentrate on the analytical possibilities of this reagent and in addition to a survey of its applications in the study of unsaturated compounds, there are sections which deal in detail with the determination of alcohols, phenols, aromatic amines, sulphonamides and other sulphur compounds. There is an additional chapter which is concerned with some examples of structure determination based on the specific allylic bromination reaction. References are grouped at the end of every chapter and an author and subject index is provided.

Advances in Chromatography, Vol. 11: J. C. GIDDINGS and R. A. KELLER (Eds.). Dekker, New York, 1974. Pp. xi + 196. $19.75.

This volume follows the format of earlier ones. The subjects reviewed are quantitative analysis by gas chromatography (J. Novák), polyamide layer chromatography (K.-T. Wang, Y.-J. Wang and I. S. Y. Wang) specifically absorbing silica gels (H. Bartels and B. Prijs) and non-destructive detection methods in paper and TLC (G. C. Barrett). The references cover approximately two decades ending in 1972. Novák's review is a discussion of the theoretical basis of quantitative interpretation of GC peaks and their dependence on the nature of the detector. That by Bartels and Prijs is a speculative review of an underdeveloped area. The other two reviews have a practical bias. Thus the volume is nicely balanced and a good addition to the series.

Talanta, Vol. 22, p. iii. Pergamon Press, 1975. Printed in Great Britain

PUBLICATIONS RECEIVED

Analysis of Water: J. RODIER. Halstead Press, 1975. Pp. xvii + 926. $82.50.

It is probably worthwhile and certainly interesting to compare this volume with two other handbooks on water analysis—*Analysis of Raw, Potable and Waste Waters* (HMSO, 1972) and *Standard Methods for the Examination of Water and Waste Waters*, 13th edition (AWWA, 1971). Wilson's monograph on The Chemical Analysis of Water (1974) is a commentary on the problems and practice of water analysis and is not comparable with but rather complementary to these other books.

The HMSO handbook (304 pp.) covers only chemical analysis, and recommends well-tried methods based on mainly titrimetry and photometry, which even the smallest laboratory should be in a position to carry out. The AWWA handbook (874 pp.) includes more instrumental methods, but deals separately with polluted waters and with relatively clean waters. It also has sections on radioactivity, bacteriological and biological examination of waters.

This new book, written, like the others, by a team of experts, is a translation of the latest edition of a widely-used French handbook. It follows the approach used by the AWWA of dealing first with natural waters (about half the book) then with waste waters (called residual waters, 100 pp.) and sea water (40 pp.). Bacteriological and biological examinations are then covered (100 pp.) followed by a section on the interpretation of the results, discussing why elements or chemical compounds are desirable or harmful and what levels they should not exceed. Finally there are some 140 pp. of appendices covering just about everything from an etymological table of the elements to procedures for purification of a well.

The authors claim that a special feature is the addition of notes to each method, pointing out snags and difficulties which may be encountered. But in fact the other two handbooks also do this, only with a different layout. The quality of the translation is on the whole good, but occasionally the standard drops. The reader will guess what a semi-plateau potential in polarography is, but I wonder if anyone knows what blanose is? And again, to omit the word "atomic" in the heading to a section on AAS is a little misleading. But one should rather concentrate on the many good features of this book—the wide range of proven methods, well documented, and the filling-in details which make it not only useful and practical, but also readable.

Handbook of Moisture Determination and Control, Vol. 3: A. PANDE. Dekker, New York, 1975. Pp. xi + 289. $33.50.

This is the third of a set of four volumes (see *Talanta*, 1975, **22**, No. 4/5, iii) leaving the reader to acquire the last to get the index. Chapters are devoted to Moisture in Textiles; Bagasse, Wood and Paper; Foods and Allied Agricultural Products; and Soils, Sands, Concrete and Silicates. As the first two volumes contain descriptions of the methodology, this part discusses the significance of moisture content in the various materials, how they may be dried, and what moisture levels should be aimed at. Instruments designed particularly for specific applications (*e.g.*, to test whether plaster is dry enough for painting or coffee beans dry enough not to lose colour on storage) are described where appropriate. There is much interesting information here which an analyst confronted with problems of moisture determination would need to know and not find in most analytical handbooks. Many references are given, but very few of these are from the last 15 years. It would be surprising if this were a balanced picture of the present state of knowledge in the field.

Atomic Absorption Spectrophotometry: M. PINTA (ed.). Hilger, London, 1975. Pp. xxii + 418. £35.00.

This is an English translation of *Spectrométrie d'Absorption Atomique* published in 1971. Little of the excellence of the French original has been lost in the translation. Since practical application of AAS is always uppermost in the treatment, most of the multitude of analytical methods described are well-tried, no attempt being made to include the newer flameless techniques. Theory and practicalities are particularly well harmonized, especially in the earlier chapters, which give a good theoretical background to the choice of instrument and technique. Later chapters are devoted successively to rocks and soils, ores, water, vegetable matter, biochemistry and toxicology, petroleum products, metals and alloys, nuclear energy, civil engineering, indirect methods and sundry applications. These chapters contain an abundance of practical detail gathered both from the laboratories of the many contributors and from the literature. Typographical mistakes are unfortunately not uncommon, but are easily recognized and are not serious. The awkward punctuation and heavy abbreviation in the description of methods is irksome, and is occasionally the cause of ambiguity. However, these minor faults do not significantly detract from this encyclopaedic work, which is of immense value to practising analysts.

Colloque International sur l'Analyse par Activation de très Faibles Quantités d'Eléments: Akadémiai Kiadó, Budapest, 1975. Pp. viii + 686. £36.10.

This weighty tome contains the papers presented at the eponymous colloquium held at C.E.N. Saclay in October 1972, and is reprinted from *J. Radioanal. Chem.*, apparently constituting Vols. 17, 18 and 19 of that journal.

Radiochemical Separation Methods (Proceedings of the 7th Radiochemical Conference, Mariánske Lázně, April 1973): T. BRAUN and E. BUJDOSÓ, eds. Elsevier, Amsterdam, 1975. Pp. 478. $64.75.

This is another reprint from *J. Radioanal. Chem.*, this time from Vol. 21. Page for page it seems to be a bit dearer than the Hungarian reprint reviewed above.

Talanta, Vol 22, p iii Pergamon Press, 1975 Printed in Great Britain

NOTICES

THE CECIL L. WILSON PRIZE

Cecil Wilson, Professor of Analytical Chemistry in the University of Belfast, died in March 1974. He graduated from Queen's with an M.Sc. in 1933 and was a member of staff from 1946 until his death. He was Professor of Analytical Chemistry from 1958. His colleagues wish to commemorate him by establishing the "Cecil Wilson Prize" to be awarded to the best first-year chemistry student each year on the basis of the June examination. This seems particularly appropriate as Cecil Wilson lectured largely to first-year classes and was always very concerned with the progress of undergraduates.

Analytical chemists throughout the world are cordially invited to contribute to the capital fund, interest from which will be used to provide the prize described above. Donations, in any currency, should be made payable to "Queen's University of Belfast" and crossed, "Cecil Wilson Prize, account No. C501CC". They may be sent to either: Dr. G. Svehla or Dr. M. A. Leonard, Department of Chemistry, Queen's University, Belfast, Northern Ireland.

22nd SPECTROSCOPY SYMPOSIUM OF CANADA

The 22nd Spectroscopy Symposium of Canada, sponsored by the Spectroscopy Society of Canada in collaboration with the Analytical Section of the Chemical Institute of Canada and the Canadian Probe Users Group, will be held in Montreal, Quebec, Canada, 27–29 October 1975, at the Sheraton-Mount Royal Hotel. Papers are solicited for approximately twelve sessions on all phases of spectroscopy. Information can be obtained from: Mr. P. J. Skerry, Symposium Chairman, Northern Electric Co. Ltd. Dept. K311, P.O. Box 6124, Montreal, Quebec, Canada H3C 3J4:

Or

Miss C. Ratzkowski, Program Chairlady, Hoffmann-LaRoche Control Laboratory, 1000 Roche Blvd., Vaudreuil, Quebec, Canada.

FIRST EUROPEAN SYMPOSIUM ON THERMAL ANALYSIS

This Symposium, organized by the Thermal Methods Group of the Analytical Division of the Chemical Society, will be held at the University of Salford, England, on 20–24 September 1976. The deadline for submission of contributions is 31 December 1975. Further information can be obtained from: Dr. D Dollimore, Reader in Physical Chemistry, University of Salford, Salford M5 4WT, England.

Talanta, Vol. 22, p iu Pergamon Press, 1975 Printed in Great Britain.

PUBLICATIONS RECEIVED

Chemical Manipulation : MICHAEL FARADAY, Halsted Press, New York, 1974. Pp. viii + 656. $35.00.

This latest addition to the Royal Institution Library of Science series is a facsimile of the copy of "Chemical Manipulation" presented to the Royal Institution by the author, and bearing his holograph corrections. It is full of practical information, written in a clear and elegant style. The Foreword to the book has a curious sentence that suggests that use of the cheeks as bellows may be helpful in transferring a spark from a Leyden Jar to a eudiometer, a feat which might be thought only possible for a certain young man of Madras. One would like to suggest that this book should be required reading for all first-year chemistry students, in the hope of (*a*) giving them a proper appreciation of the giants of the past (and indeed of all time), (b) teaching them how to write, and (*c*) teaching them some *useful* chemistry and technique.

Elektronnye spektry i struktura organicheskikh reagentov (Electronic spectra and structures of organic reagents): S. B. SAVVIN and E. P. KUZIN, Nauka, Moscow, 1974. Pp. 277 (in Russian). 1 Rb. 29 K.

This book contains details of the spectra, properties and applications of many analytically important organic reagents, together with an LCAO-MO treatment and discussion of the spectra and structure of the reagents.

The infrared spectra of minerals: ed. V. C. FARMER, Mineralogical Society, London, 1974. Pp. 539. £16:00 ($U.S. 38.00).

This volume contains 21 chapters contributed by 13 authors. They describe the origin of infrared and Raman spectra in crystalline solids and glasses. The title is somewhat misleading; the spectroscopic properties of many important synthetic products—cements, ceramics and glasses—are also described, although the coverage is not always up to the extremely high standards set by the other chapters. Lack of a good formula index may handicap efforts to find references to a specific compound. Nevertheless, it is rare to find an edited volume designed to appeal to the specialist which will also be so helpful and comprehensible to the practising chemist. This will undoubtedly remain the standard work on the subject and deserves a place on the shelf of every analyst who applies infrared spectroscopy to industrial inorganic and mineral products.

Talanta, Vol 22, pp iii–iv. Pergamon Press, 1975 Printed in Great Britain

NOTICES

AMERICAN VACUUM SOCIETY
SHORT COURSES IN VACUUM SCIENCE AND TECHNOLOGY

A four-day basic course and nine one-day specialized courses will be offered in conjunction with the *22nd NATIONAL SYMPOSIUM OF THE AMERICAN VACUUM SOCIETY*, which will be held at the Philadelphia Civic Center, Philadelphia, Pennsylvania, on 28–31 October 1975. These courses are intended for anyone working with or interested in vacuum science and technology, including laboratory technicians, production equipment operators, maintenance personnel and students. All courses will be taught by well qualified, experienced instructors.

The basic course, "*VACUUM TECHNOLOGY*", will cover vacuum technology from fundamental theory state-of-the-art concepts into 25 hours of classroom instruction.

The one-day specialized courses will start from basics and cover theory, equipment, and applications. The one-day courses to be offered are:

"Sputtering Technology"
"Partial Pressure Analysis"
"Leak Detection"
"Microcircuit Thin Films"
"Surface Analysis"
"Evaporation Methods"
"Freeze Drying"
"Optical Coating Technology"
"Vacuum Microbalance Techniques"

Course outlines and application forms can be obtained from Nancy Hammond, American Vacuum Society, 335 East 45th Street, New York, New York 10017.

WORLD CONFERENCE ON OILSEED AND VEGETABLE OIL PROCESSING TECHNOLOGY, 1976

The American Oil Chemists' Society is organizing a World Conference on Oilseed and Vegetable Oil Processing Technology to be held 1–5 March 1976, in Amsterdam.

The programme committee is currently considering specific topics and speakers for a broad-interest, five-day programme which will include exhibits, small group interaction with speakers, and social events. The program is being designed primarily for managers and operating personnel and will take on the educational nature of a broad-based short course.

Inquiries about the programme, exhibits, and special travel arrangements may be directed to James Lyon, Executive Director, American Oil Chemists' Society, 508 South Sixth Street, Champaign, Illinois 61820.

INTERNATIONAL ASSOCIATION ON WATER POLLUTION RESEARCH
8TH CONFERENCE
SYDNEY, AUSTRALIA
17–22 OCTOBER 1976

Technical sessions will provide for the presentation and discussion of selected papers on original research and development on a wide variety of topics related to marine and freshwater pollution and wastewater treatment. Instantaneous translation services—English, French and German—will be available.

Workshop sessions will review progress and discuss current problems on the following subjects—

Water resource quality management
Marine and estuarine waste disposal aspects
Ultimate disposal of solid and liquid wastes
Land surface and sub-surface disposal of wastewater

Technical visits will be conducted on an afternoon free of sessions, to wastewater treatment plants and other places of technical interest.

Further information from the Conference Secretariat: G.P.O. Box 2609, Sydney, 2001, N.S.W., Australia.

INTERNATIONAL SOLVENT EXTRACTION CONFERENCE 1977

TORONTO, ONTARIO, CANADA
10–17 SEPTEMBER 1977

The conference will bring together people from industry, government and universities with a common interest in solvent extraction. The main theme of the conference will be metallurgical applications of solvent extraction, but applications to other areas such as petrochemical and pharmaceutical industry will also be discussed. In addition, new developments in extraction equipment and solvents and new insights into the physical and chemical mechanisms of extraction will be presented.

It is proposed that about 80 papers will be presented at the Conference during five working days. There will be six plenary sessions at which papers of broad interest will be given; more specialized papers will be presented at twelve sessions which will be arranged in parallel, with three sessions simultaneously in progress.

Submissions of detailed Abstracts (200 to 300 words) are invited before **April 1st, 1976** and of complete papers before **September 1st, 1976.** They should consist of original, unpublished research results or critical reviews which fall within the scope of ISEC 77 (see above). The papers will all be subject to review by the Session Chairman and outside reviewers. Papers will be distributed to pre-registered delegates about four weeks prior to the conference.

Discussion of papers at the conference is held to be an important contribution, and it will be recorded and included in the final printed Proceedings which will appear early in 1978.

The careful reviewing and selection of papers require considerable time, so intending authors are urged to plan accurately for the deadline of **September 1st, 1976.** The Committee reserve the right not to accept papers submitted after that date.

Further information from Dr. M. H. I. Baird, Secretary, ISEC 77, Dept. of Chemical Engineering, McMaster University, Hamilton, Ontario, L8S 4L7, Canada.

Talanta, Vol. 22, pp. iii–iv. Pergamon Press, 1975. Printed in Great Britain.

PUBLICATIONS RECEIVED

Applied Spectroscopy Reviews, Vol. 8, Part A: EDWARD G. BRAME, JR., ed. Dekker, New York, 1974. Pp. vii + 147 + I–15.

This consists of a single wide-ranging monograph upon the spectroscopic methods of identification of microquantities of organic materials. In addition to the familiar techniques of mass spectrometry, ultraviolet and infrared spectrometry, nuclear magnetic resonance and optical rotatory dispersion, there are sections dealing with circular dichroism, the several varieties of electron spectroscopy, and techniques associated with ionization in the gas phase.

Applied Spectroscopy Reviews, Vol. 8, Part B: EDWARD G. BRAME, JR., ed. Dekker, New York, 1974. Pp. xiv + 144. $29.50.

This book contains three separate and diverse surveys of spectroscopic interest. The first is concerned with the structure of water as revealed by vibrational spectroscopy, the second with solvent effects on electronic spectroscopy and the third with the study of ionic crystals by infrared and Raman spectroscopy.

The Chemical Analysis of Water: A. L. WILSON, Society for Analytical Chemistry, London, 1974. Pp. viii + 188. £7.50.

This comprehensive and up-to-date guide to the analysis of water is a typical example of the clarity of thought and the systematic approach characteristic of its author. It could also well serve as a student text, for illustration of the instrumental approach to analysis, and the essential practicality of analytical chemistry in application of theory.

The Spectroscopy of Flames (2nd Ed.): A. G. GAYDON. Halsted Press, New York, 1974. Pp. xii + 412. $24.50.

Although the second edition has a similar layout to the first edition, the contents have been extensively revised and updated throughout. Several new figures and tables have been included, and some less important figures excluded. Several new or extended sections have been incorporated to cover developing topics such as the use of fluorescence and laser Raman techniques, isotopic shift studies, spectral line profiles, excitation of metal spectra in H_2–O_2–N_2 flames, organic diffusion flames, formation of nitrogen oxides, ozone decomposition flames and the mechanism of S_2 excitation. The chapters on carbon monoxide flames and analytical flame spectrophotometry have been substantially extended. In the latter chapter in particular, the author's very extensive experience stands him in good stead for making useful and relevant comments on the current "state of the art" without resorting to a detailed review. The appendix on molecular spectra has also been usefully extended. This volume provides a valuable source of background information to those concerned with analytical flame spectrometry.

Principles of Chemistry: LOREN G. HEPLER and WAYNE L. SMITH. Macmillan, New York, 1975. Pp. xiii + 609. $13.95.

This is a well-written account of the basic ideas of chemistry, with a wealth of problems intended to give the student insight. As is inevitable with a book of this type, the section on organic chemistry is highly selective and the main emphasis is on theoretical, physical, and inorganic chemistry; analytical chemistry. Analytical chemistry appears to be a non-starter.

Neutron Activation Analysis Tables: J. C. LECLERC, A. CORNU and A. GINIER-GILLET, Heyden, London, 1974. Pp. 64. £5.00, $14.00.

This is a very useful compilation for the analyst who employs neutron-activation analysis. It gives the basic radiochemical data about naturally-occurring isotopes and radionuclides, classifying the latter both in order of atomic number and by increasing energy. Finally the saturation sensitivity, practical sensitivity for longer lived nuclides and the potential interferences are tabulated. Various value judgements are necessarily made in this set of data, but they are clearly stated and reasonable. Most analysts will find the classifications used are most useful and up to date. The text is in both English and French.

Creation and Detection of the Excited State, Vol. 3: W. R. WARE (Ed.), Dekker, New York, 1974. Pp. VIII + 193. $23.50.

This volume consists of three articles on chemiluminescence in the condensed phase, single vibronic level fluorescence and photocurrents in fluids. The first of these by C. A. Heller and H. P. Richter which discusses the practical problems of making quantitative CL measurements is likely to be the one of most interest to analytical chemists.

Synthetic Reagents, Vol. 1 and 2: J. S. PIZEY, Horwood, Chichester, 1974. Pp. 411 and 353. £13.00 and £12.50.

The author's aim in this new series is to "bridge the gap between the compact encyclopaedic coverage in Fieser and Fieser's 'Reagents for Organic Synthesis' and review articles, which do not give synthetic details". Each volume of the series will feature a reductant, an oxidant, halogenating material, a solvent and/or some other important reagent. Thus in the first two volumes, dimethylformamide, lithium aluminium hydride, mercuric oxide, thionyl chloride (all in Vol. 1), *N*-bromosuccinimide, diazomethane, manganese dioxide and Raney nickel (in Vol. 2) are dealt with in considerable detail. All aspects of the uses of these reagents and solvents are well covered with numerous references, *e.g.*, over 1000

references are cited for $LiAlH_4$. The latest reference is for 1971, but there are only a few references to 1970 and 1971 papers. Each volume contains its own index, which lists compounds, reactions and techniques; there is no author index. There is no doubting the effort which the author has put into these volumes, which appear as very thorough and competent works. If the whole series maintains the standards of the first two volumes, it will be a valuable addition to libraries, even though, to the mind of the reviewer, it is only of limited value in helping to establish (quickly) the best reagent and conditions for a particular synthetic step, such as a reduction. To work through all reductants to be included in the whole series would be a laborious and time-consuming exercise. Lastly, but of importance, the cost does not appear to be too prohibitive.

Talanta, Vol 22, pp iii–iv Pergamon Press, 1975 Printed in Great Britain

PUBLICATIONS RECEIVED

Handbook of Process Stream Analysis: K. J. CLEVETT, Ellis Horwood, Chichester, 1975. Pp. xviii + 470. £15.00.

This is an impressively thorough and detailed survey of a wide field of analytical chemistry not well served by most text-books and monographs. The author groups the types of machines according to the analytical principle involved, and commences each chapter with a brief account of the theory and the normal laboratory practice of the technique The bulk of the text is, however, concerned with the many and varied forms in which the techniques have been automated for continuous use in on-line analysis. There are chapters on: Vapour-phase chromatography, Viscosity, Distillation, Flash-point, Pour- and Cloud-point, Vapour pressure, Oxygen measurement, pH and Redox measurement, Trace gas analysis, UV, visible, and IR absorption, Moisture, Density, Water quality, Gaseous fuel quality, Octane number, various other methods, and Sample-handling systems. The book is well illustrated with many line drawings of instruments, and with numbers of photographs, though these are on the whole less informative than the drawings. The assistance of many manufacturers in providing technical information has certainly helped the author to produce what must surely prove a very valuable handbook for anyone concerned with analysis and plant-control.

Handbook of Moisture Determination and Control, Vol. 1: A. PANDE, Dekker, New York, 1974. Pp. xi + 266.

This is very much a working handbook, with sufficient detail to enable the reader to follow procedures without further reference to the literature, and with plenty of comment and criticism stemming from the author's experience in the field. Results of comparative tests on different methods, and the statistical analysis of the results, are also helpful. This volume contains chapters on: Water, its properties and interaction with hygroscopic materials, Gravimetric methods, Distillation and chromatographic techniques, and the Karl Fischer titration. Volume 2 will also deal with techniques, and volumes 3 and 4 with applications.

Chemical Analysis of Organometallic Compounds, Volumes 2 and 3: T. R. CROMPTON, Academic Press, London, 1974. Pp. ix + 163 and x + 211.

These two volumes continue what now looks like becoming an encyclopaedia on the analysis of organometallic compounds. Volume 2 covers the elements titanium (2 pages), zirconium (½ page) and silicon (137 pages), and mentions that no methods exist for compounds of hafnium and thorium. Volume 3 covers the elements germanium (12 pages), tin (85 pages) and lead (91 pages). As in volume 1, methods are given for determination of elements, functional groups, and the compounds themselves, with particular emphasis on gas chromatographic and other instrumental techniques. Again, the procedures are described in detail, so that the methods can be used without recourse to the original literature, and the books will therefore be particularly useful as laboratory "recipe books". The literature is covered only up to 1970.

Annual Reports on Analytical Atomic Spectroscopy, Vol. 3, 1973: C. WOODWARD, The Society for Analytical Chemistry, London, 1974. Pp. x + 324. £6.00.

In this excellent small volume the literature for 1973 is reviewed in depth and detail. Part I deals with "Fundamentals and Instrumentation" and includes useful Tables of up-to-date information on commercial atomic absorption and fluorescence equipment as well as emission spectrometers. Part II, "Methodology" reviews the analytical applications. Tables of references arranged by element give concise but extensive details of the techniques used. In both parts an authoritative textual commentary provides an overall impression of current trends and developments otherwise obtainable only by assiduous attendance at international conferences. The text is somewhat interrupted by the interpolation of multi-page tables which could with advantage be collected at the end of the text. Errors are few and although it falls a little short of comprehensive it is still, with its bibliography of 1698 references, the most effective available source-book for analytical spectroscopist. We look forward to Vol. 4.

Advances in Chromatography, Vol. 10: J. GIDDINGS and R. A. KELLER, Dekker, New York, 1974, Pp. xi & 246. $19.75.

Three articles are contained in this volume. The one by L. S. Ettre and J. E. Purcell on Porous layer open tubular columns is critical, readable and of general interest to analytical chemists. The theory and development of these columns and especially Golay's views show how theory can lead to improved practical application. The other articles on the resolution of optical isomers by GLC (E. Gil-Av and D. Nurok) and GLC of terpenes (E. von Rudloff) are more specialized.

Gradient Liquid Chromatography: C. LITEANU and S. GOCAN, Horwood, Chichester, and Wiley, London, 1975. Pp. xii and 338. £10.50.

This is a badly organized book on an interesting subject. A lot of practical information is buried in lots of theory–there are about 430 equations. Unfortunately the theory is not well related to the practical side, and there is no attempt to make any classification on the basis of types of compounds or areas of application. This is regrettable because the authors have packed in a tremendous amount of information and learning, which the diligent reader will find of value.

Ion Exchange and Solvent Extraction, Vol. 6: J. A. MARINSKY and Y. MARCUS, Dekker, New York, 1974. Pp. xii and 301. $27.50.

This volume is very similar in format and editorial viewpoint to its predecessors. It contains good and interesting articles on the solvent extraction of drugs (G. Schill) and rare earths and tervalent actinides (B. Weaver) the dynamics of liquid–liquid extraction processes (G. G. Pollock and A. E. Johnson) and the application of the solubility concept to extraction (H. M. N. H. Irving). The authors still seem to be penalized by publishing delays; most of the work reported was published before 1970.

Chemical Phase Analysis: ROLAND S. YOUNG, Halsted Press, New York, 1974. Pp. vii + 138. $11.50.

The title of this interesting and useful little book does not really give much indication of the contents. What the book is about is the use of chemical methods for determination of the different species (metals, oxides, chemical compounds, minerals *etc.*) present in raw materials and manufactured chemical products. A variety of chemical treatments is therefore involved, based on selective dissolution or selective volatilization, the selectivity being conferred by choice of reagents and conditions. In some respects the work is complementary to the books on decomposition procedures, but in others goes beyond them in that a selection and/or combination of procedures must be made. To those who wish to put the chemistry back into analysis, this book is strongly recommended.

The Chemistry of Diacetylenes: M. F. SHOSTAKOVSKII and A. V. BOGDANOVA, Halsted Press, New York, 1974. Pp. xvii + 493. $45.00.

This compilation of material on the chemistry of the diacetylenes is a translation from the Russian and reads like one. The original text covered the literature up to 1971, and it is a pity that it was not updated during the translation period. However, for workers in this field it will serve well as a comprehensive guide.

Talanta, Vol. 22, pp. 1–15. Pergamon Press, 1975. Printed in Great Britain.

TALANTA REVIEW*

PLASMA EMISSION SOURCES IN ANALYTICAL SPECTROSCOPY—I

S. GREENFIELD, H. McD. McGEACHIN and P. B. SMITH

Albright and Wilson Ltd., P.O. Box No. 80, Oldbury, Warley, West Midlands, B69 4LN, U.K.

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Summary—A critical survey of plasma emission sources used in analytical spectroscopy, excluding conventional arc and spark sources, has been made. In Part I the concept of temperature applied to high-temperature excitation sources is considered, as are arc plasma jets. Part II will be concerned with microwave and capacitively coupled sources and in Part III inductively coupled sources will be dealt with. In the last part a comparison will also be made of all the sources reviewed, from the point of view of sensitivity, precision and freedom from matrix effects.

The analyst using emission spectroscopy for elemental analysis looks for the following desirable properties in an excitation source.

1. Capability of exciting lines of a large number of elements.
2. High sensitivity.
3. Good stability.
4. Freedom from interferences. These include spectroscopic interference, where the line of interest cannot be easily resolved from a line from another element or from a band of a molecular spectrum; chemical interference, where the presence of another element depresses the intensity of a line by reduction in the population of free atoms, owing to the formation of molecules or radicals, or where the presence of another element (usually of low ionization potential) makes a dramatic change in the electron density in the source, thereby shifting the ionization equilibrium; and contamination from the construction materials of the source.
5. Reproducibility in the introduction of samples.
6. Convenience of operation.

These desiderata are not necessarily compatible. For example, a source which can excite lines from an element for which the lowest excited energy level is high, is likely to excite many levels in elements where this energy is low and this may result in problems of spectroscopic interference. Similarly, freedom from contamination may demand some inconvenience in operation.

The temperature of the gas in flame sources is limited by the heat of combustion of the fuel. Electric discharges have no such fundamental limitation and the belief that excitation capability, sensitivity, and freedom from chemical interference increase with temperature has led to the development of plasma sources. A plasma is a gas ionized to a degree sufficient to have a significant effect on its properties. The important property of a plasma for

* For reprints of this Review, see Publisher's announcement near the end of this issue.

present purposes is that large quantities of electrical energy can be transferred to it if it is sufficiently ionized: this supply of energy can heat it to very high temperatures.

The effects of high temperatures on gases are dissociation if the gas is not monatomic, followed by a series of ionizations. For nitrogen[1] for example, at low temperatures N_2 dominates; at about 6700 K the abundances of N_2 and N are equal; the abundances of N and N^+ are equal at about 14,500 K and those of N^+ and N^{2+} are equal at about 29,000 K. At 10,000 K the relative abundances are N_2, 0·4%; N, 94·2%; N^+, 2·7% and electrons 2·7%. If we wish to break up molecules, with the double benefit of suppressing band spectra and reducing matrix effects, a temperature of over 10,000 K is desirable. However, the high electron density associated with such high temperatures results in a very high emission of continuum radiation; this is discussed in the next section.

A suitable scheme for a spectroscopic source would thus be to pass the sample through a very hot region to ensure complete dissociation into atoms and then to use the emission from a cooler position downstream where the continuum is less. Such a reduction in temperature may also allow the sample atoms to form molecules, but since dissociation energies are usually less than ionization energies and since the sample is greatly diluted by the plasma gas, a position in the tail flame may be found where there is no significant molecular association and where the continuum is weak.

Temperatures of 10,000 K and upwards are not obtainable with conventional arc and spark sources. It has long been known that radial constriction of an arc can increase its temperature and improve its stability. This has led to the development of wall-stabilized arcs. These have been excluded from this survey, which is concerned with the type of system mentioned above, in which a flame-like discharge, emerging from the hottest zone where the electrical energy is absorbed, is used as the spectroscopic source We think it may be helpful, however, before discussing the various sources, to give a simple account of what, if anything, is meant by temperature. A summary is given at the end for the benefit of those disinclined to read this section.

SPECTRA, TEMPERATURE AND EQUILIBRIUM

The electrons in an atom are distributed in discrete energy levels, which can be specified by four quantum numbers, which can themselves be defined in various ways. Here we shall use the principal quantum number n, the orbital quantum number l, the inner quantum number j and the magnetic quantum number m. In terms of Bohr's original quantum theory of the hydrogen atom, still useful for pictorial purposes, n defines the radius of the orbit occupied by the electron, and l its eccentricity. The excess of potential energy of an electron in the nth circular orbit over that of an electron in the ground state, for which $n = 1$, is given by $E = K(1 - 1/n^2)$ where K is a constant. If $n = \infty$, the radius of the orbit becomes infinite. This corresponds to ionization of the atom, and the ionization energy is given by K. Any positive integral value can be assumed by n and so there is an infinite number of energy levels, each with finite energy; the levels are very close together for large values of n.

In a proper quantum mechanical treatment, the energy of a level depends on n, l, j and m. Discrete values of l express the quantization of orbital angular momentum much as before; discrete values of j $(= l \pm \frac{1}{2})$ express in addition the quantization of the resultant of the orbital angular momentum and that due to the spin of the electron; and discrete values of m express the quantization of the orientations which the orbit can assume with respect to an external field. If the atom is in a magnetic or electric field, each permissible

quartet of quantum numbers corresponds to a different energy; levels which differ only in m are very close together. If there is no external field, the energy is independent of m. There are $2j + 1$ possible values which m can take, so that in the absence of an external field, $2j + 1$ levels have the same energy. It is often convenient to describe this as a single degenerate level; the number of levels $2j + 1$ into which it can split is known as the statistical weight g of the level. Since m is different for each of the members of the degenerate level, each can be occupied by an electron without violating the Exclusion Principle, which states that no two electrons in an atom may have identical sets of quantum numbers.

An atom emits radiation of frequency ν when an electron falls from an energy level E_i to an energy level E_j. The frequency is given by $\nu = (E_i - E_j)/h$ where h is Planck's constant. The transition probability A_{ij} for the transition $i \rightarrow j$ is defined as the fraction of the population of the level i which undergoes the transition to the level j in unit time; it depends both on how long an electron remains in the upper level i and on how well the jth level competes with other possible lower levels.

The intensity of the line of frequency ν, defined as the energy emitted per unit time at this frequency, is therefore $I = A_{ij}\, h\nu N_i$ where N_i is the number of atoms in the ith level. Thus, for a given spectroscopic line, I is proportional to N_i. The analyst engaged in elemental analysis will usually construct a calibration curve of measured intensities for known concentrations and then deduce the concentration in an unknown sample from its measured intensity. The slope of the calibration curve will depend on how N_i depends on N, the total number of atoms of the species present, as well as on the frequency and transition probability. Ratios of the intensities to those of an internal standard are often used to compensate for instabilities in the source.

The fraction N_i/N depends, in general, on source conditions in a very complicated and not easily predictable way. If the source is in thermodynamic equilibrium, however, the position is much simpler.

Thermodynamic equilibrium is a state where the principle of detailed balancing applies strictly, so that every process of energy transfer is perfectly balanced by the reverse process. This applies to all forms of energy (kinetic and potential) and all forms of energy transfer. Thermodynamic equilibrium is an idealized state which cannot be observed, for the process of observing it implies an uncompensated loss of radiation from the system. However, it is found that in certain circumstances, some laws which have been deduced for systems in thermodynamic equilibrium can be successfully applied to systems which are not. Systems where the energy distribution of particles is subject to these laws, but where the radiation is not, are said to be in local thermodynamic equilibrium (LTE). This condition is most readily achieved when the dominating mode of energy transfer is by collision between particles rather than by absorption or emission of radiation. It can be deduced from Maxwell's equations of electromagnetism that radiation exerts a pressure p on a surface and that $p = \mu/3$ where μ is the energy of the radiation per unit volume (this is not quite analogous to particle pressure, which is predicted by the kinetic theory of gases to be $2\mu/3$ where μ is now the kinetic energy per unit volume). If the system is in complete thermodynamic equilibrium, the radiation energy density is given by Stefan's law $\mu = 7{\cdot}6T^4 \times 10^{-15}$ erg/cm^3. Some idea of the relative importance of the collisional and radiative modes can be obtained by comparing the radiation pressure with the pressure due to the particles. Consider a plasma where the particle pressure is 1 atmosphere: its radiation pressure if it is in equilibrium at 10,000 K is $2{\cdot}5 \times 10^{-5}$ atmosphere and it can be taken as collision-dominated, whereas at 1,000,000 K the radiation pressure is 2500 atmospheres and it is

radiation-dominated. Small laboratory-plasmas at or near atmospheric pressure are likely to be collision-dominated.

In a system in LTE, as in complete thermodynamic equilibrium, the ratio of the particle populations in energy levels i and j is given by Boltzmann's law:

$$\frac{N_i}{N_j} = \frac{g_i}{g_j} \exp\left[- \frac{(E_i - E_j)}{kT} \right]$$

where g_i and g_j are the statistical weights of the ith and jth levels, of energies E_i and E_j, and T is the absolute temperature; this serves as a definition of temperature. Specifically, in LTE, one value of T, when substituted in Boltzmann's equation, will determine the ratios N_i/N_j for all values of i and j, and the distribution of kinetic energies of atoms, ions and electrons will be given by using the same value of T in Maxwell's equation for the distribution of kinetic energies. This value of T is called the temperature.

Usually we are interested less in the ratio of the populations of two levels than in the fraction of the total population in the ith level, N_i/N. This is given by

$$\frac{N_i}{N} = \frac{1}{Z(T)} g_i \exp\left[- \frac{E_i}{kT} \right]$$

where $Z(T) = \sum_j g_j \exp[-E_j/kT]$, the electronic partition function; this sum is over all possible states and increases with temperature. Since there is an infinite number of levels with finite energies before the ionization limit is reached, Z might be expected to be infinite. However, the effect of the electric field due to neighbouring particles is to reduce the ionization limit so that the number of energy levels is reduced to a finite number. For cool sources (2000–3000 K), the ground-state often dominates the partition function, which can then be taken as the statistical weight of the ground-state, but for higher temperatures its calculation becomes more complicated, involving a choice of assumptions and approximations and in addition a fairly complete knowledge of the atomic energy levels.[2] The reliability of the calculations deteriorates at high temperatures.

If a plasma is in LTE, the relative populations of the various excited states are given in Boltzmann's equation with a constant value of T which is the temperature of the plasma. Theory predicts and experiment confirms[3] that the most likely deviation from LTE is a relative overpopulation of the ground-state. This is known as partial LTE; the higher the levels involved, the more likely is Boltzmann's law to give the ratio of their populations. It can also happen that different particle species may follow Boltzmann's law, each with its own value of T. Thus we may have electron temperature, governing the distribution of the kinetic energy of the electrons; gas (or kinetic) temperature, governing the distribution of the kinetic energies of the atoms; excitation temperature, governing the populations of the atoms in different states of excitation, and so on. Unless the system is in LTE, these temperatures will be different. If deviations from LTE are large, relative populations depend on the individual cross-sections for excitation to the levels involved and the concept of temperature may lose its meaning.

These concepts are of fundamental importance in the investigation of plasmas by spectroscopy, but what mainly concerns us here is the use of a plasma source to excite atoms in a sample introduced usually with the object of estimating their relative abundances. The

first requirement is to produce sufficient excitation to the chosen level to give a spectroscopic line with adequate intensity. This can be done with a source in LTE with a suitably high temperature, or with a source not in LTE in which an excitation temperature exists and is suitably high, or with a source so far from LTE that the concept of temperature is inapplicable, if the cross-section for collisional excitation of the chosen level is sufficiently large. The chance of success with the first choice is predictable, with the second less predictable and with the third still less so. A second desirable feature is the elimination of interferences between atoms. At temperatures of typical flame sources, atoms of one kind often associate with those of another to form a molecule or radical and when this happens they cannot emit their characteristic radiations. They are thus lost to the spectroscopist. This loss does not arise if the kinetic energy acquired by the molecule is sufficiently high to dissociate it. A high kinetic temperature is most likely to be achieved with a system in LTE. Third, we want a system with minimum fluctuation in intensity arising from instability in the source. In LTE, N_i/N depends essentially only on temperature (although the electron density influences the partition function *via* the calculation of the drop in ionization potential, the dependence is not strong).[4] With deviations from LTE an extra factor,[5] strongly dependent on both temperature and electron density, must be introduced in Boltzmann's equation. This increases the effect of fluctuations of the source and the compensation obtained by using an internal standard, which even in LTE needs careful consideration,[6] becomes less reliable.[5]

It is possible for two reasons (but rarely likely with small plasmas) that a temperature higher than the optimum might be realized. The first reason is that with higher temperatures the radiation plays a greater part in the processes of energy transfer and this lessens (but at practicable temperatures only slightly) the likelihood of achieving LTE. The second is that as the temperature is increased, the exponential term in the expression for N_i ultimately tends to unity while $Z(T)$ continues to increase. The intensity thus goes through a maximum. The physical reason for this is that at high temperatures the atoms are distributed over more energy levels, so that the lowest levels become depopulated: in addition since N_i is properly a particle density, it decreases with temperature if the pressure is constant.

The temperature at which this maximum occurs is calculable and this can be used as a temperature calibration (subject to the plasma being in LTE). The maximum is not very sharply defined, however. The most frequently used method for the determination of the temperature of a plasma (again assumed to be in LTE) is by the measurement of the intensity ratios of two or more spectroscopic lines emitted by atoms of the same element. The ratio of the intensities yields the ratios of the populations in the excited states, if the transition probabilities are known, and from the ratio of the populations the temperature can be calculated from Boltzmann's equation. Unfortunately the transition probabilities are not usually accurately known. The greatest precision is obtained when the upper energy levels are widely separated and this has suggested the use of lines from different ionization states of the atom; but this involves the ratio of the partition functions of the two ionization states (this term cancels when only one state is involved) which are difficult to evaluate at high temperatures. Most temperature measurements are therefore not very reliable.

A temperature calculation based on observations of only one part of a cylindrical plasma results in an average temperature, for the emission will have originated in regions at different temperatures. A proper temperature profile can be reconstructed from a series of measurements across the plasma, by an Abel inversion.[7]

The temperature-dependence of the continuum radiation is a matter of practical interest. This radiation is due to transitions which involve free electrons. It consists of recombination radiation, where a free electron combines with a positive ion, and bremsstrahlung, where a free electron remains free but loses energy, typically by the decelerating effect of other particles, as the name suggests. The two types are frequently known as free–bound and free–free radiation. Because the energies of free electrons are not quantized the radiation is distributed in a continuous spectrum. The calculation of the spectrum results in a complicated formula,[2] which for frequencies near those of the visible region reduces to

$$I(\nu) = \frac{Kn_e^2}{T_e^{1/2}}$$

where K is a constant, n_e the electron density and T_e the electron temperature. If this is applied to the data for nitrogen,[1] we find that reducing the temperature from 12,000 K to 8000 K reduces the continuum by a factor of 1000, and from 12,000 K to 6000 K by a factor of over 10^6. This strong dependence on temperature *via* electron density is the main reason for not using the hottest part of the plasma as the spectroscopic source.

We may summarize this section as follows.

1. For a system in thermodynamic equilibrium, one parameter T (the temperature) determines the radiation field by Stefan's law and the distribution of the particles in different energy states, by Boltzmann's law.

2. For a system in local thermodynamic equilibrium, one parameter T (the temperature) determines the distribution of the particles in different energy states, but not the radiation field.

3. If deviations from local thermodynamic equilibrium are small, different parameters T_i will govern the distributions of the kinetic energies of different types of particle (electron temperature, gas temperature) and the populations of atoms in excited states (excitation temperatures).

4. If deviations from local thermodynamic equilibrium are large, there may exist no parameters T_i governing the populations by Boltzmann's law and the idea of excitation temperature has no meaning.

5. A source in local thermodynamic equilibrium, though not essential for spectrochemical analysis, is desirable on three counts. (*a*) The behaviour of a given element is more predictable. (*b*) A high kinetic temperature, on which freedom from chemical interference depends, is more likely. (*c*) The effect of instabilities in the source is likely to be minimized.

PLASMA JETS

The origin of the plasma jet principle is generally credited to Gerdien and Lotz.[8] In 1922, while carrying out experiments on high-intensity arcs, they inserted an anode into a copper ring cooled by a vortex water stream impinging on the inner wall. Within the ring the arc channel was constricted because its periphery was cooled by the water: this effect is the so-called thermal pinch. The current density rose to about 100 A/mm^2 and the arc temperature was the highest that had been obtained at that time. The arc burned in the water vapour and the gases emerged from the ring in a high-velocity steam plasma jet. This form of the plasma jet was refined and received considerable attention in the late 40's and early 50's, culminating in a paper by Giannini[9] in 1957 where he claimed temperatures of 30,000°F. Other good reviews on the history and development of the plasma jet have appeared.[10,11]

A plasma jet is formed when the current density to be dissipated on the surface of an arc electrode is greater than can be removed by radiation and conduction alone. Maecker,[12] by forcing an arc to burn in a narrow water pipe, showed that any constriction of an arc gives rise to a jet. If the periphery of the arc column is deliberately cooled or its diameter restricted by any means, the ionization, and hence the conductivity of the gases, in the outer regions of the plasma, will be lowered. The current in the discharge will then tend to concentrate in the hotter central region of the plasma. This increase in current density by means of a thermal pinch causes a further increase in temperature or conductivity. When the current density in the discharge becomes high enough a second pinch effect occurs, the so-called magnetic pinch. Two parallel conductors carrying current in the same direction attract each other, and similarly, charged particles flowing through a plasma jet device crowd closer together. This constricts the discharge and increases the density of the plasma even further. The benefits of constriction of the arc are greater stability, a greater concentration of energy and higher temperature.

There is a voluminous literature on plasma physics and on applications as diverse as high-temperature gas-reactions, rocket motors, cutting equipment and spheroidizing. Such papers have little bearing on analysis and have been omitted from this review. The use of the plasma jet for analytical purposes came relatively late in its development and was due to Margoshes and Scribner[13] in the United States and Korolev and Vainshtein[14,15] in Russia. The stability of the systems described was not good, coefficients of variation of several per cent being obtained. Owen[16,17] attributed the instability to the arc streamer (from the jet to the annular cathode) moving randomly over the surface of the cathode and perturbing the jet. His solution to this problem was to use an external yet integral cathode, usually made of thoriated tungsten. This electrode was electrically connected to the exit orifice of the annular cathode. After an arc had been struck between the anode and the annular cathode the plasma jet issuing from the orifice came into contact with the auxiliary thoriated tungsten electrode and the electrical path was transferred. This mode of operation is often referred to as the "transferred arc plasma jet".

The plasma jets so far described are of the type which has seen most development for quantitative analytical purposes. In some papers, particularly Russian, they are often referred to as Plasmatrons. An interesting variation is that of Valente and Schrenk,[18] who used two similar plasma jets inclined to each other at 30° and producing a common tail flame. The analytical solution was delivered to the left-hand jet by means of an argon gas stream of 1·2 l./min while pure argon was delivered to the other jet at 1·0 l./min. From their published results this would seem to produce good stability and sensitivity, and would seem to us to have possibilities of supplying different analytical solutions to the two jets at the same time for internal standard control or possibly standardization. A commercial design of the single plasma jet has been produced by SPEX Industries, and is described in detail by Mitteldorf and Landon.[19] Sirois[20,21] used this commercial plasma jet, and described the optimization of operating parameters and evaluated the equipment for the analysis of aqueous solutions.

Comparatively less attention has been paid to the Kranz Jet[22–24] or "D.C. Plasmabrenner" as it is often called. This type of plasma jet is essentially a gas-stabilized d.c. arc struck between thoriated electrodes. The coolant gas is introduced tangentially in opposite directions in both the cathode and anode parts. The horizontal path of the arc is entirely enclosed in a metal envelope except for a vertical orifice perpendicular to the arc. The "flame-like" plasma jet issuing from this orifice may reach more than 20 cm in length when

operating with nitrogen. It is claimed that this jet may be operated for many hours without contamination from the tungsten electrodes in the absence of an aerosol. Contamination is encountered when aerosols are introduced into either gas stream. Malinek and Massmann[25] claim to have overcome this difficulty and it is possible that this source will now receive more attention. The plasma jet described earlier is also relatively free from electrode consumption when running on argon or helium without an aerosol. (For a 50-kW plasma jet it is about 3×10^{-7} ppm w/w of electrode and nozzle metal in the gas stream.) For analytical purposes this is, however, academic since the injection of aerosols raised the concentration of the electrode material in the gas stream to 1% w/w or more. It thus becomes necessary to change electrodes every $\frac{1}{2}$–3 hr, to provide a constant electrode geometry.

It is not within the scope of this review to consider other types of gas-stabilized arcs or noble-gas environment arcs. These d.c. arcs are variations of the conventional arc and involve no plasma jet. The spectra examined for analytical purposes are emitted from the arc, in contrast to the plasma jet where they are emitted from the flame-like jet.

GENERATING EQUIPMENT—SUPPLIES AND OPERATING PARAMETERS

There is a very wide variation in line intensity with arc current which makes it impracticable to specify any operating parameters, since their best values depend very much on the physical size of the jet, the arc voltage and gas flows.

Vecsernyes,[26] for example, has shown that variation of arc current, for constant gas flow and arc voltage, changes the excitation conditions for the analytical lines. A plot of line intensity against arc current shows at least one maximum. For instance he records a maximum for the Mg 277·8-nm line at 28 A whereas for the Zn 307·6-nm line it occurs at 45 A. Every spectroscopic line, as might be expected, has its own maximum. This latter observation was confirmed by Valente[18] who found the calcium Ca(I) 422·7-nm line had a maximum at 9 A whereas the Ca(II) 393·4-nm line had a maximum at 14 A. A further interesting observation was made by Goto *et al.*,[27] who found that even at 400 A the Ca(II) line was still increasing in intensity although the Ca(I) line had reached a maximum. These variations have been generally attributed to the increase in temperature of the jet with arc current.

For analytical purposes the plasma jet is powered by d.c. power supplies capable of sustaining powers up to 100 kW. For 1–5 kW it is convenient to use a d.c. arc power supply of the type supplied for conventional arc spectroscopy. Above such powers a welding set or similar is used. It is relatively easy to provide a filtered d.c. supply at low powers but this becomes more difficult at high powers. With low-current designs the plasma jet will run for 2–3 hr without electrode erosion problems after the introduction of aerosols, whereas the high-current models last, at the best, only 30 min. Details of the power supplies which have been used for analytical purposes, together with certain operating parameters, are summarized in Table 1.

Introduction of liquids and solids into the plasma jet

Owen[17] has attributed the limited exploitation of plasma jet excitation for spectrochemical analysis to the inefficient and irreproducible nebulization of liquid samples into the jet. This view was confirmed by Valente and Schrenk[18] who reported a coefficient of variation of 0·7% for 15 readings of one solution continuously nebulized into the jet but 4% when the readings were made with a water wash between each.

Table 1. Typical generating equipment and operating parameters

Reference No.	Generator	Type	Ignition	Gas	Flow-rate, *l./min*	Voltage, *V*	Current, *A*	Electrodes
51	Miller Model 360-P	a.c.–d.c. Welding unit	H.f. spark	Ar	·7–30	12 39	240–800	W, C or Cu
				Air	·3–30	30–46	165-400	
				N_2	1–8	44 46	160–225	
62	—	d.c. arc	H.f. spark	Ar	·6–14	—	17	C
28	—	d.c. arc	—	He/ 30% Ar	10–30	—	90–500	C
20/21	SPEX Industries	9030		He/Ar	14	—	15–24	C
19/56	—	—	Contact	He/Ar	—	—	—	—
45	Two 600-A rectifiers in series	Welding unit	—	Ar/H_2	58	50 ~100	200 7–16	C/W C
18	Jarrell-Ash Custom Varisource	40–750	—	Ar	—	—	—	—
50	Lincoln Electric welding machine	SAE-300	H.f. spark	Various	—	50	300	—
30	240-V d.c. inductor stabilized line or rectifier source	—	—	Ar	9	—	20	W

The primary disruptive force for aerosol production in pneumatic nebulizers comes from the difference in velocity between the driving gas stream and liquid stream. The greater the differential velocity, the greater the efficiency and the smaller the droplets. The differential velocity is primarily a function of the pressure drop across the gas exit orifice. To obtain a high pressure drop across the gas exit, without excessive gas flow, requires very small orifices. These are suitable only for very dilute solutions, up to approximately 1000 ppm, because of the risk of blockage. Owen[17] concluded that ultrasonic nebulization is superior to other types; nobody appears to have applied this concept successfully to the plasma jet.

Notwithstanding the previous comments, much work has been satisfactorily carried out by use of pneumatic nebulizers with a plasma jet, as will be seen later.

There are several ways in which an aerosol can be injected into a plasma jet and all have received some attention.

The sample solution can be introduced into the plasma by nebulizing the solution through a capillary and blowing it on to the arc with a gas stream. This system has been advanced by Goto *et al.*,[27] who report satisfactory results. The injection system makes an angle of 10° with the axis of the plasma jet. A similar system has been used by Yamamoto[28] who pointed out that when the sample solution is blown into the plasma arc at this angle the plasma jet moves away from the injector. He suggested that the effect could be eliminated by the use of a magnetic field. Atsuya and Goto[29] have applied this idea and have obtained improved stability.

Several workers[16,18,30,31] have introduced the sample by using a direct injector situated on the plasma axis and injecting in the same vertical direction as the plasma. A direct nebulizing injector is one where the whole aerosol of the nebulized sample passes into the plasma.

Chapman *et al.*[32] have improved the stability of the plasma jet by replacing the direct-injection nebulizer with a premixed chamber-nebulizer. In this type the larger droplets are separated from the fine aerosol.

Kranz[24] has considered the various alternatives for the introduction of liquids and solutions into the plasma jet and concludes that of the alternatives, tangential injection with the stabilizing gas and radial injection with a breaking flow boundary layer (following Goto and Yamamoto) are the best methods.

Less information is available on the more complicated problem of the introduction of solids into the plasma jet. Kranz,[24] using heat and conductivity equations,[33] has calculated that for temperatures of 6000 K the greatest radii of particles that will still be vaporized by the time they arrive in the measuring position are $2{\cdot}4 \times 10^{-4}$ cm for water and $7{\cdot}5 \times 10^{-8}$ cm for tungsten. The concentration of elements in the plasma is determined by the volatilization rate, by the rate at which they are removed by diffusion (convection) from the plasma and by the gas flow.

The volatilization processes have been considered by Rusanov and Batova.[34] They found that, for a given element, the size of particles containing this element has a pronounced effect on spectroscopic intensity, but the size of the particles free from this element, with which they are mixed, has little effect. These authors[34] used an injection system in which the solid samples (1–90 μm in diameter) were blown through the centre of the plasma by compressed air. Observation showed that use of methods of injecting powders which do not guarantee that the powders remain in the form of isolated particles, results in the weakening of line intensity, particularly when material of low melting point is in-

jected.[35] When particles isolated from each other are injected into the plasma, no significant mutual influence on the line intensity is shown by the particles. Under these conditions, in ore analysis, gangue rock composition should not have a significant effect on line intensity of the test elements.

Yudelivich *et al.* have recently studied the effect of chemical composition on line intensities[36] and the effect of particle size on calibration curves.[37] They have also recommended the use of buffers to stabilize the ionization process, so that a single standard could be used for samples having different compositions.[38]

Vecsernyes[26] has also studied the injection of powders into a plasma jet and concluded that the construction of a feeder system producing material transport that is homogeneous in time is a very difficult problem. Several other authors[39–44] have tried to inject powders into the plasma but with limited success for analytical work.

Although it is possible to analyse solids by impregnation of one of the electrodes of the plasma jet it is obviously a rather tedious and impractical technique as the jet would have to be demounted for each determination. The injection of the material by means of gas pressure, despite the problems, seems the only practical method.

Temperature of the plasma jet

Considerable effort has been made to ascertain temperatures of plasma jets, assuming local thermodynamic equilibrium. One of the earliest attempts was by Jahn.[45] Cann and Ducati[46] had previously estimated the temperature from thrust measurements and Browning[47] from considerations of heat content. Neither of these two methods was capable of great accuracy and only gave an average temperature over the cross-section of the jet, as indeed do spectroscopic methods unless the source is scanned and an Abel inversion performed.[48] Using techniques based on the intensities of the H(α) and H(β) lines, Jahn obtained a figure of 12,600 K for a plasma jet run on argon/5% hydrogen and arc conditions of 200 A at 50 V. Much additional material on the techniques for measurement of plasma jet temperatures is given by Nagler[49] and Hottel *et al.*[50] Generally, temperatures of 5000 K upwards are quoted and at these temperatures it would appear that most refractory materials are vaporized and dissociated, subject to the reservations due to particle size mentioned earlier.

INTERFERENCE EFFECTS AND PLASMA BACKGROUND SPECTRA

When the arc is run on argon alone it will burn continuously with little destructive action on the electrode. The introduction of water or aqueous solutions produces reaction at the cathode tip and some deterioration occurs. Metallic constituents in solution often deposit on the tip but it is usually possible to run the plasma for 30 min before cleaning and readjustment are necessary.

The spectrum of the jet near the auxiliary cathode has very strong lines due to tungsten and thorium. Their intensity falls off sharply within a few mm from the cathode. The background from the argon recombination spectrum is high and presents some limitations to sensitivity. Goto *et al.*[27] used helium, which has a higher ionization energy, in place of argon, to reduce the continuum. The intensity of the lines, in general, increases to a maximum near the centre of the jet and shows minima at both ends. Increase in current increases the intensity of all lines, the ion lines showing the greatest increase. This indicates a continually increasing temperature with increasing current, which contrasts with the d.c. arc where the arc temperature/current relationship is much less sensitive.

Raisen *et al.*[51] have produced a detailed list of the presence, or absence, of 28 different molecular and atomic species for different electrodes in an argon plasma, an air plasma and a nitrogen plasma. For an argon plasma they found the following species present: for W–Cu electrodes, Ar, Ar^+, N_2, N_2^+, N, O and Cu, and for C–C electrodes, Ar, Ar^+, N_2, N, O, C_2, C and CN. For an air plasma and C–C electrodes they found N, O, C_2, C and CN, and for C–Cu electrodes, Ar, N_2, N_2^+, N, O, C_2, C, CN, Cu and Cu^+. For a nitrogen plasma and C–C electrodes they found N_2, N_2^+, N, O, C_2, C and CN. The 28 species sought were Ar, Ar^+, Ar^{2+}, N_2, N_2^+, N, N^+, O_2, O_2^+, O, O^+, C_3, C_2, C, C^+, C^{2+}, CN, CN^+, CO_2, CO, CO^+, NO, NH, NH^+, OH, OH^+, Cu and Cu^+. Thygesen,[52,53] however, has claimed that the temperature of his plasma jet is high enough to excite the spectra of Ar^+ and Ar^{2+}.

Several authors[18,54,55] have commented on the presence, or absence, of matrix effects. They agree that the presence of sodium, potassium and alkaline earth elements gives rise to varying degrees of enhancement and recommend the addition of radiation buffers. It would appear that for high accuracy similar matrices are required for samples and standards. It would also appear that, in general, refractory materials are dissociated to their constituent atoms; for instance, the well known aluminium or phosphate interference in calcium emission is eliminated.

At this stage insufficient conclusive work has been reported for it to be stated that no other matrix effects exist.

ANALYTICAL APPLICATIONS

In keeping with all plasma devices the plasma jet has a very large linear range and high inherent sensitivity. Valente and Schrenk,[18] for instance, report a linear range of 0·01–20 μg/ml for zinc and report a coefficient of variation of 0·7% for 15 measurements of a 10-μg/ml calcium solution, compared with 0·3% when a hollow-cathode lamp was used as source with the same detection system. They also found that with washing out the system between readings the coefficient of variation rose to 4%. In practice this is the sort of figure to be expected from these devices when standards and samples have to be interspersed with water washes. Lerner[56] has obtained a coefficient of variation of 0·7–1·0% for acetone solutions but comments that aqueous solutions gave worse results.

Table 2. Analytical applications of the plasma jet

Materials examined	Typical elements determined	References
Metals and alloys	Ti, Ca, Mg, Mo, Nb, Cr, Ni, Mn, Al, B	13, 44, 60, 63, 67, 73, 75, 78
Minerals and slag	La, Y, Gd, Ca, P, Zn, B, Be, S	29, 36, 59, 61, 74, 79
Blood	Mg	54
Oilfield water	Ba, B, Fe, Mn, Sn	55
Aqueous solutions	Trace elements	65, 70, 71
Gasoline	B	66
Refractory oxides	Al, La	72
Wear metals	Trace elements	77
Coal ash	Trace elements	76
Air samples	Be	62
Biological materials	Ca	64

Table 3. Detection limits obtained with plasma jets

Element	Plasma-jet detection limit, μg/ml	Wavelength, nm	Element	Plasma-jet detection limit, μg/ml	Wavelength, nm
Aluminium*	0·3	396·2	Neodymium*	3	401·2
Antimony*	0·2	259·8	Niobium*	0·4	405·9
Arsenic*	0·5	235·0	Nickel†	0·003	341·5
Barium*	0·2	553·5	Osmium*	0·7	225·6
Beryllium*	0·003	313·0	Palladium*	0·5	361·0
Bismuth*	5	306·8	Phosphorus*	0·6	253·6
Boron*	0·05	249·8	Platinum*	0·5	265·9
Cadmium†	0·03	228·8	Praseodymium*	4	414·3
Calcium†	0·002	393·4	Rhenium*	0·5	221·4
Carbon*	15	247·9	Rhodium*	0·5	343·5
Cerium*	2	415·0	Ruthenium*	0·6	372·8
Chromium†	0·003	425·4	Samarium*	0·3	360·9
Cobalt*	0·8	228·6	Scandium*	0·03	361·4
Copper*	0·2	324·8	Selenium*	2	204·0
Dysprosium*	0·3	353·2	Silicon*	0·2	251·6
Erbium*	0·6	400·8	Silver*	0·2	338·3
Europium*	0·1	382·0	Sodium*	0·02	589·0
Gadolinium*	0·7	342·2	Strontium*	0·01	407·8
Gallium*	0·1	417·2	Tantalum*	1·5	296·5
Germanium*	0·2	265·1	Tellurium*	0·7	214·3
Gold*	0·2	242·8	Terbium*	0·07	369·4
Hafnium*	0·6	264·1	Thallium*	0·4	535·0
Holmium*	0·3	345·6	Thorium*	2	401·9
Indium*	0·3	451·1	Thulium*	0·5	346·2
Iridium*	1·5	254·4	Tin*	0·6	284·0
Iron†	0·005	372·0	Titanium*	0·08	334·9
Lanthanum†	0·07	399·6	Tungsten*	2	400·9
Lead†	0·03	283·3	Uranium†	0·5	424·2
Lithium†	0·001	670·8	Vanadium*	0·2	309·3
Lutetium*	0·06	261·5	Ytterbium*	0·07	328·9
Magnesium*	0·02	279·7	Yttrium†	0·008	371·0
Manganese*	0·04	257·6	Zinc†	0·01	213·9
Mercury*	0·3	254·6	Zirconium*	0·3	339·2
Molybdenum*	0·1	281·6			

* Reference 32.
† Reference 18.

A selection of the applications of the plasma jet to analysis has been collated in Table 2.

The literature also gives typical detection limits for many elements; the best of these are those of Valente and Schrenk,[18] and of Chapman *et al.*,[32] and these are shown in Table 3.

Plasma jets have a number of disadvantages when used as spectroscopic sources. They have electrodes which operate at high temperatures and produce their own spectroscopic contamination of the sample under investigation. The high temperature precludes the use of certain gases, *e.g.*, oxygen with copper or graphite electrodes. The electrodes, although at high temperature, are at a lower temperature than the plasma and will cool it. The wandering of the contact spot and the flare may cause spectrographic problems. It is difficult to inject aerosols into the plasma jet other than by means of direct injectors, and these are by no means the ideal type of nebulizers. However, plasma jets are comparatively inexpensive and do offer a means of obtaining greater sensitivities and precisions than those obtainable by conventional sources.

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PUBLICATIONS RECEIVED

Biopharmaceutics and Pharmacokinetics An Introduction Edited by ROBERT NOTARI, Dekker, New York, 1975 Pp x + 285. $13 75

Notari's book has generally achieved the aim of its author, which is to introduce the reader to the subject of biopharmaceutics and pharmacokinetics The various underlying principles of rate processes and kinetics are introduced and discussed in chapters 2 and 3, and then are applied in chapters 5 and 6 to real-life problems, some of which are drawn from the recent literature, of dosage regimens, desirable drug blood-level values, and formulation of drugs Casual reading will not suffice to obtain the full benefit from this book, which requires the active participation of the reader by working through the various sample and practice problems set by the author For this reason the book is of limited value to most analytical chemists except those who would be in close contact with workers in this field For them this book could be recommended To quote the author's introduction "This book is meant to provide knowledge for teachers, students, biomedical practitioners and research scientists in medicinal chemistry, pharmacology, pharmacy and other biomedical disciplines" The text is generally well written, although the section on "Controlling solubility through stomach buffering", with its associated practice problem, is rather difficult to understand, and there is the occasional printer's error in the text (particularly in the last sentence of page 119) The bibliography contains an impressive number of references to works only 2–3 years old The table of natural logarithms included at the end of the book would appear to be of limited value

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NOTICES

INTERNATIONAL SYMPOSIUM ON ANALYTICAL CHEMISTRY IN THE EXPLORATION, MINING AND PROCESSING OF MATERIALS

Johannesburg, South Africa, 23–27 August 1976

This symposium, held under the auspices of IUPAC, should be of particular interest to chemists, engineers, geologists and industrialists concerned with exploration for raw materials, befeficiation, refining, and production of materials.

Details are obtainable from:

The Conference Division (IUPAC Symposium),
CSIR, P.O. Box 395, Pretoria 0001,
Republic of South Africa.

1976 INTERNATIONAL CONFERENCE: MODERN TRENDS IN ACTIVATION ANALYSIS

Munich, 13–17 September 1976

The Gesellschaft Deutscher Chemiker (GDCh) and the Institut für Radiochemie der Technischen Universität München, in association with the International Committee will hold the "1976 International Conference: Modern Trends in Activation Analysis", under the sponsorship of the Federal Ministry of Research and Technology, the Bavarian State Ministry of Education and Culture, the City of Munich and the Bureau EURISOTOP.

Scope of the Conference

A. Fundamental contributions
   Recent progress in technical development
B. Applied contributions
   1. Biological and biomedical applications
   2. Environmental and ecological applications
   3. Material sciences and industrial applications
   4. Applications in geo- and cosmo-sciences
   5. Applications in archaeology, art and forensic sciences
C. Inter-disciplinary contributions
   1. Accuracy and precision
   2. Sampling and homogeneity control
   3. Standard materials
   4. Comparisons with other analytical methods

Submission of Papers

Abstracts of up to 500 words clearly indicating the scope of the work are required by 15 January 1976 and the complete manuscript by 15 July 1976.

Further information is obtainable from:

Prof. Dr. F. Lux,
Institut für Radiochemie der Technischen Universität München,
D-8046 Garching,
F.R. Germany.

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ERRATA

In the June issue of *Talanta* (1974), on p. 533, the two lines under the heading MODE DE CALCUL PROPOSE should read

Dans l'expression empirique de la courbe analytique:[8] $I = KC^n$, I est l'intensité relative, K une constante, C la concentration dans l'échantillon et n le facteur d'émission.

On p. 534 of the same issue, the heading 4 lines up from the foot of the page should read

Détermination de K, S et C pour les deux entraineurs

ERRATUM

In the paper by W. P. Koch, D. P. Poe and H. Diehl, *Talanta*, 1975, **22**, 609, on p 610 half of Program A was accidentally omitted. The full program appears overleaf and should be inserted opposite p 610.

See overleaf

```
C        PROGRAM A
C      THIS PROGRAM FITS TITRATION DATA TO A CUBIC EQUATION,
C      USING A SUBROUTINE DEVISED BY THE AMES LABORATORY
C      COMPUTER SERVICE. THE ENDPOINT IS DETERMINED BY SETTING
C      THE SECOND DERIVATIVE OF THE COMPUTED CUBIC EQUATION
C      EQUAL TO ZERO AND SOLVING FOR THE INDEPENDENT VARIABLE.
C      THE PRINT-OUT INCLUDES: (1) THE COEFFICIENTS OF THE
C      CUBIC, (2) A LISTING OF THE INPUTTED VALUES, (3) A
C      LISTING OF THE CALCULATED VALUES OF THE DEPENDENT
C      VARIABLE FOR EACH DATA POINT, (4) THE TIME AT THE
C      ENDPOINT, (5) THE PH AT THE ENDPOINT, AND (6) THE SLOPE
C      AT THE ENDPOINT.
C      THE FORM OF THE CUBIC EQUATION IS:
C      PH = Q(1) + Q(2)*TIME + Q(3)*TIME**2 + Q(4)*TIME**3
C      NSETS = NUMBER OF SETS OF DATA TO BE READ
C      NAME = IDENTIFICATION OF INDIVIDUAL SETS OF DATA
C
C      OPLSPA SUBROUTINE
C      NDEG = DEGREE OF POLYNOMIAL (1.LT.NDEG.LT.10)
C      NPTS = NUMBER OF DATA POINTS
C      X = TIME IN SECONDS (INDEPENDENT VARIABLE)
C      Y = PH (DEPENDENT VARIABLE)
C      W = WEIGHTING FACTOR
C      Q = THE OUTPUT, A DOUBLE PRECISION ARRAY OF COEFFICIENTS
C      TUWYLO = 0.0 UNLESS LOOP THROUGH DIFFERENT NDEG'S
C      Y = Q(1) + Q(2)X + Q(3)X**2 + Q(4)X**3
C
C
      DIMENSION X(50),Y(50),W(50),YCALC(50),NAME(20)                    1
      DOUBLE PRECISION Q(10)                                            2
      DATA W/50*1.0/                                                    3
      READ(5,120) NSETS                                                 4
  120 FORMAT(I2)                                                        5
      DO 500 K=1,NSETS                                                  6
      READ(5,100)(NAME(I),I=1,20)                                       7
  100 FORMAT(20A4)                                                      8
      WRITE(6,110)(NAME(I),I=1,20)                                      9
  110 FORMAT('1',20A4)                                                  10
      WRITE(6,115)                                                      11
  115 FORMAT(1X,'PH = Q(1) + Q(2)*T + Q(3)*T**2 + Q(4)*T**3')           12
      NDEG=3                                                            13
      NQ=NDEG+1                                                         14
      TUWYLC=0.0                                                        15
      J=0                                                               16
  125 J=J+1                                                             17
      READ(5,130) X(J),Y(J)                                             18
  130 FORMAT(F7.2,F6.3)                                                 19
      IF(X(J).LT.0.0) GO TO 140                                         20
      GO TO 125                                                         21
  140 NPTS=J-1                                                          22
      CALL OPLSPA(NDEG,NPTS,X,Y,W,Q,TUWYLO)                             23
      WRITE(6,200)(I,Q(I),I=1,NQ)                                       24
  200 FORMAT(1X,' Q(',I1,') = ',E15.8)                                  25
      DO 210 I=1,NPTS                                                   26
      YCALC(I)=Q(1)+Q(2)*X(I)+Q(3)*X(I)**2+Q(4)*X(I)**3                 27
  210 CONTINUE                                                          28
      WRITE(6,230) (I,X(I),Y(I),YCALC(I),I=1,NPTS)                      29
  230 FORMAT(1X,' I = ',I2,4X,'TIME = ',F7.2,3X,'PH = ',F6.3,
     &4X,'PHCALC =',F6.3)                                               30
      ENDPT=-Q(3)/(3.0*Q(4))                                            31
      ENDPH=Q(1)+Q(2)*ENDPT+Q(3)*ENDPT**2+Q(4)*ENDPT**3                 32
      SLOPE=Q(2)+2.0*Q(3)*ENDPT+3.0*Q(4)*ENDPT**2                       33
      WRITE(6,240)ENDPT,ENDPH,SLOPE                                     34
  240 FORMAT(1X,'TIME AT ENDPOINT = ',F7.2,6X,'PH AT ENDPOINT'
     &,' = ',F6.3,//' SLOPE AT ENDPOINT = ',E13.6,'PH/SEC')             35
      CALL GRAPH(NPTS, X,Y,3,7.7,0.5,0.0,0.0,0.0,0.0,0.0,0.0,
     &'TIME;','PH;',NAME,'    PH = F(TIME);')                          36
      CALL GRAPHS(NPTS,X,YCALC,0,2,' :')                                37
      CALL GRAPHS(1,ENDPT,ENDPH,1,7,' :')                               38
  500 CONTINUE                                                          39
      STOP                                                              40
      END                                                               41
C
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