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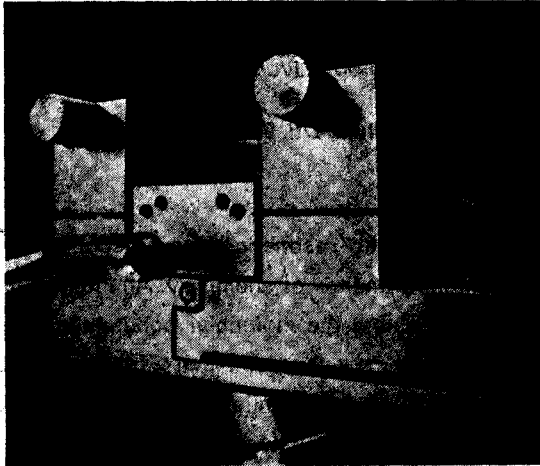
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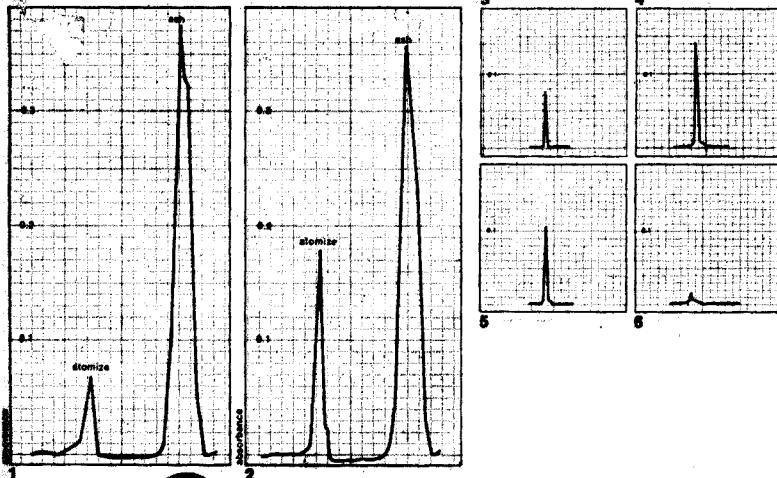
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1 2 3 4 2515

Analysis of High Resolution NMR Spectra

By R. J. ABRAHAM, *Department of Organic Chemistry, The Robert Robinson Laboratories, University of Liverpool, Liverpool, Great Britain*

1971, 334 pages, 43 tables, 147 illus., Dfl. 95.00 (ca. \$29.75)

ISBN 0-444-40846-0

High resolution nuclear magnetic resonance spectroscopy has now been applied to problems in most branches of chemistry. An integral part of these applications consists of obtaining the molecular constants, i.e. the nuclear chemical shifts and internuclear coupling constants, from the actual spectra. This is the theme of this book which essentially tries to answer the question, here is an NMR spectrum, how do I analyse it? After an introduction to the basic concepts and theory some explicit two, three and four spin systems are considered in detail. Then more general methods of analysis such as iterative computational methods and subspectral analysis are dealt with. Finally the various experimental aids to analysis are considered, in particular double resonance techniques.

This book is intended for senior undergraduate and graduate students in chemistry and research chemists with some familiarity with the basic instrumentation of high resolution NMR and the general patterns of chemical shifts and coupling constants who wish to analyse non first-order spectra without previous theoretical knowledge.

CONTENTS: Introduction. The quantum mechanical theory. The analysis of the AB, AB₂ and ABX spectra. The analysis of A₂X₂ and A₂B₂ spectra. The computer analysis of NMR spectra. Sub-spectral analysis. Aids to analysis.

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TRACE ANALYSIS FOR PLATINUM IN GLASSES BY NEUTRON ACTIVATION

DONALD A. BECKER

Activation Analysis Section, Analytical Chemistry Division, National Bureau of Standards, Washington, D.C. 20234 (U.S.A.)

(Received 28th February 1972)

A series of specially prepared glasses was analyzed for microgram quantities of platinum by neutron activation analysis. The glasses were part of a materials characterization study, in which the composition of each glass was to be correlated with its optical properties. The glasses had been prepared from the raw components in a resistance furnace under an inert gas atmosphere (argon), in platinum crucibles. In previous experiments, the use of platinum equipment in the preparation of similar type glasses had resulted in unwanted contamination of the glass melt, especially on the exposed glass surface. The series of glasses was prepared by the materials scientists in an effort to evaluate the effect of new and revised glass preparation procedures on the platinum contamination problem.

The samples as received were in the form of glass disks, 2.5 cm in diameter and averaging 3 mm thick. One surface of each sample was concave, and presumably represented the upper portion of the melt. The weights and approximate composition

TABLE I

COMPOSITION OF GLASSES FOR PLATINUM ANALYSIS

Sample no.	Wt. (g)	Approximate composition (wt. %)										
		Li ₂ O	Na ₂ O	K ₂ O	MgO	CaO	BaO	CaF ₂	Ce ₂ O ₃	Nd ₂ O ₃	Al ₂ O ₃	SiO ₂
1	6.9	1.6	10.1		0.7			2.8	0.4	2.7	5.2	76.5
2	6.2	16.1				9.6					5.0	69.4
3	6.4	1.1	7.2	11.0			6.0				2.0	72.7
4	5.6				7.0	27.6					14.5	50.9
5	8.4	1.0	6.4	9.3			5.0				1.7	76.6
6	5.5	1.7	10.5		0.8	2.1					1.8	83.1
7	6.6	1.7	11.0		0.8	2.2					5.6	78.7
8	7.1	1.6	10.2		0.7	2.0			0.4	2.7	5.2	77.2
9	8.7	1.6	10.1		0.7			2.8	0.4	2.7	5.2	76.5

of the individual samples are found in Table I. Information was desired on both the surface platinum, and on the platinum concentration in the glass matrix itself. The amounts of platinum estimated to be present in or on the glass samples were a few micrograms or less. Previous microscopic examination of the glass surfaces had ten-

TABLE II

MAJOR (n, γ) NUCLEAR REACTIONS OF PLATINUM

^{190}Pt (n, γ)	^{191}Pt
^{192}Pt (n, γ)	$^{193}\text{Pt} + ^{193\text{m}}\text{Pt}$
^{194}Pt (n, γ)	$^{195\text{m}}\text{Pt}$
^{196}Pt (n, γ)	$^{197}\text{Pt} + ^{197\text{m}}\text{Pt}$
^{198}Pt (n, γ)	$^{199}\text{Pt} + ^{199\text{m}}\text{Pt} \xrightarrow{\beta^-} ^{199}\text{Au}$

tatively identified platinum on the surface of four of the samples, but confirmatory analyses were required.

The analyses for platinum were made by neutron activation. After neutron irradiation, the six platinum isotopes present in natural platinum yield a large number of radioactive products (Table II). Of these, the reaction found to be most suitable for the analysis was ^{198}Pt (n, γ) $^{199}\text{Pt} \xrightarrow{\beta^-} ^{199}\text{Au}$. The end-product of the reaction, gold-199, has a 3.15-d half-life and γ -ray energies of 158 keV (37% abundant) and 208 keV (8% abundant)¹. The initial products of the reaction, platinum-199 and platinum-199m, have half-lives of only 31 min and 14.1 sec, respectively, and thus would not be convenient for an analysis utilizing a difficult dissolution technique and a chemical separation, as was necessary for the samples. The high level of radioactivity in the glasses, resulting from neutron activation (ca. 3 R/h at 15 cm, after 14-h decay), combined with the low-energy γ -rays of the gold-199 product necessitated the use of such a chemical separation in the analysis.

A search of the neutron activation literature for platinum (and gold) separation procedures produced a wide variety of techniques. However, the technique to be used should be rapid, quantitative and make use of the highly specific Ge(Li) detection systems now available, to reduce analysis time and difficulty. One separation technique which can be highly selective and yet very rapid is spontaneous deposition of one element on a less noble element. The technique was successfully used in this laboratory for the separation of sub-p.p.m. levels of short-lived $^{116\text{m}}\text{In}$ and ^{64}Cu from a highly radioactive gold matrix on to metallic silver². A spontaneous deposition technique was again applied, and the ^{199}Au formed from the decay of ^{199}Pt was deposited on metallic zinc granules.

EXPERIMENTAL

Reagents

The platinum standard used was NBS Standard Reference Material (SRM) 680, High-Purity Platinum. The SRM was in the form of 0.0508-cm (20 mil) diameter wire, and had a purity of 99.998%. For the analysis, a small section of the platinum SRM was dissolved in hot aqua regia, the solution was diluted to known concentration, and aliquots containing ca. 100 μg of platinum were then heat-sealed in polyethylene tubing and used as standards.

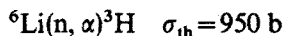
All other reagents were of ACS analytical reagent-grade quality.

Counting system

The counting system used for the analysis was a 60-cm³ Ge(Li) semiconductor, coupled with a 4096-channel pulse-height analyzer.

Irradiation conditions

Initially, approval for irradiation had to be obtained for the samples. Owing to the significant amounts of lithium contained in some of the glasses (up to 16.1% Li_2O), a series of tests had to be performed before irradiation approval was granted. This was necessary because of the large heat production from the nuclear reaction:



Since the NBSR pneumatic tube systems use polyethylene containers ("rabbits") for irradiations, steady-state temperatures must not exceed 115° . The tests were conducted on mixtures of lithium oxide with crushed quartz, in a polyethylene container identical to that to be used for the actual samples. To start, very small amounts of lithium oxide were used with the crushed quartz (ca. 8 g quartz) and irradiated for only short periods of time. The resulting temperatures were determined by irreversible temperature-indicating stickers, fastened to the outside of the polyethylene sample as previously described³. After the initial results, both the lithium oxide quantity and the length of irradiation were gradually increased. The final results showed that up to 2.2% lithium oxide (by weight) could be safely irradiated for up to 2 h in the NBSR pneumatic tube RT-4. The results indicated that one of the samples, number 2, which had a 16.1% lithium oxide concentration, could not safely be irradiated in the NBSR pneumatic tube system, and thus was dropped from the analysis program.

The samples remaining were irradiated as follows. Since the whole disks were physically too large to be irradiated in one piece, they had to be broken. To do this, individual disks were placed inside a clean polyethylene bag and fractured with a sharp blow. All the pieces were then carefully transferred to a cleaned polyethylene vial and sealed for irradiation. Iron foil flux monitors were attached to each vial for neutron flux normalization. The platinum standards, encapsulated in heat-sealed polyethylene tubing, were attached to several of the vials. All samples and standards were then irradiated for 2 h at a thermal neutron flux of $1.3 \cdot 10^{13} \text{ n cm}^{-2} \text{ sec}^{-1}$.

Chemical separation

After irradiation and a decay of about one week, the samples were quantitatively transferred to glass beakers and the surface platinum was dissolved. The solvent used was 20 ml of aqua regia (1 + 4 + 1— HNO_3 : HCl : H_2O) containing about 10 mg of gold carrier. The glass was kept in contact with the hot aqua regia for about 1 h. It had previously been determined that this procedure will dissolve milligram quantities of platinum metal.

After removal of surface platinum, the aqua regia was transferred to a clean container with several washings. Several milliliters of perchloric acid were added, and the solution taken to fumes of perchloric acid, and to incipient dryness. The residue was then taken up in several milliliters of concentrated hydrochloric acid and diluted to 30 ml (1–2 M hydrochloric acid). A small amount of washed zinc granules was then added, and if necessary, 10% sodium hydroxide solution added until cessation of vigorous zinc dissolution. The hydrochloric acid solution was then completely (including the zinc granules) transferred to a 1-cm thick zinc granule column in a microfiltration apparatus, and the zinc was separated by filtration on a glass fiber filter pad. After filtering and washing several times with distilled water, the zinc granules and the filter pad were transferred to a disposable plastic petri dish, covered,

homogenized by vigorous shaking, and counted on the Ge(Li) detector system.

For the determination of interior platinum, the residue after surface platinum removal was dissolved in a mixture of 72% perchloric acid and 48% hydrofluoric acid (4+1) containing 10 mg gold carrier using a teflon beaker; the mixture was taken to fumes of perchloric acid, then more hydrofluoric acid was added, and the cycle was repeated. This dissolution usually required 2-3 h. Occasionally, a teflon stirring rod was used to break off the insoluble calcium fluoride from the surface of the glass. The final perchloric acid solution was then evaporated to incipient dryness, taken up in several ml of concentrated hydrochloric acid, and heated to dissolve any oxides present. The resulting solution was diluted to 30 ml, and treated identically to the surface platinum solution. In this procedure the gold, platinum and other metals more noble than zinc were chemically reduced to the metals and separated with the zinc granules.

The irradiated platinum standards were quantitatively transferred and diluted with aqua regia containing 10 mg of gold carrier, and taken through the chemical separation procedure. The resulting ^{199}Au standards could be then compared directly to the samples.

Chemical yields were determined with irradiated platinum as a tracer, and were taken through the complete separation procedure. The yields were determined to be reproducible, and were always greater than 99%, averaging about 99.5%. The dissolution container, microfiltration apparatus and effluent were all checked for gold-199, with all losses found to be negligible.

RESULTS AND DISCUSSION

In order to test the analysis procedure, one sample (no. 3) was analyzed first. The procedure worked smoothly, and the results were 9.2 μg of platinum on the surface and less than 0.04 μg platinum in the interior portion. These values were determined by means of the 158-keV peak of ^{199}Au . The half-life plot and peak ratios of the two γ -rays verified the radiochemical purity of the ^{199}Au from the surface analysis. On subsequent samples, however, even though the half-life plot continued to agree, the peak ratios of the 158-keV and 208-keV γ -ray peaks did not agree with that of the standards or of the first sample. Subsequent investigation revealed the presence of an interfering radionuclide, scandium-47. This radionuclide is formed from the calcium component of the matrix by the nuclear reaction: $^{46}\text{Ca} (n, \gamma)^{47}\text{Ca} \xrightarrow{\beta} ^{47}\text{Sc}$; $T_{1/2} = 3.43 \text{ d}$, $E_{\gamma} = 160 \text{ keV}$ (73%) and was not completely removed from the zinc metal in the chemical separation employed. The γ -ray of ^{47}Sc is 160 keV, and could not be resolved from the 158-keV γ -ray from ^{199}Au with the counting system employed. However, the 208-keV γ -ray from ^{199}Au could still be used for the analysis, although with an order of magnitude lower sensitivity. The analytical results from all of the samples are found in Table III.

Thus, it was found that four of the eight samples analyzed had surface platinum contamination, ranging from 2.8 μg to 9.2 μg per sample. After two of the interior portions were analyzed and revealed no detectable platinum (less than 0.04 μg platinum in the interference-free case) it was decided that no further interior portions needed to be analyzed.

Several potential errors were investigated during the analysis, including the

TABLE III

RESULTS OF PLATINUM ANALYSIS

Sample	Total platinum content (μg)		Microscopic examination
	Surface	Interior	
1	<0.8	—	Possible
2 ^a	—	—	Yes
3	9.2	<0.04	Yes
4	6.6	—	Yes
5	4.3	—	Yes
6	<0.6	<0.4	No
7	<0.8	—	No
8	2.8	—	Probable
9	<0.6	—	No

^a This sample could not be irradiated owing to high lithium content; see text.

reproducibility of the sample counting geometry, γ -ray self-shielding owing to the relatively large mass of zinc, neutron self-shielding of the platinum standards, and possible neutron self-shielding from the lithium and other components of the glass matrix. The results of these investigations showed that the first two problems, counting geometry and γ -ray self-shielding by the zinc, were real, but were eliminated by treating the standards identically to the samples and by homogenizing the samples by effective mixing of the zinc granules.

The third problem, neutron self-shielding of the platinum, was found to be significant for the 20-mil platinum wire. Therefore, to eliminate this problem, the platinum wire was dissolved in hot aqua regia and a dilute solution used as the standard. For the last problem, neutron self-shielding of the sample was found to be negligible for the conditions of this analysis, although sample number 2, with 16.1% Li_2O , would have had a serious neutron self-shielding problem had it been irradiated.

The results of the surface analyses agree well with the microscopic examination as shown in Table III. Of the four samples on which platinum was tentatively identified as being present, three were confirmed by the neutron activation method, the fourth being rejected for analysis because of its high lithium content. The one "probable" identification was confirmed as having 2.8 μg of platinum, while the one "possible" and the three negatives were found to have less than 0.8 μg of platinum by neutron activation. Later communications with the scientists involved indicated that the analyzed samples which showed no detectable platinum on the surface were in fact the samples resulting from the improved glass production procedures under evaluation.

SUMMARY

Trace amounts of platinum were determined in eight glasses. These glasses had been prepared under special conditions, and information on both the surface and interior platinum was desired. Previous microscopic examination of the glass samples had identified platinum on the surface of at least four of the samples. The platinum

was analyzed by means of the nuclear reaction $^{198}\text{Pt}(n, \gamma)^{199}\text{Pt} \xrightarrow{\beta} ^{199}\text{Au}$. The ^{199}Au product has a 3.15-day $T_{1/2}$ and E_γ of 158 and 208 keV. Samples were irradiated in the NBSR for 2 h at $1.3 \cdot 10^{13} \text{ n cm}^{-2} \text{ sec}^{-1}$. After irradiation, the glasses were etched with aqua regia for the determination of surface platinum, and then dissolved in hydrofluoric and perchloric acids for the determination of interior platinum. The radioactive ^{199}Au was separated from the matrix by spontaneous deposition on metallic zinc. Experimental sensitivities of 0.04 μg of platinum were obtained.

RÉSUMÉ

On propose une méthode de dosage de traces de platine dans des verres. Elle est basée sur la réaction nucléaire $^{198}\text{Pt}(n, \gamma)^{199}\text{Pt} \xrightarrow{\beta} ^{199}\text{Au}$. ^{199}Au présente un $T_{1/2}$ de 3.15 jours et un E_γ de 158 et 208 keV. Après irradiation de 2 h à $1.3 \cdot 10^{13} \text{ n cm}^{-2} \text{ sec}^{-1}$, les verres sont traités par l'eau régale pour le dosage du platine en surface et ensuite dissous dans un mélange d'acides fluorhydrique et perchlorique pour le dosage du platine interne. ^{199}Au radioactif est séparé de la matrice par déposition spontanée sur zinc métallique. On est arrivé à des sensibilités expérimentales de 0.04 μg de platine.

ZUSAMMENFASSUNG

Es wurden Spuren Mengen Platin in acht Gläsern bestimmt. Die Gläser waren unter besonderen Bedingungen hergestellt worden, und es wurden Informationen über das Platin an der Oberfläche und im Innern gewünscht. Bei mindestens vier der Glasproben war durch vorhergehende mikroskopische Prüfung der Proben Platin an der Oberfläche identifiziert worden. Das Platin wurde mit Hilfe der Kernreaktion $^{198}\text{Pt}(n, \gamma)^{199}\text{Pt} \xrightarrow{\beta} ^{199}\text{Au}$ bestimmt. ^{199}Au hat eine Halbwertszeit von 3.15 Tagen, und die γ -Energien sind 158 und 208 keV. Die Proben wurden im NBSR 2 h bei $1.3 \cdot 10^{13} \text{ n cm}^{-2} \text{ sec}^{-1}$ bestrahlt. Nach der Bestrahlung wurden die Gläser für die Bestimmung des Oberflächen-Platins mit Königswasser angeätzt und dann für die Bestimmung des Platins im Innern in Fluorwasserstoff-Perchlorsäure gelöst. Das radioaktive ^{199}Au wurde von der Matrix durch Abscheidung an metallischem Zink abgetrennt. Es wurden experimentelle Empfindlichkeiten von 0.04 μg Platin erzielt.

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- 3 D. A. Becker, in P. D. LaFleur, *Activation Analysis Section: Summary of Activities, July 1968 to June 1969*, NBS Tech. Note 508, 1969, p. 14.

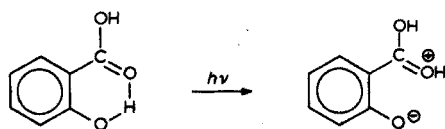
BIPROTONIC *versus* INTRAMOLECULAR PHOTOTAUTOMERISM OF SALICYLIC ACID AND SOME OF ITS METHYLATED DERIVATIVES IN THE LOWEST EXCITED SINGLET STATE

PETER J. KOVL, CONNIE L. MILLER and STEPHEN G. SCHULMAN

College of Pharmacy, University of Florida, Gainesville, Fla. 32601 (U.S.A.)

(Received 14th February 1972)

It has been shown by Weller¹ that the anomalously long wavelength of fluorescence of salicylic acid in organic solvents is the result of intramolecular proton transfer from the hydroxyl group to the carboxyl group during the lifetime of the excited state from which fluorescence arises. Because dissociation of the hydroxyl group and protonation of the carboxyl group both stabilize the excited states of phenols and aromatic carboxylic acids relative to the ground states², the zwitterion of salicylic acid, formed by phototautomerism, fluoresces at longer wavelengths than if the excited "neutral" acid were responsible for fluorescence. Recently, Schulman and Gershon³ have shown that the intramolecular proton transfer in the excited state of salicylic acid is mediated by intramolecular hydrogen bonding in the ground and Franck-Condon excited states of the latter compound:



In the latter study, it was also shown that the absorption spectra of the singly charged anion derived from salicylic acid were also indicative of intramolecular hydrogen bonding in the ground state, a result which suggested that a study of the pH-dependence of the fluorescence of salicylic acid might yield information of analytical interest.

Because of our interests in optimization of selectivity and sensitivity in trace analysis in biological fluids and in the photochemistry of photosensitizing drugs, the present study of the acidity and solvent dependences of the fluorescences of several salicylic acid derivatives was undertaken. The solvents employed in this study were water and chloroform, the latter being the solvent most often employed for extraction of drugs from urine and blood.

EXPERIMENTAL

Apparatus

Absorption spectra were taken on a Beckman DB-GT spectrophotometer. Fluorescence spectra were recorded on a Perkin-Elmer MPF2A fluorescence spectrophotometer whose monochromators were calibrated against the xenon line emission

spectrum and whose output was corrected for instrumental response by means of a rhodamine-B quantum counter. pH measurements were made on an Orion Model 801 pH meter with a Beckman silver-silver chloride-glass combination electrode.

Reagents

Chloroform (Spectroquality, Matheson, Coleman and Bell, Inc., Rutherford, N.J.), sulfuric acid, salicylic acid, and methyl salicylate (Mallinckrodt Chemical Works, St. Louis, Mo.) and *o*-anisic acid (*o*-methoxybenzoic acid; Eastman Organic Chemicals, Inc., Rochester, N.Y.) were used. Distilled deionized water containing phosphate and acetate buffers, was used to study the pH range. For very basic solutions, carbonate-free sodium hydroxide was diluted with distilled deionized water.

Acidic and basic chloroform solutions were prepared by making chloroform 2% (v/v) in trifluoroacetic acid and in morpholine, respectively.

RESULTS

The long wavelength absorption and fluorescence maxima of salicylic acid and its methylated derivatives in Hammett acidity and pH regions are presented in Table I.

The corresponding properties taken in chloroform media are listed in Table II.

TABLE I

LONG-WAVELENGTH ABSORPTION ($\bar{\nu}_a$) AND FLUORESCENCE ($\bar{\nu}_f$) MAXIMA OF SALICYLIC ACID AND RELATED COMPOUNDS IN AQUEOUS MEDIA

(Spectral maxima are reported in μm^{-1} ($\text{cm}^{-1} \cdot 10^{-4}$))

	18 M H ₂ SO ₄		0.1 M H ₂ SO ₄		pH 7		0.01 M NaOH		7 M NaOH	
	$\bar{\nu}_a$	$\bar{\nu}_f$	$\bar{\nu}_a$	$\bar{\nu}_f$	$\bar{\nu}_a$	$\bar{\nu}_f$	$\bar{\nu}_a$	$\bar{\nu}_f$	$\bar{\nu}_a$	$\bar{\nu}_f$
Salicylic acid	3.04	2.39	3.31	2.26	3.38	2.45	3.38	2.45	3.11	2.57
<i>o</i> -Anisic acid	3.12	2.38	3.38	2.75	3.58	2.90	3.58	2.90		
Methyl salicylate	3.03	2.39	3.31	2.73	3.31	2.73	3.02	2.45		
				and		and				
				2.23		2.23				

TABLE II

FLUORESCENCE ($\bar{\nu}_f$) MAXIMA OF SALICYLIC ACID AND RELATED COMPOUNDS IN ACIDIC, NEUTRAL AND BASIC CHLOROFORM MEDIA

(Spectral maxima are reported in μm^{-1} ($\text{cm}^{-1} \cdot 10^{-4}$))

	$\bar{\nu}_f$		
	CHCl ₃ + 2% TFA	Neutral CHCl ₃	CHCl ₃ + 2% morpholine
Salicylic acid	2.56 and 2.24	2.25	2.42
<i>o</i> -Anisic acid	2.49	2.94	—
Methyl salicylate	2.52 and 2.24	2.22	2.22

TABLE III

PROTOLYTIC DISSOCIATION CONSTANTS OF SALICYLIC ACID AND RELATED COMPOUNDS, DETERMINED BY ABSORPTIOMETRIC TITRATION (pK_a) AND BY FLUORIMETRIC TITRATION (pK_a^*)

(Not all of the possible excited-state protolytic equilibria were fast enough for pK_a^* values to be obtained. Assignment of the pK_a and pK_a^* values to their respective equilibria is discussed in the text)

	pK_a	pK_a^*
Salicylic acid	-8.0, 3.0, 14.0	-7.0, 16.0
<i>o</i> -Anisic acid	-7.5, 4.2	1.5
Methyl salicylate	-8.0, 9.9	-6.8

It should be noted that *o*-anisic acid does not fluoresce in alkaline chloroform.

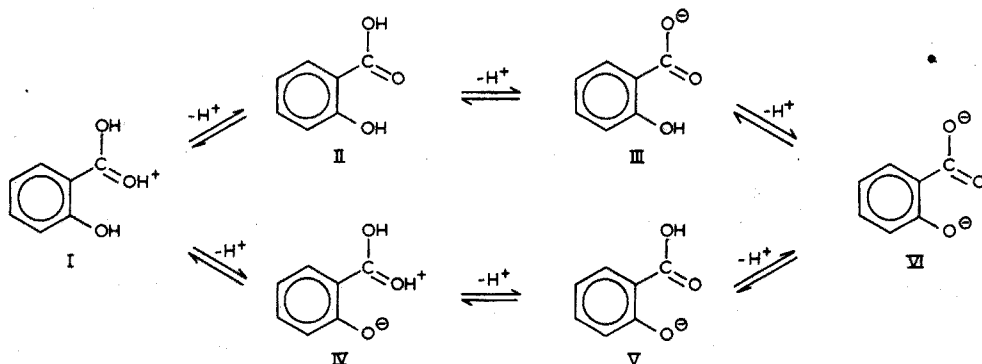
The ground (pK_a) and lowest excited state (pK_a^*) dissociation constants of salicylic acid and its derivatives as determined by absorptiometric and fluorimetric titration, respectively, are shown in Table III. In those equilibria where the conjugate species have considerably different absorption spectra (*e.g.* for *o*-anisic acid), fluorimetric titration curves were also observed in the pH regions in which the absorptiometric titration curves were obtained. This is a result of the dependence of fluorescence intensity on absorbance as well as fluorescence quantum yield. However, excited state equilibria are characterized by variations of fluorescence intensity in acidity regions where the absorption spectra are invariant⁴ and it is the latter types of fluorimetric titration curves which were employed to determine the pK_a^* values given in Table III.

DISCUSSION

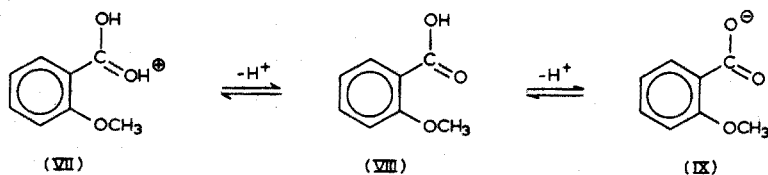
The theory of the relationship between fluorescence band shifts occurring upon protolytic dissociation and the protolytic equilibrium constants in ground (pK_a) and lowest excited singlet states (pK_a^*) has been developed by Förster⁵. Dissociation from phenolic groups enhances charge transfer from the phenolic oxygen atom to the aromatic ring in the excited state, thereby stabilizing the excited phenolate anion relative to the excited undissociated phenol. This results in a shift to longer wavelengths (or lower frequencies) of the fluorescence of a phenolic molecule upon dissociation². Dissociation from carboxyl or carboxymethyl groups inhibits charge transfer from the aromatic ring to the electron-withdrawing groups in the excited state, destabilizing the dissociated excited molecules relative to the undissociated excited molecules. This results in a shift to higher frequencies of the fluorescence of an aromatic carboxylic acid or ester, upon dissociation². Similar arguments are generally applicable to the shifts in absorption spectra occurring on protolytic dissociation^{2,6}. Since fluorescence intensities reflect the equilibrium concentrations of excited species, fluorescence shifts occurring on dissociation can be employed to indicate the site of dissociation of the excited species. Similarly absorbances reflect the equilibrium concentrations of ground state species, and absorption shifts are characteristic of the sites of protolytic dissociation in the ground state. As a result of the differences in electronic distributions in the ground and electronically excited states of the same mole-

cules, it is not a foregone conclusion that the sequence of dissociations occurring in the ground states of polyfunctional molecules, on going from acidic to basic pH, is the same as that occurring in the excited state. In light of these arguments the dissociation equilibria of salicylic acid and its derivatives in ground and lowest electronically excited singlet states will now be considered.

Salicylic acid, on going from concentrated acid to concentrated base solutions, is capable of undergoing three successive protolytic dissociations by either of two paths:



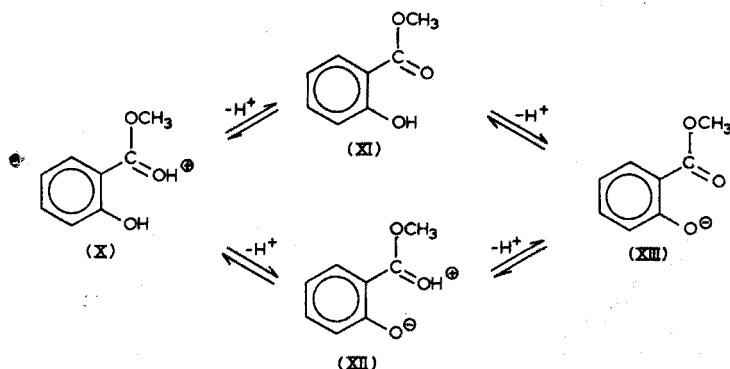
The first path entails dissociation of the protonated acid (I) from the protonated carboxyl group to form the neutral molecule (II). This is followed by dissociation from the carboxyl group again, to form the singly charged anion (III) and then dissociation from the phenolic group to form the doubly charged anion (VI). This pathway would be expected to be accompanied by successive shifts to higher frequency then again to still higher frequency and finally to lower frequency of the long wavelength absorption and fluorescence bands. This is, in fact, the sequence of frequency shifts observed in the long-wavelength absorption maxima and indicates that the latter pathway is the sequence of ionizations occurring in the absorbing (ground state) species. However, the sequence of fluorescence shifts is to lower frequency, then to higher frequency and finally, again to higher frequency. Examination of the second pathway of going from cation to doubly charged anion (I→IV→V→VI) indicates that this will produce the observed order of fluorescence shifts. This suggests that in the lowest excited singlet state, the phenolic group is more acidic than either the protonated or neutral carboxyl groups, a situation opposite to that in the ground state. The fluorescence behaviors of *o*-anisic acid and methyl salicylate support this conclusion. In *o*-anisic acid there is no hydroxyl proton. Thus only two dissociations are possible, both occurring from the carboxyl group:



It is to be expected that these dissociations will each produce shifts to higher frequen-

cies of the long-wavelength absorption maxima and the fluorescence maxima. The data of Table I indicate that this is indeed the case.

Methyl salicylate has a hydroxylic proton but no carboxylic proton in the neutral molecule. Thus two dissociative pathways are again possible; however, each of these can entail only two dissociations on going from concentrated acid to base:



The shifts to higher frequency and then to lower frequency of the long-wavelength absorption maxima indicate that the pathway $X \rightarrow XI \rightarrow XIII$ is followed in the ground state but in the excited state, the pathway $X \rightarrow XII \rightarrow XIII$, similar to that in salicylic acid, is indicated by the successive shifts to lower and then to higher frequency of the fluorescence maxima.

In the Hammett acidity range -6 to 0 , methyl salicylate shows only the low frequency emission at $2.23 \mu\text{m}^{-1}$ due to the excited zwitterion (XII). However, in the pH range $1-7$, a high-frequency fluorescence at $2.73 \mu\text{m}^{-1}$ appears in addition to the

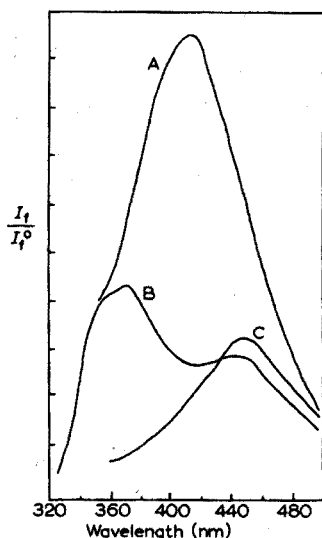


Fig. 1. Fluorescence spectra of methyl salicylate. (A) pH 9.0, (B) pH 1.0, (C) $H_0 - 0.7$. I_t/I_t^0 is the relative fluorescence intensity in arbitrary units.

low-frequency band (Fig. 1). This emission is similar in position to the neutral species derived from *o*-anisic acid (VIII) and is likely to originate from the excited neutral species (XI) derived from methyl salicylate since both (VIII) and (XI) have similar electronic configurations. In the region $H_0 - 6$ to pH 7, only the neutral, ground-state methyl salicylate is excited, so that the low-frequency emission of the zwitterion must be preceded by phototautomerism of the excited neutral molecule, a process which is apparently incomplete in methyl salicylate from pH 1 to pH 7. The observation of the low-frequency emissions of the zwitterions of salicylic acid and methyl salicylate in neutral chloroform, indicates that in this aprotic medium phototautomerism is intramolecular, involving proton transfer across the internal hydrogen bond. In dilute aqueous acid solutions, the observation of only the zwitterion fluorescence from salicylic acid suggests that phototautomerism in salicylic acid is also intramolecular. However, the phototautomerism of methyl salicylate in aqueous solutions shows an acidity dependence which indicates that phototautomerism in aqueous solutions involves diffusion-limited protonation of the carboxyl group, in the excited state, followed by dissociation of the hydroxyl group, the former step being slow and incomplete in dilute acid and resulting in some of the excited methyl salicylate fluorescing from the neutral molecular form.

That the emission properties of methyl salicylate in dilute acidic aqueous solutions are due to a kinetic rather than a thermodynamic phenomenon is apparent when the dissociation constants of the protonated species derived from salicylic acid and methyl salicylate are examined. The ground-state dissociation constants of the protonated ground-state species are identical and about 0.5 log unit more acidic than the *o*-anisic acid cation. This difference can be attributed to the intramolecular hydrogen bond stabilizing the neutral ground-state salicylic acid and methyl salicylate molecules with respect to the cations; this effect is absent in neutral *o*-anisic acid. Moreover, the excited-state dissociation constants of the salicylic acid cation and protonated methyl salicylate of -7.0 and -6.8 , respectively, are almost identical, so that the excited zwitterions giving rise to the low-frequency emission and the neutral ground-state species giving rise to the excited zwitterions, are essentially identical in the thermodynamic sense.

Although the pK_a data of Table III reflect all of the possible ground-state equilibria represented in the above schemes and studied by absorptiometry, the pK_a^* data of Table III do not contain all possible excited-state equilibria represented in these schemes. The reason for this circumstance is that the ground state has an infinite mean lifetime with respect to the acid-base equilibria while the lowest excited singlet state is often too short-lived for prototropic equilibrium to occur before fluorescence deactivates the latter electronic state. Thus the pK_a^* values of -7.0 and -6.8 correspond to the excited-state equilibria between the species I and IV derived from salicylic acid and between X and XII derived from methyl salicylate. The pK_a^* of 16.0 corresponds to the excited-state equilibrium between species V and VI derived from salicylic acid. The pK_a^* of 1.5 corresponds to the excited-state equilibrium between species VII and VIII derived from *o*-anisic acid and is the only directly observed equilibrium here in which the ground-state species and excited-state species correspond to one another. The ground-state pK_a for the latter equilibrium of -7.5 indicates that the carboxyl group is, as expected, a much stronger base in the excited state. This is also reflected in the completeness of excited-state protonation of *o*-anisic acid in

chloroform containing 2% trifluoroacetic acid. In the latter medium, salicylic acid and methyl salicylate are only partially protonated (Table II).

All fluorimetric titrations other than the ones mentioned above coincided with the absorptiometric titrations in the same pH regions, indicating that these excited state equilibria were attained too slowly to occur during the lifetimes of the excited participant species. However, that the fluorescences were always indicative of phototautomerism indicates that except for the neutral-zwitterion tautomerism of methyl salicylate, all other tautomerizations were extremely rapid and undoubtedly occurred via the intramolecular proton transfer mechanism.

SUMMARY

Salicylic acid demonstrates intramolecular proton transfer (phototautomerism) in its uncharged and singly charged anionic species in both chloroform and aqueous media. Methyl salicylate, on the other hand, exhibits intramolecular phototautomerism in chloroform but in aqueous media phototautomerism appears to be biprotonic, involving diffusion limited protonation of the carboxyl group and dissociation of the hydroxyl group by the solvent. The biprotonic process in methyl salicylate is complete, during the lifetime of the excited state in moderately concentrated acid solutions but is incomplete in dilute acid media.

RÉSUMÉ

Une étude est effectuée sur le phototautomérisme intramoléculaire de l'acide salicylique et de quelques uns de ses dérivés méthylés. On observe un tautomérisme biprotonique en milieu aqueux pour le salicylate de méthyle. Ce processus est complet durant la durée de vie de l'état excité, en solutions acides modérément concentrées; mais il est incomplet en milieu acide dilué.

ZUSAMMENFASSUNG

Salicylsäure zeigt einen intramolekularen Protonenübergang (Phototautomerie) in ihren ungeladenen und einfach geladenen anionischen Spezies sowohl in Chloroform als auch in wässrigem Medium. Andererseits zeigt Methylsalicylat intramolekulare Phototautomerie in Chloroform, jedoch scheint in wässrigem Medium die Phototautomerie biprotonisch zu sein, wobei durch Diffusion begrenzte Protonierung der Carboxylgruppe und Dissoziation der Hydroxylgruppe durch das Lösungsmittel erfolgen. Der biprotonische Prozess in Methylsalicylat ist während der Lebensdauer des angeregten Zustandes in mässig konzentrierten Säurelösungen vollständig, jedoch unvollständig in verdünnten Säuremedien.

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ATOMIC ABSORPTION AND FLUORESCENCE SPECTROSCOPY WITH A CARBON FILAMENT ATOM RESERVOIR*

PART XI. THE DETERMINATION OF IRON BY ATOMIC ABSORPTION SPECTROSCOPY

L. EBDON**, G. F. KIRKBRIGHT and T. S. WEST

Department of Chemistry, Imperial College of Science and Technology, London, SW7 2AY (England)

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The development of the carbon filament atom reservoir as an atomization device for atomic spectroscopy has been described previously in this series, and methods for the determination of several elements have been reported. This paper describes the determination of iron by atomic absorption spectroscopy with limited field viewing, an unenclosed cell and a fast response d.c. detection system.

Iron is an important trace element in numerous matrices and is, therefore, of particular analytical interest. It is less volatile than manganese¹ and has melting and boiling points of 1535° and 3000°, respectively. This latter figure is of interest because the terminal temperature obtained by the filament in these studies is *ca.* 2600°; additionally the formation of iron carbide (Fe₃C, m.p. 1837°) is well known. It may, therefore, be expected that iron would be more difficult to atomize in the carbon filament cell than more volatile elements, and that decreased sensitivity and poorer selectivity would be attained.

EXPERIMENTAL

Apparatus

The Unicam SP 900A spectrophotometer carbon filament atom reservoir and storage oscilloscope described previously¹ were used except that titanium was used in place of stainless steel for the water-cooled electrodes. Although iron atomic absorption signals were observed when the (slow) a.c. amplification system of the SP 900A was used, sensitivity was improved when this was replaced by a simple fast-response d.c. system. For this purpose, the photomultiplier circuit was modified to supply a negative EHT to the photomultiplier tube from an independent power supply (Brandenburg, Model 470 Regulated Power Supply, 2.5 kV and 5 mA) and the d.c. signal from the photomultiplier was led directly to the amplifier (K-type 20 V cm⁻¹ to 0.1 mV cm⁻¹) of the oscilloscope. Thus the use of the SP 900A amplifier, which has a time constant as long as *ca.* 0.6 sec for full-scale deflection, was avoided; in addition the need for a rotating sector, to convert the light signal to an a.c. level was

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** Present address: Department of Chemistry, Makerere University, P.O. Box 7062, Kampala, Uganda.

eliminated. Signal distortion was reduced and a faster response system obtained; full-scale deflection with the d.c. system was attained in *ca.* 0.7 msec. This enabled higher filament voltages to be used because it was possible to differentiate atomic signals from the continuum glow of the filament². The more rapid atomization which resulted also led to an improvement in sensitivity by virtue of the signal being measured by peak height rather than by area. An iron hollow-cathode lamp (Pye Cathodeon Ltd., Cambridge) was used as the spectral source. In all other respects, the apparatus and optical system used were similar to that described previously¹ and again a restricted region 0–0.7 mm above the carbon rod was observed.

Reagents and procedure

All reagents were of analytical-reagent grade and the water was glass-distilled and then de-ionized. The water used to prepare the solutions and the reagents employed in the interference studies were periodically checked for contamination by iron.

The sample pipette and all glassware were treated with "Repelcote" as described elsewhere³.

The procedure followed in routine determinations was the same as that described previously for manganese¹. In addition, the EHT was set to a predetermined optimum voltage.

Preparation of filament and nature of the signals

The carbon rods used to prepare the filaments were found to contain a large amount of iron, and it was necessary to remove this iron from new filaments before they could be used. This was successfully achieved by repeated heating of the filament for 3 sec at 12 V. The filament was heated under a tightly fitting glass dome³. This completely isolated the filament from the atmosphere, as, otherwise, slight oxidation at the ends of the filament occurred and reduced its useful life. A nitrogen shielding-gas flow-rate of *ca.* 2 l min⁻¹ was used. Filaments treated in this way gave high sensitivity for the first 15 determinations, after which the sensitivity decreased, possibly because the heating increased the porosity of the filament. The reproducibility of the signals increased, however, and after the first 25 determinations a coefficient of variation of 6% for 5- μ l samples was obtained. This was then maintained during the useful filament life. When the filament was heated for 1.5 sec at 12 V for each determination, *ca.* 200 determinations were possible before the filament required replacement.

The possibility that the absorption signals obtained might arise from non-atomic absorption of the incident source radiation was excluded by irradiating the atomic vapour with the cobalt lines at 242.5 and 252.1 nm instead of with an iron lamp. No signal was obtained from 5 μ l of a 10 μ g ml⁻¹ iron solution when a cobalt hollow-cathode lamp was used. The possibility that the signals might arise from residual iron being eluted from the filament was eliminated when no signal was obtained from blank solutions of de-ionized water or acid.

It was thought that the differing volatility of various iron salts (*e.g.* iron(III) chloride and iron(III) sulphate which decompose on heating in air to iron(III) oxide, m.p. 1565°) might result in equivalent amounts of iron from different salts giving different absorbance values. However, no difference was observed in the atomic absorption signal when equal concentrations of iron were applied to the filament as

the sulphate or the chloride. This finding was confirmed by interference studies (see Table III) and presumably arises from the strongly reducing nature of heated carbon; *i.e.* the salts are reduced to the same extent irrespective of the anions.

RESULTS AND DISCUSSION

Optimization of experimental conditions

The relationship of filament voltage to the (peak-height) signal from 5 ng of iron at 248.3 nm is shown in Fig. 1. Higher filament voltages can be used and increased sensitivity obtained compared to those for the a.c. detection system. The optimal filament voltage was 12 V. The graph of absorbance for 0.5 ng of iron at 248.3 nm *vs.* height of observation (Fig. 2) indicates that at 12 V the iron atomic vapour may exist for a few mm above the rod but that, as expected, the greatest sensitivity is obtained immediately above the rod (0–0.7 mm) where the atomic population is densest⁴.

Figure 3 shows the variation of the absorbance of 0.5 ng of iron at 248.3 nm with the nitrogen shielding-gas flow-rate. A filament voltage of 12 V and a height of observation 0–0.7 mm above the filament were employed. The optimal nitrogen flow-rate was found to be 3.9 l min⁻¹. As with manganese, no enhancement of absorption was obtained when argon was substituted as shielding gas; the optimal argon flow-rate was 4.0 l min⁻¹. Nitrogen was used as shielding gas subsequently.

Greatest sensitivity and linearity of calibration curves were obtained with a very narrow monochromator slit-width (0.01 mm), which gave the highest resolution of the 248.3-nm line from neighbouring lines. Similarly, greatest sensitivity was obtained at low hollow-cathode lamp currents. However, in order that sufficient light intensity reached the detector to prevent the need for high amplifier gains, which

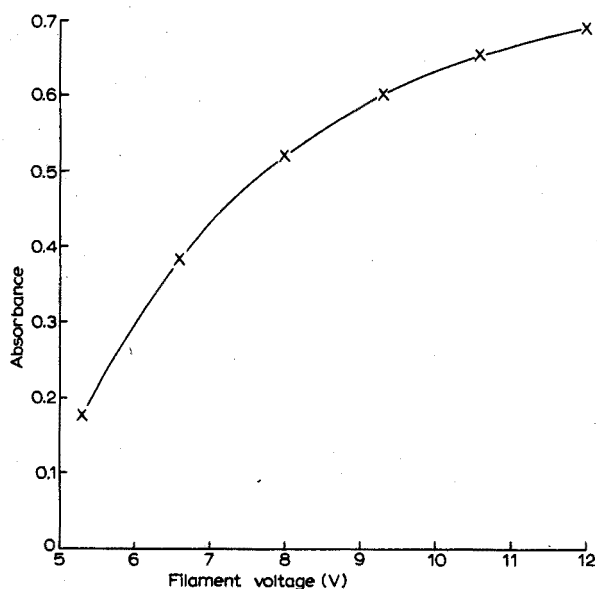


Fig. 1. Variation of absorbance at 248.3 nm with filament voltage.

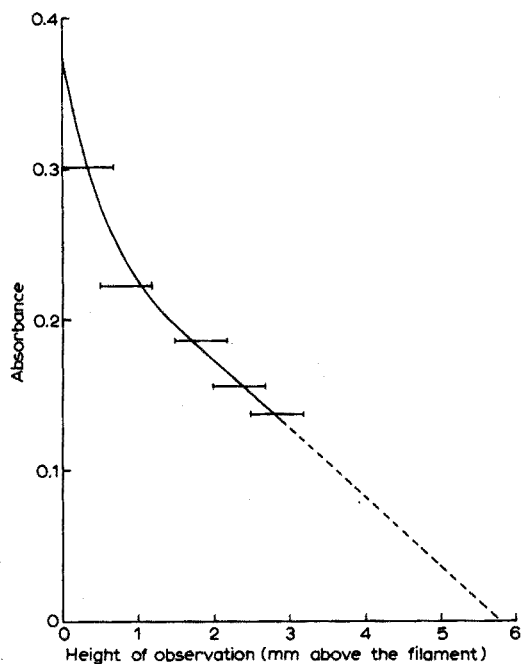


Fig. 2. Variation of absorbance at 248.3 nm with height of observation.

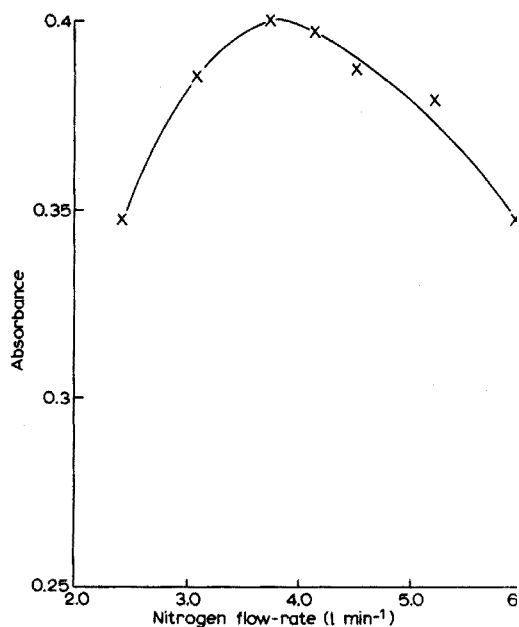


Fig. 3. Variation of absorbance at 248.3 nm with nitrogen shielding-gas flow-rate.

with this fast response system result in high noise levels, a wider slit-width and higher lamp current were preferred. The optimal slit-width was 0.02 mm (corresponding to a spectral band-pass of 0.15 nm at this wavelength) and a hollow-cathode lamp current of 15 mA was used. The optimal EHT was found to be 950 V.

Detection limits and calibration data

Under the established optimum conditions, the detection limit (signal:noise ratio of 2:1) and "sensitivity" (concentration in p.p.m. for 1% absorption) were determined at 248.3 nm. For 5- μ l samples, an 0.002 μ g ml⁻¹ iron solution corresponded to the limit of detection, *i.e.* an absolute limit of detection of $1 \cdot 10^{-11}$ g. The "sensitivity" for 1% absorption was 5 μ l of 0.001 μ g ml⁻¹ solution, *i.e.* $5 \cdot 10^{-12}$ g of iron; this was better than the limit of detection because of the relatively high noise levels experienced with limited field viewing and the fast response detection system. The limit of detection could be lowered considerably if a more intense narrow-line source were available, or with an improved optical system. The limit of detection with this system for 1- μ l samples was found to be 0.006 μ g ml⁻¹, *i.e.* $6 \cdot 10^{-12}$ g, but when the same monochromator was used for the atomic absorption of iron in an air-acetylene flame with an electrodeless discharge lamp as source⁵ it was necessary to use a sample volume of 2 ml to obtain a useful signal at the detection limit of 0.1 μ g ml⁻¹, *i.e.* $2 \cdot 10^{-7}$ g. Thus, as for other determinations with the carbon filament, the advantage in terms of absolute amounts of sample is several orders of magnitude.

The absolute limit of detection with the unmodified SP 900A amplifier (*a.c.*

detector) and the oscilloscope was found to be $1 \cdot 10^{-10}$ g iron with a sensitivity of $5 \cdot 10^{-11}$ g. The modified fast-response d.c. system thus enables an improvement of an order of magnitude in sensitivity to be made. This is because the fast-response system enables a higher filament voltage to be used (12 V for the d.c. system and 7 V for the a.c. system) resulting in narrower and higher absorption peaks, and also because the d.c. system causes less distortion of signals. The detection limits obtained for iron atomic absorption at 248.3 nm are summarized in Table I.

TABLE I

DETECTION LIMITS AND "SENSITIVITIES" AT 248.3 nm

<i>Atom cell</i>	<i>Detection* limit ($\mu\text{g ml}^{-1}$)</i>	<i>Sensitivity (for 1% absorption) ($\mu\text{g ml}^{-1}$)</i>
Carbon filament with d.c. detection system:		
5- μl sample	0.002 ($1 \cdot 10^{-11}$ g)	0.001 ($5 \cdot 10^{-12}$ g)
1- μl sample	0.006 ($6 \cdot 10^{-12}$ g)	0.003 ($3 \cdot 10^{-12}$ g)
Carbon filament with a.c. detection system:		
5- μl sample	0.02 ($1 \cdot 10^{-10}$ g)	0.01 ($5 \cdot 10^{-11}$ g)
Air-acetylene flame and this apparatus	0.1 ($2 \cdot 10^{-7}$ g)	0.9
Air-acetylene flame ⁶	0.005	0.062

Linear calibration curves were obtained for atomic absorption to high absorbance values when narrow monochromator slit-widths and low hollow-cathode lamp currents were employed with limited field viewing. It has already been noted that with limited field viewing the optimal slit-widths and currents for the optimal signal-to-noise ratios were somewhat larger, *i.e.* 0.02 mm and 15 mA; these settings decreased the range of linearity in the calibration curve and slightly reduced the attainable sensitivity. For practical analyses, however, the effects were quite tolerable and calibration curves for atomic absorption were linear over the range 0.05–5 ng of iron and passed through the origin.

Determination of iron at other wavelengths

Iron exhibits a relatively complex atomic absorption spectrum with a large number of resonance lines and lines which arise from intermediate lower levels lying very close to the ground state. Thus there are many lines at which iron atomic absorption may be observed, although the sensitivities at these lines vary greatly, mainly because of their differing transition probabilities. Smith and Frank⁷ have reported 31 usable lines for iron atomic absorption spectroscopy with a flame cell. In the present study, atomic absorption signals for iron were observed at 27 different lines. These are listed in Table II, together with the energy level transitions to which they correspond; also listed are the limits of detection and "sensitivities" for 1% absorption obtained in the present study using the carbon filament and the d.c. detection system. The "sensitivity" data are largely dependent on the transition probability

and the population of the level from which the transition arises. The detection limits are dependent on a number of other factors, including the intensity of the hollow-cathode lamp at that line (which determines the amplifier gain needed), and therefore the relative line intensities reported by other workers⁷⁻¹⁰ using air-acetylene and oxyhydrogen flames are also shown. In a few instances, at lines reported by these workers, the particular line could not be isolated from the hollow-cathode source, and in two instances where a reported line was isolated no absorption was observed.

It can be seen from Table II that no absorption was observed for lines resulting from transitions arising from the 0.11 and 0.858 eV (888 and 6928 cm^{-1}) energy

TABLE II

IRON ATOMIC ABSORPTION "SENSITIVITIES" AND LIMITS OF DETECTION AT VARIOUS WAVELENGTHS^a

Wave-length (nm)	Transition ^b (eV)	Relative line intensity	Carbon filament		Reported "sensitivity" in flame cells (p.p.m.)			
			"Sensi- tivity" (p.p.m.)	Detection limit (p.p.m.)	Air-C ₂ H ₂		O ₂ -H ₂	
					Ref. 10	Ref. 7	Ref. 8	Ref. 9
248.33	0 -4.99	100	0.001	0.002	0.01	0.1	0.10	0.8
248.82	0.052-5.04	60	0.0014	0.004	0.02	0.2		1.2
252.29	0 -4.92	70	0.0012	0.0026		0.2	0.21	1.25
252.74	0.052-4.95	44	0.01	0.02		0.6		
271.90	0 -4.55	124	0.002	0.0026	0.04	0.4	0.34	3.5
275.01	0.052-4.55	50	0.12	0.26				
275.63	0.052-4.548	50	0.15	0.32				
279.50	0 -4.43	70	0.2	0.8				
293.69	0 -4.22	44	0.03	0.08	0.47		2.35	
294.79	0.052-4.25	46	0.03	0.08	0.64			
296.69	0 -4.17	140	0.02	0.016	0.07	1.2	0.82	9.0
297.32	0.052-4.22	90	0.2	0.26	0.28			
298.36	0 -4.15	72	0.13	0.2	0.23			
299.44	0.052-4.195	72	0.03	0.04	0.24			
300.10	0.082-4.21	76	0.24	0.26	0.48			
302.06	0 -4.10	392	0.003	0.003	0.03	0.5	0.37	2.8
304.76	0.082-4.15	96	0.02	0.008	0.29			
344.06	0 -3.60	940	0.03	0.02		2.8	1.65	8.0
349.06	0.052-3.60	256	0.23	0.3				
367.99	0 -3.36	188	0.2	0.8			8.9	
370.56	0.052-3.39	304	0.33	0.3				
371.99	0 -3.34	26,400	0.006	0.0016	0.05	1.0	0.67	3.3
373.71	0.052-3.36	22,000	0.033	0.015				6.1
374.56	0.082-3.36	1,480	0.066	0.02				
382.44	0 -3.24	860	0.66	0.2			8.7	
385.99	0 -3.21	1,680	0.009	0.004	0.13	2.0	1.12	6.0
388.63	0.052-3.24	760	0.25	0.08				
273.73	0.11 -4.64	42	—	—	1.61			
358.12	0.858-4.32	520	—	—	0.55			

^a "Sensitivities" (for 1% absorption) and limits of detection (signal:noise 2:1) quoted in $\mu\text{g ml}^{-1}$. The values quoted for the carbon filament are those obtained in this study with 5- μl samples.

^b References 11 and 12.

levels. Furthermore the sensitivity obtained for the 252.74, 297.32 and 300.10 nm lines resulting from transitions arising from the 0.052 and the 0.082 eV energy levels using the carbon filament atom cell are poorer relative to that of the principal resonance line at 248.33 nm than those reported using flame cells. This is consistent with the lower temperature of the atoms in the carbon filament cell and consequent lower populations of these low-lying levels close to the ground state. A comparison of the sensitivities obtained for iron atomic absorption at different lines using the same instrumentation, but with different flame cells and the carbon filament atom reservoir could, with careful control of experimental conditions, yield useful information as to the energy level distribution of the iron atoms above the filament, and hence the environmental temperature.

From this study, it was confirmed that 248.3 nm was the most sensitive atomic absorption line for iron and this line was preferred for most measurements. However, the emission from the hollow-cathode source at 372.0 nm was *ca.* 260 times more intense, which enabled higher scale-expansion factors to be used before equivalent noise levels were obtained. This resulted in a lower detection limit, $0.0016 \mu\text{g ml}^{-1}$ for iron (*i.e.* $8 \cdot 10^{-12}$ g on a 5- μl sample), being obtained at this wavelength. Different wavelengths having differing sensitivities for iron atomic absorption offer varied analytical working ranges and under certain conditions measurements may be made at a line less sensitive than 248.3 nm to avoid the necessity for sample dilution.

Interference studies

An extensive examination was made of the effect of foreign ions on the absorbance recorded for iron; 5- μl aliquots of a $0.4 \mu\text{g ml}^{-1}$ solution of iron containing 1000, 100 or 10-fold amounts (by weight) of 22 different foreign ions were employed. The previously determined optimal conditions and the d.c. detection system were used. The results are shown in Table III; only interferences which resulted in a change of signal of more than 5% were taken to be significant.

Two interesting interference phenomena were noted. Aqueous ammonia and ammonium phosphate solutions were found to enhance iron absorption. This was shown not to be due to molecular absorption or iron impurity in the solutions employed; *e.g.* $400 \mu\text{g ml}^{-1}$ of the ammonia solutions produced no signal when added to the filament alone. The interference was removed by the addition of excess of acid to the test solutions. Ammonia and ammonium phosphate probably enhanced the signal for iron by forming colloidal iron hydroxide or phosphate which cannot readily penetrate into the porous carbon of the filament; atomization of the iron from the surface is thus speeded up, resulting in higher peak heights than normal. The removal of these effects by acidification is consistent with this explanation. The effects of various solutions containing ammonia on iron absorption signals are summarized in Table IV.

Nickel ions added as the nitrate produced, in 100-fold amounts, a 50% suppression of signal, but a 1000-fold amount gave an enhancement of +70%. Pure nickel nitrate solution gave no signal when $400 \mu\text{g ml}^{-1}$ solutions were applied to the filament. Nickel chloride in 1000-fold amounts gave a suppression of signal of -50%. The interference effects of cobalt and nickel solutions are shown in Table V.

From Table II it should be noted that only two ions (Co^{2+} and Cr^{3+}) seriously interfere at the 10-fold excess level (20 ng), the interference from diammonium

TABLE III

INTERFERENCE IN THE DETERMINATION OF IRON BY ATOMIC ABSORPTION WITH THE CARBON FILAMENT

Ion	Salt	% Change in signal from $2 \cdot 10^{-9}$ g Fe by 1000, 100 and 10-fold weight amount		
		1000	100	10
Al	$\text{Al}_2(\text{SO}_4)_3$	-24	-14	0
Ca	$\text{CaCO}_3/\text{HNO}_3$	0	0	0
Co ^a	CoCl_2	-85	-45	-20
Cr	CrCl_3	-80	-45	-20
Cu	$\text{Cu}(\text{NO}_3)_2$	-50	-40	0
K	KCl	-20	0	0
Mg	MgCl_2	-70	0	0
Mn	MnCl_2	-70	0	0
Na	NaCl	-50	-15	0
Ni ^a	NiCl_2	-50	-45	0
Pb	$\text{Pb}(\text{NO}_3)_2$	0	0	0
Si	Si/HF/ HNO_3	0	0	0
Th	$\text{Th}(\text{NO}_3)_4$	0	0	0
Ti	Ti/HF	0	0	0
V	V/ HNO_3	0	0	0
W	W/HF/ HNO_3	0	0	0
Zn	ZnSO_4	0	0	0
NH_4^{4+}	$\text{NH}_4\text{OH}/\text{HCl}$	0	0	0
Cl^-	HCl	0	0	0
NO_3^-	HNO_3	0	0	0
PO_4^{3-}	H_3PO_4	0	0	0
SO_4^{2-}	H_2SO_4	0	0	0

^a See Table V.^b See Table IV.

hydrogen phosphate and ammonia at this level being removed by the addition of excess of acid. At the 100-fold level (200 ng) several cations interfere, largely those of equivalent volatility to that of iron. At 1000-fold levels (2 μg) most of the cations studied, except the most involatile elements, produce serious depressions; no inter-

TABLE IV

EFFECTS OF VARIOUS AMMONIA SOLUTIONS ON IRON ATOMIC ABSORPTION

Solute	% Change of signal from 1000, 100 and 10-fold amounts of NH_4^+		
	1000	100	10
NH_4OH	+50	+50	+40
$(\text{NH}_4)_2\text{HPO}_4$	+70	+18	+13
$(\text{NH}_4)_2\text{SO}_4$	0	0	0
$\text{NH}_4\text{OH} + \text{excess HCl}$	0	0	0
$(\text{NH}_4)_2\text{HPO}_4 + \text{excess HCl}$	0	0	0

TABLE V

EFFECT OF NICKEL AND COBALT SOLUTIONS ON IRON ATOMIC ABSORPTION

Solute	% Change of signal from 1000, 100 and 10-fold amounts of Ni ²⁺ and Co ²⁺		
	1000	100	10
Ni(NO ₃) ₂	+70	-50	—
NiCl ₂	-50	-45	—
Co(NO ₃) ₂	-40	-50	-20
CoCl ₂	-85	-45	-20

ference was observed at this level from any of the anions studied. A few elements, notably magnesium, silicon, titanium and tungsten, produced peaks which appeared to be caused by particulate scatter at the 2- μ g level. These scatter peaks, however, did not interfere with the iron determination as they did not occur at the same time as the iron absorption peak; the fast response d.c. detection system was able to separate the absorption and apparent scatter peaks. As usual, all solutions of diverse ions were examined for iron contamination and tendency to produce apparent scatter peaks at the concentration levels employed. As observed for other elements with the carbon filament, less severe interference was observed for 1000-fold excesses of foreign ions when the iron concentration employed was lower.

CONCLUSION

This study shows that the carbon filament atom reservoir offers a sensitive method for the determination of iron by a.a.s. The fast d.c. recording system increases the attainable sensitivity. It is apparent that the tendency for iron to form a stable carbide and to have a boiling point *ca.* 400° in excess of the terminal temperature of the carbon filament does not lead to any lack of sensitivity. The technique yields a detection limit and "sensitivity" between one and two orders of magnitude better than those claimed for flame-based techniques when the results are quoted in terms of concentration and many orders of magnitude when quoted in terms of absolute amounts.

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SUMMARY

The atomic absorption behaviour of iron in the carbon filament atom reservoir is described. With limited field viewing and an open cell, used in conjunction with direct presentation of a d.c. absorption signal on an oscilloscope, a detection limit of $1 \cdot 10^{-11}$ g Fe ($2 \cdot 10^{-3}$ p.p.m.) and "sensitivity" of $5 \cdot 10^{-12}$ g Fe ($1 \cdot 10^{-3}$ p.p.m.) is obtained at 248.3 nm using 5- μ l volumes of sample solution. The effect of the presence of 22 cations and anions in 10–1000-fold amounts is examined. Nine metals

interfere at the 1000-fold level, but only two (Co and Cr) interfere at the lower level. Atomic absorption signals were observed for iron at 27 lines by the carbon filament technique.

RÉSUMÉ

On examine le comportement du fer, en absorption atomique, avec réservoir atomique à filament de carbone. Dans les conditions décrites, on arrive à une limite de détection de $1 \cdot 10^{-11}$ g Fe ($2 \cdot 10^{-3}$ p.p.m.) et une "sensibilité" de $5 \cdot 10^{-12}$ g Fe ($1 \cdot 10^{-3}$ p.p.m.), à 248.3 nm, avec des volumes d'échantillon de 5 μ l. On examine l'influence de 22 cations et anions, en quantités 10 à 1000 fois supérieures. A une concentration 1000 fois supérieure, neuf métaux gênent; cependant seuls cobalt et chrome interfèrent à des concentrations inférieures. Avec cette technique, le fer présente 27 lignes d'absorption.

ZUSAMMENFASSUNG

Das Atomabsorptionsverhalten von Eisen im Kohleheizfaden-Atomreservoir wird beschrieben. Mit begrenztem Blickfeld und einer offenen Küvette, die in Verbindung mit direkter Darstellung eines Gleichstrom-Absorptionssignals auf einem Oszilloskop angewendet werden, wird eine Nachweisgrenze von $1 \cdot 10^{-11}$ g Fe ($2 \cdot 10^{-3}$ p.p.m.) und eine "Empfindlichkeit" von $5 \cdot 10^{-12}$ g Fe ($1 \cdot 10^{-3}$ p.p.m.) bei 248.3 nm erhalten, wenn das Volumen der Probenlösung 5 μ l beträgt. Der Einfluss von 22 Kationen und Anionen in 10–1000-fachem Überschuss wird geprüft. Neun Metalle stören in 1000-facher Menge, jedoch nur zwei (Co und Cr) bei geringerer Menge. Atomabsorptionssignale für Eisen wurden bei dem Kohleheizfaden-Verfahren bei 27 Linien beobachtet.

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DETERMINATION OF LEAD IN PETROLEUM AND PETROLEUM PRODUCTS BY ATOMIC ABSORPTION SPECTROMETRY WITH A CARBON ROD ATOMIZER

M. P. BRATZEL, JR.* and C. L. CHAKRABARTI

Department of Chemistry, Carleton University, Ottawa, Ontario K1S 5B6 (Canada)

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The application of atomic absorption, atomic emission, and atomic fluorescence spectrometry to the analysis of petroleum and petroleum products for trace metal content has been reported in the literature¹⁻⁶. The conventional procedure for analysis is to dilute the petroleum sample with an appropriate organic solvent before flame spectrometric analysis to obtain a solution of sufficiently low viscosity so that it can be nebulized into a burner. Additionally, standards must be prepared in a solvent which closely matches the viscosity and composition of the samples to be analyzed so that the analytical signal observed is not affected by differences in nebulization rates and efficiencies. Trent⁷ and Kashiki *et al.*⁸ have analyzed gasoline for lead, and have found that different volatile organo-lead compounds evaporate at different rates in the spray chamber of a premix burner; hence, standard solutions of the same concentration prepared from different lead compounds give different absorbances. Also, the differences vary from one solvent to another. Correction, either by addition of a normalizer, or by proper experimental design, or by proper experimental conditions, is necessary.

Emission spectrography is often employed for qualitative and semiquantitative analysis of crude oils and other petroleum products, but sample preparation generally includes time-consuming ashing or calcining, with the possibility that some metal may be lost by volatilization in the process.

Slavin² published a review of petroleum analysis by atomic absorption spectrometry with reference to some problems encountered. More recent work by atomic absorption spectrometry, flame emission spectrometry, and emission spectrography has been reviewed^{9,10}.

The recent development of the nonflame carbon rod atomizer cells¹¹⁻¹⁵ presents an attractive alternative to conventional flame spectrometric or emission spectrographic analysis in that many of the problems and limitations are avoided, in addition to the inherently greater sensitivity, lower detection limits, and smaller sample volumes required. Kirkbright¹⁶ has recently reviewed the field.

Matousek and Stevens¹³ have applied a carbon rod atomizer to the determination of magnesium, iron, copper, lead, and zinc in blood and plasma. Bratzel *et al.*¹⁵ have used this atomizer for the analysis of rocks and metallurgical products for gold and silver. Brodie and Matousek¹⁴ have used it for the determination of sil-

* Present address: Bureau of Community Environmental Management, 550 Main Street, Cincinnati, Ohio 45202, U.S.A.

ver, aluminum, copper, chromium, magnesium, nickel, and lead in synthetic lubricating oils, as well as vanadium in fuel oil, and zinc in lubricating and motor oils. They used aqueous standards for the analysis of spiked organic solutions and obtained good recoveries. The above studies indicate that a carbon rod as an atomization device is rapid and simple, and gives high sensitivity and accuracy.

In the present study, the authors have extended the work of Brodie and Matousek¹⁴ for lead from just synthetic samples to a variety of real samples. A routine procedure for the direct analysis of various petroleum products is presented. Also studied is a simple one-step sample preparation procedure involving organic-to-aqueous extraction if the carbonaceous matrix and the viscosity of the sample are too great for direct analysis, or if the metal concentration is too low and preconcentration is necessary. The effect of different lead compounds used in preparing standard solutions, of solvent, and of a hydrogen diffusion flame on the sensitivity obtained with a "mini-Massmann" carbon rod atomizer, as well as a comparison of the sensitivity obtained with the lead resonance lines at 217.00 nm and 283.31 nm is presented. This study also presents the detection limit, the effect of cations and anions as potential interferences, and the results of analysis of gasoline, used bunker fuel oil, used jet engine lubricating oil, and crude oil for lead content.

EXPERIMENTAL

Apparatus

The atomic absorption spectrometer and the carbon rod unit (Model AA-5 and Model 61, respectively, Varian Techtron Pty. Ltd., Melbourne, Victoria, Australia) and its operation have been described elsewhere¹³⁻¹⁵. Sampling was with a micro-liter hypodermic syringe (No. 75 SN, The Hamilton Company, Whittier, Calif.). The tip of the syringe was inserted through an injection port of the carbon rod and the sample placed directly in the transverse sample-cell hole at which radiation from the source was focussed. The sample was dried, ashed, and atomized sequentially by passage of an electric current through the carbon rod. The duration of the atomic absorption signal (and thus the residence time of the atomic population in the optical path) was about 1 sec. Radiation was detected with a R-106 response phototube, and the slit width was 0.100 mm, corresponding to a spectral bandpass of 0.33 nm. Some preliminary studies were also made with the same instrumental system but with a Techtron 10-cm premix air-acetylene burner.

Reagents and samples

Chemicals of analytical reagent-grade purity were used without further purification, including lead cyclohexanebutyrate (Pb-CHB) (Eastman Organic Chemicals, Rochester, N.Y. 14650), tetraethyl lead (TEL) (Ethyl Corp., New York, N.Y. 10017), nickel cyclohexanebutyrate (Eastman), tris(1-phenyl-1,3-butanediono)-iron (Eastman), and copper cyclohexanebutyrate (Eastman).

Distilled water was passed through an ion-exchange column to remove both cations and anions (including lead) before use. The suppliers of the various samples analyzed for this study are given in the footnotes of Table II.

Operating conditions

The time and the voltage settings for the dry, ash, and atomize portions of the

atomization cycle were quickly determined and were such that the solvent and the organic matrix were removed before the atomization step, and that the sample was completely atomized and removed from the sample cell with each firing. An adequate rate of argon flow to provide effective sheathing of the carbon rod but not so high as to remove the atomic vapor too quickly from the optical path was about 1 l min^{-1} . The effect of a hydrogen diffusion flame (in conjunction with the carbon rod) is discussed below.

Optimization of the extraction system

The solvent extraction of lead complexes from aqueous to organic solvents has been discussed^{17,18}. A reverse extraction, *i.e.*, an organic-to-aqueous extraction consisting of a xylene-aqueous nitric acid extraction system was studied. Xylene was selected because of its immiscibility with aqueous solutions. Standard organo-lead solutions were prepared by dissolving TEL and Pb-CHB in xylene. Lead was extracted into aqueous nitric acid solution with a single extraction. Flame atomic absorption spectrometry indicated that the lead from the TEL was completely extracted into aqueous nitric acid solutions at acid concentrations greater than about 30% (v/v), and that the Pb from Pb-CHB was completely extracted into aqueous nitric acid solutions at acid concentrations greater than about 20% (v/v). Studies were made at lead concentrations of about $40 \mu\text{g ml}^{-1}$. All subsequent extractions of lead from a xylene solution were made with an aqueous solution which was 40% (v/v) nitric acid. Standard solutions containing $0.2 \mu\text{g Pb ml}^{-1}$ were taken through this extraction procedure and analyzed with the carbon rod. The analyses confirmed that the lead from TEL was completely extracted under these conditions; the organic phase gave no signal after the extraction. The lead from Pb-CHB, however, was only partially extracted; the organic phase gave a lead signal after extraction, but the signal was smaller than that observed without the extraction step. Solid dithizone was then added to the extraction system which resulted in the rapid and complete extraction of lead from the organic into the aqueous phase. These results indicate that the rate of extraction of lead from Pb-CHB is slow and that dithizone increases the rate of reaction, possibly by forming the complex lead dithizonate, which is more readily extracted into the aqueous nitric acid solution. For all extraction studies conducted with petroleum samples, solid dithizone was therefore added to facilitate the extraction. As a general rule, however, it appears that lead from petroleum and petroleum products should be extractable from xylene into 40% (v/v) nitric acid. If a particular organo-lead compound is to be used as a standard or is suspected to be present in the sample, then that particular compound should be studied to verify the complete extraction of lead.

The effect of volume of the organic to the aqueous phase was studied for volumes ranging from 1:25 to 250:25. Extraction was complete over the entire range with a single extraction and was independent of the volume of the two phases.

Experimental procedure

Many petroleum samples can be analyzed directly, simply by diluting with xylene in order to reduce the amount of carbonaceous matrix of the oil sample and to give a lead concentration in the appropriate range. In case the carbonaceous matrix and/or the viscosity of the sample are too high, the lead can be extracted by the procedure discussed above and summarized below. A sample of petroleum is weighed

out and diluted with xylene to reduce the viscosity, dithizone is added, and the lead is extracted into a known volume of 40% (v/v) nitric acid. The dilution with xylene is not strictly necessary but facilitates the extraction. Usually the sample size was about 4–10 g and the volume of the aqueous phase 25–50 ml, but these quantities can be increased or decreased to give a lead concentration in the optimal range.

Standard solutions of lead, prepared either from TEL or from Pb-CHB, were used for the analysis of the organo-lead (organic phase), and lead nitrate for the analysis of aqueous lead solutions. Blank solutions of xylene or 40% (v/v) nitric acid gave no signal, even with full ($\times 10$) scale expansion. No background correction with a deuterium source for molecular band absorption and/or scatter was found necessary for any of the samples analyzed.

RESULTS AND DISCUSSION

Sensitivity and detection limit

The effects of the hydrogen diffusion flame, the solvent type, and the chemical nature of the lead compound on the sensitivity of the lead signal, and a comparison of the sensitivity of the two lead lines at 217.00 nm and at 283.31 nm were studied. The results are presented in Table I. It may be concluded that the hydrogen diffusion flame, the solvent type, and the chemical nature of the lead compounds used have no effect on the sensitivity at either wavelength. However, the use of the hydrogen diffusion flame is recommended because it prolongs the life of the carbon rods by preventing atmospheric oxygen from burning the rods. Further, any standard lead compounds can probably be used for constructing analytical working curves; also, either xylene, methyl isobutyl ketone (MIBK), or 40% (v/v) nitric acid can be used as solvents for the construction of working curves. The independence of the lead signal from the type of lead compound and from the type of solvent is a decided advantage over flame atomic absorption spectrometry, in which the lead signal is dependent on the nature of the lead compound and the solvent^{19–21}. Although the 217.00-nm line exhibits greater sensitivity than the 283.31-nm line, the greater noise at the former wavelength precludes its use with very low concentrations of lead. The noise at 283.31 nm was

TABLE I

EFFECT OF SOLVENT TYPE, LEAD SALT TYPE, HYDROGEN DIFFUSION FLAME, AND LEAD LINE ON SENSITIVITY OF LEAD

	Sensitivity, <i>g (absolute)</i> ^{a,b}			
	217.00 nm		283.31 nm	
	Flame ^c	No flame	Flame ^c	No flame
Pb-CHB in xylene	—	—	$2 \cdot 10^{-11}$	—
TEL in xylene	$1 \cdot 10^{-11}$	$1 \cdot 10^{-11}$	$2 \cdot 10^{-11}$	$2 \cdot 10^{-11}$
TEL in MIBK	$1 \cdot 10^{-11}$	—	$2 \cdot 10^{-11}$	—
Pb nitrate in 40% (v/v) nitric acid	$1 \cdot 10^{-11}$	$1 \cdot 10^{-11}$	$2 \cdot 10^{-11}$	$2 \cdot 10^{-11}$

^a Sensitivity is defined as the mass in g (absolute) giving 1% absorption.

^b Sample size = 2 μ l.

^c Hydrogen flow for diffusion flame = 1.0 l min⁻¹.

about ninefold less than at 217.00 nm; the greater noise was mainly the result of the increased photomultiplier voltage required to detect the signal at the lower wavelength.

The detection limit (defined as $S/N=2$, where S = signal and N = root-mean-square noise) for lead at 283.31 nm with the carbon rod atomizer was $2 \cdot 10^{-12}$ g (absolute). This value compares favorably with the value of $2 \cdot 10^{-12}$ g (absolute) obtained by L'vov²², and $5 \cdot 10^{-12}$ g (absolute) obtained by Brodie and Matousek¹⁴ with a carbon rod atomizer identical to that used in the present study.

Interferences

One-thousand fold mass excesses of Ba^{2+} , Ca^{2+} , Ce^{3+} , Co^{2+} , Cr^{3+} , Cu^{2+} , Fe^{3+} , Mg^{2+} , Na^+ , Ni^{2+} , and Zn^{2+} , prepared from the nitrate salt, and chloride or phosphate, prepared from the sodium salt, were added to aqueous solutions containing $0.2 \mu\text{g Pb ml}^{-1}$ and the lead was determined by means of the carbon rod. Any change in absorbance signal due to these ions was less than 10%, and therefore was considered to be tolerable. One-hundred fold mass excesses of Cu^{2+} , Fe^{3+} , and Ni^{2+} , prepared from the organometallic salts given above, and Ag^+ prepared from the nitrate salt dissolved in the presence of triisooctyl phosphorothioate, were added to xylene solutions containing $0.2 \mu\text{g Pb ml}^{-1}$ and lead was determined. The presence of foreign species produced signal changes of less than 10% and therefore were not considered to interfere.

Matousek and Stevens¹³ and Brodie and Matousek¹⁴ experienced difficulties with absorption signal reproducibility for nearly neutral aqueous solutions of various metals with the carbon rod. They attributed the difficulty to differing viscosity of the solutions, which resulted in the aqueous solutions of samples soaking into the rod to a different extent each time. One solution to the problem adopted by them was to syringe $3 \mu\text{l}$ of xylene onto the carbon rod prior to the addition of the $0.5\text{-}\mu\text{l}$ sample, thus impregnating the rod and preventing the aqueous sample from soaking into the rod. Another solution they adopted was to syringe the sample slowly onto the carbon rod during the drying cycle so that the solvent would evaporate on contact with the heated surface of the rod. This procedure, however, could result in the sample evaporating within the tip of the syringe, causing poor reproducibility.

In this study, this problem was also encountered with lead nitrate solutions prepared in 1% (v/v) nitric acid: the signal was highly irreproducible and always smaller than that obtained for lead in 40% (v/v) nitric acid solutions, which showed typical coefficients of variation of less than 5% for almost the entire range of lead concentration studied. From this, it may be concluded that the high concentration of nitric acid functions in a manner similar to xylene and MIBK, giving better reproducibility than nearly neutral aqueous solutions.

Analysis of petroleum and petroleum products

The results of analysis of petroleum and various petroleum products are presented in Table II, along with results from other studies. All samples were analyzed directly after dilution (if necessary) with xylene to give a lead concentration in the appropriate range. The removal of the carbonaceous matrix during the ashing cycle presented no problem. The used bunker oil, the used jet engine oils, and the crude oils were also analyzed by following the extraction procedure described above. Extraction

TABLE II

RESULTS OF ANALYSIS OF PETROLEUM SAMPLES FOR LEAD

Sample description	Concentration	
	This study ^a (no extraction)	Other studies ^c
Esso "Regular" Gasoline	2.9 ± 0.2 ml TEL/U.S. gal.	3.00 ml TEL/U.S. gal. ^b
Esso "2000" (Low Lead) Gasoline	0.49 ± 0.05 ml TEL/U.S. gal.	≤ 0.50 ml TEL/U.S. gal. ^b
Texaco Bunker C No. 6 Heating Fuel Oil	2.0 ± 0.2 µg Pb/g oil	—
U.S.A.F. Jet Engine Lubricating Oil No. 68-1	11.9 ± 0.3 µg Pb/ml oil	1.8 ^{c,d} ; 10.8 ^{c,e} µg Pb/ml oil ^g
U.S.A.F. Jet Engine Lubricating Oil No. 70-2A	4.4 ± 0.1 µg Pb/ml oil	0.5 ± 0.5 ^{c,d} ; 2.4 ± 1.3 ^{c,e} µg Pb/ml oil
U.S.A.F. Jet Engine Lubricating Oil No. 70-3A	3.7 ± 0.1 µg Pb/ml oil	0.5 ^{c,d} ; 2.2 ± 1.0 ^{c,e} µg Pb/ml oil
Venezuela Crude Oil - Guanipa	0.31 ± 0.02 µg Pb/g oil	—
Venezuela Crude Oil - T.V. 102	0.17 ± 0.02 µg Pb/g oil	—

^a Standard deviations are shown as ±.

^b Values supplied by Imperial Oil Ltd., Montreal, Quebec.

^c Analysis by various U.S.A.F. Central Labs and Base Labs.

^d Value obtained by spark atomic emission.

^e Value obtained by flame atomic absorption.

was complete for the bunker oil sample and the crude oil samples; no signal was obtained from the organic phase after the extraction, and the same concentration of lead was obtained by following the extraction procedure as by following the nonextraction procedure. The jet engine oil samples gave lower results when the extraction procedure was followed, and the analysis of the organic phase after the extraction indicated only partial extraction of lead. The lead was not readily extracted, presumably because it was present as particulates suspended in the organic phase rather than in a dissolved form. For particulate lead to be extracted, it must first be dissolved, which occurs slowly as the particulate species come into contact with the highly acidic aqueous phase. The percent extracted and the rate of extraction would also be a function of the size distribution of the particulate lead in the sample. The large scatter of results obtained by other workers (see Table II) for analysis of these jet oil samples would support the above presumption for particulate lead. In the case of particulates, the results would therefore be highly dependent on the solution preparation and pretreatment as well as the method of analysis. The fact that a larger lead signal was obtained by using the carbon rod than by using flame or spark atomization devices indicates that the carbon rod is a more efficient atomizer of particulates.

Recovery studies with the crude oil samples showed that TEL added to the crude oil was completely extracted.

The coefficients of variation of replicate determinations with the extraction procedure were significantly larger than those obtained by using the direct analysis procedure. Because of the increased uncertainty introduced by the additional (extraction) step, the additional time involved, and the nonquantitative extraction of particulate lead in the used jet engine oil samples, the extraction procedure is not re-

commended for general application but does appear to be useful for samples in which the lead is completely dissolved, *e.g.* crude oil, or for samples in which the lead concentration is too low.

CONCLUSIONS

The analysis of petroleum and petroleum products for lead with the carbon rod atomizer directly in the organic matrix has been demonstrated to be fast, accurate, sensitive. Many of the problems normally encountered in sample and standard preparation for flame atomic absorption analysis are avoided entirely. No real problems were encountered with the carbon rod in the routine analysis of petroleum products. Preliminary studies in this laboratory indicate that the determination of most other metals normally present in petroleum matrixes is also feasible. Analysis of extremely low concentrations of metals should be possible with preconcentration by extraction from a large petroleum sample into a small volume of aqueous solution.

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SUMMARY

The use of a carbon rod atomizer for the analysis of lead in petroleum and petroleum products is described. Variables affecting sensitivity studied include: type of lead salt and type of solvent for standard and sample preparation, hydrogen diffusion flame, choice of analytical wavelength and interferences. For the 217.00-nm line, a sensitivity of $1 \cdot 10^{-11}$ g (absolute) and for the 283.31-nm line, a detection limit of $2 \cdot 10^{-12}$ g (absolute) are reported. Results of analysis of gasoline, used bunker heating oil, used jet engine lubricating oil, and crude oil for lead content are presented. An organic-to-aqueous solvent extraction system for lead is described.

RÉSUMÉ

Un nouveau type d'atomiseur est proposé pour le dosage du plomb dans le pétrole et dans des produits dérivés. On examine les divers paramètres pouvant affecter la sensibilité. On arrive à une sensibilité de $1 \cdot 10^{-11}$ g, à 217.00 nm; et à une limite de détection de $2 \cdot 10^{-12}$ g, à 283.31 nm. On propose en outre une méthode d'extraction du plomb.

ZUSAMMENFASSUNG

Die Anwendung einer Graphitstab-Küvette für die Bestimmung von Blei in Erdöl und Erdölprodukten wird beschrieben. Zu den untersuchten Variablen, die die Empfindlichkeit beeinflussen, gehören: Art des Bleisalzes und des Lösungsmittels für die Vergleichs- und Probenlösungen, Wasserstoffdiffusionsflamme, Wahl der analytischen Wellenlänge und Störungen. Bei 217.00 nm ist die Empfindlichkeit $1 \cdot 10^{-11}$ g (absolut) und bei 283.31 nm die Nachweisgrenze $2 \cdot 10^{-12}$ g (absolut). Die Analyseergebnisse von Benzin, gebrauchtem Bunkerheizöl und Düsen-Schmier-

öl sowie Rohöl werden vorgelegt. Ein System für die Extraktion von Blei aus organischer in wässrige Phase wird beschrieben.

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DETERMINATION OF MICROAMOUNTS OF LEAD IN COPPER, NICKEL AND ALUMINIUM METALS AND IN COPPER-BASE ALLOYS BY SOLVENT EXTRACTION AND ATOMIC ABSORPTION SPECTROMETRY

I. TSUKAHARA and T. YAMAMOTO

Furukawa Electric Co., Ltd., Central Research Laboratory, 2-9-15, Futaba, Shinagawa-ku, Tokyo (Japan)

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Until recently, the determination of lead in copper, nickel and aluminium metals, and in copper-base alloys has usually been performed by gravimetry based on electrodeposition of lead peroxide, colorimetry with dithizone, polarography, or emission spectroscopy. However, these methods have inherent disadvantages. The gravimetric method is time-consuming and insensitive. The colorimetric method is sensitive, but technically complex. Polarography is relatively time-consuming and less sensitive. Emission spectroscopy is rapid, but is subject to matrix interferences and regular calibration against similar samples of known lead content is necessary. A rapid and sensitive method for the determination of lead in the above materials is therefore considered to be desirable.

Atomic absorption spectrometry has recently become an increasingly important tool in a field of trace analysis for impurities in metals and alloys. Elwell and Gidley¹ have reported the determination of larger amounts (0.05–5%) of lead in copper-base alloys and steels by direct atomic absorption spectrometry. In general, for the sensitive and satisfactory determination of trace amounts (0.001% levels or less) of lead, a preconcentration or a separation of lead is usually required. Burke² and Dagnall *et al.*³ successfully used a coprecipitation technique to concentrate lead and determined microamounts of lead in nickel or in steels, brass and bronze by atomic absorption spectrometry, but these procedures are relatively time-consuming.

A solvent extraction technique in conjunction with atomic absorption spectrometry has great advantages because it enables rapid and sensitive determination of lead through extraction and concentration of microamounts of lead into an organic solvent and spraying it directly into the flame; moreover, interferences from matrix elements are avoided by selective extraction. The present paper describes an atomic absorption method for the determination of microamounts of lead in copper, nickel, aluminium metals, and copper-base alloys. The proposed method involves the extraction of lead with a methyl isobutyl ketone solution of a liquid anion-exchanger and the direct spraying of the extract into the flame, which have been successfully used by the authors⁴ for the determination of cadmium and zinc in copper, nickel, aluminium and uranium metals. The method is simple, rapid and sensitive, and could perhaps be advantageously applied to other metals and alloys. The optimal conditions for the extraction and determination of lead are discussed.

EXPERIMENTAL

Apparatus

A Hitachi 208 atomic absorption spectrophotometer with a three-slot 10-cm long burner and a lead hollow-cathode lamp was used with the following operating conditions:

Wavelength	283.3 nm	Air pressure	1.8 kg cm ⁻²
Slit width	0.18 mm	flow rate	15 l min ⁻¹
Burner height	2-position	Acetylene pressure	0.5 kg cm ⁻²
Lamp current	10 mA	flow rate	1.5 l min ⁻¹

An automatic recorder readout was used with scale expansion.

Reagents

All the reagents used were of JIS-special grade.

Liquid anion-exchanger solution (0.2–10 v/v%). Dissolve tri-*n*-octylamine (commercial name Farmin T-08; Kao Soap Co., Ltd.) or methylbenzylaurioctylammonium chloride (MBLOAC; commercial name Moonion A-9Q-08; Kao Soap Co., Ltd.), in methyl isobutyl ketone (MIBK), *n*-butyl acetate, or ethyl acetate. Change MBLOAC to the bromide-form (MBLOAB) in the following manner: transfer the solution to a separatory funnel and shake vigorously with 1 M hydrobromic acid. Discard the aqueous layer and shake again with 1 M hydrobromic acid. Discard the aqueous layer and centrifuge the organic layer in order to separate completely the aqueous layer.

Standard lead solution. Dissolve 0.100 g of high-purity lead metal in 5 ml of nitric acid (1 + 1). Make basic with ammonia, filter precipitated lead hydroxide and wash the precipitate with diluted ammonia. Dissolve the precipitate with 30 ml of 4 M hydrobromic acid and dilute the solution to 100 ml with water (stock solution). Standardize the stock solution by titration with EDTA. Before use, dilute the stock solution to the appropriate concentration.

Recommended procedures

Determination of lead in copper and nickel metals. Dissolve 1.0 g of sample in 15.0 ml of nitric acid (1 + 1). Add 15.0 ml of sulfuric acid (1 + 1) and evaporate the solution to fumes in order to expel nitric acid. Transfer with 10.0 ml of 1 M hydrobromic acid to a 100-ml separatory funnel and make up to 50 ml with water. Shake vigorously with 10.0 ml of 3% (v/v) MBLOAB–MIBK solution for 5 min. Discard the aqueous layer. Transfer the organic layer to a 10-ml volumetric tube and make up to 10 ml with MIBK. Spray into the flame in the usual way and determine the amount of lead from the calibration curve (see below).

Determination of lead in aluminium metal. Decompose 1.0 g of sample with 15.0 ml of 20% (w/v) sodium hydroxide solution and make acidic with 15.0 ml of sulfuric acid (1 + 1) and 10.0 ml of 1 M hydrobromic acid. Transfer to a 100-ml separatory funnel and make up to 50 ml with water. Determine the amount of lead as described above.

Determination of lead in copper-base alloys. Dissolve 0.1–0.3 g of sample according to its zinc content (the presence of more than 80 mg of zinc in the sample taken is undesirable because of its interference with the determination of lead) in 5.0

ml of nitric acid (1 + 1). Add 10.0 ml of sulfuric acid (1 + 1) and evaporate the solution to fumes in order to expel nitric acid. Complete the determination of lead as described above.

Preparation of calibration curves. Transfer aliquots of the standard lead solution, containing appropriate amounts of lead according to the lead content in the sample to be analyzed, to 100-ml separatory funnels. To each solution and a blank (water), add 10.0 ml of 1 M hydrobromic acid and make the volumes up to 50 ml with water. Extract the lead and measure the relationship between the scale reading and the amounts of lead as described above.

RESULTS AND DISCUSSION

Effects of solvent and hydrobromic acid concentration

It is well known that bromo- and chloro-complexes of lead can be extracted from aqueous solution into organic solvents with the secondary and tertiary amine and quaternary ammonium salts of high molecular weight which have become familiar as liquid anion-exchangers. In this study, the effects of different extractants for lead (solutions of tri-*n*-octylamine or of MBLOAB) in different diluents (MIBK, *n*-butyl acetate and ethyl acetate), and of the concentration of hydrobromic acid on the extraction were investigated. A series of solutions containing 20 μg of lead was prepared and the hydrobromic acid concentration of each solution was adjusted; the final volume of the aqueous phase was 50 ml. Lead was extracted with 10 ml of the solvents and the atomic absorption of lead was measured in the usual way after the volume of organic layer was adjusted to 10 ml with the corresponding diluent.

The results (Figs. 1 and 2) show that lead could be best extracted from 0.5 M hydrobromic acid with the tri-*n*-octylamine solutions and with MBLOAB-ethyl acetate solution, and from 0.2–1.0 M hydrobromic acid with the MBLOAB-MIBK

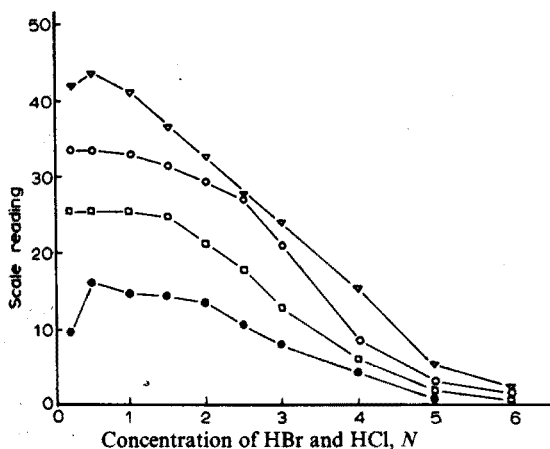


Fig. 1. Effects of solvent, and of hydrobromic and hydrochloric acids concentration on the extraction of lead. Pb taken 20 μg ; volume of aq. phase 50 ml; solvent used 10 ml; concentration of MBLOAB and MBLOAC in diluents 3% (v/v). (▽) MBLOAB-ethyl acetate-HBr; (○) MBLOAB-MIBK-HBr; (□) MBLOAB-butyl acetate-HBr; (●) MBLOAC-MIBK-HCl.

and MBLOAB–butyl acetate solutions; in general, the scale readings with the MBLOAB solutions were higher than those with the tri-*n*-octylamine solutions in corresponding diluents.

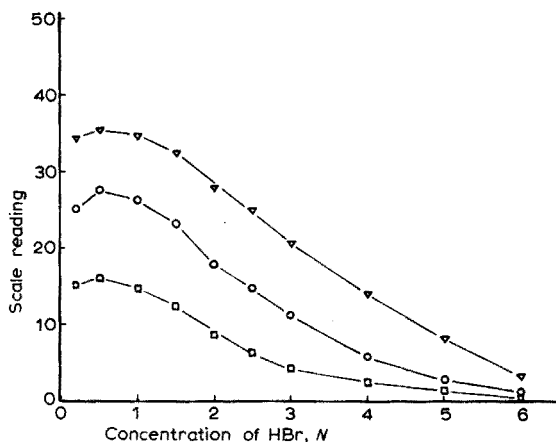


Fig. 2. Effects of solvent and hydrobromic acid concentration on the extraction of lead. Pb taken 20 μ g; volume of aq. phase 50 ml; solvent used 10 ml; concentration of tri-*n*-octylamine in diluents 3% (v/v). (V) Tri-*n*-octylamine–ethyl acetate; (O) tri-*n*-octylamine–MIBK; (□) tri-*n*-octylamine–butyl acetate.

Differences in the scale readings between MIBK, *n*-butyl acetate and ethyl acetate at the respective optimal hydrobromic acid concentrations were also observed; the scale readings with MIBK and *n*-butyl acetate as the diluent were about 75% and 50% with respect to that with ethyl acetate. These differences may not be due to the differences in extractability of lead, but are probably due to the differences in the aspiration rate among these diluents owing to their viscosities. Benzene, xylene, and isoamyl alcohol were also investigated for the diluent, but they were unsuitable because of lower scale readings than MIBK or because of fluctuations of the scale readings.

The extraction of lead from hydrochloric acid solution with MBLOAC–MIBK solution was found to be unsuitable because of the lower extractability of lead (Fig. 1).

From these results, the MBLOAB–ethyl acetate–HBr system appeared to be best for the extraction and determination of lead, but it had a disadvantage in that the solubility of ethyl acetate in the aqueous phase was large and the initial volume (10 ml) of the MBLOAB–ethyl acetate phase decreased to about 5 ml on the extraction of lead. Therefore, the MBLOAB–MIBK–HBr system was adopted for the extraction of lead in this study.

Effects of air and acetylene flow rates

The effects of the air and acetylene flow rates on the atomic absorption of lead were investigated. The results are given in Fig. 3. The scale reading decreased with an increase in the air flow rate, and for larger acetylene–air flow ratios, the flame was yellow and fluctuations of recorder readouts were observed. These may be due to a reducing condition of the flame with incomplete combustion of the organic solvent. For lower acetylene–air flow ratios, the flame was blue and steady recorder readouts

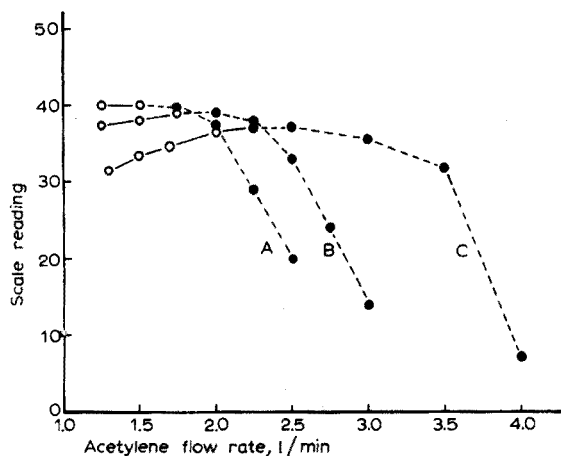


Fig. 3. Effects of air and acetylene flow rates on the atomic absorption of lead. Pb taken $20 \mu\text{g}$; solvent used 3% (v/v) solution of MBLOAB in MIBK; air flow rate: (A) 13 l min^{-1} , (B) 14 l min^{-1} , (C) 15 l min^{-1} . White and black circles represent blue and yellow flames respectively. Solid and dotted lines represent steady and fluctuating recorder readouts respectively.

were obtained. In this study, 1.5 l min^{-1} of acetylene flow rate and 15 l min^{-1} of air flow rate were chosen.

The effects of burner height and lamp current were also investigated, but proved to be very small.

Effect of MBLOAB concentration

The effect of the concentration of MBLOAB in MIBK on the scale reading was investigated. The results are shown in Fig. 4. With solutions of MBLOAB below 2%, the scale reading increased rapidly with an increase in the MBLOAB concentration,

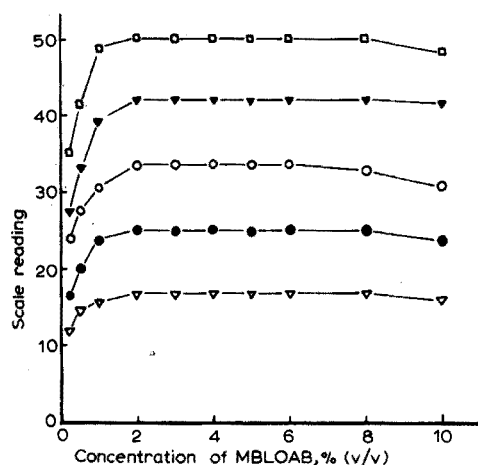


Fig. 4. Effect of MBLOAB concentration on the atomic absorption of lead. Diluent used MIBK; solvent used 10 ml; volume of aq. phase 50 ml; hydrobromic acid concentration 0.2 M. Element taken: (O) $20 \mu\text{g Pb}$, (●) $15 \mu\text{g Pb} + 1 \text{ g Cu}$, (∇) $10 \mu\text{g Pb} + 50 \text{ mg Zn}$, (▼) $25 \mu\text{g Pb} + 1 \text{ g Ni}$, (□) $30 \mu\text{g Pb} + 1 \text{ g Al}$.

and finally reached a plateau. This increase may be due to an increase in extractability of lead with an increase in the MBLOAB concentration. With 10% MBLOAB concentration, the scale reading decreased slightly, possibly because of a decrease in sample aspiration rate with the increased viscosity of the solvent. In this study, a 3% solution of MBLOAB in MIBK was chosen.

Effects of diverse acids

The effects of diverse acids in the aqueous phase on the extraction of lead were investigated. The results (Fig. 5) show that up to 3 M sulfuric acid had no effect, but hydrochloric, nitric, and perchloric acids diminished the extraction. In further investigations, it was found that more than 0.01 M nitric or 0.001 M perchloric acids interfered. There was no interference from 0.3 M phosphoric acid.

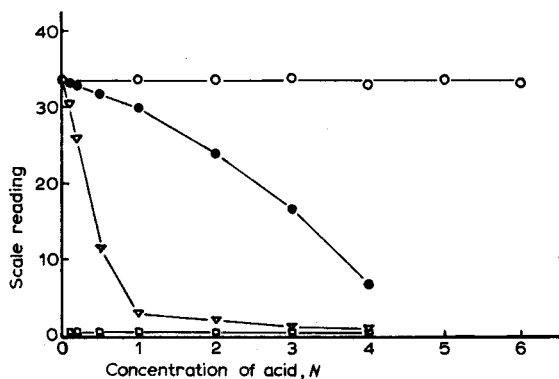


Fig. 5. Effects of diverse acids on the extraction of lead. Pb taken 20 μ g; volume of aq. phase 50 ml; hydrobromic acid concentration 0.2 M; solvent used 10 ml of 3% (v/v) MBLOAB-MIBK solution. Acid added: (○) H₂SO₄, (●) HCl, (▽) HNO₃, (□) HClO₄.

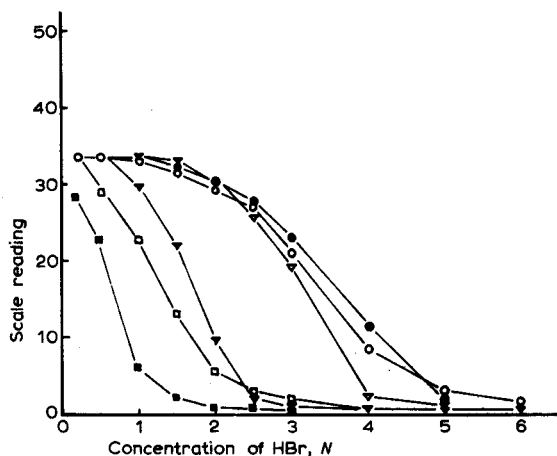


Fig. 6. Effects of copper, nickel, aluminium and zinc on the extraction of lead. Pb taken 20 μ g; volume of aq. phase 50 ml; solvent used 10 ml of 3% (v/v) MBLOAB-MIBK solution. Additions: (○) no addition, (▽) 1 g Al, (●) 1 g Ni, (▽) 1 g Cu, (□) 50 mg Zn, (■) 500 mg Zn.

Effects of various elements

As it was intended to determine lead in copper, nickel and aluminium metals, and in copper-base alloys, the effects of large amounts of copper, nickel, aluminium, and zinc on the determination of lead were first studied. The results obtained are shown in Fig. 6 and Table I. As shown in Fig. 6, 1 g of nickel or aluminium did not interfere with the determination of lead. The presence of 1 g of copper, or of 50 mg of zinc narrowed the optimal hydrobromic acid concentration range for the extraction. Especially, in the presence of 0.5 g of zinc, the scale reading fell off rapidly with an increase in the hydrobromic acid concentration. These effects may be due to a decrease in extractability of lead because of extraction of a bromo-complex of copper or zinc, as shown in Fig. 7.

From these results, a hydrobromic acid concentration of 0.2 M was chosen

TABLE I

EFFECT OF ZINC ON THE DETERMINATION OF LEAD

(Pb taken 20 μg ; MBLOAB-MIBK solution used 10 ml; hydrobromic acid concentration 0.2 M; final volume of aqueous phase 50 ml)

Addition (mg)	Scale reading	Addition (mg)	Scale reading
Zn 0	33.5	Zn 0, Cu 0	33.5
Zn 20	33.5	Zn 20, Cu 80	33.2
Zn 40	33.3	Zn 40, Cu 60	34.0
Zn 80	33.0	Zn 80, Cu 20	33.5
Zn 100	31.2	Zn 100, Cu 900	31.5
Zn 200	30.5	Zn 200, Cu 800	30.8
Zn 300	29.8	Zn 300, Cu 700	29.8
Zn 400	28.8	Zn 400, Cu 600	28.5
Zn 500	28.1	Zn 500, Cu 500	27.8
Zn 600	25.5	Zn 600, Cu 400	25.1

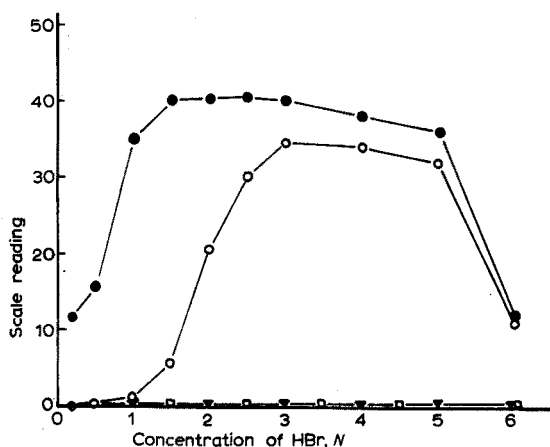


Fig. 7. Extractabilities of copper, nickel, aluminium and zinc from hydrobromic acid solution with MBLOAB-MIBK solution. Volume of aq. phase 50 ml; solvent used 10 ml of 3% (v/v) MBLOAB-MIBK solution. Element taken: (○) 5 μg Cu, (□) 100 μg Ni, (▼) 1000 μg Al, (●) 1 μg Zn.

for the extraction of lead. At this concentration, 1 g of copper, nickel and aluminium did not interfere. However, as shown in Table I, more than 80 mg of zinc interfered, even when lead was extracted from 0.2 M hydrobromic acid solution. The presence of more than 80 mg of zinc in a sample taken is therefore undesirable.

The interfering effects of other elements found generally in copper, nickel, aluminium metals, and copper-base alloys were then investigated. Amounts of 10 mg of As(III), Bi³⁺, Cd²⁺, Co²⁺, Cr³⁺, Fe³⁺, Ga³⁺, In³⁺, Mg²⁺, Mn²⁺, Sb(III), Se(VI), Sn⁴⁺, Ti⁴⁺, V(V), and 0.1 mg of Ag⁺ did not interfere.

TABLE II

ANALYTICAL RESULTS FOR COPPER, NICKEL, ALUMINIUM METALS, AND COPPER-BASE ALLOYS

Sample	Composition (%)	Pb determined (p.p.m.)	
		Proposed method	Other method
Copper metal (VMC)	Cu > 99.99	1, 1, 2	< 3 ^a
Copper metal (tough pitch)	Cu > 99.90	26, 26, 27	28 ^a
Copper metal (electrolytic)	Cu > 99.96	8.0, 7.8, 7.8	10 ^a
Copper metal (electrolytic)	Cu > 99.96	0.5, 0.5, 0.4	< 3 ^a
Nickel metal (electrolytic)	Ni > 99.9	0.8, 0.8, 0.9	0.8 ^b
Nickel metal (electrolytic)	Ni > 99.9	3.6, 3.4, 3.7	3 ^b
Aluminium metal (high-purity)	Al > 99.99	1, 2, 2	
Aluminium metal	Al > 99.0	10, 10, 11	
Brass	Cu: 60.62 Zn: balance	176, 178, 182	170 ^b
Brass	Cu: 78.08 Al: 2.03 As: 0.048 Si: 0.22 Zn: balance	12, 12, 13	10 ^b
Nickel silver	Cu: 55.11 Ni: 18.20 Mn: 0.27 Zn: balance	23, 24, 25	29 ^b

^a Emission spectrophotometric method.

^b Colorimetric method with dithizone.

Analytical results for copper, nickel, aluminium and copper-base alloys

Lead was determined in a variety of copper, nickel and aluminium metals, and copper-base alloys by the proposed method. The results (Table II) were in good agreement with those determined by other methods. The precision of the method was good, and the detection limit by this method was 0.2 µg of lead. The proposed method is rapid and sensitive, and considered to be satisfactory.

SUMMARY

A rapid and sensitive method has been developed for the determination of microamounts of lead in copper, nickel and aluminium metals, and copper-base alloys. Optimal conditions have been established for the extraction and determination of lead. Lead is extracted with a methyl isobutyl ketone solution of methylbenzyl-lauryloctylammonium bromide and determined by atomic absorption spectrometry. As little as 0.5 p.p.m. of lead in copper, nickel and aluminium metals, and 5 p.p.m. of lead in copper-base alloys can be determined.

RÉSUMÉ

Une méthode rapide et sensible est proposée pour le dosage de microquantités de plomb dans le cuivre, le nickel et l'aluminium, ainsi que dans des alliages à base de cuivre. Le plomb est extrait au moyen d'une solution de bromure de méthylbenzyl-lauryloctylammonium dans la méthylisobutylcétone et dosé ensuite par spectrophotométrie d'absorption atomique. On peut déterminer ainsi 5 p.p.m. de plomb dans des alliages de cuivre.

ZUSAMMENFASSUNG

Für die Bestimmung von Mikromengen Blei in Kupfer-, Nickel- und Aluminiummetall sowie in Kupferlegierungen wurde eine schnelle und empfindliche Methode entwickelt. Die optimalen Bedingungen für die Extraktion und die Bestimmung von Blei wurden ermittelt. Blei wird mit einer Lösung von Methylbenzyl-lauryloctylammoniumbromid in Methylisobutylketon extrahiert und durch Atomabsorptionsspektrophotometrie bestimmt. Es können so geringe Mengen wie 0.5 p.p.m. Blei in Kupfer-, Nickel- und Aluminiummetall sowie 5 p.p.m. Blei in Kupferlegierungen bestimmt werden.

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MICRODETERMINATION OF LEAD WITH DITHIZONE AND THE RING-OVEN TECHNIQUE

A. D. SHENDRIKAR and PHILIP W. WEST

Coates Chemical Laboratories, Louisiana State University, Baton Rouge, La. 70803 (U.S.A.)

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Lead and its compounds represent an occupational hazard of considerable importance. The toxicology of lead is very complex. It is a general metabolic poison and cumulative in human beings. It is known to inhibit enzyme systems necessary for the formation of hemoglobin. Traces of lead are frequently determined in air¹, blood², and biological materials³ by various analytical instruments. The most favored instrument is the atomic absorption spectrometer which is relatively expensive and requires time-consuming sample preparation. If the boat technique or a heated graphite atomizer is used, the sample preparation step can be avoided but there is an additional increase in the cost of equipment. The work reported here was carried out with the aim of developing a sensitive, inexpensive, and rapid analytical method for the determination of traces of lead, particularly in air. Because the ring-oven technique in general meets the above mentioned criteria, it was chosen for the study.

Although the ring-oven technique was introduced in 1954 by Weisz⁴, its earlier applications were limited to qualitative analysis. During the last decade, however, the technique has been frequently used for the determination of various elements in trace quantities⁵⁻⁹. The methods usually apply to microgram to nanogram levels and accuracies of the results are comparable with those obtained by emission spectroscopy and polarography. Fugas and Paukovic¹⁰ have developed a ring-oven method for determination of lead as chromate and have applied this method for determining lead in smoke. They have tested the reliability of the ring-oven data by simultaneously analyzing smoke samples by the ring-oven method and by atomic absorption spectrometry and found good agreement. Using the ring-oven technique, Jungreis and West¹¹ have described a method for the microdetermination of lead and found this method to be suitable for determining lead in air.

EXPERIMENTAL

Reagents and solutions

In general, great care was taken to ensure that reagents and solutions used (including distilled water) were free from possible lead contamination. In the course of this study, ammonia liquor was found to be contaminated with traces of lead and, therefore, distilled ammonia was used.

Diphenylthiocarbazone (dithizone) solution. Dithizone was purified by the recommended procedure¹² and a 0.05% (w/v) solution in carbon tetrachloride was prepared.

Standard lead solution. A solution containing 1.00 mg ml^{-1} was prepared by dissolving 1.00 g of pure lead in a minimal volume of nitric acid. The solution was boiled to expel oxides of nitrogen and finally made to 1 l with distilled water. The stock solution was further diluted as required for preparing standard working solutions.

Alkaline ammonium acetate solution. A 15% (w/v) solution of ammonium acetate was adjusted to pH 8.00 with lead-free ammonia solution.

Wash solution. A mixture of 0.2% (w/v) sodium cyanide and 2% (v/v) ammonia liquor was used to remove the excess of dithizone from the filter paper.

Interfering ion solutions. $10 \mu\text{g ml}^{-1}$ solutions were prepared and used in the interference studies.

Apparatus

Ring oven. A trace oven with accessories (Arthur H. Thomas, Co., Philadelphia) and surface thermometer (Pacific Transducer Corporation, Model No. 311F) were used. A spray-on "Jet-Pak" power unit (Sprayon Products, Inc.) was used to spray dithizone solution. Filter papers were dried by holding them in front of a hair drier.

The Perkin Elmer 303 atomic absorption spectrophotometer was used for the comparison study. A lead hollow-cathode lamp (Perkin Elmer) with lamp current 7 A, wavelength 283.3 nm, air-acetylene flame and single slot burner, was used. The conventional procedure for the determination of lead was followed¹³.

General procedure

Place the filter paper, the center of which was previously marked with a sharp pin, on the ring oven maintained at about 95° . The temperature of the ring oven is easily adjusted by means of a powerstat and measured with a surface thermometer placed on the hot surface of the ring. Add the appropriate volume of the standard or unknown solution in the center of the paper with a calibrated μl pipet. Add $15 \mu\text{l}$ of alkaline ammonium acetate and $15 \mu\text{l}$ of aqueous 15% (w/v) sodium thiosulfate and wash to the ring with distilled water. The usual precautions of allowing sufficient time between the addition of each solution to permit normal diffusion through the pores of the paper and avoid flooding of the rings are assumed. Also, avoid any diffusion of solution beyond 1 mm from the heating block. Allow the ring to dry thoroughly and then add another $15 \mu\text{l}$ of alkaline ammonium acetate and wash to the ring with distilled water. Add $15 \mu\text{l}$ of aqueous 1.5% (w/v) sodium cyanide solution and again wash to the ring with water. After the ring is completely dry, remove the filter paper from the ring oven and spray the ring area with dithizone solution. Wait about 15 sec for the organic solvent to evaporate, then dip the paper into the wash solution placed in a petri dish. Shake the contents for 3–6 min to remove the excess of dithizone. Wash the filter paper under tap water, then press it between two filter papers and dry thoroughly in a stream of warm air from a hair dryer. The intensity of color of the ring is proportional to the lead concentration.

Analysis of unknown

The general procedure described was followed for the preparation of rings from unknown sample solutions. The standard scale was conveniently prepared by making rings with 0-, 1-, 2-, 4-, 6-, 8-, and $10\text{-}\mu\text{l}$ drops of lead solution containing

0.1 $\mu\text{g Pb } \mu\text{l}^{-1}$. The standard rings were covered with a watch glass and stored in the dark. Rings treated this way were stable for at least 4–6 days.

Three rings made from a different number of microliter drops of the solution are sufficient for each unknown solution. The color intensity of the three rings is visually compared to that of standard rings. The sum of microliter drops of standard solution divided by the sum of the number of microliter drops of the three rings made from unknown solution equals the concentration of the unknown solution. When this quotient is multiplied by the concentration of the standard solution used to prepare standard rings, the concentration of the unknown solution is obtained¹⁴. The accuracy and reproducibility of this method for the microdetermination of lead was ascertained by the procedure described above and the results are shown in Table I.

The limit of detection of lead by the recommended procedure is 0.04 μg while the range recommended for optimal accuracy in quantitative work is 0.05–1.00 μg of lead.

TABLE I

DETERMINATION OF LEAD

<i>Taken (μg)</i>	<i>Found (μg)^a</i>
0.1	0.098 \pm 0.011 ^b
0.2	0.192 \pm 0.013

^a Based on averaging 5 values calculated from three rings each by the method¹⁴ described above.

^b Calculated at 90% confidence level.

RESULTS AND DISCUSSION

Various qualities of filter papers were examined and those checked were found free of lead. Whatman No. 1 was chosen for its wet strength, desired speed of diffusion, regular texture and sensitivity for the lead dithizone reaction. However, Whatman No. 41 was found to be equally suitable, and therefore, tests can also be carried out with Whatman dust tapes.

Dithizone reacts with a number of metal ions under identical conditions and, therefore, in devising an analytical procedure one must take into account all such reacting metals. Because the developed method was to be used for the determination of lead in air, special consideration was given to the interfering species that were most likely to be present together with lead in the air. Preliminary investigations showed that iron would be a potential interference in the lead dithizone reaction, and therefore, must be masked; otherwise, this method would have serious limitations, particularly in air pollution studies. Iron reacts with dithizone producing a red or brick red color similar to that of the lead reaction. Attempts to mask the iron–dithizone reaction with cyanide failed; also, use of other masking agents for iron did not succeed. Of the many masking agents studied only alkaline ammonium acetate (pH 8.00) was found to be effective. It was found to precipitate iron basic acetate quantitatively in the center of the ring without affecting lead. Then lead could be washed to the ring zone with water.

Further experiments showed that the pH of the alkaline ammonium acetate

solution should not be more than 8.50; otherwise, a portion of lead is occluded with the iron hydroxide precipitate, thus affecting the determination of lead.

During the interference studies of cations, copper was found to interfere by reacting with dithizone to produce a gray ring. However, sodium thiosulphate solution was found to mask copper quantitatively. Further, it was also found that sodium thiosulphate enhanced the sensitivity of the lead dithizone reaction by five times and, therefore, the addition of this salt was incorporated in the general procedure.

Dithizone is susceptible to air oxidation and the reaction rate is enhanced during exposure on the hot ring oven. The oxidation products of this reagent appear as dark yellow stains on the filter paper and thus were found to interfere in the quantitative estimation of lead. Therefore, the dithizone solution was sprayed on the ring area from a "Jet-Pak" sprayer after the test rings had been removed from the oven surface. This step was found to be of a great advantage as it eliminated oxidation of the reagent by heat and permitted the relatively easy removal of the excess of dithizone by subsequent washing of the filter paper in a wash solution.

Interference

The effect of interfering ions was investigated by preparing two rings for each ion. The first ring contained 20 μg of the potential interfering ion and the second, 0.2 μg of lead in the presence of 20 μg of the interfering species. The ion was established as non-interfering when the first ring was identical to the blank and the second matched the 0.2- μg lead ring of the standard scale.

The possible interfering effects of the following ions were investigated:

- Group I. Li^+ , Na^+ , K^+ , Cu^{2+} , Rb^+ , Cs^+ , Au^{3+}
- Group II. Be^{2+} , Mg^{2+} , Ca^{2+} , Sr^{2+} , Zn^{2+} , Cd^{2+} , Hg^{2+}
- Group III. BO_2^- , $\text{B}_4\text{O}_7^{2-}$, Al^{3+} , Ce^{3+} , Ce^{4+}
- Group IV. CO_3^{2-} , SiO_3^{2-} , GeO_3^{2-} , Zr^{4+} , Sn^{4+} , Th^{4+}
- Group V. NO_3^- , NO_2^- , HPO_4^{2-} , VO_3^- , As^{5+} , Sb^{5+} , Bi^{3+}
- Group VI. SO_3^{2-} , SO_4^{2-} , $\text{S}_2\text{O}_3^{2-}$, SeO_4^{2-} , TeO_3^{2-} , Cr^{3+} , MoO_4^{2-} , TeO_4^{2-} , WO_4^{2-} , UO_2^{2+}
- Group VII. F^- , Cl^- , ClO_3^- , ClO_4^- , BrO_3^- , I^- , IO_3^- , Mn^{2+}
- Group VIII. Fe^{3+} , Co^{2+} , Ni^{2+} , and Pt^{4+}

Twenty micrograms of molybdenum and tin interfered; however, when the concentration of these two cations was reduced to 10 μg , no interference was observed. The interference of cobalt in the lead dithizone reaction was eliminated by using a 20% sodium nitrite solution. Palladium and tellurium also interfered, even at low concentrations, but the presence of these two elements is of very little significance in air pollution studies.

Ligands such as diethylene glycol, mannitol, malonate, oxalate, tartrate, citrate, lactate, phthalate, sorbitol, inositol, and adipate did not interfere in the determination of lead.

Determination of lead in air

The method thus developed was applied to the determination of lead in air. Mexican air samples (supplied by National Health and Welfare Center of Canada) were analyzed for their lead content. Sampling was done either on membrane filters

or glass fiber paper. An aliquot portion of each air sample was cut out with a hole puncher and fixed in the center of the filter paper placed on the ring oven. The lead content was then determined by following the general procedure described above. Three more discs from different quadrants of the sample were punched and lead was determined. From the original weight of the sample and weight of the four portions analyzed, the lead content of the entire air sample (4.6 cm in diameter) was calculated.

Ring-oven methods in general are often regarded as only semiquantitative. Therefore, the air samples were analyzed simultaneously by ring oven and atomic absorption spectrometry. The data obtained (see Table II) clearly reflect the accuracy and the reliability of the ring-oven technique.

Each air sample was analyzed for its lead content by the ring-oven method as discussed above and total lead was calculated. The remaining portion (weighed) of each sample was then treated with nitric acid, boiled, cooled and filtered and the solution was made up to a known volume. The lead was then determined by conventional atomic absorption spectrometry. Standard lead solutions were treated in a manner similar to that used on the sample solutions for the construction of calibration curves. The total lead content of each sample was calculated and the data compared with that obtained by the ring-oven method. Table II records these values which show good agreement.

TABLE II

LEAD CONTENT OF MEXICAN AIR SAMPLE

Sample no.	ng Pb m ⁻³ by ring oven	ng Pb m ⁻³ by a.a.s.
1	17.20	18.90
2	8.80	8.90
3	5.70	6.00
4	5.30	5.60
5	4.30	4.70
6	8.20	9.10

SUMMARY

A method for the microdetermination of lead with dithizone by the ring-oven technique is presented. The limit of detection is 0.04 μg and the range is 0.05–1.0 μg of lead with no interference from other species that are of significance in air pollution studies. The determinations can be made directly on samples collected on sequential tapes. The applicability and reliability of this method for air pollution studies were verified by analyzing Mexican air samples simultaneously by atomic absorption spectrometry and the ring oven. The data show good agreement. This method is especially recommended for field studies because it is sensitive, rapid, reliable and far less expensive than methods currently in use for lead determinations.

RÉSUMÉ

Une méthode est proposée pour le microdosage du plomb par la dithizone, au moyen de la technique du four circulaire. La limite de détection est de 0.04 μg . On

peut ainsi doser de 0.05 à 1.0 μg de plomb, sans interférence lorsqu'il s'agit de pollution de l'air. Les résultats concordent très bien avec ceux obtenus par spectrophotométrie d'absorption atomique. Cette méthode est spécialement recommandée pour des essais sur le terrain ; elle est sensible, rapide, sûre et beaucoup moins coûteuse que les méthodes généralement utilisées.

ZUSAMMENFASSUNG

Es wird eine Methode für die Mikrobestimmung von Blei mit Dithizon nach dem Ringofen-Verfahren beschrieben. Die Nachweisgrenze ist 0.04 μg , und der Bereich, in dem keine Störungen durch andere, für Luftverunreinigungsuntersuchungen signifikante Spezies auftreten, ist 0.05–1.0 μg Blei. Die Bestimmungen können direkt an Proben vorgenommen werden, die auf fortlaufenden Streifen gesammelt worden sind. Die Anwendbarkeit und Zuverlässigkeit dieser Methode für Luftverunreinigungsuntersuchungen wurden belegt, indem mexikanische Luftproben gleichzeitig durch Atomabsorptionsspektrometrie und nach dem Ringofen-Verfahren analysiert wurden. Die Werte stimmen gut überein. Diese Methode wird besonders für Aussenuntersuchungen empfohlen, da sie empfindlich, schnell, zuverlässig und viel weniger aufwendig als gängige Methoden für Bleibestimmungen ist.

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THE ROLE OF PERCHLORATE ION IN THE CHLOROFORM EXTRACTION OF ZINC WITH OXINE

SHŌHACHIRŌ ŌKI and ISAO TERADA

Faculty of Engineering, Shizuoka University, Hamamatsu (Japan)

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Although it has been stated that zinc oxinate (oxine=8-hydroxyquinoline, HOx) can be extracted with chloroform¹, details of the experimental conditions were not known. Somewhat later, there were no reports supporting the opinion² and it was thought for a while that zinc oxinate could not, or not quantitatively, be extracted with chloroform^{3,4}. It is only in the last decade that zinc oxinate has again been reported to be extracted quantitatively with chloroform⁵⁻⁸. Even now, however, it is not always clear under which conditions zinc oxinate is quantitatively extracted with chloroform without addition of any particular reagent. In order to obtain a better understanding of the extraction stoichiometries of zinc oxinate with chloroform, it was decided to reinvestigate the extraction system. The work described below has shown the important role of perchlorate, which was thought not to have any particular effect on the extraction system in previous work⁵⁻⁸.

EXPERIMENTAL

Materials and apparatus

All the reagents and chemicals were of G.R. grade. Chloroform containing 0.5% (v/v) ethanol was used. A ⁶⁵Zn radiotracer was used in all the distribution ratio measurements.

The apparatus used included a Shimadzu-Bausch-Lomb Spectronic 20 colorimeter and the accessory 0.5-in. diameter test-tubes, a Horiba Model P pH meter, a Kobe AN-10 γ -ray spectrometer equipped with a well-type NaI(Tl) crystal, a Toshiba-Beckman NF-1A atomic absorption spectrophotometer for determination of zinc, and a Toyo GC-S-7.8 gas chromatograph connected with a Yanagimoto Model GP-1000 pyrolysis apparatus for the determination of organic solvents adsorbed in the oxine complex isolated from organic extracts.

Extraction of zinc

A volume (10 ml) of 0.1 M solution of oxine in chloroform and an equal volume of an aqueous solution containing zinc ion labelled with ⁶⁵Zn at a constant ionic strength of 0.1 were equilibrated in a glass-stoppered cylindrical tube for 1 h. The pH of the aqueous phase was adjusted by addition of perchloric, hydrochloric or nitric acid and sodium hydroxide, and the ionic strength was kept constant by addition of sodium perchlorate, chloride or nitrate. The mixture was then centrifuged for 5 min and the radioactivity was measured for aliquots (2 ml) of both phases. The distribution ratio of zinc was defined as the ratio of the radioactivity of the aliquot of

the organic phase to that of the aqueous phase. The pH measurement was carried out with the residual aqueous phase. If necessary, the absorbance (400 nm) of the organic phase was measured against reagent blank. The concentration of hydrogen ion was calculated as $\text{pH} = -\log [\text{H}^+]$.

The extraction experiments were carried out in a temperature-controlled room at 20°.

Isolation of the zinc-oxine complex from the organic extract

To 60 ml of 0.2 M solution of oxine in chloroform were added 30 ml of 0.1 M zinc solution in dilute perchloric acid, 12 ml of 1 M sodium perchlorate solution, 9 ml of 0.5 M sodium hydroxide solution and 9 ml of water in that order. The mixture was then shaken in a separatory funnel for 1 h. The final pH value of the aqueous phase became 3.3–3.4 by this procedure. The organic extract was filtered through a filter paper to remove insoluble suspensions. Then carbon tetrachloride, benzene or *n*-hexane was added gradually to the filtered extract until a white turbidity appeared. The volume of an organic solvent required to precipitate the zinc-oxine complex in the extract amounted to 1–2 times the volume of the extract. After 30–60 min, the precipitate was filtered off on a filter paper and washed with the organic solvent used for precipitating the complex until oxine in the filtrate disappeared. The product was then dried in a vacuum desiccator with the aid of a water-jet pump until constant weight was obtained. About 30% of the zinc was obtained as the zinc-oxine complex by this procedure.

Analysis of zinc-oxine complex in chloroform extract

To 10 ml of a sample organic extract were added aqueous solutions of 5 ml of 0.4 M potassium dihydrogenphosphate (the pH was adjusted to 5.8 by addition of sodium hydroxide) and 5 ml of 0.01 M EDTA. The mixture was then shaken for 30 min to back-extract zinc and perchlorate completely into the aqueous phase. The back-extract was transferred to a suitable volumetric flask and diluted to an appropriate concentration with water. Zinc was determined by the atomic absorption spectrometric method and perchlorate by the absorption spectrophotometric method of Uchikawa⁹.

Analysis of isolated zinc-oxine complex

About 200 mg of the isolated complex was weighed accurately, dissolved in 10 ml of 2 M sulfuric acid, and transferred to a 100-ml volumetric flask, and the volume was made up to the mark with water. Oxine was determined by the bromometric titration of the sample solution. The sample solution was then diluted to an appropriate concentration with water, and zinc and perchlorate were determined as described above. The organic solvents contained in the complex were determined separately by heating the complex at 200° in the pyrolysis-gas chromatographic apparatus.

RESULTS

Extraction of zinc

Figure 1 shows the effect of the concentration of perchlorate ion and pH in the

aqueous phase on the extraction of zinc with 0.1 M oxine in chloroform. The pH ranges for complete extraction were 4.0–5.9 for 0.1 M and 4.3–5.0 for 0.01 M perchlorate solutions. Only incomplete extraction was obtained for the lower concentration of perchlorate ion. It is noticeable that even from the solutions containing chloride ion only, zinc ion could be extracted though only in very small amount.

In order to establish the role of perchlorate ion, the molar ratio of perchlorate to zinc of the extracted complex was determined. The results are summarized in Table I. Blank determinations carried out for the perchlorate analysis showed that a small amount of perchlorate (below $4 \cdot 10^{-6}$ M) was also extracted in the absence of zinc in the initial aqueous phase. It can be seen from Table I that under various conditions the molar ratio of perchlorate to zinc of the extracted complex is 1:2. This fact indicates that the extracted complex is a binuclear or polynuclear one.

Isolated zinc-oxine complex

Since the extracted complex seemed to have a somewhat complicated composition, an attempt was made to isolate the complex directly from the organic extract. The method of the isolation was successfully devised from the fact that the complex was extracted with chloroform but not with carbon tetrachloride, benzene or *n*-hexane; the complex was expected to be precipitated by diluting the chloroform extract with these solvents. The complex thus obtained was a lustrous yellow flocculent precipitate.

The analytical results for the isolated complex are given in Table II. It can be seen that the molar ratio of perchlorate to oxine to zinc of the isolated complex is

TABLE I

COMPOSITION OF EXTRACTED ZINC-OXINE COMPLEX

$C_{HOx}(M)^a$	$C_{ClO_4}(M)^b$	pH ^c	$[Zn]_0(M)$	$[ClO_4]_0(M)$	$[ClO_4]_0/[Zn]_0$
0.1	0.01 ^d	4.94	$9.82 \cdot 10^{-5}$	$4.80 \cdot 10^{-5}$	0.489
0.1	0.1	4.14	$1.04 \cdot 10^{-3}$	$5.05 \cdot 10^{-4}$	0.486
0.2	0.2	3.40	$3.40 \cdot 10^{-3}$	$1.66 \cdot 10^{-3}$	0.488
0.2	0.2	3.56	$3.25 \cdot 10^{-3}$	$1.65 \cdot 10^{-3}$	0.508

^a Initial concentration of oxine in organic phase.

^b Initial concentration of perchlorate ion in aqueous phase.

^c pH after extraction.

^d Containing 0.09 M of chloride ion.

TABLE II

COMPOSITION OF ISOLATED ZINC-OXINE COMPLEX

Zn(%) (I)	HOx(%) (II)	ClO ₄ (%) (III)	(I) + (II) + (III) (%)	$\frac{(HOx)^a}{(Zn)}$	$\frac{(ClO_4)^a}{(Zn)}$	Solvent ^b
11.4	74.6	9.48	95.5	2.95	0.544	CCl ₄
11.1	72.4	8.63	92.1	2.93	0.508	CCl ₄
10.6	69.7	8.42	88.7	2.94	0.520	C ₆ H ₆
10.9	75.9	8.75	95.5	3.12	0.523	<i>n</i> -C ₆ H ₁₄

^a Molar ratio. ^b Solvent used to precipitate complex.

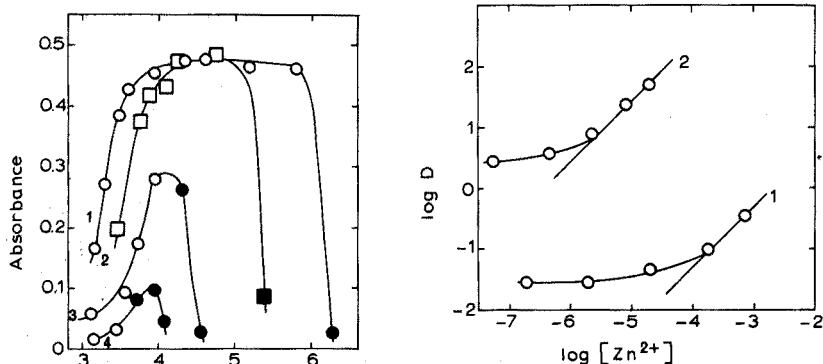


Fig. 1. Extraction curve of zinc with oxine solution in chloroform. $C_{\text{HOx}} 0.1 M$; $C_{\text{Zn}} 2 \cdot 10^{-4} M$; C_{ClO_4} : (1) 0.1 M, (2) 0.01 M, (3) 0.001 M, (4) 0 M. Ionic strength was adjusted to 0.1 by addition of NaCl. Closed symbols show that precipitate appeared between aqueous and organic phases.

Fig. 2. Distribution ratio of zinc as a function of $[\text{Zn}^{2+}]$. $C_{\text{HOx}} 0.1 M$; $C_{\text{ClO}_4} 0.1 M$. pH at equilibrium: (1) 3.00, (2) 4.00. Limiting slope is 1.0 when $[\text{Zn}]_0 \geq 10^{-4.8} M$.

1:6:2. As the molar ratio of perchlorate to zinc is not changed by precipitation, the composition of the zinc-oxine complex in the organic phase is assumed to be $\text{Zn}_{2n}(\text{Ox})_{3n}(\text{HOx})_{3n}(\text{ClO}_4)_n$, where $n = 1, 2, 3 \dots$, considering the electrical neutrality principle.

Distribution data analysis

Since zinc(II) is the predominant zinc-containing species in the aqueous phase at the lower pH range, the mixed equilibrium constant of the extraction of zinc may be given by

$$K = \frac{[\text{Zn}_{2n}(\text{Ox})_{3n}(\text{HOx})_{3n}(\text{ClO}_4)_n]_0 [\text{H}]^{3n}}{[\text{Zn}]^{2n} [\text{HOx}]_0^{6n} [\text{ClO}_4]_0^n} \quad (1)$$

where the subscript 0 indicates the organic phase concentrations, lack of subscripts indicates the aqueous phase, and charges are omitted for simplicity. The distribution ratio of zinc, D , is given by

$$D = \frac{2n [\text{Zn}_{2n}(\text{Ox})_{3n}(\text{HOx})_{3n}(\text{ClO}_4)_n]_0}{[\text{Zn}]} \quad (2)$$

When eqn. (2) is introduced into eqn. (1), the following equation results

$$K = \frac{D [\text{H}]^{3n}}{2n [\text{Zn}]^{2n-1} [\text{HOx}]_0^{6n} [\text{ClO}_4]_0^n} \quad (3)$$

The distribution data are given in Table III. The data can be divided into 11 groups depending on the concentrations of zinc ion, oxine and perchlorate ion and on the inert salts used. Groups 1–5 present the data on the extraction with 0.1 M solutions of oxine in chloroform from aqueous 0.1 M perchlorate solutions. When the data of groups 1–5 were plotted against pH for every group, the distribution ratio at a desired pH was obtained by interpolation for each initial concentration of zinc ion. The distribution ratios at pH 3 and 4 taken from the log D –pH plot were plotted as a

TABLE III

DISTRIBUTION DATA

No: $\log C_{Zn}$, $\log C_{HOx}$, $\log C_{ClO_4}$, *salt*^a: *pH* (*log D*): *Symbol*^b

1:	-3.00, -1.00, -1.00,—: 2.92(-0.74), 3.11(-0.11), 3.36(0.51), 3.61(1.00), 3.95(1.59), 4.03(1.73), 4.26(2.04):○
2:	-3.70, -1.00, -1.00,—: 3.00(-0.94), 3.16(-0.32), 3.53(0.45), 3.76(0.93), 3.94(1.26), 4.56(2.21):⊖
3:	-4.70, -1.00, -1.00,—: 3.01(-1.16), 3.14(-0.82), 3.47(-0.05), 3.75(0.51), 4.13(1.10), 4.50(1.56):●
4:	-5.70, -1.00, -1.00,—: 2.80(-2.20), 2.96(-1.58), 3.16(-0.98), 3.45(-0.63), 3.53(-0.25), 3.95(0.53), 4.38(1.22), 4.56(1.47), 4.99(1.93)
5:	-6.70, -1.00, -1.00,—: 3.17(-1.16), 3.30(-0.82), 3.51(-0.42), 3.80(0.16), 4.22(0.71), 4.49(1.07)
6:	-4.70, -0.52, -1.00,—: 3.12(0.62), 3.95(2.25):●
7:	-3.00, -1.00, -2.00, NaCl: 3.39(-0.02), 4.09(1.33), 4.15(1.38):□
8:	-3.00, -1.30, -2.00, NaCl: 3.95(0.09):⊠
9:	-3.00, -0.70, -2.00, NaCl: 3.40(1.03):⊠
10:	-3.00, -1.00, -2.00, NaNO ₃ : 3.33(-0.06), 3.65(0.56), 4.10(1.28):△
11:	-3.00, -0.70, -2.00, NaNO ₃ : 3.23(0.71), 3.65(1.49):▽

^a Inert salt used to adjust ionic strength 0.1.

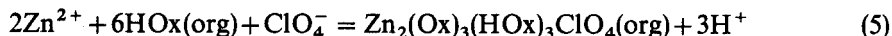
^b Symbol mark used in Fig. 3.

function of the equilibrium concentration of zinc ion in the aqueous phase in Fig. 2. The equilibrium concentration of zinc ion was calculated by eqn. (4), assuming that zinc(II) was predominant in the aqueous phase.

$$[Zn] = C_{Zn}/(1 + D) \quad (4)$$

where C_{Zn} is the initial concentration of zinc ion in the aqueous phase. It can be seen that $\partial \log D / \partial \log [Zn]$ was close to unity when the apparent organic phase concentration of zinc at equilibrium was higher than about $10^{-4.8}$ M. From eqn. (3), this signifies the presence of the binuclear complex ($n=1$) as the sole species at the higher zinc concentration in the organic phase.

In order to test the reaction



$\log D$ was plotted against $\log [Zn] + 6 \log [HOx]_0 + \log [ClO_4] + 3pH$, where (org) refers to the organic phase. The distribution data of groups 1–3 and 7–11 in Table III are plotted in Fig. 3. Chloride and nitrate ions are regarded as inert ions*. The equilibrium organic phase concentration of oxine was calculated from eqn. (6):

$$\log [HOx]_0 = \log C_{HOx} - \log \left(1 + \frac{[H]}{K_1 D_R^0} + \frac{1}{D_R^0} + \frac{K_2}{D_R^0 [H]} \right) \quad (6)$$

where C_{HOx} is the initial organic phase concentration of oxine, and K_1 , K_2 and D_R^0 are the acid dissociation constants of oxinium and oxine and the distribution coefficient

* Nitrate ion practically does not form complexes with zinc ion in the aqueous phase¹¹. The effect of chloride ion under the experimental conditions also seems to be very small in the aqueous phase judging from the stability constants of zinc-chloride complexes¹¹. Moreover, the zinc-oxine complexes extracted from an aqueous solution of 0.01 M perchlorate and 0.09 M chloride also had a molar ratio of perchlorate to zinc of 1:2.

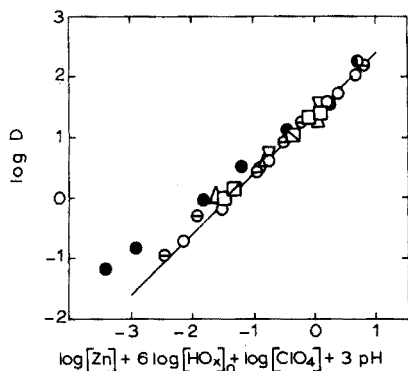


Fig. 3. Determination of K . Refer to Table III for symbols.

of oxine, respectively. The values $pK_1 = 5.14$, $pK_2 = 9.74$, and $\log D_R^0 = 2.64$ were used¹⁰.

The points for various concentrations of perchlorate ion and oxine fell on a single straight line with unit slope when the apparent equilibrium concentration of zinc in the organic phase was higher than $10^{-4.8} M$, indicating the validity of eqn. (5). The data of group 3 deviated from the straight line at the low $\log D$ range where the apparent concentration of zinc in the organic phase was lower than $10^{-4.8} M$. This is due to the presence of a mononuclear zinc-oxine complex in the organic phase in addition to the binuclear complex. From the straight line it was possible to calculate the constant for eqn. (5)

$$K = \frac{[\text{Zn}_2(\text{Ox})_3(\text{HOx})_3\text{ClO}_4][\text{H}]^3}{[\text{Zn}]^2[\text{HOx}]_0^6[\text{ClO}_4]} = 10^{1.10} \quad (7)$$

DISCUSSION

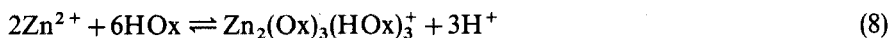
Several workers have successfully extracted zinc with oxine in chloroform from aqueous perchlorate solutions and have developed theoretical treatments of the extraction system regarding perchlorates as inert salts⁵⁻⁸. On the other hand, some workers have failed to extract zinc-oxine complexes with chloroform from some aqueous buffer solutions not containing perchlorates^{3,4}. As shown in Fig. 1 a complete extraction of zinc occurs in the presence of a large excess of perchlorate anion, but a poor extraction in the presence of chloride only. The extractability of zinc can be interpreted from the standpoint of the extraction of an ion-association complex; oxine reacts with zinc ion to form a binuclear cation, $\text{Zn}_2(\text{Ox})_3(\text{HOx})_3^+$, which is extracted by the use of an appropriate counter anion such as perchlorate. Thus, it stands to reason that the large perchlorate anion causes complete extraction, while the small chloride or nitrate anions cause poor extraction. It also follows that many of the common solvents, such as carbon tetrachloride, benzene, toluene, etc., used in the solvent extraction of uncharged chelates do not extract the polar ion-association complex.

Zinc ion was reported to be extracted from aqueous perchlorate solutions with oxine solutions in chloroform in the form of $\text{Zn}(\text{Ox})_2\text{HOx}^6$ or $\text{Zn}(\text{Ox})_2\text{HOx}^{5,8}$. However, it should be pointed out that these conclusions were derived on the false

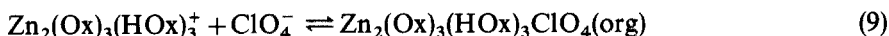
assumptions that the distribution ratio of zinc was independent of the zinc concentration system and that perchlorate was an inert salt.

As shown in Fig. 2, the distribution ratio of zinc becomes independent of the zinc concentration with decreasing concentrations of zinc ion, indicating the presence of a mononuclear zinc-oxine complex in the organic phase. However, the present authors have not yet found comprehensible regularities in the distribution data of zinc at very low concentrations except that perchlorate ion is also indispensable for complete extraction. Zinc ion at a concentration of $10^{-6.3}$ M in the initial aqueous phase was reported⁷ to be extracted in the form of $Zn(Ox)_2HOx$. This conclusion, however, seems also to be incorrect because the important role of perchlorate was disregarded. As for the distribution system, studies are now under way.

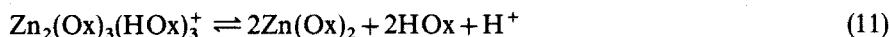
The sudden drops in extraction resulting in the formation of the precipitate between the phases were observed above pH 6.0 (0.1 M perchlorate in the aqueous phase), 5.2 (0.01 M), 4.0 (0.001 M) and 3.5 (0.1 M chloride), respectively. The precipitate could not be re-extracted with oxine in chloroform at any pH even in the presence of a large excess of perchlorate. The precipitate was verified to be the familiar complex of bis-(8-hydroxyquinolino)zinc dihydrate, $Zn(Ox)_2 \cdot 2H_2O$, by infrared measurement. The sudden drops in extraction may be explained as follows. In the aqueous phase at the lower pH range, where the concentration of oxinate anion is low, an equilibrium exists between zinc ion and oxine:



The binuclear cation is extracted with chloroform forming the ion-association complex:



In the aqueous phase at the higher pH range, where the concentration of oxinate anion is relatively high, $Zn(Ox)_2$ is formed in addition to the binuclear cation by the following equilibria:



If the concentration of $Zn(Ox)_2$ amounts to a certain level in the aqueous phase, the irreversible hydration of $Zn(Ox)_2$ takes place, which removes zinc from the distribution system as the precipitate of $Zn(Ox)_2 \cdot 2H_2O$.

Thus, the sudden drop in extraction occurs at the pH range where $Zn(Ox)_2$ begins to appear as a dominant species in the aqueous phase, and perchlorate ion tends to broaden the optimal pH range for extraction.

The sum of the values of weight per cent of zinc, oxine and perchlorate amounts neither to 100% nor to constant value (the 4th column of Table II). This was found to be partly because the complex was unstable but largely because the complex adsorbed organic solvents. Though the complex was dried to constant weight by the aid of a water-jet pump for several days at room temperature, the organic solvents adsorbed in the complex were not completely removed unless it was heated above 150°. However, a much larger inevitable weight loss was observed when the complex was heated at 150°, which was verified by infrared measurements to be due to the partial decomposition of the complex.

SUMMARY

Zinc ion was completely extracted with 0.1 M oxine solution in chloroform from 0.1 M perchlorate solution at pH 4.0–5.9, but was practically unextracted from chloride or nitrate solution. The extracted complex from the perchlorate solution was isolated and the composition was determined to be $Zn_2(Ox)_3(HOx)_3ClO_4$. The equilibrium, $2Zn^{2+} + 6HOx(org) + ClO_4^- \rightleftharpoons Zn_2(Ox)_3(HOx)_3ClO_4(org) + 3H^+$, is proposed; the equilibrium constant was found to be $10^{1.10}$ at 20°. The extracted complex is considered to be an ion-association complex, $[Zn_2(Ox)_3(HOx)_3^+, ClO_4^-]$, from the extraction behavior.

RÉSUMÉ

Le zinc peut être extrait quantitativement par l'oxine 0.1 M dans le chloroforme, en milieu perchlorate 0.1 M à pH 4.0–5.9; il n'est pratiquement pas extrait en milieu chlorure ou nitrate. On a pu isoler le complexe extrait et déterminer sa composition: $Zn_2(Ox)_3(HOx)_3ClO_4$. L'équilibre $2Zn^{2+} + 6HOx(org) + ClO_4^- \rightleftharpoons Zn_2(Ox)_3(HOx)_3ClO_4(org) + 3H^+$ est proposé; la constante trouvée est de $10^{1.10}$ à 20°.

ZUSAMMENFASSUNG

Zinkionen wurden mit 0.1 M Oxinlösung in Chloroform aus 0.1 M Perchloratlösungen bei pH 4.0–5.9 vollständig extrahiert, wurden jedoch praktisch nicht extrahiert aus Chlorid- oder Nitratlösung. Der extrahierte Komplex aus der Perchloratlösung wurde isoliert und seine Zusammensetzung zu $Zn_2(Ox)_3(HOx)_3ClO_4$ ermittelt. Es wird das Gleichgewicht $2Zn^{2+} + 6HOx(org) + ClO_4^- \rightleftharpoons Zn_2(Ox)_3(HOx)_3ClO_4(org) + 3H^+$ vorgeschlagen; die Gleichgewichtskonstante bei 20° ist $10^{1.10}$. Der extrahierte Komplex wird auf Grund des Extraktionsverhaltens als Ionenassoziationskomplex $[Zn_2(Ox)_3(HOx)_3^+, ClO_4^-]$ angesehen.

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DETERMINATION OF SILICA IN SILICATES CONTAINING PHOSPHORUS, TITANIUM AND ZIRCONIUM

O. A. OHLWEILER, J. O. MEDITSCH, CARMEM L. P. SILVEIRA and SANDRA SILVA

Instituto de Química, UFRGS, Pôrto Alegre (Brasil)

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The classical method for the determination of silica in silicates, based on the precipitation of polymerized silicic acid by dehydration with mineral, is extremely laborious. The separation is rarely complete, even when two precipitations are made; any silica escaping two dehydrations may not be recovered in a third consecutive dehydration with acid. A recovery of silica as quantitative as possible is critical with the usual 0.5000-g samples, for 2 mg of unrecovered silica causes a relative error of 0.4%. Some authors recommend the use of 2.000-g samples; but larger samples make the fusion and further treatment of the product more difficult. In most accurate analyses, the residual (dissolved) silicic acid must be determined colorimetrically in the filtrate. The silica normally obtained is never a pure phase; the weighed impure silica is treated with hydrofluoric and sulfuric acids in order to eliminate silicon and evaluate the nonvolatile impurities. Because of the difficulties outlined, determinations of silica on a single sample of silicate by different analysts almost invariably result in variations up to 1% or more¹⁻³.

Various gravimetric methods for the determination of silica based on the precipitation of 12-molybdosilicic acid with organic bases have been described. In all these methods it is essential to convert completely the silicic acid to the monomeric form. Only monosilicic acid produces the desired 12-molybdosilicic acid when ammonium molybdate is added to the correctly acidified solution (pH 1.3-1.5). Different organic bases have been used for the precipitation of *e.g.* 8-hydroxyquinoline (oxine)⁴, pyramidone⁵, pyridine⁶, hexamethylenetetramine⁷, 2,4-dimethylquinoline⁸ and quinoline⁹. Recently, Harzdorf¹⁰ studied the precipitates obtained with 33 organic bases, giving special attention to pyridine.

The most important of those methods is the one based on the precipitation of 12-molybdosilicate with oxine in strongly acid solution, originally proposed by Volynets⁴. Later Merz¹¹ prescribed more definite working conditions. The gravimetric factor for silica, empirically determined for precipitates dried at 140°, is 0.02510. The formula of the compound deduced from the silica factor is $4C_9H_7ON \cdot H_4SiMo_{12}O_{40}$. The gravimetric factor is extraordinarily favorable and permits the use of relatively small samples. The results obtained with the method indicate high precision and accuracy. Germanium(IV), phosphorus(V), arsenic(V) and vanadium(V) interfere by also forming hetero-12-molybdates; titanium(IV) and zirconium(IV) hydrolyse, and considerable quantities of uncomplexed fluoride hinder the development of 12-molybdosilicate.

Brabson *et al.*¹² attempted to adapt the method based on oxine 12-molybdo-

silicate to the determination of silica in materials containing fluorine and phosphorus. Fluoride ion was complexed with boric acid. Silicon and phosphorus were converted to their respective 12-molybdo acids; the oxine precipitation gave a mixture of the two 12-molybdo acids. It was therefore necessary to determine phosphorus separately by a conventional method, and to make an appropriate correction. With regard to the phosphorus interference, the effective contribution of Brabson *et al.* was the evaluation of the gravimetric factor of oxine 12-molybdophosphate for the correction when silicon and phosphorus are precipitated together.

Experimentally, a factor of 0.03174 was found in comparison with the theoretical value of 0.031395 for the compound $3C_9H_7ON \cdot H_3PMo_{12}O_{40}$; the difference was attributed to a slight solubilization of the phosphorus precipitate in the wash solution (saturated with oxine 12-molybdosilicate). With respect to the titanium(IV) and zirconium(IV) interferences, Brabson *et al.*¹² suggested that silicon and phosphorus might be separated from those elements in alkaline medium; however, in alkaline medium the precipitation of titanium(IV) and zirconium(IV) hydroxides invariably entrains silicic acid and causes low results in the determination of silica.

In short, the method based on oxine 12-molybdosilicate presents two important advantages: it allows the use of small samples and the results indicate high precision and accuracy. However, a more extensive utilization of these advantages depends on overcoming the interferences of phosphorus, titanium and zirconium, elements that occur in many silicate minerals and rocks. Phosphorus and titanium are invariably present in igneous and metamorphic rocks. The quantity of P_2O_5 usually runs from 0.10 to 1.0%, but occasionally amounts to several per cent. The amount of TiO_2 varies usually from 0.1 to about 2.0%, but may be up to 5–6%. Zirconium is also present in many rocks, usually in amounts of less than 0.20% as ZrO_2 , but occasionally as much as 2%.

This paper presents a specially developed procedure for applying the oxine 12-molybdosilicate method to the determination of silica in silicates containing phosphorus, titanium and zirconium. The procedure essentially involves the fusion of the sample with boron trioxide and the use of ion-exchange resins to remove the cations and anions arising from the sample. Boron trioxide was chosen as the flux because it dissolves in water forming boric acid ($K_1 = 5.8 \cdot 10^{-10}$), a very slightly ionized compound that does not introduce ions into the solution, which is favorable for the subsequent application of the ion-exchange resins. The cake is dissolved in 0.01 M hydrochloric acid containing ethylenediaminetetraacetic acid in order to avoid hydrolysis of titanium(IV) and zirconium(IV), and in contact with a strongly acidic cation-exchange resin in the hydrogen form, *e.g.* Amberlite IR-120 (H^+). When the cake has dissolved, the solution is treated with a strongly basic anion-exchange resin in the hydrogencarbonate form, *e.g.* Amberlite IRA-400 (HCO_3^-). Finally, the solution, from which the interfering substances have been removed, is used for the precipitation as oxine 12-molybdosilicate.

EXPERIMENTAL

Reagents

Boron trioxide. Dehydrate boric acid by fusing the reagent in a platinum dish. When the formation of bubbles has ceased, cool suddenly to cause the resultant

boron trioxide to crack into pieces. Then, crush the material in a Plattner mortar and, finally, powder it in a mullite mortar. Boron trioxide is hygroscopic and must be stored in an air-tight vessel.

Amberlite IR-120 (H^+ ; 30–50 mesh).

Amberlite IRA-400 (HCO_3^- ; 30–50 mesh). Prepare by passing, first, a 5% sodium hydrogencarbonate solution through a column of Amberlite IRA-400 (Cl^-) and, then, a 1% solution. Finally, drain the resin in a Büchner funnel.

Sodium hydroxide. In pellets, silica-free.

Thymol blue solution. Dissolve 0.2 g of thymol blue in 10 ml of freshly prepared 5% sodium hydroxide solution in a platinum dish. Dilute to 125 ml and neutralize with dilute hydrochloric acid to an orange color; avoid excess lest the indicator be precipitated. Dilute the solution to 250 ml in a volumetric flask.

Ammonium molybdate solution. Dissolve 50 g of the salt, $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$, in 500 ml of water, allow to stand for 24 h and filter into a polyethylene flask. The solution must be renewed weekly.

8-Hydroxyquinoline solution. Dissolve 14 g of oxine in 20 ml of 6 M hydrochloric acid, dilute to 100 ml, filter and dilute to 1 l.

Saturated wash solution. Dilute a mixture of 12 ml of glacial acetic acid and 143 ml of concentrated hydrochloric acid to 2 l. Fuse a 0.1-g sample of quartz with boron trioxide and proceed as described below. Dissolve, however, simply in 0.01 M hydrochloric acid. Precipitate the silica from an aliquot containing about 20 mg of SiO_2 and filter. Transfer a portion of the unwashed precipitate to a 1-l round-bottom flask, and add about 800 ml of the acid solution. Boil for 10 min under a reflux condenser. If all the precipitate dissolves, cool slightly, add more precipitate, and continue heating. Cool to room temperature, allow to stand overnight, and filter before use.

Procedure

Transfer 0.1000 g of the finely powdered sample (< 200 mesh) to a 30-ml platinum crucible. Add 1.0 g of boron trioxide and 0.10 g of lithium carbonate and mix intimately with a short glass rod with rounded ends. Set the crucible in a silica triangle and heat, first, carefully with a small flame until any water is completely expelled. Then, cover the crucible and heat with a strong oxidizing flame (ca. 1000°) for 30 min. Remove the burner and, with the aid of a crucible tongs, cool suddenly by putting the bottom of the crucible in contact with cold water, so that the fused mass rapidly solidifies forming a transparent glass; if necessary, repeat the thermal shock, but avoiding any refusing of the material, until the glass is completely detached from the walls of the crucible.

Transfer 0.1000 g of the finely powdered sample (< 200 mesh) to a 30-ml and 0.10 g of ethylenediaminetetraacetic acid to a 1500-ml beaker placed on a magnetic stirrer. Rinse off the cover of the crucible into the beaker with a stream of 0.01 M hydrochloric acid and suspend the crucible in the liquid. Place a magnetic bar inside the liquid, cover the beaker and put the stirrer in action at a convenient rate; the complete dissolution of the cake, when perfectly detached from the crucible, needs about 2 h. When the cake has dissolved, remove and rinse the crucible with a stream of 0.01 M hydrochloric acid. Add 10 g of Amberlite IRA-400 (HCO_3^-) and stir for more 30 min. The second resin may be placed into a small bag of fine cloth

in order to simplify the regeneration of the two resins; in this case a longer stirring time is necessary.

Filter the solution through paper (S&S 589, white ribbon) into a 1-l volumetric flask, wash with distilled water and dilute to the mark. Transfer an aliquot of 200 ml (containing 5–25 mg of silica) to a 600-ml polyethylene beaker. Add about 1 g of sodium hydroxide and stir until the reagent has completely dissolved. Add 8 drops of thymol blue solution and then concentrated hydrochloric acid, dropwise, until the color changes from yellow to red. Successively add 8 ml of (1+9) hydrochloric acid, 5 ml of (1+2) acetic acid and 20 ml of ammonium molybdate solution; stir the solution vigorously for 1 min after the addition of the last reagent. Allow 15 min for the formation of the 12-molybdosilicic acid.

Add 40 ml of (1+1) hydrochloric acid and precipitate the silica by adding 60 ml of 8-hydroxyquinoline solution from a buret, stirring constantly during the addition. Cover the beaker, and heat in a water bath at 60° for 10 min, stirring occasionally.

Cool to room temperature in a water bath, allow the precipitate to settle, and filter through a weighed glass filtering crucible. Transfer all the liquid before washing is begun. Wash twice by decantation with 25-ml portions of wash solution and transfer the precipitate to the crucible. Police the beaker thoroughly with the wash solution and wash the precipitate with the wash solution 10 times after the transference has been completed. Wash once with 5 ml of water. Dry the precipitate for 1 h at 140°.

Cover the hot crucible with a watch glass, and cool the precipitate for 30 min in an evacuated desiccator. Weigh rapidly to eliminate errors from absorption of moisture. Subtract a blank representing the weight of precipitate obtained by taking equal quantities of all the reagents through the steps of the procedure.

Calculate the quantity of silica: weight of the precipitate of oxine 12-molybdosilicate $\cdot 0.02510 =$ weight of SiO_2 .

DISCUSSION

Quantity of sample

The quantity of sample to be weighed was fixed in accordance with the characteristics of the oxine 12-molybdosilicate precipitate and the desired accuracy. It is recommended to precipitate between 5 and 25 mg of silica; the precipitates obtained with those extreme quantities weigh about 0.2 and 1 g, respectively. Precipitates obtained with more than 25 mg of silica are very large and more difficult to filter, wash and dry. Practically, the accuracy in the determination of silica, by the proposed method depends on the precision in weighing the sample. For errors less than 0.1%, which are readily attainable by the method, it is necessary to weigh at least a 0.1000-g sample or better a 0.2000-g sample. Then, the silica is precipitated in a suitable aliquot of the solution prepared for the analysis. To simplify the fusion and the treatment of the cake, the procedure was developed for 0.1000-g samples.

Fusion of the sample

The choice of boron trioxide as the flux has been already explained. The reagent is a powerful non-oxidizing flux; it fuses at red heat giving a very viscous

liquid that dissolves metallic oxides to form borates; with silicon dioxide, it forms borosilicates. Nearly all silicates succumb to fusion with boron trioxide.

Obviously, in the fusion with boron trioxide, the conditions must be correct for the ultimate solubilization of silicic acid and the complete conversion of the silica to the monosilicic acid which produces the 12-molybdosilicate complex. Preliminary experiments based on fusions of quartz (0.1000 g) with boron trioxide (*ca.* 1 g) at 1000° for 30 min, showed that treatment of the fusion product with 0.01 *M* hydrochloric acid always left a residue of gritty particles, which indicated incomplete attack. Larger quantities of flux or longer fusion times did not overcome the difficulty. However, complete dissolution was achieved by adding a certain minimal quantity of sodium carbonate (0.10 g) to the flux.

Nevertheless, the determinations of silica directly in solutions so obtained showed a recovery of no more than 95–98%. There is evidence that, even when sample decomposition appears complete, fragments of the silicon–oxygen crystal framework remain intact after the glass has been dissolved in dilute acid, as was observed by Maesson and Boumans¹³ in silicate analysis. It is also possible that a partial restoration of bonding occurs during the glass cooling.

For a complete recovery of silica, the solution must be made strongly alkaline just before the pH adjustment which, in the recommended procedure, precedes the development of the 12-molybdosilicate complex. In 0.1 *M* sodium hydroxide, complete depolymerization of silicic acid takes place; then, after the solution has been properly acidified, all silica will be present as monosilicic acid which reacts with molybdate quantitatively. In a series of experiments where the glass dissolution immediately followed the fusion, 100 ± 0.1% recoveries were obtained. In an isolated experiment the dissolution was performed 70 h after the fusion; then, the vitreous mass became opaque and the recovery of silica, despite the treatment with sodium hydroxide, attained scarcely 98.9%.

When fusion with a mixture of boron trioxide and sodium carbonate was applied to silicate decomposition, the cakes obtained did not dissolve satisfactorily in dilute acid. The use of lithium carbonate instead of sodium carbonate was successful. Indeed the fusion of a 0.1000-g sample of silicate with boron trioxide (*ca.* 1 g) and lithium carbonate (0.10 g) produced a glass that dissolved completely in 0.01 *M* hydrochloric acid.

It is very important to reduce the sample to a fine powder (< 200 mesh) and to mix the sample intimately with the flux; the melt is very viscous and local concentrations of silica disperse slowly. The flux–sample ratio specified above (*i.e.*, 10:1) was the most satisfactory. Lower flux–sample ratios produced glasses that dissolved more slowly; higher ratios required longer times for the cakes to dissolve. The fusions were performed in platinum crucibles by heating at about 1000° for 30 min; 15-min fusions did not give good results.

Preparation of the solution

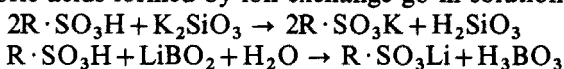
The cake must be dissolved so that polymerization of silicic acid and hydrolysis of cations from the sample do not occur. Metallic hydroxides, if produced by hydrolysis, would entrain silicic acid and, therefore, cause low results in the determination of silica.

The solubility of silicic acid in distilled water has been reported to be 110–140

p.p.m. SiO_2 at 25° . The solubility is not affected by changes in pH in the range 0–9. At pH 1–8, in concentrations less than about 110–140 p.p.m. SiO_2 , the stable form is the unionized monosilicic acid, $\text{Si}(\text{OH})_4$. Above pH 9, the solubility rises sharply owing to the formation of silicate, $\text{SiO}(\text{OH})_3^-$. In solutions more concentrated than 110–140 p.p.m. SiO_2 , polymerization occurs. Polymerization of two $\text{Si}(\text{OH})_4$ molecules may lead to the formation of dimeric silicic acid; further polymerization will lead to the formation of trimeric silicic acid, and condensation and elimination of water will lead to branched-chain and ring polymers. Continued increase in size gives rise to the formation of colloidal particles and, under suitable conditions, a gel. Silicic acid is most stable at pH 1–3. At pH below 1, the polymerization rate increases; at pH 3–8 the rate of polymerization is at its maximum, being particularly high between 5 and 6. According to Alexander¹⁴ monosilicic acid in 0.1 M solution at 2° polymerizes almost instantly at pH 6 and is most stable at pH 3.2. Polymerization below pH 3.2 is a third-order reaction, giving linear or openly branched polysilicic chains, whilst above pH 3.2 the polymerization is a second-order reaction and depolymerization–polymerization rearrangement gives rise to cyclic or cross-linked polymers. Monosilicic and polysilicic acids are such weak acids that they do not furnish hydrogen ions to aqueous solutions.

The procedure described above involves the dissolution of the fusion product in 800 ml of 0.01 M hydrochloric acid. Thus, the silicic acid concentration in the solution is always below the equilibrium solubility. And the pH of the solution will be between 1 and 3, the range of greatest stability of the monosilicic acid. With 0.001 M hydrochloric acid, dissolution of the glass takes more time; with 0.1 M hydrochloric acid, dissolution is faster, but the action of the ion-exchange resins would be hindered.

The addition of a strongly acidic cation-exchange resin in the hydrogen form, *e.g.*, Amberlite IR-120 (H^+), favors dissolution of the glass by the removal of the cations from the solution. The ion-exchange dissolution technique was used in silicate analysis by Govindaraju¹⁵. The fusion product is stirred with a suspension of the strongly acidic cation exchanger in the solution used for dissolving the cake. Silicic and boric acids formed by ion exchange go in solution:



As the solution is 0.01 M in hydrochloric acid, the removal of cations in this stage attains only an equilibrium condition.

The addition of a strongly basic anion-exchange resin in the hydrogencarbonate form, *e.g.*, Amberlite IRA-400 (HCO_3^-), when the glass dissolution goes to completion, is principally intended to remove phosphate ion from the solution. The resin takes up the strong acids, phosphoric acid included, but leaves the silicic acid in solution¹⁶. Consequently, the hydrogen ion concentration decreases to about pH 6. This pH change favors the removal of cations from the solution by the first resin.

The cation-exchange resin alone does not ensure the removal of titanium(IV). But titanium(IV), if present, must be removed from the solution because it tends to hydrolyze forming polymeric colloidal species, which are not adsorbed by the resin and entrain silicic acid. Zirconium(IV) also forms polymeric species in weakly acid solution.

Titanium(IV) was removed by means of ethylenediaminetetraacetic acid added

to the solution used for dissolving the cake. Titanium(IV) forms with EDTA at pH 1.0–2.5 the neutral TiY complex¹⁷. Pecsok and Maverick¹⁸ have shown that the TiY complex is in equilibrium with the TiO^{2+} ion; above pH 2.5, $TiOY^{2-}$ complex is the predominant species, but as the pH is increased above 3, the TiO^{2+} ion becomes increasingly hydrolyzed to colloidal TiO_2 . The satisfactory results experimentally obtained proved that EDTA inhibits the titanium(IV) hydrolysis, and that the ionic species in equilibrium with the TiY complex are retained by the resins before the increase in pH caused by the second resin action can hydrolyze the TiO^{2+} ion to colloidal TiO_2 .

The quantity of the cation-exchange resin specified in the recommended procedure (10 g) was established empirically, so as to ensure the removal of relatively high contents of titanium(IV). The quantity of anion-exchange resin (10 g) was somewhat higher than required to bring the solution at about pH 6. The quantity of EDTA (0.10 g) was somewhat lower than required to attain the equilibrium solubility of the reagent in the acidic solution.

The dissolution of the cake must be performed immediately after the fusion so that, as observed above, harmful irreversible changes do not occur in the vitreous mass. The development of 12-molybdosilicic acid, in its turn, must be preceded by a

TABLE I

RESULTS OBTAINED IN THE DETERMINATION OF SILICA IN SILICATE STANDARD SAMPLES

Sample	Composition (%)	SiO_2 found (%)	Relative error (%)
Soda feldspar (U.S. National Bureau of Standards, no. 99)	SiO_2 , 68.66; Al_2O_3 , 19.06;	68.74	0.12
	Fe_2O_3 , 0.067; MgO , 0.053;	68.63	0.04
	CaO , 0.36; Na_2O , 10.73; K_2O ,	68.58	0.08
	0.41; TiO_2 , 0.017; P_2O_5 ,	68.57	0.13
	0.142; MnO , < 0.001; BaO , 0.01		
Plastic clay (U.S. National Bureau of Standards, no. 98)	SiO_2 , 59.11; Al_2O_3 , 25.54;	59.06	0.08
	Fe_2O_3 , 2.05; TiO_2 , 1.43;	59.04	0.12
	ZrO_2 , 0.041; P_2O_5 , 0.08; V_2O_5 , 0.025; Cr_2O_3 , 0.021; CaO , 0.21; MgO , 0.72; K_2O , 3.17; Na_2O , 0.28; SO_3 , 0.07; MnO , 0.005; CuO , 0.009		
Flint Clay (U.S. National Bureau of Standards, no. 97)	SiO_2 , 42.87; Al_2O_3 , 38.77;	42.85	0.05
	Fe_2O_3 , 0.98; TiO_2 , 2.38;	42.82	0.12
	ZrO_2 , 0.25; P_2O_5 , 0.08; V_2O_5 , 0.040; Cr_2O_3 , 0.079; CaO , 0.10; MgO , 0.26; K_2O , 0.54; Na_2O , 0.33; SO_3 , 0.042; MnO , 0.002; CuO , 0.003		
Burnt refractory (U.S. National Bureau of Standards, no. 76)	SiO_2 , 54.69; Al_2O_3 , 37.67;	54.65	0.07
	Fe_2O_3 , 2.38; TiO_2 , 2.21;	54.62	0.13
	ZrO_2 , 0.07; MgO , 0.58; CaO , 0.27; K_2O , 1.37; Na_2O , 0.38; P_2O_5 , 0.069; V_2O_5 , 0.021		

transitory alkalization of the solution (0.1 M in sodium hydroxide) to complete the depolymerization of silica to monosilicic acid. Alkali may be added even several hours after the glass dissolution and its depolymerization effect is practically immediate.

Subsequent stages

The stages of the recommended procedure following the depolymerization by sodium hydroxide correspond exactly to the procedure described by Brabson *et al.*^{1,2}.

RESULTS AND CONCLUSIONS

The procedure described above for the determination of silica in silicates containing phosphorus, titanium and zirconium, was first tested with analyzed samples issued by U.S. National Bureau of Standards. The results obtained indicate high precision and accuracy (Table I); the relative errors are about 0.1%.

The tolerance limits for phosphorus, titanium and zirconium were fixed by analyzing samples of a soda feldspar, practically free from those elements, to which known quantities of phosphorus, titanium and zirconium were added (Table II).

TABLE II

TOLERANCE LIMITS FOR PHOSPHORUS, TITANIUM AND ZIRCONIUM

Sample	SiO ₂ found (%)	Relative error (%)
Soda feldspar	65.49	—
	65.48	—
	65.49	—
	Mean: 65.49	
Soda feldspar + 0.5% of P ₂ O ₅ (added)	65.44	-0.08
1.6%	65.41	-0.12
2.0%	65.36	-0.20
2.5%	65.32	-0.25
3.0%	65.27	-0.33
5.0%	65.24	-0.37
Soda feldspar + 3.0% of TiO ₂ (added)	65.43	-0.09
5.0%	65.37	-0.18
Soda feldspar + (2.2% of TiO ₂ and 1.0% of ZrO ₂) (added)	65.41	-0.12

If a 0.2% relative error in the determination of silica is considered permissible, then the tolerance limits for phosphorus and titanium are 2% P₂O₅ and 5% TiO₂, respectively. The last result included in Table II allows the conclusion that the tolerance limit fixed for titanium can be taken also as approximately valid for titania plus zirconia.

SUMMARY

A procedure based on precipitation of oxine 12-molybdosilicate has been examined for the determination of silica in silicates containing phosphorus, titanium and zirconium. Boron trioxide and lithium carbonate are used in the flux. The fusion product is dissolved in 0.01 M hydrochloric acid containing EDTA, in contact with Amberlite IR-120 (H^+). The resultant solution, after stirring with Amberlite IRA-400 (HCO_3^-), is used for the precipitation of silica as oxine 12-molybdosilicic acid.

RÉSUMÉ

Les auteurs ont adapté la méthode de précipitation de l'oxine-12-molybdosilicate au dosage de la silice dans des silicates renfermant phosphore, titane et zirconium. On procède d'abord à une fusion au moyen d'anhydride borique. Le produit de la fusion est dissous dans l'acide chlorhydrique 0.01 M, en présence d'EDTA et d'Amberlite IR-120 (H^+). Puis, après traitement de cette solution avec l'Amberlite IRA-400 (HCO_3^-), on précipite la silice sous forme d'oxine-silico-12-molybdate.

ZUSAMMENFASSUNG

Die Methode der Ausfällung von Oxin-12-Molybdatosilikat wird auf die Bestimmung von Kieselsäure in phosphor-, titan- und zirkoniumhaltigen Silikaten angewendet. Die Proben werden mit Bortrioxid und Lithiumcarbonat aufgeschlossen. Das Schmelzprodukt wird in 0.01 M, EDTA-haltiger Salzsäure in Gegenwart von Amberlite IR-120 (H^+) gelöst. Nach Schütteln der erhaltenen Lösung mit Amberlite IRA-400 (HCO_3^-) wird das Oxin-12-Molybdatosilikat ausgefällt.

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COMPLEXIMETRIC TITRATIONS BASED ON 2:1 METAL-LIGAND COMPLEX FORMATION

F. FREESE, G. DEN BOEF and G. J. VAN ROSSUM

Laboratory for Analytical Chemistry, University of Amsterdam, Amsterdam (The Netherlands)

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For some years ligands which form complexes with metal ions with a metal-ligand ratio of 2:1 have been known. The best known example is triethylenetetramine-hexaacetic acid (TTHA). Recently, Harju and Ringbom^{1,2} have published theoretical considerations on titrations based on this type of complex formation. They restricted themselves to the use of indicators for the end-point detection.

In the present paper, the theory for instrumental end-point indication methods in which the signal linearly depends on the concentration of one or more of the reacting compounds, is discussed. The theory is illustrated by the photometric titration of copper(II) with diethylenetriaminepentaacetic acid (DTPA).

THEORY

The equations, leading to the titration curves, given in the same notation as in recent publications^{3,4} for 1:2 complex formation, are

$$f = \frac{c_L}{c_M} = l + m_2l + ml; \text{ and } m + ml + 2m_2l = 1$$

$$Z_1 = K_1 c_M = \frac{ml}{m \cdot l}; \text{ and } Z_2 = K_2 c_M = \frac{m_2l}{ml \cdot m}$$

in which K_1 and K_2 are the conditional stability constants for the first and second steps of the complex formation, and c_M and c_L are the analytical concentrations of the required metal M and the titrant L. The relative concentrations with respect to c_M are:

$$m = \frac{[M]}{c_M}; l = \frac{[L]}{c_M}; ml = \frac{[ML]}{c_M}; m_2l = \frac{[M_2L]}{c_M}$$

It is again supposed that the volume does not change during the titration.

For those cases where M_2L complex formation was studied, the stability constant for the first step was usually much larger than that for the second step. It should, however, be noted that side-reactions may affect K_1 and K_2 differently; particularly side-reactions of L affect K_1 but not K_2 . Under certain conditions the conditional stability constant K_1 can therefore be smaller than K_2 . In this paper the reaction of ML with M is not considered as a side-reaction in the formation of M_2L , and both $M + L \rightleftharpoons ML$ and $ML + M \rightleftharpoons M_2L$ are considered as main reactions. The result is that the conditional stability constants K_1 and K_2 are both independent

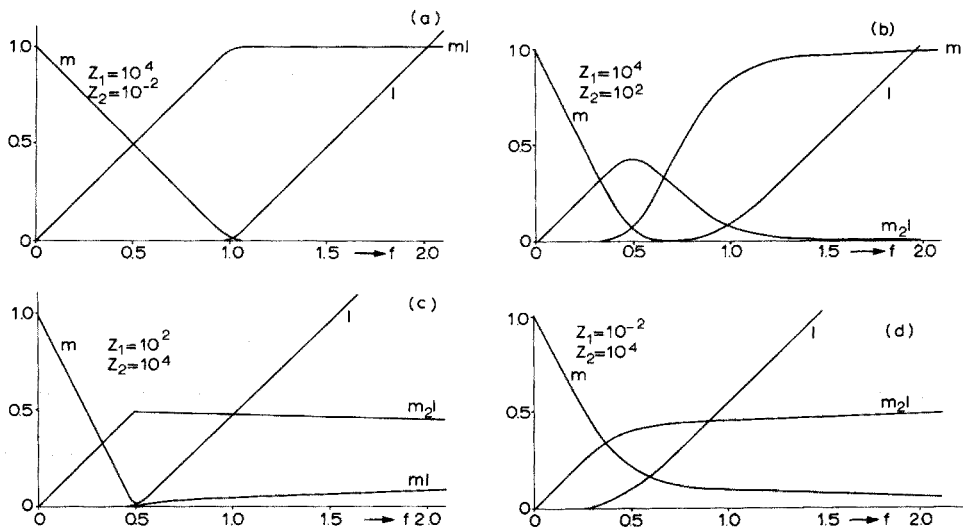


Fig. 1. f - l , f - m , f - ml and f - m_2l curves under different conditions.

of the analytical concentration of the metal c_M . Figure 1 gives a survey of the different possible titration curves.

The f - m curve

Elimination of the other variables from the basic equations leads to

$$f = \frac{1}{Z_1} \frac{1-m}{m} \frac{1}{1+2Z_2m} + (1-m) \frac{1+Z_2m}{1+2Z_2m} \quad (1)$$

For $Z_2 \gg 1$, the case of interest, eqn. (1) reduces to

$$f = \frac{1}{Z_1} \frac{1-m}{m} \frac{1}{1+2Z_2m} + \frac{1-m}{2}$$

for not too low values of m . The titration curve is roughly a straight line from $m=1$ at $f=0$ to $m=0$ at $f=0.5$. The intersection of the two straight parts of the curve is at $f=0.5$. The curvature near the equivalence point and resulting titration errors can easily be found by means of eqn. (1). When $Z_1 \gg 1$, values of $Z_2 > 100$ will permit end-point determination at $f=0.5$, provided that only points far from the equivalence point are used for the two straight parts of the curve.

For $Z_2 \ll 1$, eqn. (1) reduces to

$$f = \frac{1}{Z_1} \frac{1-m}{m} + 1-m$$

which is the equation when no M_2L is formed. An end-point occurs at $f=1$, if $Z_1 \gg 1$. Intermediate values of Z_2 , of the order of 1, do not produce titration curves suitable for end-point determination.

The f - l curve

Elimination yields

$$f = l + \frac{1}{2} - \frac{1 - (Z_1 l)^2}{4Z_1 Z_2 l} W_1 \quad (2)$$

in which

$$W_1 = \frac{1}{2} \left[\left\{ 1 + \frac{8Z_1 Z_2 l}{(1 + Z_1 l)^2} \right\}^{\frac{1}{2}} - 1 \right]$$

When $8Z_1 Z_2 l / [(1 + Z_1 l)^2] \ll 1$ this leads to

$$f = l + \frac{Z_1 l}{1 + Z_1 l}$$

which is the formula for the titration of M with L without the intermediate formation of M_2L . This simplification of eqn. (2) is justified for the larger part of the titration curve when $Z_1 \gg Z_2$. An end-point is obtained at $f=1$.

For $Z_1 \ll 1$ and $Z_1 Z_2 \gg 1$, the M_2L complex is formed exclusively and eqn. (2) then reduces to $f=l+\frac{1}{2}$, and a suitable end-point occurs at $f=\frac{1}{2}$.

In intermediate cases good end-points may be obtained with the $f-l$ curve at $f=1$ provided that $R \gg 1$ and at $f=0.5$ when $R \leq 1$ and $Z_1 Z_2 \gg 1$, but the exact eqn. (2) has to be used for drawing the theoretical curve.

The $f-ml$ curve

From the basic equations it is found that

$$f = ml + \left[\frac{1}{Z_1} + \frac{2}{R} ml \right] \frac{ml}{1 - ml} + (1 - ml) \frac{Z_2 ml}{1 + 2Z_2 ml} \quad (3)$$

in which $R = Z_1/Z_2$.

For $Z_2 \gg 1$, the case of interest, the first and third term of eqn. (3) can be taken together for not too small values of ml , leading to

$$f = \frac{1 + ml}{2} + \left[\frac{1}{Z_1} + \frac{2}{R} ml \right] \frac{ml}{1 - ml}$$

As, in general, $Z_1 \gg 1$ and $R \gg 1$, the second term can be neglected for values of ml far from unity. We then have

$$f = \frac{1 + ml}{2}$$

a curve consisting of a straight branch from $ml=0$ ($f=0.5$) to $ml=1$ ($f=1$) and two horizontal branches at either end of this straight line. End-points at $f=0.5$ and at $f=1$ are observed. In order to compute deviations from linearity the exact eqn. (3) has to be used. The second term reflects the curvature near $f=1$ and the third term the deviations from linearity near $f=0.5$. Systematic titration errors are obtained with the same formula.

The $f-m_2l$ curve

Elimination yields

$$f = m_2 l + (1 - W_{m_2 l})(1 - 2m_2 l) + \frac{1}{Z_1} \frac{1 - W_{m_2 l}}{W_{m_2 l}} \quad (4)$$

in which

$$W_{m_2l} = \frac{1}{2} \left[1 \pm \left(1 - \frac{4m_2l}{Z_2(1-2m_2l)^2} \right)^{\frac{1}{2}} \right]$$

These formulae reflect the fact that the f - m_2l curve passes a maximum and that for $m_2l_{\max} > m_2l > 0$, two f values exist for every value of m_2l .

It is also obvious that m_2l_{\max} follows from

$$\frac{4m_2l}{Z_2(1-2m_2l)^2} = 1,$$

which gives

$$m_2l_{\max} = \frac{1}{2} - \frac{(2Z_2 + 1)^{\frac{1}{2}} - 1}{2Z_2}$$

Substitution in eqn. (4) gives the corresponding value of f :

$$f = \frac{1}{2} + \frac{1}{Z_1}$$

For $m_2l < m_2l_{\max}$, the actual curve, the expression W_{m_2l} can be expanded in a series, which for values largely below m_2l_{\max} can be approximated by

$$W_{m_2l(-)} = \frac{m_2l}{Z_2(1-2m_2l)^2} \text{ and } W_{m_2l(+)} = 1 - \frac{m_2l}{Z_2(1-2m_2l)^2}$$

Substitution in eqn. (4) leads to

$$f_{(+)} = m_2l + \frac{1}{Z_2} \frac{m_2l}{1-2m_2l} + \frac{1}{Z_1} \left(\frac{Z_2(1-2m_2l)^2}{m_2l} - 1 \right)^{-1}$$

for the rising part of the curve and

$$f_{(-)} = 1 - m_2l - \frac{1}{Z_1} - \frac{1}{Z_2} \frac{m_2l}{1-2m_2l} + \frac{1}{R} \frac{(1-2m_2l)^2}{m_2l}$$

for the descending branch of the curve.

For values of $Z_2 \gg 1$, the value of m_2l_{\max} is near its maximum of 0.5 at $f=0.5$ and the curve f - m_2l is nearly straight from $f=0$ ($m_2l=0$) to $f=0.5$ ($m_2l=0.5$), provided that $Z_1Z_2 \gg 1$, too, which will nearly always be so. At the latter point a sharp bend occurs, suitable for end-point determination. In practice a limit is set by $Z_2 > 100$ and $Z_1Z_2 > 100$. The shape of the curve for larger values of f depends largely on Z_1 and R . Another end-point may occur at $f=1$ but only when $R \gg 1$.

All these conclusions can be attributed to particular terms in $f_{(+)}$ and $f_{(-)}$.

EXPERIMENTAL

The theory was applied to the photometric titration of copper(II) with diethylenetriaminepentaacetic acid (DTPA) in which complexes of the type M_2L may be formed.

A Zeiss PMQ II spectrophotometer provided with a 2-cm titration cell was used.

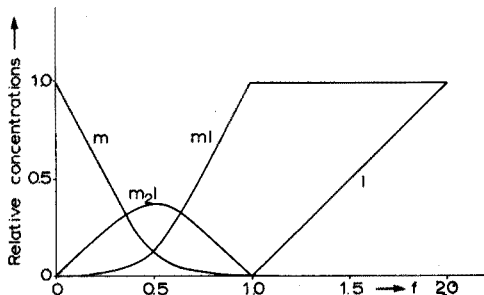


Fig. 2. f - m , f - l , f - ml and f - m_2l curves for $Z_1 = 2.2 \cdot 10^8$ and $Z_2 = 24$.

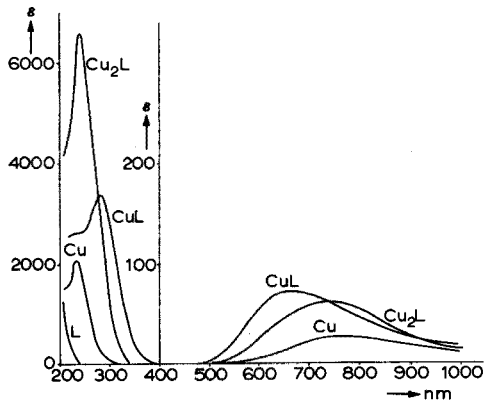


Fig. 3. Absorption spectra of Cu(II), CuDTPA, Cu_2 DTPA and DTPA.

The following stability constants were taken from the literature: $\log K_{CuL} = 20.5$; $\log K_{Cu_2L}^{Cu} = 5.5$; $\log K_{CuHL}^H = 5.0$.

In Fig. 2 the relationships between f and ml , m_2l , m and l are graphically represented for the titration of $10^{-3} M$ copper(II) with DTPA in a $0.1 M$ acetate buffer of pH 5.5. Under these conditions $Z_1 = 2.2 \cdot 10^8$ and $Z_2 = 24$. Figure 3 shows the spectra of copper(II), CuDTPA, Cu_2 DTPA and DTPA. In most experiments 330 nm was selected for the titration, as at this wavelength, mainly CuDTPA absorbs. The values of the molar absorptivities at this wavelength are 1180 for CuDTPA, 140 for Cu_2 DTPA and 4 for copper(II).

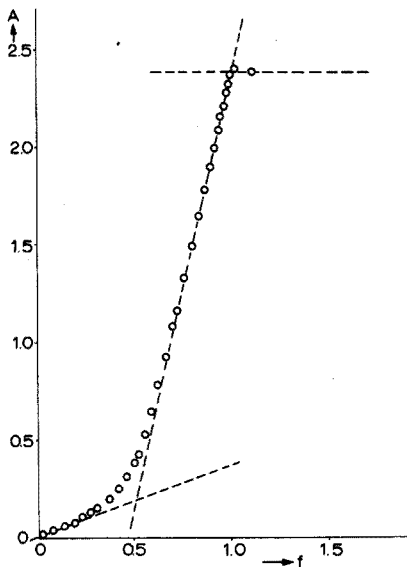


Fig. 4. Theoretical photometric titration curve of $10^{-3} M$ copper(II) with DTPA at 330 nm.

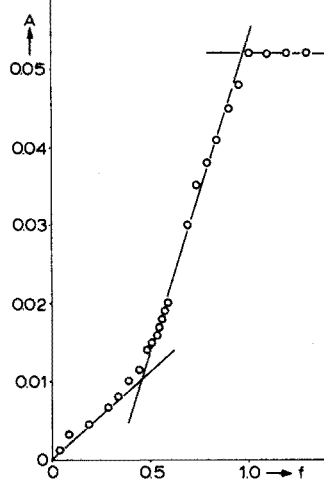


Fig. 5. Experimental photometric titration curve of $1.8 \cdot 10^{-5} M$ copper(II) with DTPA at 330 nm.

The corresponding theoretical photometric titration curve, calculated by means of a desk computer is given in Fig. 4. The experimental curve agrees with the theoretical curve, but for the end-point at $f=0.5$, which turns out to be very much sharper than was expected theoretically. Therefore, some titrations were carried out at lower concentrations. Figure 5 shows that the titration is successful even for $1.8 \cdot 10^{-5} M$ copper(II). More dilute solutions could not be titrated at this wavelength because the change in absorbance during the titration became too small.

A few titrations were carried out at 250 nm, where the absorbance of Cu_2DTPA reaches its maximum. Curves of a different shape occurred and as the sensitivity was slightly larger under these conditions, determinations of $5 \cdot 10^{-6} M$ copper(II) appeared to be possible.

As the experimental titration curves were sharper at $f=0.5$ than was expected, the data on the equilibrium constants appear to be incomplete or even incorrect.

SUMMARY

Mathematical expressions are given for the titration curves of compleximetric titrations of a metal M with a ligand L, resulting in 2:1 complexes of the type M_2L . The theory is illustrated with the titration of copper(II) with DTPA.

RÉSUMÉ

Des expressions ont été calculées pour les courbes de titrage complexométrique du type $2\text{M} + \text{L} \rightleftharpoons \text{M}_2\text{L}$ donnant la relation entre le paramètre de titration f et les différentes concentrations. La théorie est illustrée par le titrage du cuivre(II) avec DTPA.

ZUSAMMENFASSUNG

Für die Titrationskurven komplexometrischer Titrationsen, bei denen ein Metall M mit einem Liganden L zu einem 2:1 Komplex M_2L reagiert, werden mathematische Beziehungen abgeleitet. Die Brauchbarkeit der Formeln wird am Beispiel der Titration von Kupfer(II) mit DTPA erläutert.

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SOME POSSIBILITIES OF REDOX TITRATIONS WITH IRON(II) SULPHATE IN AN ALKALINE MANNITOL MEDIUM

JAN DOLEŽAL* and F. J. LANGMYHR

Department of Chemistry, University of Oslo, Oslo 3 (Norway)

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Some previous communications have dealt with reductimetric titrations with iron(II) sulphate in alkaline media of triethanolamine (TEA)¹⁻⁶. The formation of a very stable iron(III)-TEA complex causes a very negative value of the formal potential of the system Fe(II)/Fe(III)-TEA and offers the possibility of extending the use of iron(II) solutions in titrimetric analysis.

In alkaline media containing triethanolamine and some other aminopolyalcohols, the formal redox potential of the system of complexes of iron(II) and iron(III) is given by the value -1.01 V (S.C.E.) (0.5 M TEA and 0.5 M potassium hydroxide); thus in the medium given, an iron(II) salt can be used for the quantitative reduction of *e.g.* divalent copper¹, bismuth¹, silver, gold, mercury, tetravalent platinum, iridium (reduction to the metal)², hexavalent chromium (Cr(VI)→Cr(III)), tellurate (Te(VI)→Te(IV)), trivalent manganese (Mn(III)→Mn(II))¹, tetravalent manganese (Mn(IV)→Mn(III)→Mn(II))³ and, among organic systems, nitro-, nitroso-, azo-compounds etc., even on a microscale^{4,5}. Conversely, the colourless complex of manganese(II) with triethanolamine can be oxidized quantitatively with potassium hexacyanoferrate(III) to form a green manganese(III) complex⁶.

The investigation of the polarographic behaviour of the complexes of di-, tri- and tetravalent manganese and other metals with mannitol was the subject of a previous communication dealing with the structure of the complexes and their analytical use⁷. In a recently published communication the results were utilized in polarographic analysis and also in the oxidimetric determination of manganese(II) with hexacyanoferrate(III)⁸.

In the present paper the formation of stable complexes of iron(II) and iron(III) with mannitol in an alkaline medium is applied for reductimetric potentiometric titrations of some redox systems, *e.g.* Cr(VI)/Cr(III), Mn(IV)/Mn(III), Mn(III)/Mn(II), Co(III)/Co(II), and Cu(II)/Cu(I).

EXPERIMENTAL

Reagents

0.05 M Iron(II) sulphate solution. This was prepared by weighing 13.901 g of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (Merck, p.a.) and dissolving it in 1 l of 0.05 M sulphuric acid. The titre of the solution was determined by titration with dichromate in 3 M sulphuric acid.

0.05 M Manganese sulphate solution. 8.45 g of $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ (Merck, p.a.) was

* On leave from Department of Analytical Chemistry, Charles University, Prague, Czechoslovakia.

weighed and dissolved in 1 l of distilled water. The titre of this solution was determined compleximetrically.

0.1 N Potassium dichromate solution. 4.9037 g of $K_2Cr_2O_7$ (Merck, p.a.) was dissolved in 1 l of distilled water.

0.05 M Cobalt sulphate solution. 7.0275 g of $CoSO_4 \cdot 7H_2O$ (Merck, p.a.) was dissolved in 1 l of distilled water; the titre was determined compleximetrically.

1.0 M Mannitol solution. This was prepared from the commercial reagents (Norsk Medicinal Depot and Koch Light Laboratories Ltd., England) which were purified by the method of Smith and Montgomery⁹.

The other chemicals were all of reagent-grade purity (Merck).

Apparatus

The potentiometric measurements were carried out with an E 396 B pH-meter (Metrohm, Herisau, Switzerland) with a vessel for titrations in inert atmosphere. The indicator electrode was a platinum wire, and the reference electrode a saturated calomel electrode. To obtain reproducible results for potential measurement in alkaline media, the platinum electrode must be immersed in a 0.1 M solution of iron(II) sulphate in 3 M sulphuric acid for at least 10 min after each titration. If the electrode is left in the air or in distilled water after washing, the results showed very poor reproducibility. The instrument was calibrated against a normal Weston cell.

RESULTS

The mannitol complexes of iron(II) and iron(III) in alkaline media yield an irreversible anodic polarographic wave with $E_{\frac{1}{2}} = -1.22$ V (S.C.E.) and a cathodic double-wave with $E_{\frac{1}{2}} = -1.15$ and -1.65 V (S.C.E.) in a medium containing 3 M potassium hydroxide and 0.5 M mannitol (Fe(II) and Fe(III) concentrations were $5 \cdot 10^{-3}$ M). The $E_{\frac{1}{2}}$ values suggest that the iron(II) salt will be a strong reducing agent in this medium, similar to its solution in the presence of triethanolamine¹⁻⁵. The dichromate reduction was chosen as a model titration.

The titration of dichromate

During the potentiometric monitoring of the course of the dichromate reduction, the dependences on the concentrations of potassium hydroxide and mannitol were followed. After adding a 0.1–0.01 N potassium dichromate solution to 30–50 ml of x M potassium hydroxide and x M mannitol, oxygen was removed from the solution by passing nitrogen for 10–20 min; nitrogen was also passed during titrations. The best results were obtained in a medium 1–3 M in potassium hydroxide and 0.5 M in mannitol. The effect of the potassium hydroxide concentration on the reaction course, and the formal redox potential values of the system Fe(II)–mannitol/Fe(III)–mannitol are shown in Fig. 1 and Table I. Potential values stabilize practically instantaneously in 1–4 M potassium hydroxide. If the hydroxide concentration is less than 1 M, potentials stabilize within 30 sec during the titration; 1 min must be allowed at the equivalence point. The largest potential break at the end-point was observed in 4 M potassium hydroxide containing 0.5 M mannitol ($\Delta mV/\Delta ml = 9,000/0.02$ ml of 0.05 M iron(II) sulphate). The same results were obtained in the 1 M potassium hydroxide + 0.25 M mannitol medium. At lower mannitol concentrations than 0.25 M, the potential values stabilize very slowly and turbidity appears in the solution (in-

TABLE I

THE DEPENDENCE ON THE CONCENTRATION OF POTASSIUM HYDROXIDE*

 $(T=20^\circ$; total volume 25–30 ml; 0.5 M mannitol; 5 ml of 0.01 N $K_2Cr_2O_7$; Pt-S.C.E.)

Concn. of KOH (M)	$\Delta mV/\Delta ml$ 0.02 ml 0.05 M $FeSO_4$	Error (%)	$E_f Fe(II)/Fe(III)$ (mV) (S.C.E.)	$E_{eqn.}$ (mV) (S.C.E.)
0.5	1.500	+1.00	- 880	-760
1	2.000	+0.5	- 940	-800
2	4.600	± 0.5	-1,010	-845
3	6.800	± 0.1	-1,050	-860
4	9.000	± 0.5	-1,180	-870

* The values are averages of 5 measurements.

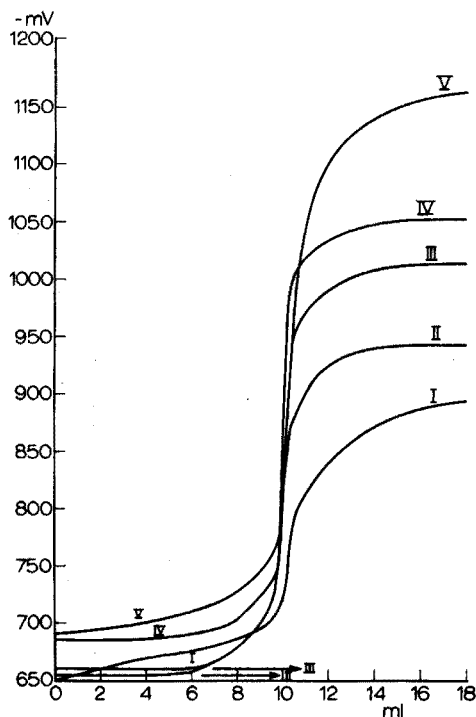


Fig. 1. Titration curves for the reduction of dichromate with iron(II) solution in the KOH-mannitol medium. 5 ml of 0.01 N $K_2Cr_2O_7$ in 30 ml x M KOH + 0.5 M mannitol. $T=20^\circ$; Pt-S.C.E. (I) 0.5 M KOH; (II) 1 M KOH; (III) 2 M KOH; (IV) 3 M KOH; (V) 4 M KOH.

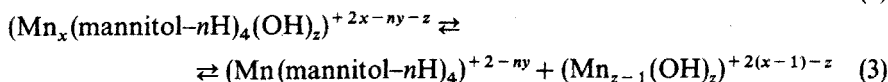
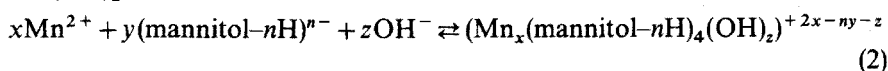
sufficient complexing agent). The results obtained are very well reproducible and correspond exactly to the results of the dichromate determination with iron(II) sulphate in an acid medium.

An advantage of this newly proposed determination is its sensitivity; its disadvantage is the necessity of maintaining a completely inert atmosphere. If the titration is performed in the presence of air, the results are subject to errors up to

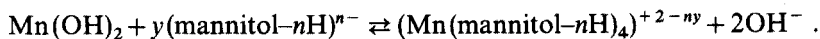
+ 50%. Nitrogen must be passed for at least 10 min. The titration can also be reversed, *i.e.* iron(II) can be determined by titration with dichromate in a 2 M potassium hydroxide–0.5 M mannitol medium (it is difficult to maintain an inert atmosphere in this case). The determination is not disturbed even by a 200-fold excess of chloride (KCl), nitrate (KNO₃), sulphate (Na₂SO₄), or perchlorate (NaClO₄). Vanadate, which is not reduced by iron(II) in the 2 M potassium hydroxide–0.5 M mannitol medium, does not interfere in the dichromate determination, if present under the molar ratio Cr₂O₇²⁻:VO₃⁻ = 1:5. At higher concentrations of vanadate, the determination is subject to a positive error (*e.g.* at Cr₂O₇²⁻:VO₃⁻ = 1:10, the error is + 10%).

The titration of manganese

On the basis of the results of the polarographic study of the manganese(II) oxidation at a dropping mercury electrode in an alkaline mannitol medium⁷, the following reactions have been established



For $x=1$ and $z=2$,



This complex can be quantitatively oxidized with potassium hexacyanoferrate(III) to the brown manganese(III)–mannitol complex, or to the ruby red manganese(IV)–mannitol complex. The best medium is 1 M potassium hydroxide–0.5 M mannitol. The oxidation can also be effected by oxygen or hydrogen peroxide⁸. Both from the polarographic behaviour of the mannitol complexes of di-, tri-, and tetravalent manganese, and from the oxidimetric determination of manganese(II) with potassium hexacyanoferrate(III) in an alkaline mannitol medium it follows that, by titration with iron(II) sulphate only the manganese(IV)–mannitol→manganese(III)–mannitol reduction could be quantitatively followed. This assumption was verified by a number of experiments, in which both hexacyanoferrate(III) and lead dioxide were used for the manganese(II) oxidation. From the dependences on the potassium hydroxide concentration it follows that a solution containing 1–3 M potassium hydroxide and 0.5 M mannitol is the most suitable medium for the reductimetric determination of the manganese(IV) complex with iron(II) sulphate. The first step, corresponding to the reduction of manganese(IV)–mannitol (a ruby red solution) to manganese(III)–mannitol (a brown solution), is accompanied by a perceptible potential break, $\Delta mV/\Delta ml = 1,500/0.02$ ml of 0.05 M iron(II). The iron(II) consumption corresponding to the Mn(III)–mannitol→Mn(II)–mannitol reduction exhibits a considerable positive error, + 10% to + 25%, according to the alkalinity of the solution. The sharp potential break in this case has a slope of $\Delta mV/\Delta ml = 2,000/0.02$ ml of 0.05 M iron(II). The potentials stabilize almost instantaneously during the titration, and within 60 sec at the equivalence point.

The following procedure was used in the determinations: (a) The deaerated manganese(II) sample solution (2–20 mg) was added to 30 ml of a deaerated solution

which was 1–2 *M* in potassium hydroxide and 0.5 *M* in mannitol. Then the oxidation with 0.05 *M* potassium hexacyanoferrate(III) was carried out under potentiometric control. Immediately when the indicator electrode potential reached +150 mV (S.C.E.), titration with 0.05 *M* iron(II) sulphate was carried out in an inert atmosphere (Fig. 2). (b) A manganese(II) sample was transferred to a 100-ml volumetric flask which was then mixed with potassium hydroxide and mannitol, to give a final concentration of 2–3 *M* hydroxide and 0.5 *M* mannitol. The solution was transferred to an Erlenmeyer flask and manganese(II) was preoxidized to manganese(III) with air or oxygen (the originally weakly brownish turbid solution turns intensely brown).

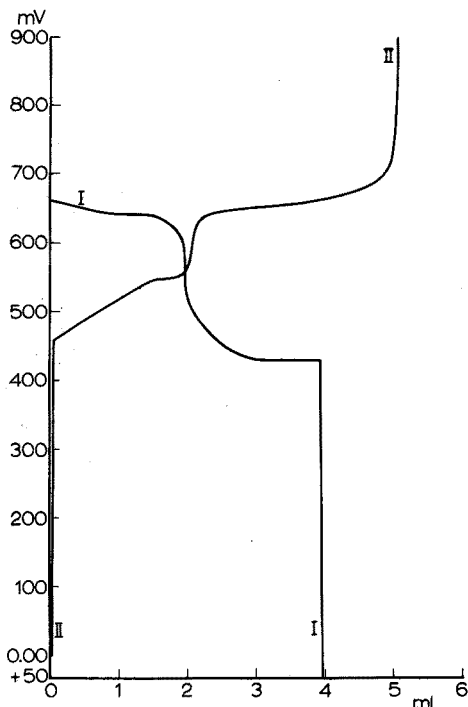


Fig. 2. Titration curves for the oxidimetric and reductimetric determination of manganese. (I) 30 ml 1 *M* KOH and 0.5 *M* mannitol + 2 ml 0.05 *M* Mn(II); titration with 0.05 *M* $K_3\{Fe(CN)_6\}$. (II) Reduction of Mn(IV)–mannitol complex with 0.05 *M* $FeSO_4$. $T = 20^\circ$; Pt–S.C.E. Theoretical consumption corresponding to the oxidation $Mn(III) \rightarrow Mn(IV)$ and the reduction $Mn(IV) \rightarrow Mn(III) = 2.00$ ml. Found: ml 0.05 *M* $K_3\{Fe(CN)_6\} = 2.00$; ml 0.05 *M* $FeSO_4 = 2.005$.

Fig. 3. Titration curve for the reduction of the manganese(IV)–mannitol complex (oxidation with PbO_2) with iron(II) sulphate. 25 ml 3 *M* KOH + 0.5 *M* mannitol; 2.5 ml 0.05 *M* Mn(IV); titration with 0.05 *M* $FeSO_4$. $T = 20^\circ$; Pt–S.C.E.

Then 1–2 g of lead dioxide was added and the oxidation $Mn(III) \rightarrow Mn(IV)$ was carried out with vigorous stirring for 15–20 min (the brown solution turned ruby red). The solution was filtered through a G4 sintered glass filter and an aliquot part was titrated, after deaeration, with 0.05 *M* iron(II) sulphate in an inert atmosphere, under potentiometric control. It is recommended to carry out the filtration in duplicate.

It follows from the results obtained that the oxidation proceeds more easily

in 0.5–1 *M* hydroxide than in solutions 2–4 *M* in hydroxide and 0.5 *M* in mannitol (*cf.* the titration of $K_2Cr_2O_7$). The large positive error of the iron(II) salt consumption for the Mn(III)–complex \rightarrow Mn(II)–complex reduction must be ascribed to the equilibria expressed by eqns. (1)–(3). This was proved experimentally in the reduction of the manganese(III)–complex.

Consequently, in both cases the concentration is calculated from the consumption of the iron(II) sulphate standard solution corresponding to the Mn(IV)–complex \rightarrow Mn(III)–complex reduction. Figure 2 shows the oxidation of the manganese(II)–complex with potassium hexacyanoferrate(III) in the 2 *M* hydroxide–0.5 *M* mannitol medium and the following redoximetric determination (Mn(IV) \rightarrow Mn(III)) with iron(II) sulphate. The reduction of the manganese(IV) complex with iron(II) sulphate in a medium of 3 *M* hydroxide and 0.5 *M* mannitol is shown in Fig. 3. The oxidation was carried out with lead dioxide.

The results of this determination of manganese (1–20 mg Mn in 30 ml) are subject to an error of -1% , provided that the titration is carried out within 30 min after the end of the oxidation. After 120-min standing of the manganese(IV)–mannitol solutions, the results were subject to a negative error, apparently caused by an auto-photoreduction.

TABLE II

DETERMINATION OF MANGANESE IN 2–3 *M* HYDROXIDE–0.5 *M* MANNITOL MEDIUM

($T = 20^\circ$; total volume = 25 ml; titration with 0.05 *M* $FeSO_4$. The results are averages of 3 measurements)

<i>Mn</i> taken (mg)	<i>Mn</i> found (mg)	Error (%)
1.35(9)	1.36(5)	+0.47
2.71	2.69	-1.02
5.43	5.43	—
8.15(4)	8.12(3)	-0.39
8.15(4)	8.12(6)	-0.42
15.65(7)	15.02(2)	-4.08
15.65(7)	15.65(7)	—

For example, the determination of 7.35 mg of manganese in 3 *M* hydroxide and 0.5 *M* mannitol exhibited an error of -25% after 24-h standing of the solution. Some results of determinations of manganese are given in Table II.

The titration of cobalt

Solutions of the mannitol complexes of di- and trivalent cobalt have different colours depending on the alkalinity of the solution and the degree of oxidation with atmospheric oxygen. In solutions containing 1–4 *M* potassium hydroxide and 0.5 *M* mannitol, the complexes of cobalt(II) are sky-blue, and those of cobalt(III) are olive-green or blue-green. The degree of oxidation with atmospheric oxygen or with pure oxygen was followed by titration of the cobalt(III) complex with iron(II) sulphate. It was found that, after 1 hour of passing oxygen through the solution containing 0.5 *M* mannitol, the oxidation was completed to about 58% in the presence of 2 *M*

hydroxide, about 48% in 3 M hydroxide, and about 44% in 4 M hydroxide. Quantitative oxidation of the cobalt(II) complex was achieved in a solution 3–4 M in hydroxide and 0.5 M in mannitol by the 15-min action of lead dioxide. The results of the oxidation in 0.5–2.5 M hydroxide–0.5 M mannitol were always subject to a negative error, the value of which decreased with increasing hydroxide concentration. Similar to the case of the manganese(IV) complexes, an auto- or photoreduction of the cobalt(III)–mannitol complex was observed.

The following titration procedure was used: in a 100-ml volumetric flask, potassium hydroxide and mannitol of the desired concentrations were added to a cobalt(II) sample (1–20 ml of 0.05 M Co^{2+}). The solution was mixed and transferred to an Erlenmeyer flask, 2 g of lead dioxide were added and the solution was oxidized for 20 min with vigorous stirring. The solution was filtered twice on a G4 sintered glass filter, an aliquot part (25–30 ml) was deaerated by passing nitrogen for 20 min, and immediately afterwards, the titration with 0.05 M iron(II) sulphate was carried out in an inert atmosphere. Potentials stabilized practically instantaneously during the titration (2–4 M hydroxide–0.5 M mannitol) and the end-point was shown by a sharp potential break ($\Delta mV/\Delta ml = 3,000/0.02$ ml of 0.05 M iron(II); Fig. 4). The results obtained in the oxidation and the reductimetric determination of cobalt in a medium of 3–4 M hydroxide and 0.5 M mannitol were subject to an average error of 2%. The oxidation of the mannitol complexes of cobalt(II) with potassium hexacyanoferrate(III) was also followed. However, the complexes of di- and trivalent

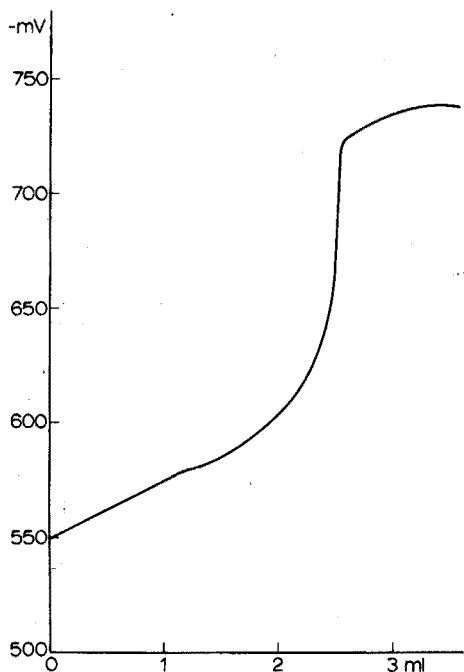


Fig. 4. Titration curve for the reduction of the cobalt(III)–mannitol complex (oxidation with PbO_2) with iron(II) sulphate. 25 ml 4 M KOH + 0.5 M mannitol; 1.25 ml 0.05 M Co(III) ; titration with 0.05 M FeSO_4 . $T = 20^\circ$; Pt–S.C.E.

cobalt apparently catalyze the mannitol oxidation so that the end of the cobalt(II) oxidation is not shown by a potential break as was the case for the oxidation of the mannitol complexes of $\text{Mn(II)} \rightarrow \text{Mn(III)} \rightarrow \text{Mn(IV)}$.

Copper

The copper(II) complexes with triethanolamine are reduced to the metal with iron(II) sulphate¹. It was found that, in an alkaline medium (0.5–4 M hydroxide–0.5 M mannitol), the intense blue mannitol complexes of copper(II) are reduced by iron(II) sulphate to the complexes of copper(I), or to copper(I) hydroxide. The reduction was followed potentiometrically in an inert atmosphere. The potential values stabilize within 60 sec during the titration, but 2 min must be allowed at the equivalence point. The end-point is clearly defined; for example, in a 2 M hydroxide–0.5 M mannitol solution, $\Delta mV/\Delta ml = 3,000/0.02$ ml of 0.05 M iron(II). The results, however, showed an error up to +5% (30 ml of 1–3 M hydroxide–0.5 M mannitol, 1–10 ml of 0.05 M Cu^{2+}) because of the formation of a precipitate in the solution.

DISCUSSION

It is obvious from the formal redox potential values of the system $\text{Fe(II)}\text{--mannitol}/\text{Fe(III)}\text{--mannitol}$ (Fig. 1, Table I) that iron(II) sulphate is a relatively strong reducing agent in an alkaline mannitol medium, with which it is possible to titrate potentiometrically *e.g.* dichromate ($\text{Cr}_2\text{O}_7^{2-} \rightarrow \text{Cr(III)}$), the manganese(IV)–mannitol complex ($\text{Mn(IV)} \rightarrow \text{Mn(III)}$), the cobalt(III)–mannitol complex ($\text{Co(III)} \rightarrow \text{Co(II)}$), and the copper(II)–mannitol complex ($\text{Cu(II)} \rightarrow \text{Cu(I)}$). The titration can be performed even on the micro-scale. Further possibilities of application will be followed, *e.g.* the determination of tellurate and some organic systems, etc., in a similar way as has been done in the case of the titrations with iron(II) sulphate in alkaline triethanolamine. The spectrophotometric study of the coloured mannitol complexes of manganese, cobalt and copper will be discussed in a later paper.

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SUMMARY

The possibility of titrations with iron(II) sulphate in a strongly alkaline medium of mannitol has been studied. From the titration curves of the dichromate reduction, the formal redox potential values of the redox system of the mannitol complexes of iron(II) and iron(III) were measured, in their dependence on the potassium hydroxide concentration. The course of the reduction of the mannitol complexes of tri- and tetravalent manganese, trivalent cobalt, and divalent copper was investigated.

RÉSUMÉ

On examine les possibilités de titrage rédox avec sulfate de fer(II) en milieu

fortement alcalin-mannitol. En se basant sur les courbes de titrage de réduction du dichromate, on effectue des mesures de potentiels du système rédox, complexes mannitol de fer(II) et de fer(III), en fonction de la concentration en hydroxyde de potassium. On examine également les phénomènes de réduction des complexes mannitol/manganèse(III) et (IV), du cobalt trivalent et du cuivre divalent.

ZUSAMMENFASSUNG

Die Möglichkeit von Titrationsen mit Eisen(II)-sulfat in einem stark alkalischen, mannithaltigen Medium wurde untersucht. Aus den Titrationskurven der Dichromatreduktion wurden die formalen Redoxpotentialwerte des Redoxsystems der Mannitkomplexe von Eisen(II) und Eisen(III) als Funktion der Kaliumhydroxidkonzentration ermittelt. Der Verlauf der Reduktion der Mannitkomplexe von drei- und vierwertigem Mangan, dreiwertigem Kobalt und zweiwertigem Kupfer wurde untersucht.

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POLAROGRAPHIC DETERMINATION OF TIN IN COPPER-, ALUMINUM- AND ZIRCONIUM-BASE ALLOYS

TOMOYUKI MUKOYAMA, TAKESHI YAMANE, NOBUTOSHI KIBA and MASAO TANAKA

Department of Chemistry, Yamanashi University, Takeda, Kofu-shi (Japan)

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The various methods commonly employed for the determination of tin are not completely satisfactory. The widely used iodimetric method has several disadvantages: tin(II) is so easily oxidized that the reduction of tin(IV) is always incomplete, and numerous ions interfere. In the spectrophotometric technique, the results depend on the experimental conditions employed, and the procedures are complicated and tedious¹⁻³.

Polarographic methods have several interfering metal ions, such as arsenic(III), bismuth(III), antimony(III) and especially lead(II) in Lingane's supporting electrolyte^{4,5}.

In most of the methods reported, it is necessary to separate the tin from lead and other metals before the final determination. Therefore, many separation methods such as extraction^{6,7}, distillation^{8,9} and co-precipitation⁹⁻¹³ have been investigated. In the co-precipitation method the use of EDTA has been found effective in making the method selective¹⁴. Problems such as selectivity, simplicity or saving of time have, however, remained.

The present paper describes an investigation of the determination of tin in copper-, aluminum- and zirconium-base alloys. In an attempt to improve the convenience and reliability of the method, the co-precipitation method with beryllium hydroxide and an alternating-current polarographic technique have been studied in detail.

EXPERIMENTAL

Reagents

Standard tin solutions. Dissolve 0.500 g of pure tin metal (99.999%) in 250 ml of 6 M hydrochloric acid in the presence of platinum wire as catalyst, and then dilute with water to 500 ml (1 ml \equiv 1 mg of tin). Prepare more dilute solutions from this stock solution by appropriate dilution with 3 M hydrochloric acid.

Beryllium solution. Dissolve 0.50 g of pure beryllium metal (above 99%) in 250 ml of 6 M hydrochloric acid, and dilute with water to 500 ml.

Wash solution. Dissolve 5 g of EDTA in 1000 ml of 0.3 M ammonia solution. All reagents should be of the highest grade of purity obtainable.

Apparatus

Polarograms were recorded with a Yanagimoto Polarograph Type PA 101;

a cell with a mercury pool reference electrode was employed. In all cases, the cell was maintained at $25.0 \pm 0.2^\circ$ in a thermostatted bath.

The drop time, measured in 3.0 M hydrochloric acid solution at a mercury height of 64.0 cm and at a peak potential of -0.47 V vs. the mercury pool anode, was 5.0 s. Dissolved oxygen was removed from the solution by passing hydrogen through the cell for 5–10 min.

Dissolution of samples

Copper alloy. Dissolve in 20 ml of mixed acid (nitric acid + hydrochloric acid + water = 1 : 2 : 4).

Aluminum alloy. Dissolve in 20 ml of 6 M hydrochloric acid with dropwise addition of 1 ml of 30% hydrogen peroxide.

Zirconium alloy. Dissolve in 20 ml of 9 M sulfuric acid with dropwise addition of 1 ml of 42% hydrofluoroboric acid.

Procedure

Transfer a suitable weight of sample (Note 1) to a 100-ml beaker, and dissolve the sample as described above. Add 8 ml of the beryllium solution and an adequate volume of aqueous 10% (w/v) EDTA (disodium salt) solution (Note 2). Boil gently for 3 min (Note 3) and adjust the pH to 8.0 with 7.5 M ammonia solution. Boil for 2 min, remove from the hot plate, allow the precipitate to settle, and filter the solution through a filter-paper. Wash the precipitate thoroughly with 30 ml of wash solution.

Pierce a hole in the filter-paper with a pointed glass rod, and wash out the precipitate into the calibrated flask with addition of 25 ml of 6 M hydrochloric acid. Dilute to 50 ml with water.

Transfer 2–3 ml of this solution to the cell and remove oxygen by passing hydrogen. Measure the peak height of the tin wave at -0.47 V vs. mercury pool.

Notes. 1. It is recommended that 1.0 g of sample be taken for an expected tin content of 0.002–0.25%, and a 0.1 g of sample for tin contents of 0.25–25%.

2. If the 1 : 1 metal–EDTA chelate is completely formed, the calculated amount of EDTA (disodium salt) is 5.8 g for 1 g of copper, 13.8 g for 1 g of aluminum and 4.1 g for 1 g of zirconium. The volume of EDTA solution used is 6 ml for 1 g of copper, 14 ml for 1 g of aluminum-, and 4.5 ml for 1 g of zirconium-base alloy.

3. Some metal ions, e.g. aluminum, react slowly with EDTA at room temperature. When the sample is aluminum alloy, the heating time is 10 min.

Calibration

Transfer suitable amounts of standard tin solution for the construction of two calibration graphs to cover the ranges 0.002–0.025% and 0.025–0.25% of tin.

Introduce into each flask 25 ml of 6 M hydrochloric acid and make up to 50 ml with water. Complete the determinations as outlined above.

RESULTS AND DISCUSSION

Separation of tin

Experiments were carried out to determine the effect of varying the amounts of beryllium and EDTA and the acidities at which the precipitation was made.

Wash solutions also were investigated.

Tests showed that the degree to which tin was co-precipitated was largely dependent on the concentration of acid and amount of beryllium. Co-precipitation of tin ranging from 20 to 2500 μg was practically quantitative above 7 mg of beryllium and at pH 8.0. The effect of pH on the recovery of 50 μg of tin was studied for 8.0 mg of beryllium; 100% recovery was obtained in the pH range 7–10.

Contamination of the precipitate by other metal ions could be completely eliminated by addition of EDTA before precipitation and by washing the precipitate. A small excess over the calculated amount of EDTA was sufficient to form the chelates with large amounts of base metal, and also it appeared that some of the other interfering ions could be masked by this addition (see below).

Of several wash solutions examined, the best was 0.3 M ammonia solution containing 0.5% EDTA. When small amounts of wash solutions were used, considerable amounts of base metal remained in the precipitate, but excess of wash solution tended to redissolve the precipitate; 30 ml of this solution was sufficient to complete the separation.

Polarographic measurements

It is convenient to determine tin polarographically in the tetravalent state, for difficulties are encountered in the reduction and in maintaining tin(II) during polarography. Lingane⁴ proposed that tin(IV) should be polarographed in the presence of an excess of chloride or bromide ions. Kallmann *et al.*⁹ used only hydrochloric acid, in preference to Lingane's supporting electrolyte.

With consideration of the working solution from the separation technique, some experiments were made on the alternating-current polarographic determination of tin in hydrochloric acid as supporting electrolyte. It was shown that the height of the diffusion wave of tin(IV) was independent of the concentration of hydrochloric acid in the range 2–5 M, and that reproducible well-defined polarograms were obtained.

The peak potential and peak height of the tin wave were completely unaffected by the inclusion of beryllium and EDTA in amounts up to 20 mg per 50 ml and 1000 mg per 50 ml, respectively. On the basis of these observations, a potential of -0.47 V vs. Hg pool, and a 3 M hydrochloric acid solution as supporting electrolyte, was chosen; measurements were made directly after dissolution of precipitate with hydrochloric acid.

Interference study

Lead in hydrochloric acid supporting electrolyte is reduced at about -0.46 V, hence trace amounts of lead cause high results. Several determinations were carried out in the presence of lead, as described under *Procedure*, with synthetic samples prepared from 1 g of copper, aluminum or zirconium. Some typical results are shown in Table I. It was, therefore, necessary to verify that lead is completely separated from tin, and consequently does not interfere.

In this supporting electrolyte, copper, arsenic, antimony, bismuth and molybdenum are also reduced at about -0.25 , -0.30 and -0.6 , -0.15 , -0.10 and -0.25 V, respectively. The presence of these ions distorted the tin wave and caused low results. Both cadmium and tungsten are reduced at about -0.65 V. The presence

TABLE I

EFFECT OF LEAD ON RECOVERY OF TIN ADDED TO 1 g OF ZIRCONIUM
(100.0 μg Sn was used in all cases)

Lead added (%)	Tin found (μg)	Error (%)
1.00	100.2	+0.2
1.50	100.8	+0.8
2.00	101.4	+1.4
2.50	103.0	+3.0

of these ions obscures the base line, and the effect is particularly serious when the concentration of tin is low. To determine the recoveries of tin, measurements were made on synthetic samples containing 1 g of pure copper and various amounts of these elements; no interferences were found in the determination of 200.0 μg of tin when 1.0 or 10.0% of arsenic(III), antimony(III), bismuth(III), molybdenum(VI), tungsten(VI) or cadmium(II) were added. It is therefore clear that a good separation of tin from many of the interfering ions is possible by a single co-precipitation of tin by the described method.

Determination of tin in the sample

The proposed method was applied to Chemical Analysis Standard (Japan) samples for copper-base alloys, to British Chemical Standard sample for aluminum-base alloys and to National Bureau of Standard samples for zirconium-base alloys. The results are shown in Tables II and III. It is evident from these results that there is good agreement between the results by the proposed and established procedures. The reproducibility of the results is good; for samples containing 1.77 and 0.0285% of tin, the standard deviation is 0.04 and 0.0003, respectively.

The proposed method for the determination of tin in these alloys is very simple, selective and accurate, and the method appears to be applicable to the determination of small amounts of tin in other metals and alloys.

TABLE II

TIN CONTENTS FOUND BY PROPOSED METHOD IN COPPER ALLOYS
(Each Sn result is the average of 10 determinations)

Sample	Composition (%)	Sn found average (%)	Standard deviation
A	Tin, 0.65; copper, 58.9; lead, 2.28; iron, 0.23; zinc, ad 100	0.653	0.002
B	Tin, 1.00; copper, 62.2; lead, 0.0066; iron, 0.01; zinc, ad 100	1.003	0.002
C	Tin, 0.02; copper, 60.6; lead, 1.23; iron, 0.04; zinc, ad 100	0.0285	0.0003

TABLE III

TIN CONTENTS FOUND BY THE PROPOSED METHOD IN ALUMINUM AND ZIRCONIUM ALLOYS

Sample	Certificated value (%)	Tin found average (%) ^a	Standard deviation
<i>Aluminum alloy</i>			
B.C.S. No. 216-1	Tin 0.05	0.0565	0.0004
<i>Zirconium alloys</i>			
N.B.S. 1214	Tin, 1.60; iron, 0.067; chromium, 0.10; nickel, 0.05	1.59	0.01
N.B.S. 1213	Tin, 1.76; iron, 0.06; chromium, 0.05	1.77	0.04

^a Average of 10 determinations.

SUMMARY

An alternating-current polarographic method is described for determining tin in copper-, aluminum- and zirconium-base alloys. With EDTA as masking agent and co-precipitation with beryllium hydroxide, tin is separated selectively from other metal ions and determined polarographically in a 3 M hydrochloric acid as supporting electrolyte. The method is simple, selective and accurate. A single determination takes about 45 min.

RÉSUMÉ

Une méthode polarographique à courant alternatif est décrite pour le dosage de l'étain dans des alliages de cuivre, d'aluminium et de zirconium. On sépare l'étain, sélectivement des autres ions métalliques, en présence d'EDTA et par coprecipitation avec l'hydroxyde de béryllium; il est ensuite dosé polarographiquement en milieu acide chlorhydrique 3 M, comme électrolyte de base. Cette méthode est simple, sélective et précise. Un dosage demande environ 45 min.

ZUSAMMENFASSUNG

Es wird eine wechselstrompolarographische Methode für die Bestimmung von Zinn in Kupfer-, Aluminium- und Zirkoniumlegierungen beschrieben. Mit EDTA als Maskierungsreagenz wird Zinn durch Mitfällung mit Berylliumhydroxid selektiv von anderen Metallionen abgetrennt und in 3 M Salzsäure als Trägerelektrolyt polarographisch bestimmt. Die Methode ist einfach, selektiv und genau. Eine einzelne Bestimmung dauert etwa 45 min.

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DETERMINATION OF RHODANASE ACTIVITY WITH CYANIDE ION-SELECTIVE ELECTRODES UNDER FLOW-STREAM CONDITIONS

W. R. HUSSEIN, L. H. VON STORP and G. G. GUILBAULT

Department of Chemistry, Louisiana State University in New Orleans, New Orleans, La. 70122 (U.S.A.)

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Enzyme-catalyzed chemical reactions have found wide applications in analytical chemistry. The determination of enzyme activity by reaction rate measurements with ion-selective electrodes has recently received considerable attention¹⁻⁵.

The enzyme rhodanase was discovered by Lang⁶ in 1933; it catalyzes the reaction:



Thus far, only spectrophotometric analytical procedures have been described for the assay of the activity of rhodanase. These methods are based on the reaction of the thiocyanate produced with iron(III) to give a red complex^{7,8}. Apart from the rather involved procedure the main limitation of this method lies in the large excess of iron(III) that is required to ensure formation of a rather unstable 1:1 iron(III)-thiocyanate complex⁹.

Thiocyanate ion which is produced according to reaction (1) could be monitored with a thiocyanate ion-selective electrode except that cyanide ion is a serious interference¹⁰.

An alternative approach is to follow the decrease in cyanide concentration with a cyanide electrode. Interferences from thiocyanate and sulfite ions ($K_{\text{CN}^-/\text{SO}_3^{2-}} = 10^{-3}$, $K_{\text{CN}^-/\text{SO}_3^-} = 5 \cdot 10^{-4}$) are very small, and the additional response of the electrode towards thiosulfate ions is compensated for by using a second cyanide electrode as a reference in a flow-stream.

The work described is concerned with the continuous analysis of rhodanase activity as a rapid, accurate and sensitive method of analysis.

EXPERIMENTAL

Potentiometric measurements were made with the Orion digital pH meter (Model 801). In order to observe small drifts in electrode potential the signal was displayed on a potentiometric recorder (Sargent Model SRLG) which incorporated a back-off device.

Cyanide electrodes were prepared in this laboratory from plexiglas tubes onto which a cyanide-sensitive membrane was fitted. The pressed membranes consisted of silver iodide and silver sulfide salts of a 1:1 ratio. A silver wire in 10^{-2} M silver nitrate solution was used as internal reference (Fig. 1).

For measurements in a flow stream two cyanide electrodes were used as refer-

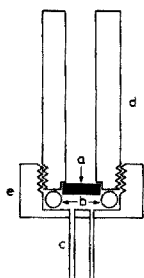


Fig. 1. Flow-through electrode design. (a) Membrane; (b) o-ring; (c) stainless steel capillary; (d) electrode body; (e) flow-through cap. Volume of flow-through chamber: 0.1 ml.

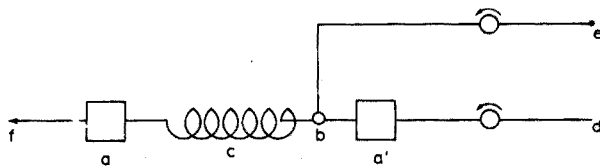


Fig. 2. Flow diagram for continuous assay of rhodanase activity. (a, a') Indicating cyanide electrode and reference cyanide electrode, respectively; (b) mixing chamber, (c) delay coil, (d) 1.5 ml min^{-1} substrate solution; (e) 0.5 ml min^{-1} enzyme solution; (f) waste.

ence and indicating electrodes, respectively. They were modified by fitting a flow-through cap onto the membrane face (Fig. 1).

The flow system is shown in Fig. 2. The enzyme solution was introduced into the substrate via a mixing chamber after the first electrode (reference CN^-) and passed through a delay coil which permitted a reaction time of 1 min before the change in substrate concentration was monitored by the second indicating CN^- electrode. The delay coil was kept in a controlled temperature bath. The outflow was gravity-fed to waste.

A Sage peristaltic pump (Model 375) was used. The flow rates were 1.5 ml min^{-1} and 0.5 ml min^{-1} for the substrate and enzyme solutions, respectively.

All chemicals used were reagent grade. The rhodanase (beef liver, Sigma Chemical Co., St. Louis) was assayed spectrophotometrically⁷⁻⁹ and was found to have an activity of 1.55 units per mg (one unit equals $1 \mu\text{mole of SCN}^-$ formed per mg of enzyme per min at pH 8.6 and 25°). Solutions of rhodanase were prepared in 0.25% albumin solution¹¹. All solutions were prepared on the day of measurement.

RESULTS AND DISCUSSION

Calibration of cyanide electrodes

The cyanide electrodes were calibrated in stationary stirred solutions containing equimolar concentrations of thiosulfate and cyanide ions in 0.5 M phosphate buffer at pH 8. The reference cyanide electrode was immersed in a $5 \cdot 10^{-4} \text{ M}$ solution of cyanide and thiosulfate while the solution concentrations at the indicating cyanide electrode were varied in the range of 10^{-2} – 10^{-4} M in cyanide and thiosulfate ions. The reference and test solutions were connected via an agar salt bridge. The calibration graph (Fig. 3) gave a slope of 56 mV/decade. By using this type of electrode arrangement the interference of thiosulfate at a cyanide electrode was completely eliminated.

Measurements of rhodanase activity

For reaction rate determinations 5 ml containing various concentrations of enzyme were injected into 50 ml of a solution containing 10^{-3} M cyanide and thiosulfate ions (see Table I). The reaction was followed as the potential change with time

TABLE I

COMPARISON OF ENZYME ACTIVITY ASSAY BY POTENTIOMETRIC AND SPECTROPHOTOMETRIC METHODS

Rhodanase concn. (mg ml ⁻¹) ^a	$\Delta E \text{ min}^{-1}$	Calculated enzyme (units mg ⁻¹)	
		Potentiometric	Spectrophotometric
2	9.5	1.60	1.55
1	4.4	1.62	1.58
0.5	2.2	1.61	1.56

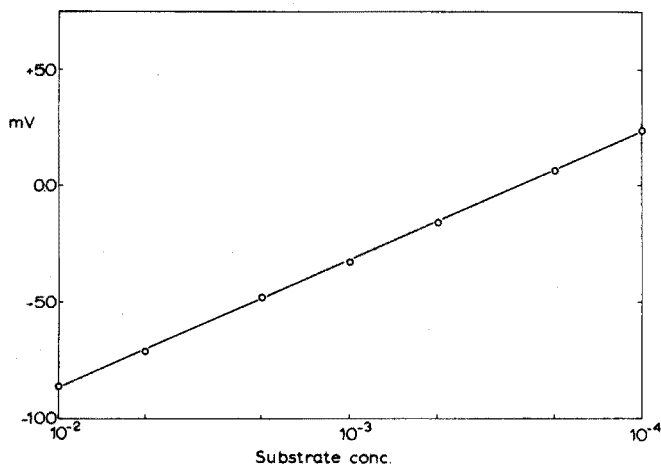
^a Concentration in stock solution used.

Fig. 3. Electrode calibration in equimolar mixtures of cyanide and thiosulfate solution concentrations.

at the indicating electrode *vs.* the reference CN^- electrode. The enzyme activity values which were calculated from the calibration graph agreed well with those obtained spectrophotometrically (Table I). The cyanide electrodes were then modified for measurements in a flowing stream.

Effect of temperature, pH, buffer

Optimal conditions such as temperature, pH, type of buffer and substrate concentration were determined for assay of the enzyme activity.

The optimal temperature is dependent on the source of enzyme and its preparation¹². Measurements were carried out with $10^{-3} M$ cyanide and thiosulfate in $0.5 M$ phosphate buffer at pH 8. A 0.25% albumin solution was used for the preparation of the enzyme sample (20 mg/50 ml) as well as for the blank solution used for all potential measurements. An increase in enzyme activity was observed with increase in temperature (Fig. 4) which corresponds well with the values already obtained. Above 40° a rapid denaturation of the enzyme was observed. The error of electrode response, however, increased with higher temperature thus giving an optimal temperature range of $25\text{--}30^\circ$.

From preliminary spectrophotometric determinations of enzyme activity in

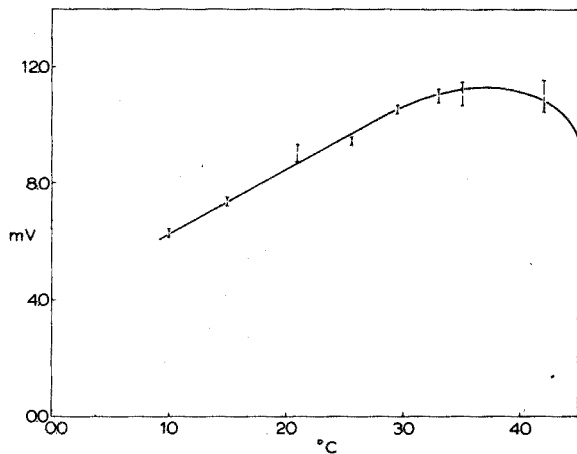


Fig. 4. Effect of temperature on the enzymic activity.

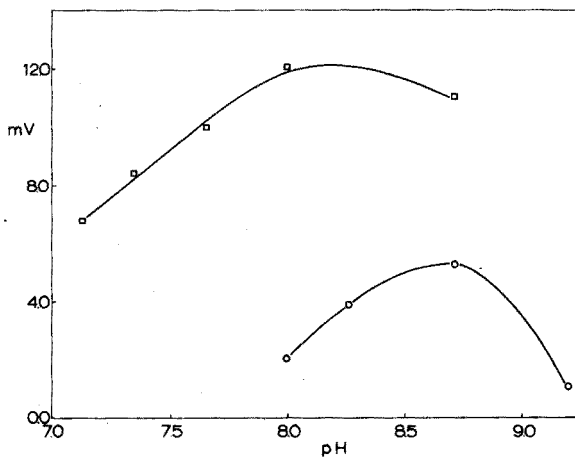


Fig. 5. Enzymic activity dependence on nature of buffer and pH. (○) 0.5 M TRIS buffer; (□) 0.5 M phosphate buffer.

this laboratory with potassium hydrogenphthalate, TRIS, borax, and phosphate buffers, it was evident that TRIS and phosphate buffers provided the most favorable medium for measuring enzyme activity. In order to evaluate the most suitable buffering medium for potentiometric determinations, phosphate and TRIS buffers were used at various pH values (Fig. 5). The results indicated that phosphate buffer at pH 8 provides the optimum conditions for both enzyme activity and electrode response.

Theoretical considerations

The correlation between enzyme activity and substrate concentration is given by the Michaelis-Menten equation, *i.e.*

$$\frac{-dS}{dt} = \frac{k_3[E]S}{K_m + S} \quad (2)$$

where E and S represent the concentration of enzyme and substrate, respectively, k_3 the rate constant for disproportionation of the enzyme-substrate complex into free enzyme and product, K_m the Michaelis constant, and t the time.

Reaction rate measurements of enzyme activity are usually carried out with a high substrate concentration. In this case the reaction rate is directly proportional to enzyme activity and independent of the substrate concentration ($K_m \ll S$).

At very low substrate concentration most of the enzyme molecules are in the free state, *i.e.*, only a small number are present in the enzyme-substrate complex form the formation of which controls the reaction rate, which in turn is proportional to the substrate concentration.

The optimal concentration range for cyanide electrodes, however, is between 10^{-2} and 10^{-4} M in cyanide ion¹³. At this concentration the substrate concentration is approximately equal to the K_m .

The decrease in cyanide concentration is monitored after a constant time (60 sec) and as a result, eqn. (2) can be integrated over the time interval t :

$$\int_{S_0}^S (K_m + S) \frac{-dS}{S} = k_3 [E] \int_{t_0}^t dt \quad (3)$$

where S_0 represents the initial substrate concentration and t the reaction time. Thus

$$-k_3 [E] t = K_m \ln S + S - (K_m \ln S_0 + S_0) \quad (4)$$

The determination of the optimal substrate concentration was carried out with equimolar mixed cyanide-thiosulfate solutions over the concentration range $5 \cdot 10^{-3}$ to 10^{-4} M . The substrate was buffered at pH 8 with 0.5 M phosphate buffer and the electrode response was measured with various enzyme concentrations. The concentration ratio of $CN^-/S_2O_3^{2-}$ of 1:1 was taken to be optimum¹². It should be pointed out, however, that variations of this ratio have no bearing on the potential difference between the two cyanide electrodes placed in a flow-stream because the

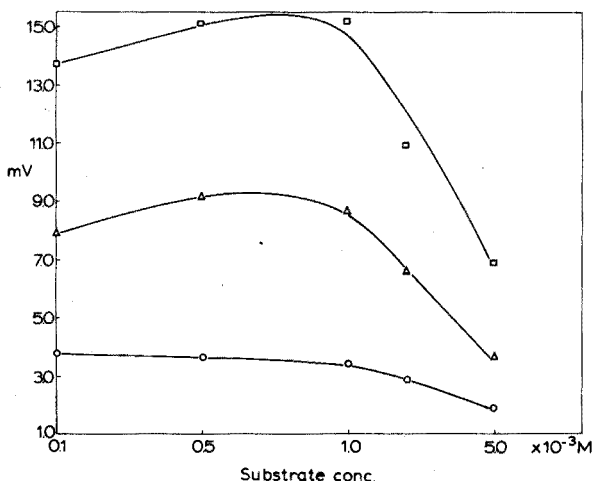


Fig. 6. Dependence of enzymic activity on substrate concentrations using enzymic activities of: (\square) 0.40 units; (\triangle) 0.20 units; (\circ) 0.08 units.

interference from thiosulfate is compensated for by the use of a cyanide electrode as reference.

According to Fig. 6, the optimal substrate concentration was observed to be within the range of 10^{-3} – $5 \cdot 10^{-4}$ M cyanide and thiosulfate.

The decrease of the electrode response below 10^{-4} M can be attributed to the decreased electrode sensitivity, whereas the decrease in electrode potential change at concentrations of cyanide and thiosulfate greater than 10^{-3} M may be due to enzyme inhibition at higher substrate concentrations or the Nernstian relationship of the electrode response. This effect is not a consequence of the integrated Michaelis equation which can be explained by differentiating eqn. (4),

$$-d[E] \cdot t \cdot k_3 = K_m(1+S)d \ln S \quad (5)$$

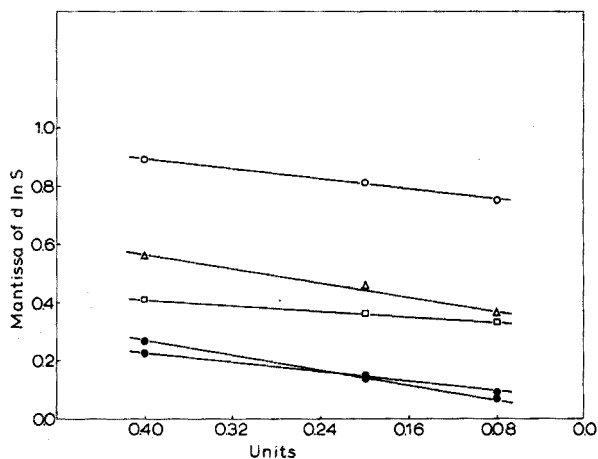


Fig. 7. First derivative of eqn. (4) plotted against $d \ln S$ with substrate concentration S_0 : (O) $2 \cdot 10^{-3}$ M, (Δ) $5 \cdot 10^{-4}$ M, (□) $5 \cdot 10^{-3}$ M, (⊙) $1 \cdot 10^{-3}$ M, (●) $1 \cdot 10^{-4}$ M.

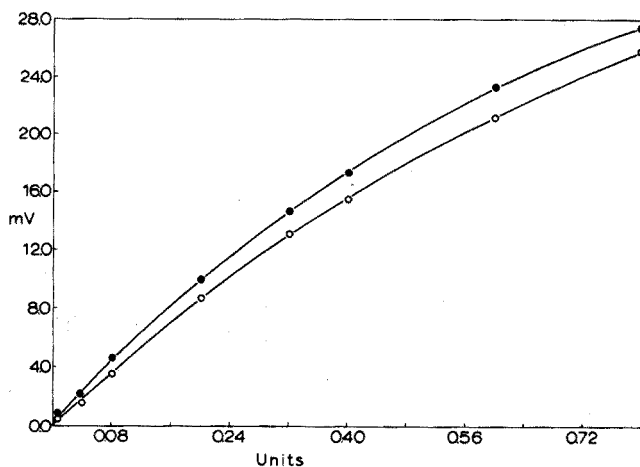


Fig. 8. Calibration of electrode response vs. enzymic activity with different ratios of silver sulfide to silver iodide in the cyanide-sensitive membrane. (●) 10:1 Ag_2S/AgI ; (O) 1:1 Ag_2S/AgI .

If the change in substrate concentration, $d \ln S$, is plotted against the change in enzyme concentration, dE , a family of curves is obtained (Fig. 7) the slope of which is dependent on the factor $K_m(1+S)/tk_3$.

An increase in substrate concentration theoretically should yield steeper curves, whereas experimentally, the opposite effect was observed when a substrate concentration of greater than 10^{-3} M cyanide ion was used.

Rhodanase assay

The electrode response towards rhodanase activity was calibrated under optimal conditions, *i.e.*, substrate concentration of 10^{-3} M cyanide and thiosulfate in 0.5 M phosphate buffer at pH 8. The reaction temperature was maintained at 28° . The enzyme concentration range was 0.008–0.8 units (Fig. 8).

At low enzyme concentrations a linear dependence of electrode response towards enzyme activity was observed which is in agreement with eqn. (5), taking into consideration that the term $d \ln S$ is proportional to the electrode potential difference. At higher enzyme concentrations, however, a slight curvature is observed which is due to the non-linearity of eqn. (4).

The average potential error for the enzyme determination was ± 0.1 mV which corresponds to an error of ± 0.002 units. The sensitivity limit was found to be 0.008 units, the average response time being *ca.* 2 min. The sensitivity of this technique, however, can be improved by extending the enzyme reaction time.

Cyanide-selective membranes

The responses of cyanide electrodes are dependent on stirring and flow rate¹³. In order to reduce this effect, pellets of a 2:1, 5:1, and 10:1 ratio of silver sulfide to silver iodide were prepared and calibrated in stationary stirred solutions in 10^{-1} M sodium hydroxide media for cyanide concentrations over the range 10^{-2} – 10^{-4} M. Electrode potentials were measured against a Beckman saturated calomel electrode. The calibration graphs obtained are shown in Fig. 9. The electrode made

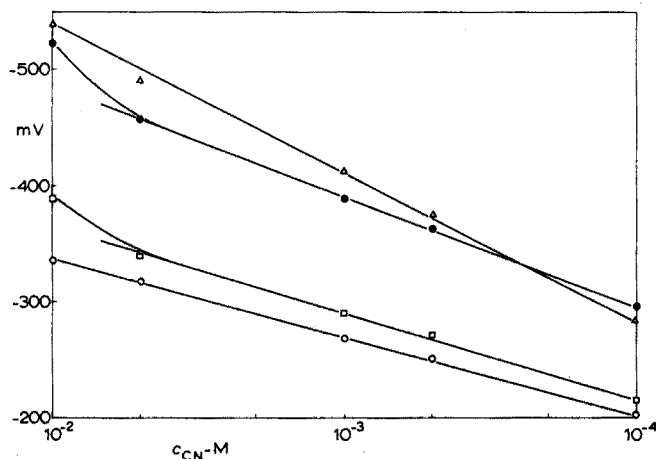


Fig. 9. Calibration graphs of cyanide electrodes with membranes containing various silver sulfide to silver iodide ratios. (Δ) 10:1 Ag_2S/AgI ; (\bullet) 5:1 Ag_2S/AgI ; (\square) 2:1 Ag_2S/AgI ; (\circ) 1:1 Ag_2S/AgI .

with the highest silver sulfide to silver iodide ratio exhibited the highest slope of 121 mV, whereas lower mixture ratios resulted in a slope of the calibration between 120 and 60 mV. This effect may be due to the highly sensitive electrode response towards silver ion which is in equilibrium with a constant amount of silver cyanide complex¹⁴ which is formed from the reaction



and held in the diffusion layer at the electrode surface.

Although the flow rate dependence of the cyanide electrode is greatly improved by the new 10:1 membrane, the response time of this type of membrane is considerably longer (10–15 min) than usually observed with ion-selective electrodes (30–60 sec).

Pellets of the ratio 10:1 in silver sulfide to silver iodide subsequently were used for electrode potential measurements of enzyme activity in a flow-stream.

Under these conditions, however, the expected increased sensitivity which is due to the 120 mV slope of the calibration graph could not be achieved. From the calibration of enzyme activity in Fig. 9, it is evident that only a small increase in sensitivity takes place which may be due to a more efficient washing of the membrane face in flow-streams leading to a lower silver cyanide complex concentration at the electrode surface.

Conclusions

The electrochemical determination of rhodanase with cyanide-selective electrodes which monitor the decrease in concentration provide a sensitive and accurate method of analysis which compares favorably with spectrophotometric procedures. This method requires less sample preparation and is easily adapted to automated systems.

The financial assistance from the National Institute of Health, Grant No. GM 17268 is gratefully acknowledged.

SUMMARY

An electrochemical assay procedure for rhodanase, which uses cyanide-selective electrodes that monitor the decrease in cyanide concentration, provides a sensitive and accurate method of analysis which compares favorably with spectrophotometric procedures. The method requires less sample preparation and is easily adapted to automated systems.

RÉSUMÉ

On propose une méthode électrochimique pour la détermination de rhodanase ; elle est basée sur l'utilisation d'électrodes sélectives, indiquant la diminution de la concentration en cyanure. Elle permet d'obtenir une sensibilité et une exactitude comparables à celles des méthodes spectrophotométriques. En outre, elle exige moins de substance et peut s'adapter facilement à des systèmes automatiques.

ZUSAMMENFASSUNG

Es wird ein elektrochemisches Verfahren zur Bestimmung der Aktivität von Rhodanase beschrieben, bei dem cyanidselektive Elektroden die Verminderung der Cyanidkonzentration verfolgen. Die Methode ist empfindlich und genau und erweist sich als günstig im Vergleich zu spektrophotometrischen Verfahren. Sie erfordert weniger Probenvorbereitung und kann leicht automatisierten Systemen angepasst werden.

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SOME SOLID-STATE PERCHLORATE SELECTIVE ELECTRODES

M. SHARP

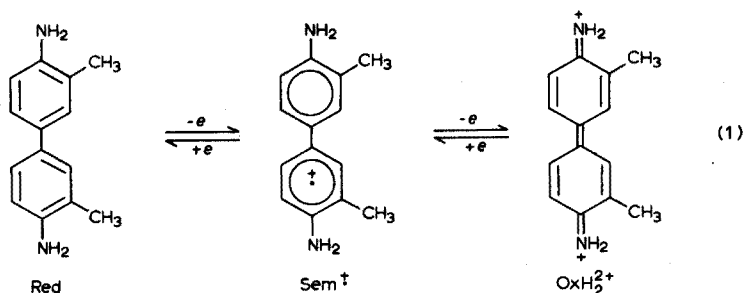
Department of Analytical Chemistry, University of Umeå, S-901 87 Umeå (Sweden)

(Received 5th April 1972)

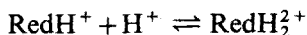
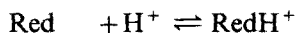
The encouraging results obtained with organic radical-anion salts as electro-active substances in solid-state cation sensitive electrodes^{1,2} have led to the consideration of whether a similar approach might provide acceptable electrodes sensitive to anions. In this instance a relatively stable organic radical-cation is required which is capable of forming sparingly soluble salts with suitable anions. In extension of the arguments applicable to the radical-anion salts studied earlier, such materials would be expected to exhibit sufficient electrical conductivity for electrode purposes.

In this initial investigation, Wurster salts of the radical-cations of derivatives of *p*-phenylenediamine and benzidine were considered suitable for assessing general electrode performance. Since the early investigations of Michaelis *et al.*³⁻⁶, who prepared and studied the behaviour of salts of *p*-phenylenediamine derivatives and discussed the factors affecting stability, many studies have been carried out to determine the properties of these and related compounds both in the solid state and in solution. A recent monograph contains a brief summary of the general results and provides a source of the principal references⁷. Details of the oxidation behaviour of organic compounds have been given by Adams⁸, by Weinberg and Weinberg⁹ and by Clark¹⁰. An article by Szwarc¹¹ summarizes the chemistry of radical-ions.

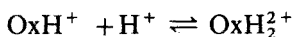
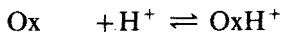
Under suitable conditions, chemical or electrochemical oxidation of certain *p*-diamines results in the formation of semiquinone radical-cations, Sem⁺, which may be regarded as intermediates in the redox equilibrium between the corresponding reduced form, Red, and the higher oxidized species, OxH₂²⁺, which exists in solution. This equilibrium may be illustrated for *o*-tolidine by



Both reduced and oxidized forms take part in further acid-base equilibria by protonation of the amino groups,

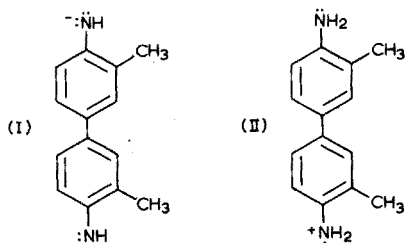


and



(2)

Among the possible pH-dependent forms which may be written for the semiquinone, stabilization by resonance is favoured in only two cases:



of which (I) would predominate only in alkaline solutions. The structure of the radical-cation may therefore be taken as that shown by (II) for the conditions discussed below. In addition, the semiquinone may exist only in limited pH regions and in the form of dimers or higher aggregates even at very low concentrations.

The higher oxidized species, OxH_2^{2+} , in equilibrium (1) is a quinonediimine which is normally highly unstable and readily undergoes irreversible reactions at higher pH values. Rapid removal of OxH_2^{2+} , *e.g.*, by reaction with the solvent, may cause the semiquinone radical-cation, with which it is in equilibrium, to exist only transiently in certain solutions whereas from theoretical considerations and observations in more favourable systems the species is in fact quite stable. By considering equilibria (1) and (2) jointly and including the possibility of semiquinone dimerization, it is apparent that the stability of the radical-cation species is determined by the pH and concentration of the solution and by the nature of the solvent.

In the solid state, however, the semiquinone form may be stabilized for considerable periods through careful choice of the anion with which it undergoes salt formation. Controlled oxidation of the parent *p*-diamine under well-defined conditions and in the presence of an excess of the appropriate anion leads to precipitation of the semiquinone as a sparingly soluble solid. The exact configuration of the semiquinone, *i.e.*, whether it exists as a free radical-cation or in the form of a dimer or higher aggregate, is not firmly established in the majority of cases.

With reference to the *p*-diamines studied below, recent work by Kuwana and Strojek¹², and Johnson and Øverby¹³ includes interpretations of the redox and concentration equilibria for *o*-tolidine and an earlier article by Oldfield and Bockris¹⁴ deals with the redox systems of benzidine, *o*-tolidine and *o*-dianisidine.

Numerous studies of solid salts derived from these diamines and analogous compounds by spectral and e.s.r. methods may be found in the literature.

EXPERIMENTAL

Materials

The perchlorate salts of the following commercially available *p*-diamines were successfully synthesized by the methods described.

N,N,N',N'-Tetramethyl-*p*-phenylenediamine (Eastman-Kodak). The dihydrochloride of the parent amine was oxidized with aqueous bromine in the presence of sodium perchlorate employing the quantities and conditions of Michaelis and Granick⁶. The blue solid perchlorate has been reported to be stable for periods of many months. Electronic spectra in methanol gave sharp peaks at 567 nm and 615 nm characteristic of the radical-cation.

N,N,N',N'-Tetra-*n*-butyl-*p*-phenylenediamine. Stoichiometric amounts of *p*-phenylenediamine and tri-*n*-butylphosphate were allowed to react; the actual procedure was an adaptation of a method outlined by Vogel¹⁵. Separation and purification of the product followed the procedure given. The dark oil obtained gave a characteristic blue colouration on oxidation in methanol with aqueous bromine. This suggested the presence of the radical-cation or its dimer. Electronic absorption spectra in methanol showed two sharp peaks at 575 nm and 624 nm and a shoulder centred at 530 nm, which is in substantial agreement with the spectra of semiquinones of other *N,N,N',N'*-tetra-alkylated *p*-phenylenediamines⁵. (The corresponding spectrum for the oxidation product of *p*-phenylenediamine shows sharp peaks at 462 nm and 479 nm.) Subsequent attempts to prepare the perchlorate salt of the tetra-*n*-butyl-*p*-phenylenediamine by the Michaelis method failed, however, the resulting product exhibiting a solubility in water which was too high for precipitation to occur at the concentrations employed.

o-Tolidine (B.D.H.) and *o*-dianisidine (Eastman-Kodak). The perchlorates were obtained by an adaptation of the Michaelis method cited above. The products were isolated as dark blue solids and were apparently stable for a period of several months. Electronic spectra in methanol gave broad bands centred at 420 nm and 438 nm for *o*-tolidine perchlorate and *o*-dianisidine perchlorate, respectively.

Benzidine (Baker & Co) and *N,N,N',N'*-tetramethylbenzidine (Eastman-Kodak). These diamines were first converted to the corresponding bromide salts by the method of Milligan¹⁶. The bromides were dark-blue and dark-green solids, respectively. That derived from benzidine was found to be quite stable in the solid state for several months but the tetramethylbenzidine derivative decomposed within a few days to a pale yellow solid. For this reason the bromide was converted to the relatively more stable perchlorate as quickly as possible after preparation. Both bromides were sufficiently soluble in water or water-methanol mixtures to enable the perchlorates to be prepared by metathesis. Filtered solutions of the appropriate bromides when mixed with aqueous solutions containing excess of sodium perchlorate yielded the required products as sparingly soluble precipitates. After filtration the solids were washed with water, methanol and dry ether and dried under vacuum at 60°. Electronic spectra in methanol gave a broad band centred at 413 nm followed by a broad shoulder centred at 580 nm for benzidine perchlorate, and three sharp peaks at 437 nm, 457 nm and 473 nm for tetramethylbenzidine perchlorate.

Attempts were made with both the Michaelis method and the Milligan procedure to obtain the perchlorate salts of *N,N,N',N'*-tetraphenylbenzidine and *N,N,N',N'*-

tetraphenyl-*p*-phenylenediamine. Both methods failed to give the required product. Modifications of these methods were not examined thoroughly. Oxidation of the *p*-phenylenediamine derivative with bromine in tetrahydrofuran produced a green colouration which suggested the presence of the radical-cation. No solid perchlorate was recovered.

Preparation of electrodes

The electrode construction used in this study differed significantly from that employed in previous investigations of radical-ion salts^{1,2} and a brief description is accordingly given. The electrode was basically similar to that described by Ružička and Lamm¹⁷ and termed by him "Selectrode". Such electrodes are not yet commercially available. One "Selectrode" was kindly supplied by its originator and was used in the initial stages of this work. A later modification, which was constructed from PVC and commercially available carbon-impregnated teflon (5–10% C) as shown in Fig. 1, also functioned satisfactorily. The method of applying the electroactive substance has been described by Ružička. Typical resistances for the assembled electrodes were of the order of 2000 ohms. This form of electrode is admirably suited to testing procedures involving new solid materials and where very small quantities of such substances are available.

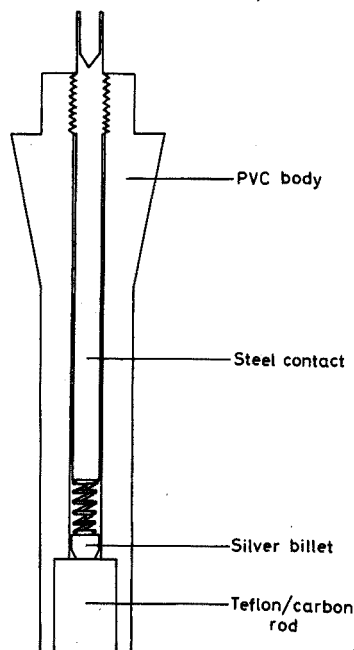


Fig. 1. Schematic diagram of electrode construction.

Measuring procedure

Unbuffered aqueous solutions of sodium perchlorate were used to determine the response of the electrodes towards the reference ion, ClO_4^- . Responses to other anions were also determined in aqueous solutions of the appropriate sodium salts.

Variations in cell potential were measured at 25° with an Orion model 701 digital pH-meter. The reference was an Orion model 90-02 double liquid-junction electrode with an outer-chamber filling of aqueous 10% (1.25 M) ammonium nitrate. Its potential was +240 mV versus N.H.E. Single ion activities were calculated from the extended Debye-Hückel¹⁸ relation with the ion-size parameters of Kielland¹⁹. The variations in liquid-junction potential at the reference electrode-electrolyte interphase were estimated with the Henderson²⁰ equation and were found to be small (total variation of ca. 4 mV over six activity decades of the test solution). No corrections were therefore applied to the measured potentials except for the H⁺ response at pH=1 where a correction of +8 mV was made.

Response towards hydrogen ion was measured for the *o*-tolidine perchlorate and *o*-dianisidine perchlorate electrodes with 10⁻¹ M hydrochloric acid and standard buffer solutions of pH values 3.00, 4.00, and 6.00 (P-H Tamm, Altuna, Sweden).

Spectra were recorded with a Unicam SP 1800 u.v./vis. spectrophotometer.

RESULTS

The results obtained with the different materials studied are most conveniently discussed by considering each substance individually.

N,N,N',N'-Tetramethyl-*p*-phenylenediamine perchlorate

This solid was found to be too soluble in aqueous solutions for stable and

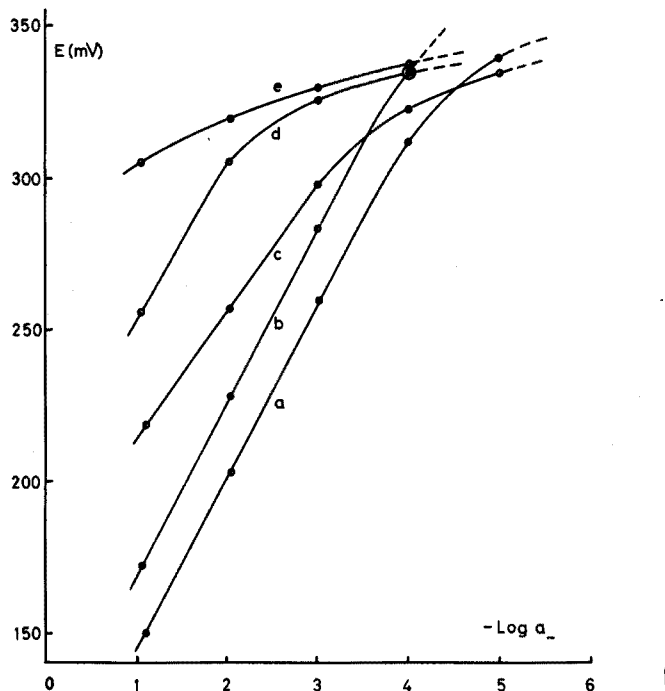


Fig. 2. Response of *o*-tolidine perchlorate electrode towards the following anions: (a) ClO₄⁻, (b) I⁻, (c) Br⁻, (d) NO₃⁻, (e) Cl⁻.

reproducible potentials to be measured. Since radical-cations derived from N,N,N',N' -tetra-alkylated *p*-phenylenediamine exhibit considerable stability, attempts were made to reduce the solubility by substituting larger hydrophobic groups at the nitrogen atoms such that as little disturbance to the π -electron system (involving ring and nitrogen atoms in the radical-cation) as possible resulted. For this purpose the perchlorate salt of N,N,N',N' -tetra-*n*-butyl-*p*-phenylenediamine was prepared. Its solubility was found to be too high to allow this material to be used as an electrode-sensing substance in aqueous solutions.

o-Tolidine perchlorate

Figure 2 shows the response behaviour of the *o*-tolidine perchlorate electrode towards the reference ion and various anions. The linear region of the perchlorate response between $10^{-1} M$ and $10^{-4} M$ corresponds to a slope of $56 \text{ mV decade}^{-1}$. It can be seen that selectivity towards perchlorate ion prevails. Response times in perchlorate solutions were relatively fast, the electrode requiring *ca.* 1 min to attain stable potential values. These potentials were observed to remain steady for several minutes (total drift of less than 1 mV); at $10^{-5} M \text{ ClO}_4^-$ the potential did not change for a period of 3–5 min, whereas at $10^{-1} M \text{ ClO}_4^-$ the stable period exceeded 20 min. The relatively shorter period of stability at the lower concentrations may arise from leakage from the reference electrode, the direction of drift being compatible with this.

Approximate selectivity coefficients were evaluated from the cell potentials observed for reference ion and interference ion activities of $10^{-1} M$ according to

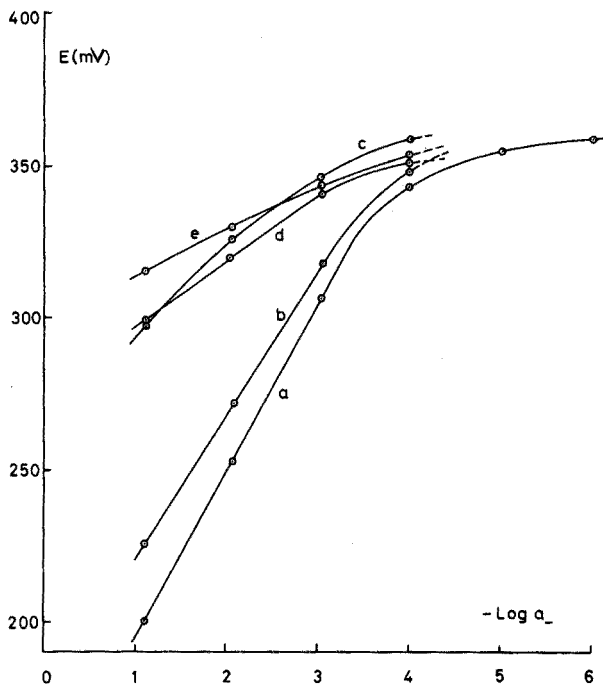


Fig. 3. Response of *o*-dianisidine perchlorate electrode towards the following anions: (a) ClO_4^- , (b) I^- , (c) Br^- , (d) NO_3^- , (e) Cl^- .

$$\log K_{\text{ref/interf}} = \frac{(E_{\text{ref}} - E_{\text{interf}})}{RT} \cdot F$$

where $RT/F = 59.2$ mV for singly-charged ions. It should be emphasized that the factors so determined, whilst being strictly incorrect mathematically (non-parallel slopes of response curves which are furthermore not equal to 59.2 mV decade⁻¹), provide an estimate of the selectivity valid only at the activity of 10^{-1} M to which the potentials, E_{ref} and E_{interf} , refer. It can be clearly seen from Fig. 2 that poorer selectivity results at the lower concentrations of the perchlorate ion.

Response times in the interference ion solutions were larger than for the reference ion but steady potentials were reached within *ca.* 5 min. Upon returning the electrode to perchlorate solutions from those of the interfering anions, the original calibration curve was reproduced to within 2 mV. Different electrodes, prepared in the same way, were also reproducible within this margin of uncertainty.

o-Dianisidine perchlorate

Figure 3 shows the response behaviour observed for the *o*-dianisidine perchlorate electrode. Curves corresponding to reference and interfering ion responses are included. It is evident that this electrode also shows selectivity towards perchlorate ions. The perchlorate ion response curve shows a linear region between 10^{-1} and $10^{-3.5}$ M perchlorate with slope 55 mV decade⁻¹. Approximate selectivity coefficients were calculated as above and are included in Table I. Response times were essentially the same as observed for the *o*-tolidine electrode and the stabilities of the potentials were equally good. In 10^{-5} M sodium perchlorate, the potential remained constant with 1 mV for a period of at least 6 min after attaining that value within 1 min of immersion in the test solution. Reproducibility was within 2 mV for different electrode examples and for repeated calibration curves.

TABLE I

APPARENT SELECTIVITY COEFFICIENTS FOR $a_{\text{ClO}_4^-} = 0.1$ M IN UNBUFFERED AQUEOUS SOLUTIONS

Anion	Electrode		
	<i>o</i> -Tolidine perchlorate	<i>o</i> -Dianisidine perchlorate	Tetramethylbenzidine perchlorate
ClO ₄ ⁻	1	1	1
I ⁻	0.39	0.36	1.66
Br ⁻	0.066	0.020	0.034
NO ₃ ⁻	0.014	0.018	0.029
Cl ⁻	0.002	0.009	0.003

N,N,N',N'-Tetramethylbenzidine perchlorate

Figure 4 shows the response of this electrode towards perchlorate ions and towards several interfering anions. The perchlorate ion response curve was linear over the range 10^{-1} – $10^{-3.5}$ M perchlorate and of slope 54 mV decade⁻¹. Selectivity towards perchlorate ions over all the other anions except iodide was observed.

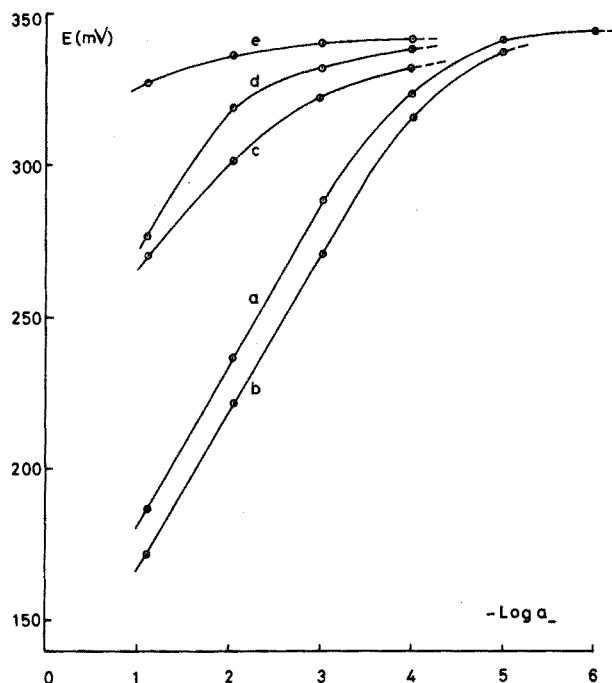


Fig. 4. Response of tetramethylbenzidine perchlorate electrode towards the following anions: (a) ClO_4^- , (b) I^- , (c) Br^- , (d) NO_3^- , (e) Cl^- .

Corresponding selectivity parameters are collected in Table I. The response times were generally less than 1 min and the stability of the potentials (within 1 mV) was maintained for at least 5 min. Reproducibility of different calibration curves was within 3 mV and different electrode examples also showed this degree of reproducibility.

Benzidine perchlorate

Electrodes prepared from benzidine perchlorate were examined with respect to their response to perchlorate solutions only. Reproducibility was, in general, poor and linear response curves, covering very narrow activity ranges, showed slopes which varied considerably within $30\text{--}50\text{ mV decade}^{-1}$. In view of the difficulties in obtaining acceptable calibration curves further investigations with this electrode were abandoned.

DISCUSSION

It is the purpose of the following discussion to examine the behaviour of the radical-cation electrodes studied above on the basis of the redox and acid-base equilibria which occur in aqueous solution. Only in the case of *o*-tolidine are sufficient quantitative data available from the literature to enable a more detailed analysis to be carried out. Analogous arguments may be expected to apply to the other systems studied in view of the close similarities of these diamines to *o*-tolidine.

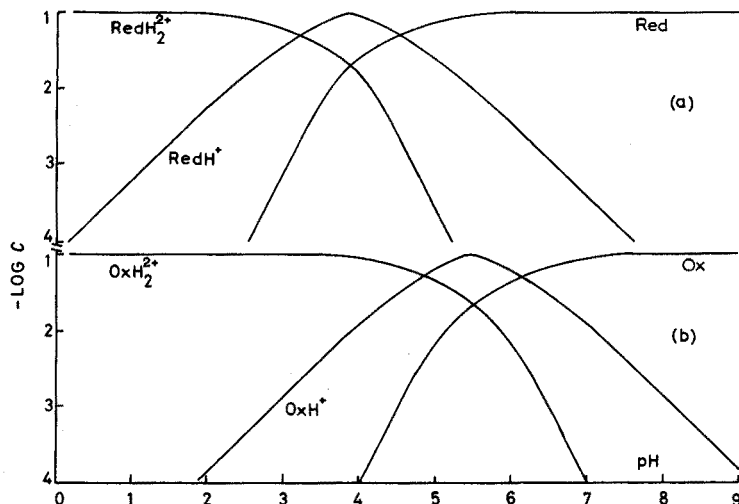
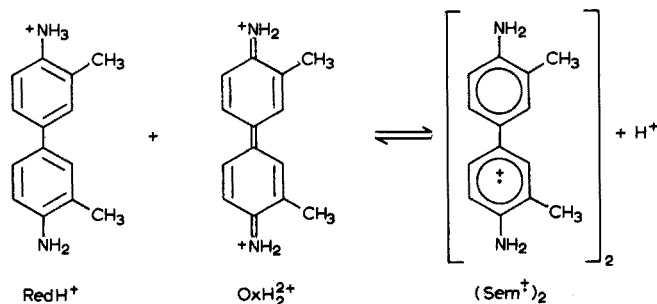


Fig. 5. Distribution of species originating from the reduced form (a) and the quinonediimine form (b) of *o*-tolidine as a function of pH. C refers to molar concentration.

The values for the acid dissociation constants for both the reduced and oxidized forms of *o*-tolidine in aqueous solution, tabulated by Clark¹⁰, allow insight into the nature and relative proportions of the different species which predominate at a particular pH value. Figures 5a and b illustrate the distribution of species where an arbitrary value of 0.1 M has been assumed for the total concentration in each case. If any interaction between the reduced and oxidized species is neglected—an assumption which is known to be definitely invalid within certain pH regions—the actual situation in solution will be represented by an appropriate superposition of these two plots. Account may however be taken of complexation between the reduced and oxidized forms, for pH regions where such association is prevalent, by means of the equilibrium constants deduced by Kuwana and Strojek¹².

The association between reduced and oxidized species of *o*-tolidine in the region $3.5 < \text{pH} < 4.6$ may be written on the basis of Figs. 5a and b in the form



which is in agreement with the reaction scheme proposed by Kuwana and Strojek¹². The association is seen to be pH dependent and values for the apparent formation constant of $K'_{\text{eq}} \approx 10^5$ have been observed, *i.e.*, the formation of the complex is strongly

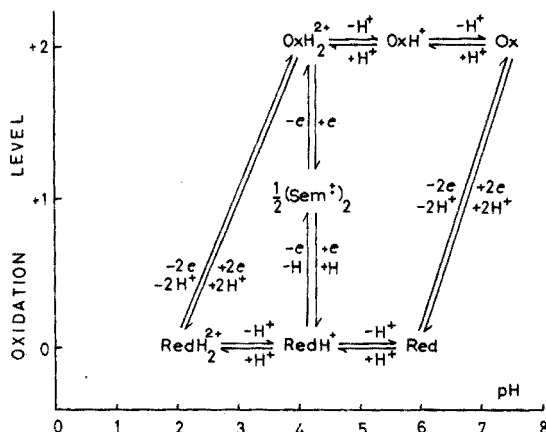


Fig. 6. Schematic diagram showing the predominating species of *o*-tolidine with respect to oxidation level and pH.

favoured¹². The configurations of the *o*-tolidine molecules comprising the complex are not clearly defined; but interpretations based on charge-transfer interactions^{21,22} and on radical-cation dimerization²³ have been suggested for closely related Wurster salts. For the purposes of further discussion the complex will be referred to as a semiquinone- or radical-cation dimer but it is to be noted that exact structural knowledge is not required for an explanation of electrode behaviour. It is sufficient that, taken as a whole, the complex conforms with *o*-tolidine molecules at the first oxidation level, *i.e.*, the oxidation level of the semiquinone radical-cation.

Combination of the information concerning species distribution provided by Figs. 5a and b with the experimental results of Kuwana and Strojek concerning complexation, allows an approximate schematic diagram to be constructed which relates the predominating species through their acid-base and redox equilibria. Such a diagram is shown in Fig. 6 where suitably chosen axes refer to solution pH and to the oxidation level of *o*-tolidine. Oxidation of *o*-tolidine in aqueous solutions of pH less than 3 has been shown to be a two-electron process^{12,14}; the formation of species at the intermediate semiquinone oxidation level has not been observed. In addition, the results of Kuwana and Strojek did not extend beyond an upper pH value of 4.6 so that formation of stable semiquinone entities above this value was not established. Spectral investigations were therefore undertaken and these showed that in aqueous solutions buffered at pH values of 6 and 7, no semiquinone dimer species, with absorption peaks at 365 nm and 630 nm¹², resulted after partial oxidation of *o*-tolidine with aqueous bromine. Absorption peaks corresponding to the reduced and fully oxidized quinonediimine species at *ca.* 280 nm and 440 nm¹², respectively, were, however, clearly defined. Similar observations at pH 4 confirmed the presence of the blue dimer but on transferring to a solution at pH 6 rapid loss of colour resulted. No dimer absorptions were detected in the solution which again showed clearly the peaks corresponding to the reduced and quinonediimine forms. It was thus concluded that, in the absence of stabilizing agents, the blue semiquinone dimer does not exist as a stable entity in solutions of pH greater than 6. Oxidation of *o*-tolidine in solutions above pH 6 thus effectively involves a two-electron process

as shown in Fig. 6 and no significant amounts of semiquinone dimer are formed.

Thus Fig. 6 indicates that *o*-tolidine is oxidized to a stable semiquinone radical-cation level only within certain pH limits. Further, if such oxidations are performed over a range of pH values in the presence of perchlorate ions, an insoluble product is obtained only within the pH region where the semiquinone dimer species predominates¹². Exhaustive oxidation to the quinonediimine level or transference of the solid to solutions of higher pH results in redissolution to give pale yellow solutions. Hence a further solubility equilibrium involving the semiquinone dimer species and perchlorate ions must be taken into account for pH regions where the former are stable. This equilibrium may be written



Under sufficiently high dilution, dissociation of the dimer into monomer radical-cations may occur. Such a dissociation is not, however, a prerequisite for an explanation of electrode behaviour.

In the light of the information contained in Fig. 6 it is possible to examine the expected behaviour of the *o*-tolidine perchlorate electrode and compare it with the experimental observations. The blue *o*-tolidine perchlorate solid used as electroactive material has been shown to conform with the presence of the semiquinone dimer species on the basis of stoichiometry and paramagnetic measurements²⁴. The structure of this material may thus be represented formally by $(\text{Sem}^{\cdot+})_2(\text{ClO}_4^-)_2$.

In aqueous solutions below pH *ca.* 3 the semiquinone dimer at the electrode surface will be rapidly converted into the corresponding diprotonated reduced and oxidized forms of *o*-tolidine according to



The resulting redox equilibrium between the products, RedH_2^{2+} , and OxH_2^{2+} may be written,



which predicts an electrode response

$$E = E_0 + \frac{RT}{2F} \ln \frac{[\text{OxH}_2^{2+}][\text{H}^+]^2}{[\text{RedH}_2^{2+}]}$$

where the brackets strictly denote the activities of the species enclosed. Since decomposition of the semiquinone leads to equal activities of the oxidized and reduced forms at the electrode surface the response equation may be rewritten:

$$E = E_0 + \frac{RT}{F} \ln [\text{H}^+]$$

which conforms with Nernstian response to changes in hydrogen ion activity. Figure 7 shows the pH dependence of the cell potentials observed with electrodes based on *o*-tolidine perchlorate and *o*-dianisidine perchlorate. Nernstian response to hydrogen ion is evident in accordance with the above equation. The standard potentials are in full agreement with the values quoted by Clark¹⁰: $E_0(o\text{-tolidine}) = +873$ mV vs. N.H.E.; $E_0(o\text{-dianisidine}) = +850$ mV vs. N.H.E. Measurements in 10^{-2} M perchloric acid further supported the prediction that response should be

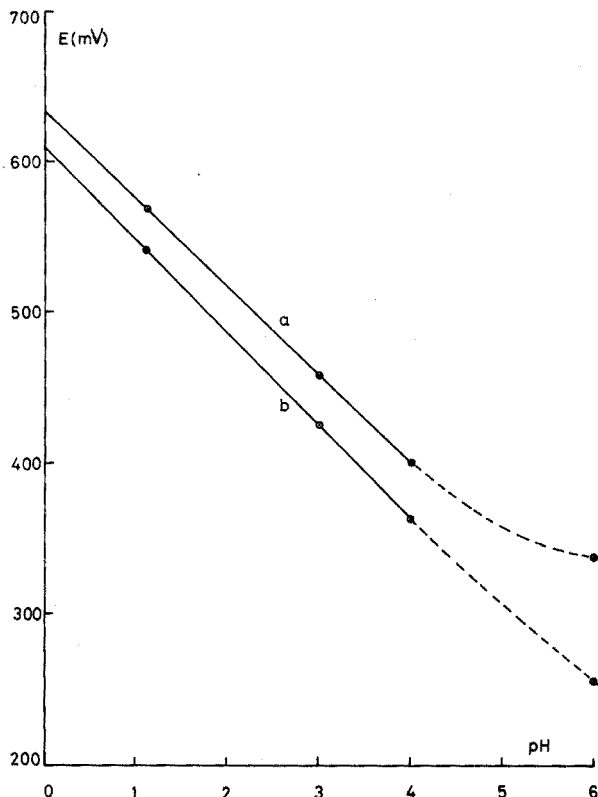
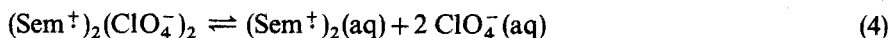
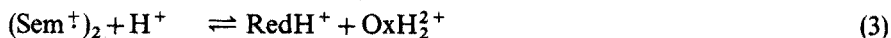


Fig. 7. pH response of *o*-tolidine perchlorate (a) and *o*-dianisidine perchlorate (b) electrodes at 25°. Respective slopes were 58 mV decade⁻¹ and 61 mV decade⁻¹.

solely towards hydrogen ion at this pH value: $E_{(\text{obs})}$ for 10^{-2} M perchloric acid was +754 mV vs. N.H.E. for the *o*-tolidine perchlorate electrode.

At intermediate pH values, $3.5 < \text{pH} < 4.6$, where the semiquinone dimer has been shown to be stable, Fig. 6, together with the solubility equilibrium involving this species, suggests that two equilibrium processes determine the activity of the radical-cation species at the electrode surface. These may be written



the first representing the pH dependence of semiquinone dimer formation and the second representing the solubility equilibrium of the *o*-tolidine perchlorate salt. The activity of the semiquinone dimer in the interphase region between the solid electrode material and the solution is thus determined by both the pH and perchlorate ion activity. The electrode potential may be expressed as a function of the activities of semiquinone dimer in the interphase region and in the solid according to

$$E = \text{const} + \frac{RT}{2F} \ln \frac{[(\text{Sem}^{\dagger})_2]_{\text{aq}}}{[(\text{Sem}^{\dagger})_2]_{\text{cryst}}}$$

and since $[(\text{Sem}^+)_{2}]_{\text{cryst}}$ may be assumed constant,

$$E = \text{const}' + \frac{RT}{2F} \ln [(\text{Sem}^+)_{2}]_{\text{aq}}$$

At constant pH, changes in the activity of the semiquinone dimer in the interphase region will be controlled by the solubility equilibrium so that by introducing the solubility product

$$K_{\text{sp}} = [(\text{Sem}^+)_{2}]_{\text{aq}} \cdot [\text{ClO}_4^-]^2$$

into the response equation, Nernstian behaviour with respect to changes in perchlorate ion activity is predicted, *i.e.*

$$E = \text{const}'' - \frac{RT}{F} \ln [\text{ClO}_4^-]_{\text{aq}}$$

Perchlorate ion response was indeed observed in the present investigation although the pH values of the unbuffered test solutions were in the range $6 < \text{pH} < 7$, *i.e.*, pH values where the semiquinone dimer has been shown to be unstable and consequently where no perchlorate response would be expected. At first sight it appears difficult to reconcile these observations, but it must be remembered that conditions at the interphase between electrode and solution may differ appreciably from those pertaining to homogeneous solution. In particular, upon immersion of the *o*-tolidine perchlorate electrode into an aqueous solution of pH greater than about 5, the first quantities of semiquinone dimer which dissolve may be expected to decompose rapidly according to



where the species Red and Ox conform with Fig. 6. Liberation of hydrogen ion during this decomposition will cause an increase in acidity at the electrode surface and consequently stabilization of the semiquinone species^{2,5}. The latter now takes part in the semiquinone-perchlorate solubility equilibrium and perchlorate ion response will result. One further aspect of such a process is of importance. The quinonediimine species, Ox, formed by the decomposition undoubtedly undergoes further irreversible reaction with the solvent at a finite although possibly small rate. Such a removal of Ox from the interphase region will promote further decomposition of the semiquinone dimer with its attendant increase in acidity. It is reasonable to expect that the result of these processes will be a "buffering" effect whereby the pH at the electrode surface is maintained essentially constant. (Removal of Ox causes further decomposition of $(\text{Sem}^+)_{2}$ which in turn leads to increased acidity and stabilization of $(\text{Sem}^+)_{2}$ and Ox.) Experimental results tend to support such a proposition since Nernstian response towards perchlorate ion would hardly be expected if large changes in pH occurred in the interphase region.

Consideration of the above equilibria (3) and (4) shows that at sufficiently low activities of perchlorate ion, the activity of the semiquinone dimer species at the electrode surface will be determined by the pH of the interphase region. Electrode response thus changes from anion to cation control. The pH at the electrode surface consequently determines the limiting potential towards which the perchlorate ion response curve approaches at lower activities. The observed limiting potential of +350 mV *vs.* S.C.E. for the perchlorate response of the *o*-tolidine perchlorate electrode

thus reflects an interphase pH value of *ca.* 5 on the basis of a standard potential of +633 mV vs. S.C.E. and Nernstian response towards hydrogen ion. At this pH, the blue semiquinone dimer is stable, as is readily verified by partial oxidation of *o*-tolidine with aqueous bromine in an appropriate buffer solution. These observations add further support to the explanation of electrode behaviour outlined above.

Although it was not examined experimentally in the present investigation, at pH values greater than *ca.* 7, response to hydrogen ion would be expected to prevail.

From the above considerations, although speculative in some respects, it is possible to summarize briefly the overall electrode behaviour with particular reference to the *o*-tolidine perchlorate system.

(a) Response to perchlorate ions results from a solubility equilibrium which involves the semiquinone dimer. For Nernstian response the pH at the electrode surface must remain essentially constant. Response to perchlorate would not be expected in pH regions where the semiquinone dimer is not stable. Strongly acidic (pH < 3) and alkaline (pH > 7) solutions are therefore to be avoided if anion response is required. The electrode potential in such solutions is determined by the hydrogen ion activity.

(b) The lower activity limit of perchlorate ion response is determined by the pH at the electrode surface. At low activities of perchlorate the electrode potential changes from being anion-controlled to being cation-controlled. The variations in limiting potential with the nature of the test solution observed in Fig. 2 may reflect differences in background pH.

(c) Response to anions other than perchlorate may depend upon solubility equilibria involving the anion and semiquinone dimer. Mixed solubility and pH dependent equilibria appear to operate for anions which show lower degrees of interference.

The results summarized above show that it is possible to prepare solid-state anion-selective electrodes by applying the same approach used for the previously studied cation-selective electrodes derived from TCNQ and related compounds. The pH dependence of the electrode potential encountered for the diamines employed may, however, limit their practical application. In addition the instability of N,N,N',N'-tetramethylbenzidine perchlorate limits the suitability of this material even further. Freshly prepared electrodes functioned satisfactorily for only a few days. Nevertheless, the investigations appear to be of value in that the behaviour observed and the explanations advanced, although necessarily tentative, permit the choice of further substances for study to be made more efficiently. In particular, the removal of functional groups such as -NH₂ or -OH from the prospective radical-cation would be expected to eliminate the undesirable pH dependence of the electrode potential. Many radical-cations of this type have been described in the literature. Preliminary studies employing such systems have shown that electrode behaviour is in fact improved in this respect. The results obtained will form the substance of a later report.

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SUMMARY

Solid perchlorate salts derived from the radical-cations of several *p*-diamines have been examined with respect to their use in solid-state anion-sensitive electrodes. Nernstian behaviour was approached over activity ranges 10^{-1} – $10^{-3.5}$ *M* perchlorate for three of the materials studied and selectivity for perchlorate ions over some common anions observed. Electrode response was fast and the stabilities of potentials acceptable. For the electrode containing *o*-tolidine perchlorate, an explanation of the observed behaviour has been attempted on the basis of acid–base and redox equilibria.

RÉSUMÉ

On examine divers perchlorates solides de *p*-diamines en vue de leur utilisation pour des électrodes sélectives. La réponse de l'électrode est rapide et les stabilités des potentiels sont suffisantes. Une explication du comportement de l'électrode au perchlorate d'*o*-toluidine est fournie, basée sur les équilibres acide–base et rédox.

ZUSAMMENFASSUNG

Feste Perchloratsalze, die sich von den Radikalkationen verschiedener *p*-Diamine ableiten, wurden im Hinblick auf ihre Verwendung in anionenempfindlichen Festkörperelektroden untersucht. Bei drei der untersuchten Substanzen wurde Nernstsches Verhalten im Aktivitätsbereich 10^{-1} – $10^{-3.5}$ *M* Perchlorat erreicht und eine Selektivität für Perchlorationen gegenüber einigen der üblichen Anionen beobachtet. Die Elektroden sprachen schnell an, und die Stabilität der Potentiale war annehmbar. Das beobachtete Verhalten der mit *o*-Tolidinperchlorat hergestellten Elektrode wurde versuchsweise auf der Grundlage von Säure–Base- und Redox-Gleichgewichten erklärt.

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THE CALIBRATION OF GLASS ELECTRODES IN CELLS WITH LIQUID JUNCTION

H. S. DUNSMORE and D. MIDGLEY

Chemistry Department, The University, Glasgow G12 8QQ (Scotland)

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In determining hydrogen ion activity or concentration from electrochemical measurements on cells with liquid junction, it is often impossible to obtain a linear calibration between pH and the observed e.m.f., because the liquid junction potential varies with the composition of the sample solution. In such cases, calibration by means of a single buffer solution and the Nernstian slope will introduce errors which increase with the difference in pH between the buffer and the sample. This procedure is also liable to errors arising from non-Nernstian behaviour of the glass electrode. Calibration with two buffer solutions spanning the pH range under study will reduce the errors.

Standard buffer solutions provide a calibration in terms of hydrogen ion activity, whereas for many purposes, such as the investigation of stoichiometric equilibrium constants in a constant ionic medium, a calibration in terms of concentration is more convenient¹. A calibration curve may be established by means of standard solutions of a strong acid, made up to the desired ionic strength with a suitable salt. If the calibration is non-linear, an unknown pH can be obtained from the observed e.m.f. by interpolation, either graphically, which is inconvenient if many data are to be handled, or by means of an empirically derived polynomial relating the pH to the e.m.f. If the polynomial is to be a good calibration, many data may be required to determine it, thus increasing the amount of computation necessary to obtain the coefficients.

A linear calibration may be obtained if the observed e.m.f. is corrected for liquid junction potential, but since the size of the correction depends on the pH, an unknown pH can be found only by an iterative procedure. In this paper, the pH values given by corrected and uncorrected calibrations are compared, and the effect of different pH values on the calculation of the dissociation constants of a dibasic weak acid is demonstrated.

EXPERIMENTAL

Reagents

Distilled water was obtained from an all-glass still. Sodium chloride, potassium hydrogenphthalate, and D-tartaric acid (AnalaR, B.D.H.) were recrystallized from distilled water. Tetramethylammonium chloride (reagent grade, Hopkin and Williams, Ltd.) was recrystallized from methanol-ether² or methanol. Tetramethylammonium hydroxide solution was prepared by reacting tetramethylammonium

chloride solution with freshly prepared silver hydroxide. Sodium hydroxide solution was obtained by dilution of a saturated solution made up from pellets (AnalaR, B.D.H.). Hydrochloric acid solutions were prepared by dilution of the constant-boiling acid. The composition of the hydrochloric acid was checked gravimetrically as silver chloride and by potentiometric titration with standard sodium hydroxide solution.

Apparatus

Measurements of e.m.f. were made on a Pye 7565 precision potentiometer, with a Vibron model 33B electrometer (Electronic Instruments Ltd.) as a null detector. Type GC33B glass electrodes (Electronic Instruments Ltd.) were used. The reference half-cell consisted of a Wilhelm Bridge³ containing a silver-silver chloride electrode. The salt bridge solution was a tetramethylammonium chloride solution of the same ionic strength as the sample, *i.e.* 0.1, 0.2, or 0.4 *M*. The liquid junction was formed at the end of a J-shaped capillary immersed in the sample solution.

All volumetric glassware was of grade A standard and its calibration had been checked.

The titration cell and Wilhelm Bridge were immersed in a water bath at $25 \pm 0.05^\circ$. The room in which all the experiments were performed was maintained at $25 \pm 1^\circ$.

Calibration procedure

Hydrochloric acid, made up to the desired ionic strength with tetramethylammonium chloride, was added from a burette to tetramethylammonium chloride solutions (0.1, 0.2, or 0.4 *M*). Alternatively, hydrochloric acid-tetramethylammonium chloride solutions were titrated with sodium hydroxide solution, in which case an equal volume of double-strength tetramethylammonium chloride solution was added from a second burette in order to maintain the ionic strength. Nitrogen was bubbled through hydrochloric acid, sodium hydroxide, and tetramethylammonium chloride (twice) at the same temperature and ionic strength as the sample solution, and then passed continuously through the test solution in order to prevent absorption of carbon dioxide and to effect stirring. Individual experiments were normalized with respect to the mean of the e.m.f. values observed with 0.05 *M* potassium hydrogenphthalate solution before and after each titration.

Tartaric acid titration

Tetramethylammonium hydroxide solution was added from a burette to 0.2 *M* tetramethylammonium chloride solution containing tartaric acid. The ionic strength was maintained with 0.4 *M* tetramethylammonium chloride solution added from a second burette. As in the calibration titrations, readings were taken with phthalate buffer solution before and after the run and nitrogen was passed continuously.

Titration in cells without liquid junctions

Hydrochloric acid solution was added from a burette to a cell containing a glass and a silver-silver chloride electrode immersed in distilled water. Nitrogen

was passed through the solution throughout the titration. Apart from the absence of the Wilhelm Bridge, the apparatus was the same as that described above.

CALCULATION OF THE LIQUID JUNCTION POTENTIAL

Henderson⁴ derived an equation for the liquid junction potential in continuous mixture junctions, assuming the constancy of ionic mobilities and activity coefficients within the junction:

$$-E_j = \frac{RT}{F} \frac{\sum \lambda_i (c_i^{\text{II}} - c_i^{\text{I}}) / z_i}{\sum \lambda_i (c_i^{\text{II}} - c_i^{\text{I}})} \ln \frac{\sum \lambda_i c_i^{\text{II}}}{\sum \lambda_i c_i^{\text{I}}} \quad (1)$$

where c_i , λ_i , and z_i are the concentration, ionic mobility and charge number respectively of the i th ion. The superscripts I and II refer to the left- and right-hand sides, respectively, of the electrochemical cell. Even in the case where the ionic strength is constant across the junction, the assumptions necessary to eqn. (1) are invalid, and Spiro⁵ and Covington⁶ have calculated additional terms to deal with the variation of activity coefficients.

In practice, liquid junctions are usually of the free diffusion type and the calculation of activity coefficient terms is seldom practicable, except for simple systems. On the basis of the Henderson equation, Biedermann and Sillén⁷ have developed an empirical correction for the liquid junction potential. In the case of the cell

reference electrode | m M BA | | h M HA, $(m-h)$ M BA | pH electrode,

they simplify the Henderson equation to

$$-E_j = \frac{RT}{F} \ln \left(1 + \frac{d \cdot h}{m} \right) \quad (2)$$

where $d = (\Lambda_{\text{HA}} - \Lambda_{\text{BA}}) / \Lambda_{\text{BA}}$. The e.m.f. of the above cell is given by

$$E = E^0 + E_j - k \log(h)$$

assuming that activity coefficients are constant and that k is equal to $2.3RT/F$. A plot of $E + k \log(h)$ against h gives, on extrapolation to $h=0$, the value of E^0 , enabling E_j to be calculated for each value of h . Equation (2) can be transformed to

$$\text{antilog}(-E_j/k) - 1 = d \cdot h/m \quad (3)$$

A plot of the left-hand side of eqn. (3) against h should be linear and of slope d/m . It has been found^{7,8} that the empirically obtained d differs from that predicted by theory, because the effects of the variation of activity coefficients have been included in the liquid junction term. Regardless of the effects included in the value of d , provided that the plot is linear, a simple correction can be applied to the observed e.m.f. to give an electrode calibration linear in hydrogen ion concentration.

Application of the correction in determining pH

In order to calculate the liquid junction correction for the e.m.f. observed with a solution of unknown pH, it is necessary to know the hydrogen ion concentration; this problem can be solved by adopting an iterative procedure. An initial estimate of

the pH is made by means of an approximate calibration and the estimate is improved by iterative application of the Biedermann and Sillén correction until the required precision is attained.

RESULTS

The plots to find E^0 and d are shown in Figs. 1 and 2, respectively, for two different electrodes, "Y" and "A". The results of calibrations in different media are given in Table I.

The calibration was tested by doing another titration in 0.2 M medium with

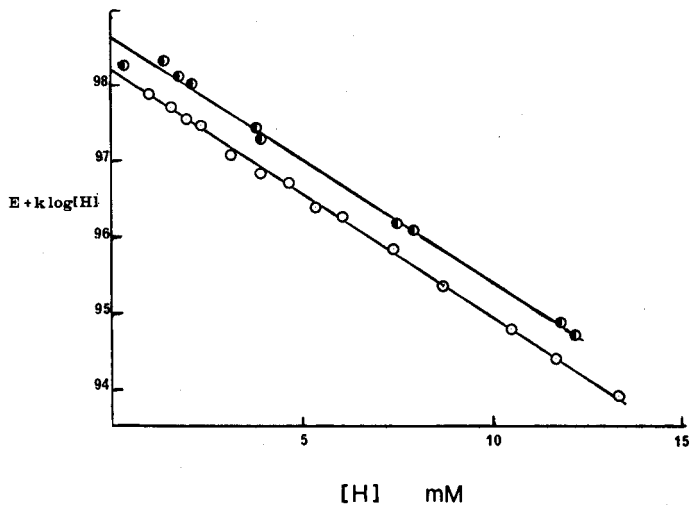


Fig. 1. Extrapolation to find E^0 . Glass Electrode "Y" (●), $E^0 = 98.7$ mV. Glass Electrode "A" (○), $E^0 = 79.3$ mV (points displaced vertically by 19 mV). 0.2 M (Me_4N)Cl medium at 25°.

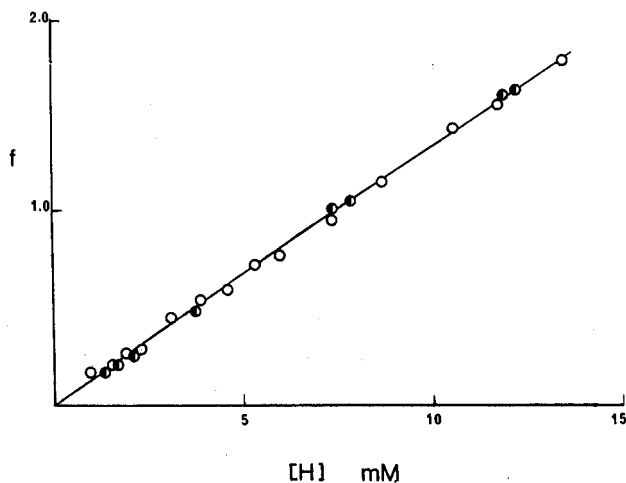


Fig. 2. Determination of the Biedermann and Sillén d coefficient in 0.2 M (Me_4N)Cl medium at 25°. Electrode "Y" (●) and Electrode "A" (○). $f = 10(-1 + \text{antilog}(E_1/k))$.

TABLE I

CALIBRATION OF GLASS ELECTRODES AT 25°

$$(E_{\text{phthalate}} - E = C + k \cdot \text{pH})$$

Ionic strength, M	0.1	0.2 ^a	0.2 ^b	0.4
Number of runs	2	5	8	2
Number of points	23	54	80	28
d	2.57	2.79	2.79	2.36
Std. deviation in d	0.02	0.01	0.01	0.06
k (mV/pH unit)	-59.39	-59.28	-59.18	-59.50
Std. deviation (mV/pH unit)	0.06	0.08	0.08	0.08
C (mV)	237.94	249.10	247.93	253.06
Std. deviation (mV)	0.17	0.26	0.24	0.23

^a Electrode "Y".

^b Electrode "A".

TABLE II

GLASS ELECTRODE "Y" AT 25° AND $I=0.2 M$

$-\log[H]$	$e.m.f.$ (mV)	$\text{p}a_{\text{H}}^a$	pH^{0b}	pH^1	E_j (mV)	pH
2.8916	73.23	2.704	2.898	2.893	0.45	2.893
2.4189	45.64	2.237	2.435	2.413	1.35	2.412
2.1306	29.86	1.971	2.170	2.130	2.55	2.126
1.9285	19.34	1.793	1.993	1.934	3.93	1.925
1.7755	11.80	1.665	1.866	1.789	5.42	1.773
2.1016	28.27	1.944	2.143	2.100	2.72	2.096
2.3986	44.60	2.220	2.417	2.395	1.41	2.394
2.6711	60.00	2.480	2.676	2.665	0.76	2.664
3.1548	88.80	2.967	3.159	3.159	0.25	3.159
3.4583	106.30	3.263	3.453	3.456	0.13	3.456

^a $E_{\text{phthalate}} = 150.39 \text{ mV}$.

^b $E_{\text{phthalate}} - E = 249.76 - 59.56 (\text{pH}^0)$.

electrode "Y", hydrochloric acid being added first and then sodium hydroxide solution. The results are given in Table II. The figures for $\text{p}a_{\text{H}}$ in column 3 were obtained by taking the pH of phthalate buffer as 4.008 and using the Nernstian slope, those in column 4 from the uncorrected calibration, and those in column 5 are the results of first order corrections for the liquid junction potential. The final values for the liquid junction potential and the pH are given in columns 6 and 7.

The effect of using an uncorrected "linear" calibration in determining the dissociation constants of a dibasic weak acid by Speakman's method⁹ is shown in Fig. 3, in which $X = K_1 \cdot Y + K_1 \cdot K_2$, where X and Y are functions of the acid and base concentrations and the pH. The experimental data are given in Table III, uncorrected and corrected pH values being in columns 3 and 4, respectively. The dissociation constants obtained with the uncorrected calibration are $K_1 = 1.46 \cdot 10^{-3} \text{ mole l}^{-1}$ and $K_2 = 1.20 \cdot 10^{-4} \text{ mole l}^{-1}$. With corrections, the results are $K_1 = 1.54 \cdot 10^{-3} \text{ mole l}^{-1}$ and $K_2 = 1.16 \cdot 10^{-4} \text{ mole l}^{-1}$.

TABLE III

TARTARIC ACID TITRATION

$10^3 [H_2Tar]$ ($mol\ l^{-1}$)	$10^3 [Me_4NOH]$ ($mol\ l^{-1}$)	pH^0	pH
6.029	1.435	2.776	2.768
5.957	1.895	2.838	2.831
5.887	2.340	2.900	2.896
5.846	2.603	2.939	2.935
5.819	2.776	2.964	2.961
5.779	3.030	3.006	3.003
5.753	3.198	3.033	3.030
5.714	3.447	3.075	3.073
5.688	3.611	3.103	3.102
5.650	3.857	3.146	3.145
5.624	4.019	3.176	3.176
5.562	4.417	3.250	3.251
5.268	6.288	3.659	3.664
5.213	6.641	3.750	3.755
5.191	6.779	3.785	3.791
5.159	6.985	3.843	3.849
5.138	7.120	3.882	3.889
5.106	7.322	3.941	3.948
5.075	7.519	4.003	4.011
5.055	7.650	4.047	4.054
5.034	7.779	4.092	4.100
5.004	7.971	4.163	4.171
4.984	8.098	4.214	4.222
4.955	8.287	4.295	4.304

Measurements in the cell without liquid junction show a linear dependence of the e.m.f. on $-\log[H][Cl] - 2 \log f$, where f is the activity coefficient calculated by means of the Davies equation¹⁰, the slope being equivalent to 58.1 mV/pH unit.

DISCUSSION

Table II shows the unsuitability of pa_H for calibration in constant ionic media, since it differs from $-\log[H]$ not only considerably but by a variable amount. An uncorrected "linear" calibration may give fair results over a small pH range, but is not generally satisfactory. The corrected calibration is much superior, even when only a first-order correction is made. It follows from eqn. (2) that the effect of the liquid junction potential on the calibration is more severe, the lower the concentration of the ionic medium. This has been found in practice, since the values of d differ only slightly in the different media.

Figure 2 shows that d , and, therefore, the deviations from linearity of the uncorrected calibrations, are independent of the characteristics of individual elec-

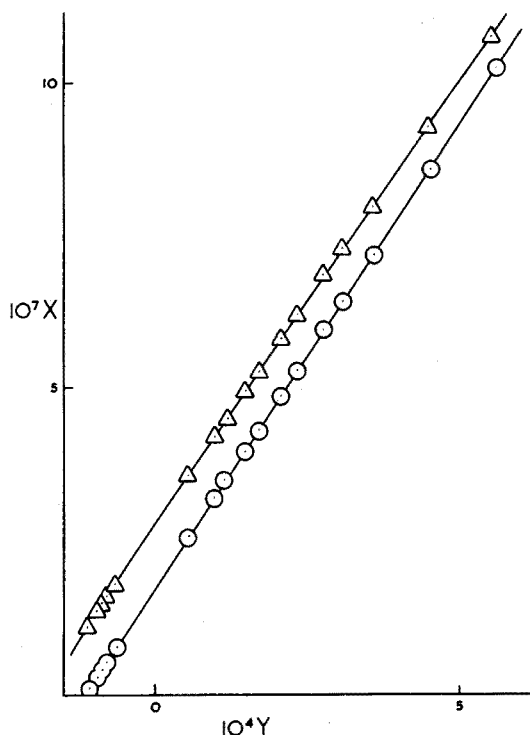


Fig. 3. Speakman plots for D-tartaric acid in 0.2 M $(\text{Me}_4\text{N})\text{Cl}$ medium at 25° calculated from corrected (○) and uncorrected (Δ) calibrations. The latter is displaced by 1 unit on the X-scale.

trodes. Further proof is the linearity of response when there is no liquid junction.

The values of dissociation constants for weak acids calculated from potentiometric data are considerably affected by the choice of calibration, as can be seen from the present results for tartaric acid. The use of an uncorrected calibration introduces curvature into the Speakman plot (Fig. 3).

Although the liquid junction correction can be calculated readily on a desk calculator, when large numbers of data are involved the use of an electronic computer is desirable. The program used, written in ALGOL, is available on request.

SUMMARY

The accuracy of different methods of calibrating glass electrodes in cells with liquid junctions is discussed and the effect of different calibrations on the determination of the dissociation constants of a weak acid demonstrated. A calibration corrected for liquid junction potential by Biedermann and Sillén's method is the best of those studied; an ALGOL program can be used to apply this correction to potentiometric data for determining pH.

RÉSUMÉ

On examine l'exactitude de diverses méthodes de calibrage d'électrodes de

verre en cellules à jonction liquide ; ainsi que l'influence du calibrage sur la détermination des constantes de dissociation d'un acide faible. Le calibrage selon Biedermann et Sillén est le meilleur parmi ceux qui ont été étudiés. Un programme d'ordinateur, écrit en ALGOL, permet d'appliquer cette correction aux données potentiométriques de détermination de pH.

ZUSAMMENFASSUNG

Die Genauigkeit verschiedener Methoden für die Eichung von Glaselektroden in Zellen mit Überführung wird diskutiert und der Einfluss verschiedener Eichungen auf die Bestimmung von Säuredissoziationskonstanten aufgezeigt. Eine Eichung, die für das Berührungspotential mittels der Methode von Biedermann und Sillén korrigiert wird, ist die beste der untersuchten Methoden. Ein Rechenprogramm wurde in ALGOL geschrieben, um diese Korrektur auf die potentiometrischen Daten für die pH-Bestimmung anzuwenden.

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SHORT COMMUNICATION

Nanogram determination of iodide by means of isotope exchange

ANN-BRITT GABRIELSSON and PER BERONIUS

Division of Physical Chemistry, University of Umeå, S-901 87 Umeå (Sweden)

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The use of the isotope exchange reaction between methyl iodide and sodium iodide,



in acetone solution to determine microgram amounts of iodide ion has been discussed previously^{1,2}. When iodide ion concentrations between $5 \cdot 10^{-5} M$ and $5 \cdot 10^{-3} M$ and 40–200 μl sample volumes were used, iodide in the range 1–26 μg could be determined with an error usually less than 3%.

This communication reports the results obtained in further investigations on the possibility of employing this method to determine nanogram quantities of iodide. Several samples containing between 25 and 550 ng of iodide have been analyzed. The results indicate that amounts down to 50 ng may be determined with only a few per cent error.

Reagents

Methyl iodide and sodium iodide were treated as reported previously¹. Acetone containing about 0.005% by weight of water was prepared^{2,3}.

Acetone solutions of methyl iodide of known concentrations were prepared immediately before use². The method used to prepare solutions of sodium iodide labelled with ¹³¹I has been reported⁴. The solutions were protected from light and handled in such a way that contamination from atmospheric moisture was avoided.

Procedure

A known volume (5–42 μl) of methyl iodide solution was transferred by means of a calibrated Hamilton micro-syringe to a reaction vessel consisting of a Pyrex test-tube of 2.5 mm inner diameter fitted with a ground-glass stopper; Fig. 1 shows the test-tube mounted in a scintillation detector for activity measurement. Test-tubes of different effective volumes between 20 and 85 μl were used. An equivalent volume of sodium radioiodide solution ($< 1 \mu\text{Ci } ^{131}\text{I}$) was then added by means of another calibrated micro-syringe in such a way that effective mixing was achieved. The test-tube was immediately closed and the reaction mixture allowed to stand in the dark at 25° for a period exceeding the calculated time required to attain the equilibrium

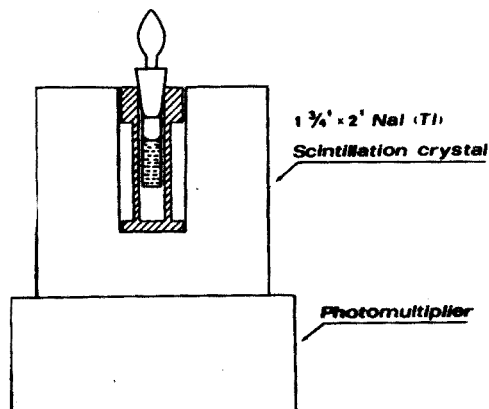


Fig. 1. Arrangement used for reproducible mounting of the reaction vessel in a NaI(Tl) scintillation detector.

concentration of radioactive methyl iodide to within 0.1%. The latter time was calculated as follows.

According to the McKay equation⁵ the concentration, x , of radioactive methyl iodide in reaction (1), which is second-order in acetone solution⁶, depends on the reaction time, t , as follows:

$$\ln(1 - x/x_{\infty}) = -(a + b)kt \quad (2)$$

where x_{∞} is the concentration of radioactive methyl iodide at exchange equilibrium, a is the total concentration of methyl iodide, b is the total concentration of sodium iodide, and k is the second-order rate constant.

If exchange equilibrium is considered to have been attained in practice when the concentration of radioactive methyl iodide deviates from the equilibrium concentration by no more than 0.1%, then,

$$x/x_{\infty} = 0.999 \quad (3)$$

If the corresponding reaction time is denoted by $t_{0.999}$, then from eqns. (2) and (3):

$$t_{0.999} = \frac{3 \ln 10}{k(a + b)} \quad (4)$$

When the second-order rate constant for reaction (1) ($k = 491 \text{ M}^{-1} \text{ min}^{-1}$ in acetone at 25°)⁶ is inserted, eqn. (4) yields,

$$t_{0.999} = \frac{0.01407}{a + b} \quad (5)$$

where a and b are molar concentrations.

Reaction times calculated by means of eqn. (5) are quoted in the penultimate column of Table I, which shows the experimental conditions used.

After attainment of exchange equilibrium the test-tube was mounted in a plastic holder in the well of a lead-shielded scintillation detector (Fig. 1) and the total radioactivity, A_0 , of the organic and inorganic iodides in the reaction mixture was determined. The solution was then evaporated to dryness as previously described^{1,2}

TABLE I

EXPERIMENTAL CONDITIONS

Expt. no.	Vol. of reaction mixture (μ l)	$a \cdot 10^4$ (M)	$b \cdot 10^4$ (M)	Reaction time (min)	
				Calcd.	Used
1	42.18	1.138	1.027	65	85
2	42.18	1.292	1.011	61	81
3	83.04	0.609	0.4050	139	200
4	83.04	0.670	0.4020	131	222
5	42.18	0.553	0.4050	147	203
6	42.18	2.755	0.3995	45	68
7	42.18	0.539	0.3995	150	160
8	21.98	0.811	0.5085	107	131
9	21.98	0.459	0.3890	166	222
10	9.96	0.811	0.5085	107	141
11	9.96	0.573	0.4045	144	158

TABLE II

RESULTS

Expt. no.	I^- taken (ng)	I^- found ^a (ng)	Relative error (%)
1	549.7	567.2	+3.2
2	541.2	532.5	-1.6
3	426.8	424.2	-0.6
4	423.6	413.4	-2.4
5	216.8	221.2	+2.0
6	213.8	217.6	+1.8
7	213.8	215.1	+0.6
8	141.8	141.3	-0.4
9	108.5	105.6	-2.7
10	64.27	69.18	+7.6
11	51.13	53.26	+4.2

^a Average of duplicate determinations.

to separate the methyl iodide from the sodium iodide, and the equilibrium activity, A_{∞} , of the latter was then measured². Sufficient counting time was used to reduce the standard deviation of the counting rate to 0.4% or less.

Activity readings were corrected for dead-time losses, background counts, and decay of ¹³¹I; the concentration of sodium iodide, equal to $aA_{\infty}/(A_0 - A_{\infty})$, and hence the amount of iodide ion in the reaction mixture were then calculated.

Results and discussion

Results for amounts of iodide between 51 and 550 ng are shown in Table II; it can be seen that the relative error is usually less than 3% for amounts of iodide above 100 ng and slightly larger for the 50–100 ng range. Repeated calibrations of the micro-syringes used indicated that the main source of irreproducibility in these measurements arose from the uncertainty in determining sample volumes.

Attempts were made to increase the sensitivity of the method by further reduction of the concentration of sodium iodide in the reaction mixture. However, when the iodide concentration was decreased below the minimal value of about $4 \cdot 10^{-5} M$ in Table I, the amounts of iodide found were invariably larger than the predetermined values. For example, values of 38.1 and 34.0 ng of iodide were found for taken amounts of 32.0 and 25.5 ng, respectively, when 10- μ l sample volumes and sodium iodide concentrations of $2.5 \cdot 10^{-5}$ and $2.0 \cdot 10^{-5} M$, respectively, were used.

These systematically positive deviations indicate non-attainment of exchange equilibrium. Hence, to avoid systematic errors a minimum sodium iodide concentration of about $4 \cdot 10^{-5} M$ is indicated.

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SHORT COMMUNICATION

Instrumental neutron activation analysis of germanium

F. ADAMS, W. MAENHAUT* and J. HOSTE

Institute for Nuclear Sciences, Ghent University, Ghent (Belgium)

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During 1970, the Organization for Economic Cooperation and Development (OECD) organized a project on the characterization of pure materials. The general object of the program was the comparison of trace characterization measurements by several methods such as mass spectrometry, activation analysis, spectroscopy, electrical measurements, diffraction measurements and microscopy on the materials potassium chloride, copper, germanium and gallium arsenide. It was hoped that the program could assess the state-of-the-art by establishing confidence limits for different methods and bringing inadequacies to light. Participants were supplied with a few carefully selected samples and with directions on the sample pretreatment procedure preferentially to be used. The general results of the program are available in a report of the OECD of restricted circulation only, and a general "overview" paper about the exchange is in the planning stage¹.

The present paper describes the determination of trace impurities in germanium by instrumental neutron activation analysis with a high resolution Ge(Li) detector. Measurements less than 3 weeks after the irradiation were precluded by the high matrix activity. Two types of samples were analysed: one was an intrinsic germanium sample with a resistivity of more than $50 \Omega \text{ cm}$ at 20° and a charge carrier density of less than 10^{13} cm^{-3} . The other was a gallium-doped single crystal with a resistivity of *ca.* $20 \Omega \text{ cm}$ at 20° and a charge carrier density of *ca.* $2 \cdot 10^{14}$ atoms Ga cm^{-3} . Each sample consisted of a $20 \times 2 \times 2 \text{ mm}$ (0.5 g) rod cut from a known position from a large Czochralski-type single crystal. The samples will be referred to as Ge 7 and Ge 8 for the intrinsic germanium, and Ge(Ga)8 and Ge(Ga)9 for the gallium-doped material.

Experimental

Instrumentation. A true coaxial detector with 5.5% efficiency was used (ORTEC). The detector was connected to an ORTEC 120 preamplifier and ORTEC 450 research amplifier used at integration and differentiation time constants of $3 \mu\text{s}$. An Intertechnique BM 96 analyser and CA 13 analog-to-digital converter (20 MHz) were used. The characteristics of the apparatus were: energy resolution 2.3 keV, a resolution at FWTM of 4.5 keV and a peak-to-Compton ratio of 23:1, all at 1.33

* Research Associate of the N.F.W.O.

MeV. The measurements were carried out in a 5-cm thick lead castle lined with 1 cm of old lead free of ^{210}Pb . The temperature of the counting room was stabilized at $22^\circ \pm 0.5^\circ$. The stability of the equipment was adequate over long counting periods of more than 100 h, so that peak-broadening effects from zero or gain shift were insignificant.

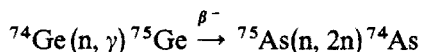
Procedure. The samples were transferred from the polythene bag in which they were encapsulated, to a nuclear-grade graphite container. In the same container were placed quartz vials containing mg amounts of Co–Al alloy with 2% cobalt, gold, indium and nickel oxide. Cobalt, gold and indium were used to provide information on the thermal and epithermal neutron flux, and nickel was used to serve as a flux monitor for the fast neutron flux. Contrary to the recommendations, no pretreatment was applied because the standard cleaning procedure was not available at the time of analysis.

The irradiation took place in the BR-2 reactor (Mol, Belgium) at a thermal neutron flux of about $10^{14} \text{ n cm}^{-2} \text{ sec}^{-1}$ during an irradiation time of nearly 13 days. After irradiation the samples were cooled during 10 days to reduce the radiation intensity to acceptable levels, and etched in a solution consisting of 3 parts of 14 M nitric acid and 1 part of 50% hydrogen fluoride. After each etching the samples were washed with deionized water until the etching solution was neutral. The samples were placed on aluminium discs, and covered with polythene tape for measurement. Measurements were started 20 days after the irradiation for 20–50 h and then about 100 days after the irradiation for 100 h.

As standards, quartz tubes of 3 mm inner diameter were filled to about 12 mm with dilute solutions of each element to be determined. These standards were of nearly the same dimensions as the germanium samples but were of circular instead of rectangular cross-section. The detection efficiencies for samples and standards were assumed to be nearly identical. The standards were irradiated in the Thetis reactor (University of Ghent), together with a cobalt flux monitor in an irradiation position with a $\Phi_{\text{epi}}/\Phi_{\text{th}}$ ratio similar to the irradiation site of the samples. The difference between Φ_{epi} and Φ_{th} in both irradiation positions was too small to make any correction necessary. The difference in γ -intensity attenuation between sample and standard was also neglected.

Results and discussion

A first series of measurements of the germanium samples three weeks after the end of the irradiation gave rise to a very high matrix activity from ^{71}Ge . This isotope decays to the ground level of ^{71}Ga and the X-rays can easily be prevented from reaching the germanium detector by putting a thin lead slab (2 mm) between source and detector. Other intense matrix radiation was due to ^{77}As , which prevented the detection of any impurities below about 300 keV. In this series of measurements it was still possible to detect the 438-keV radiation of $^{69\text{m}}\text{Zn}$, which is formed through a (n, α) reaction of ^{72}Ge . The identity of this peak was proved by decay measurements which gave a half-life of 14–16 h. ^{74}As was also present in the spectra. This isotope can only be formed from the germanium matrix by the following series of nuclear transmutations:



The hypothesis that a large concentration of arsenic is present in all the samples at about the same concentration is very unlikely. Above the 634-keV radiation of this isotope, the most intense spectral components were due to background radiation.

A second measurement of each sample was performed for *ca.* 100–130 h about 100 days after the end of the irradiation. A background spectrum for the same time of measurement allowed the easy analysis of the background components in the spectra.

The results, mostly as lower detection limits, for 13 elements are shown in Table I; a representative spectrum of the second count of the Ge(Ga)8 sample is

TABLE I

RESULTS FOR 13 TRACE CONSTITUENTS IN GERMANIUM

Element	Isotope	Photon energy (keV)	Concentration or detection limit (ng/g)			
			Ge 7	Ge 8	Ge(Ga)8	Ge(Ga)9
Co	⁶⁰ Co	1332.5	< 1.1 · 10 ⁻³	<u>1.5 · 10⁻³</u>	< 0.81 · 10 ⁻³	< 0.8 · 10 ⁻³
	⁶⁰ Co	1173.2				
In	^{114m} In	558.2	< 0.35	< 0.23	< 0.23	< 0.28
Ni	⁵⁸ Co	810.7	< 0.67	< 0.42	< 0.44	< 0.54
Sb	¹²⁴ Sb	1690.9	< 8.0 · 10 ⁻³	< 4.7 · 10 ⁻³	<u>≤ 5.1 · 10⁻³</u>	< 6.1 · 10 ⁻³
Zn	⁶⁵ Zn	1115.5	< 0.048	< 0.035	<u>0.17</u>	< 0.042
Cr	⁵¹ Cr	320.1	< 0.069	< 0.047	< 0.049	< 0.059
Ir	¹⁹² Ir	467.9				
	¹⁹² Ir	316.5	< 0.022 · 10 ⁻³	< 0.017 · 10 ⁻³	< 0.020 · 10 ⁻³	< 0.020 · 10 ⁻³
Se	⁷⁵ Se	264.6				
	⁷⁵ Se	279.5	< 0.013	< 0.011	< 0.035	< 0.012
	⁷⁵ Se	400.6				
Sc	⁴⁶ Sc	889.4	< 0.11 · 10 ⁻³	< 0.075 · 10 ⁻³	< 0.071 · 10 ⁻³	< 0.091 · 10 ⁻³
Ag	^{110m} Ag	657.8	< 0.0032	< 0.0023	< 0.0024	< 0.0026
	^{110m} Ag	884.6				
Ta	¹⁸² Ta	1188.8				
	¹⁸² Ta	1221.4	< 1.3 · 10 ⁻³	< 0.95 · 10 ⁻³	< 0.94 · 10 ⁻³	< 1.1 · 10 ⁻³
Hf	¹⁸¹ Hf	482.2	< 2.1 · 10 ⁻³	< 1.3 · 10 ⁻³	< 1.3 · 10 ⁻³	< 1.7 · 10 ⁻³
U	¹⁰³ Ru	497.9				
	⁹⁵ Zr	724.1	< 0.072	< 0.050	<u>0.36</u>	< 0.058
	⁹⁵ Zr	756.7				

shown in Fig. 1, together with the background spectrum. The detection limit is defined as $4.65 \cdot (Bkgd)^{\frac{1}{2}}$. In Ge(8) only cobalt was detected, whereas zinc, uranium and possibly antimony were present in Ge(Ga)8. Since the other germanium samples did not reveal the presence of these elements, it can be assumed that they are present as micro inclusions in the germanium, or else were introduced by contamination. Renewed etching of the sample did not remove or appreciably decrease the activity. Also, to test the possible hypothesis of contamination of the samples with radioactive isotopes, the ⁹⁵Zr–⁹⁵Nb activity ratio was measured. The ratio corresponded, within the statistical uncertainty of the measurements, to the formation of ⁹⁵Zr during the irradiation period. It should be noted that the detection limits were extremely low and represent an extreme case of what can be obtained by neutron activation analysis.

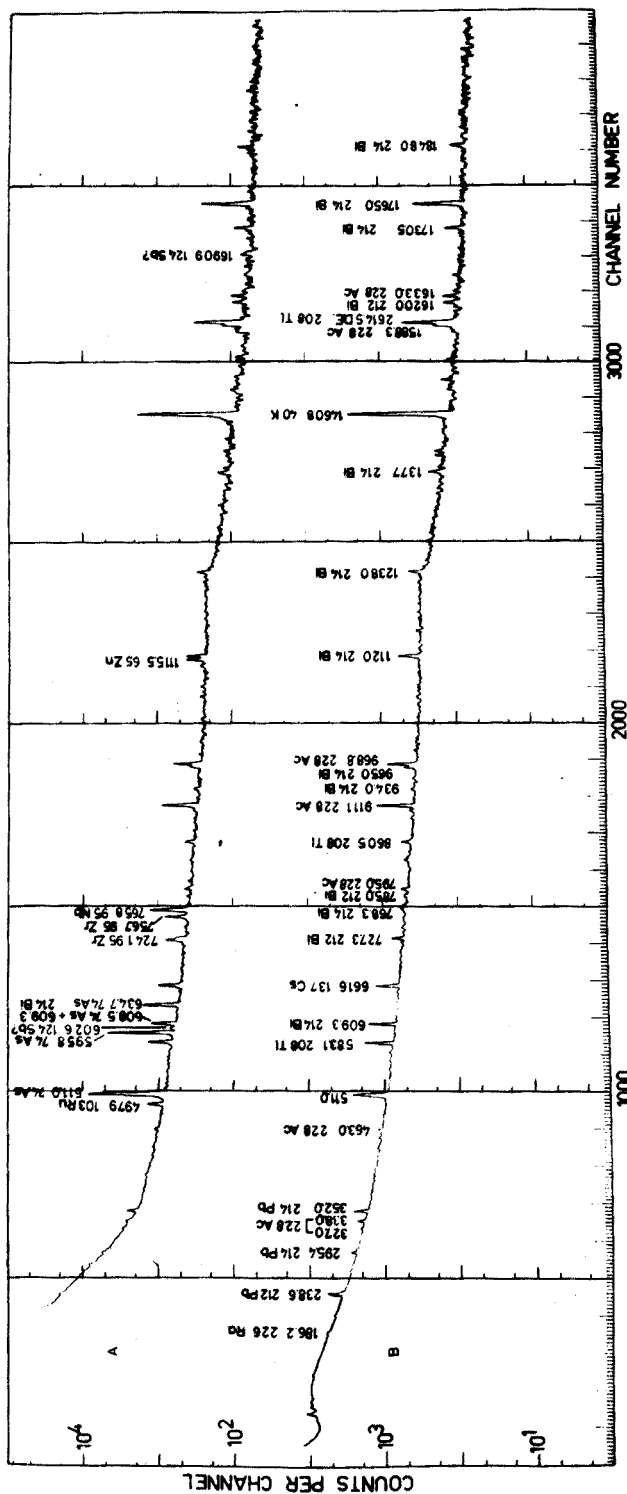


Fig. 1. Ge(Li) spectrum of sample Ge(Ga)₈, measurement time 130 h about 100 days after irradiation (A) and of the background for 140 h (B).

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Anal. Chim. Acta, 61 (1972)

SHORT COMMUNICATION

Atomic absorption and fluorescence spectroscopy with a carbon filament atom reservoir**Part XII. The determination of nickel in crude and residual fuel oils by atomic absorption spectrometry**

J. F. ALDER* and T. S. WEST

Chemistry Department, Imperial College of Science and Technology, London, SW7 2AY (England)

(Received 2nd March 1972)

In an earlier communication¹ the application of the carbon filament method of sample atomization to the determination of copper and silver in lubricating oils by atomic absorption measurements has been described. By applying a variation of this technique, it has now been found possible to solve the more intractable problems posed by the direct determination of nickel in both crude and residual fuel oils, thus demonstrating the practical utility of this versatile technique.

Instrumentation

The carbon filament atom reservoir. The unenclosed filament² was used in this study, the filament being sheathed by argon. A recess 3–4 mm long, and *ca.* 1 mm deep, was made in the middle of the filament to locate the oil; a shallow longitudinal groove was made at the bottom of the recess, to help stop the oils from flowing over the side of the filament.

When the residual fuel oils were evaporated from the filament, a residue, which appeared to be carbonaceous, was left behind; on heating to *ca.* 2700°, this resulted in a glaze being formed on the filament, and creeping of the next oil sample then occurred. To overcome this problem, the filament was rendered porous. The recess was made and the filament fixed into the cell; then, without argon flowing, the filament was heated open to the atmosphere to *ca.* 3000° for a few seconds. The argon flow was resumed and the cell was used subsequently in the normal way. The applied oil samples then soaked into the partly oxidized, porous filament, and surface creeping was minimized, resulting in improved reproducibility.

Spectrometer, amplifiers, hollow-cathode lamps and signal display. These have been described previously^{1,3}. The Unicam SP900A monochromator was used, in conjunction with a d.c. amplifier and a storage oscilloscope display. An ASL (Melbourne, Australia), high-intensity, nickel hollow-cathode lamp was employed, but

* Present address: Département de Chimie, I.N.S.A., Avenue Albert Einstein, 69-Villeurbanne, France.

the boost electrodes were not used and the primary cathode current was maintained at 20 mA.

Calibration solutions. Nickel standards were prepared from a 5.4% nickel naphthenate solution in a heavy oil. Solutions were made up by weight dilution in an SAE 10 metal-free base-oil. (Nickel naphthenate and base-oil were supplied by The British Petroleum Company, Limited.)

Procedures

The oil samples were introduced on to the filament by various means, depending on the nature of the oil. The calibration solutions were applied by a calibrated¹ 1- μ l glass pipette. All the samples, except the Libyan oil, contained too much nickel for direct analysis and were therefore diluted with SAE 10 oil before application. The more fluid oils (Iranian and Kuwait crude oils), could be handled with a "Hamilton" syringe or with glass pipettes without dilution, whereas the thicker oils (residual fuel oil and Libyan oil) could not. The Libyan oil was weighed directly onto the filament with a small weighing loop of 7 mm diameter, made from 0.5-mm diameter wire, attached to a hook for suspension from the balance, or from a suitable support on the pan. This method of weighing was suitable for the residual fuel oil and thicker crude oils, but the more fluid ones evaporated too quickly for accurate weighing. Since the nickel content of the residual fuel oil was too high for direct determination, these oils were diluted and the glass pipettes used.

The pipettes were calibrated for each oil solution applied, by weighing the amount of the oil which each delivered.

The operating conditions for the determination of nickel are summarized in Table I. The sample was introduced on to the filament which was then heated up to about 320° for 10 sec to remove the bulk of the oil. The temperature was increased to about 800° for 10 sec and then to about 1000° for 5 sec to remove the last trace of organic material. The oscilloscope was then triggered, the filament flash-heated to about 2700°, the nickel atomized and the absorption signal recorded. The peak height of the absorption signal was measured and from that and the 100% transmission reading, the absorbance was calculated. The coefficients of variation on the absorption

TABLE I

EXPERIMENTAL PARAMETERS IN THE DETERMINATION OF NICKEL IN OILS

Absorption lines	232.0 nm, 231.1 nm
Monochromator bandpass	0.2 nm
Lamp current	20 mA
Argon flow	1900 cm ³ min ⁻¹
Pre-heating sequence	10 sec—320°, 10 sec—800°, 5 sec—1000°
Atomization temperature	2700°
<i>Calibration curves</i>	
Sensitivity for 1% absorption (Ni naphthenate in SAE 10 oil)	1 · 10 ⁻¹⁰ g at 232.0 nm, 3 · 10 ⁻¹⁰ g at 231.1 nm
Limit of detection (Ni naphthenate in SAE 10 oil)	8.4 · 10 ⁻¹⁰ g at 232.0 nm, 4 · 10 ⁻⁹ g at 231.1 nm

signals thus obtained were $\pm 7\%$. Four or five replicates were run for each solution yielding per cent standard errors of about $\pm 3.5\%$. For the Libyan oil, which was weighed onto the filament, the standard error, on three weighings, was as high as $\pm 14\%$. This indicates a lack of precision of the sampling method rather than the measurement technique.

Results

The limit of detection and absorption "sensitivity" for nickel as naphthenate in SAE 10 base-oil are shown in Table I. Because the instrumentation employed yielded noisy signals, the limits of detection are poor, though the "sensitivity" is quite good. The results may be compared with the data for the technique with aqueous solutions on a grating spectrometer in which a more detailed examination of other lines was made³. Only the resonance lines at 232 and 231.1 nm were employed here; calibration curves are shown in Fig. 1. As in the case of the copper and silver¹, the

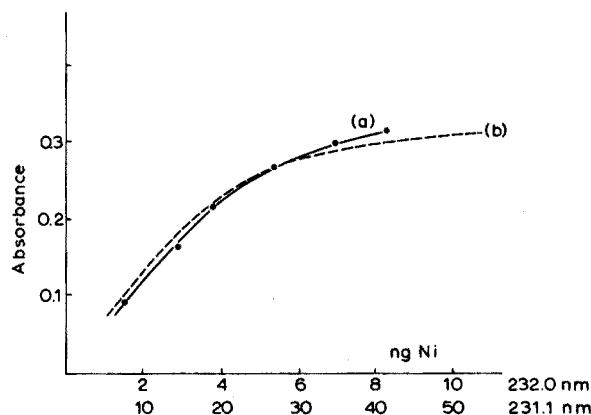


Fig. 1. Calibration curves for Ni in SAE 10 oil at (a) 232.0 nm and (b) 231.1 nm.

TABLE II

DETERMINATION OF NICKEL IN CRUDE AND RESIDUAL FUEL OILS

Sample	Dilution factor ^a (SAE 10 oil)	Spark emission result (p.p.m. Ni)	Carbon filament absorption (p.p.m. Ni)
Residual fuel oil 1	7.50	36 \pm 10%	41 \pm 0.3
Residual fuel oil 2	7.85	37 \pm 10%	35 \pm 0.2
Iranian 1 (light)	2.20	12 \pm 10%	12 \pm 0.1
Iranian 2 (heavy)	8.25	34 \pm 10%	42 \pm 0.2
Kuwait	1.85	10 \pm 10%	9 \pm 0.1
Libyan ^b	—	4 \pm 0.4	4.4 \pm 0.6

^a All samples were prediluted with SAE 10 oil to give a final nickel concentration ca. 4–5 p.p.m.

^b This oil was weighed directly onto the filament. The result given is the average of 3 determinations, for which 670, 1580 and 710 μ g of sample were weighed, and results of 5.7, 3.9 and 3.9 p.p.m. Ni, respectively, were found.

curves do not go through the origin; this apparent blank is probably due to carbon particle scatter from the hot filament. As it cannot be allowed for, it is included in the limit of detection. The 232.0-nm line was used to determine the nickel in the crude and residual fuel oils.

Four crude oils and two commercially available residual fuel oils were analysed using this method. The results are shown in Table II and compared to the results for the analysis by spark emission spectrography. The agreement between these two quite different techniques is judged to be acceptable.

Conclusions

Nickel can be readily determined in both crude oils, and residual fuel oils at the levels normally met in these analyses. Oils of varying viscosities can be accommodated and no sample pretreatment is required, except for dilution, if the concentration of nickel is too high. Figure 1 shows that higher concentrations of nickel could alternatively be determined without dilution by using the less sensitive line at 231.1 nm, although the curvature above 30 ng of nickel becomes rather pronounced.

We are grateful to the British Petroleum Company for the award of a grant to J.F.A. and to I.C.I. Limited for a grant for the purchase of the spectrometer.

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SHORT COMMUNICATION

The determination of traces of aluminium in lithium fluoride

J. T. H. ROOS

Department of Chemistry, University of Rhodesia, Salisbury (Rhodesia)

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In the course of a research project on the properties of lithium fluoride, it was necessary to determine traces of aluminium in the sample as rapidly as possible, and with a high degree of precision. Atomic absorption spectrophotometry appeared to be the most suitable technique.

The determination of aluminium by atomic absorption spectrophotometry was greatly facilitated by the introduction of the nitrous oxide-acetylene flame¹, and atomic absorption has since been used for the determination of aluminium in a wide variety of samples, including steel², ferrites³, cement⁴, and silicate minerals^{5,6}. A major disadvantage associated with the aluminium determination, however, is the comparatively poor sensitivity normally attainable. This is a particular problem when trace quantities of aluminium are to be determined; in such cases it is necessary first to concentrate the aluminium. Because of the small quantity of aluminium expected to be present in the lithium fluoride samples, the possibility was investigated of developing a combined solvent extraction-atomic absorption procedure for this determination.

With 8-quinolinol, aluminium forms a stable chelate which may be extracted into a variety of organic solvents such as chloroform, amyl acetate, and methyl isobutyl ketone. The optimal pH range for extraction is reported⁷ to be 4.5-11.5, although the rate of extraction over the range 6.5-8 is very small, extraction being complete only after several hours. Extraction with 8-quinolinol is not very selective for aluminium, but this presents no difficulty in atomic absorption analysis (provided that there is sufficient reagent to satisfy all the competing reactions) and may, in some cases, be advantageous.

Apparatus and reagents

A Unicam SP90 atomic absorption spectrophotometer fitted with a nitrous oxide control unit, was used in conjunction with both a Unicam SP20 recorder and a Philips PM 2422 digital multimeter. Hollow-cathode lamps were obtained from Pye Unicam Limited. pH was measured with a Pye Model II pH meter, and a Griffin-Christ "Universal Junior III" centrifuge was used to hasten the separation of organic and aqueous phases.

Stock aluminium solution ($100 \mu\text{g Al ml}^{-1}$). High-purity aluminium foil (0.100 g) was dissolved in the minimal volume of (1 + 1) hydrochloric acid and the

solution was diluted to 1 l. To prepare a secondary stock solution ($10 \mu\text{g Al ml}^{-1}$), this solution was diluted by a factor of ten with water.

Reagent solution. Analytical-reagent-grade 8-quinolinol (2.5 g) was dissolved in 250 ml of amyl acetate, and the solution was stored in a glass container in the dark.

Procedures

Calibration standards. To five 50-ml centrifuge tubes fitted with ground-glass stoppers, add 0, 1.0, 2.0, 4.0 and 6.0 ml of aluminium solution ($10 \mu\text{g ml}^{-1}$). Add 3 ml of (1+1) sulphuric acid and dilute each solution to about 20 ml with water. Add 1–2 drops of phenolphthalein indicator solution, then add concentrated ammonia solution dropwise, and with constant swirling, until the appearance of the first definite pink coloration (pH *ca.* 9). Cool if necessary, add 2 ml of the 8-quinolinol solution, and shake the stoppered tube for 2 min. Separate the layers by centrifuging for about 5 min at 1500–2000 r.p.m.

Sample preparation. Weigh 2.00 g of the lithium fluoride into a PTFE beaker (50–100 ml capacity). Wash down the sides of the beaker with about 10 ml of water, add 10 ml of (1+1) sulphuric acid, and heat the beaker on a hot-plate until fumes of sulphur trioxide are evolved. Continue to fume for about 1 h. Cool the beaker and dissolve the residue in about 15 ml of water (with heating). Transfer the sample solution quantitatively to a centrifuge tube (about 50 ml capacity as before), add 1–2 drops of indicator solution and complete the extraction as described for the standard solutions.

Analysis. Aspirate the upper organic layers directly for aluminium using the instrumental settings given in Table I.

TABLE I

INSTRUMENTAL SETTINGS FOR ALUMINIUM

Wavelength	309.3 nm
Burner	5 cm Nitrous oxide
Fuel	Acetylene, 3.2 l min^{-1}
Oxidant	Nitrous oxide, 5 l min^{-1}
Slitwidth	0.1 mm
Observation height	0.5 cm
Scale expansion	as required

Results

In order to confirm the reliability of the proposed procedure, recovery tests were performed on a sample of laboratory-grade lithium fluoride. The results are shown in Table II. The precision of the method was ascertained by taking 9 separate 2-g portions of lithium fluoride through the proposed procedure; the average result was $2.7 \mu\text{g}$ of aluminium, the standard deviation being $0.4 \mu\text{g}$ or 16%. The limit of detection* of the method, as written, is about $1 \mu\text{g}$ of aluminium, which corresponds

* Defined as the concentration of aluminium required to produce a signal equal to $3 \times$ the standard deviation of the background.

TABLE II

RECOVERY OF ALUMINIUM

Added (μg)	Found (μg)	Recovery	
		μg	%
0	~0.2, ~0.2	—	—
2.0	2.2, 2.6	2.0, 2.4	100, 120
5.0	5.4, 5.4	5.2, 5.2	104, 104
10.0	11.4, 10.6, 11.2, 9.8	11.2, 10.4, 11.0, 9.6	112, 104, 110, 96

TABLE III

ALUMINIUM CONCENTRATION IN VARIOUS SAMPLES OF LITHIUM FLUORIDE

Sample	Aluminium found (p.p.m.)
Laboratory grade (1)	0.2
Laboratory grade (2)	12.2
Aluminium-treated	48.7

to 0.5 p.p.m. of aluminium in the original sample. Analytical results are shown in Table III.

Discussion

A well-known limitation of atomic absorption spectrophotometry is the ease with which burner slots can become blocked by deposition of solid matter between the burner jaws as an analysis progresses. This is particularly noticeable with a nitrous oxide-acetylene flame if the sample solutions contain more than about 2% of total dissolved solids. This clearly limits the amount of sample which can be dissolved in a given volume of solvent, and is particularly troublesome when the analysis involves the determination of trace impurities in the sample material. In such cases solvent extraction may be used both to separate the desired constituents from the matrix material, and to increase their concentration to a level suitable for determination. By using an immiscible solvent which is lighter than water, the extraction may be performed rapidly in a centrifuge tube. Centrifugation hastens the separation of the phases, and the upper organic layer can then be aspirated directly from the tube without having first to separate the phases physically. Thus the danger of contamination may be kept to a minimum.

Fluoride ion is reported⁷ to interfere with the extraction of aluminium into an organic solvent with chelating agents such as 8-quinolinol. It was therefore necessary to remove fluoride from the sample before extraction of the aluminium. This could be done most conveniently by fuming with sulphuric acid, which also served to convert the insoluble lithium fluoride into soluble lithium sulphate from which the aluminium

could be extracted without any difficulty. Neutralization of the remaining sulphuric acid with ammonia solution to the first pink colour of phenolphthalein indicator furnished the required ammonia-ammonium sulphate buffer system with a pH of 9-9.5.

A similar extraction procedure could probably be used for the determination of aluminium in many other inorganic salts. In most cases, it would not be necessary to fume with sulphuric acid before extracting the aluminium.

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Anal. Chim. Acta, 61 (1972)

SHORT COMMUNICATION

Concentration of dilute solutions at p.p.b. level by non-boiling evaporation in quartz and teflon

C. BOUTRON

Laboratoire de Glaciologie, 2, rue Très-Cloîtres, 38-Grenoble (France)

(Received 19th March 1972)

In this communication a technique for preconcentration of dilute solutions at the p.p.b. level (for the present purpose, p.p.b. is defined as 10^{-9} g g⁻¹) in the presence of acids is described. The method was developed in order to allow the determination of Na, Mg, K, Ca, Mn and Fe by flame atomic absorption spectrometry in snow samples collected in Antarctica^{1,2}.

Effect of air purity

To minimize the danger of contamination of the sample (see Table I), the concentration was carried out in a vertical laminar-flow clean work station featuring HEPA filters and exclusively made of plexiglass, polypropylene and formica. The investigator wore a particle mask, polyethylene sleeves, and PVC gloves.

TABLE I

INFLUENCE OF LABORATORY ATMOSPHERE ON THE RESULTS OF CONCENTRATION OF THE SAME 10 p.p.b. STANDARD (ALL RESULTS ARE IN p.p.b.)

(Results are expressed as the concentration of the concentrated (factor 40) sample divided by this factor)

Na	Mg	K	Ca	Fe	
10.2	10.0	10.5	9.1	9.3	All operations in clean work station
13.8	12.4	13.7	9.1	20.6	All operations in laboratory atmosphere

Concentration in quartz in the presence of aqua regia

The sample (200–500 ml) was evaporated to 10 ml (3–7 h) in a 2000-ml high-purity quartz bulb placed in a double-walled pyrex vessel connected by teflon tubing to a Colora HT 39 ultrathermostat (Fig. 1). A silicone fluid (Rhodorsil 43 V 120) was circulated. Great care was taken to avoid any boiling (temperature of the solution under evaporation 85°). Suprapur-grade concentrated aqua regia (12 ml) was then added, and the evaporation continued to 1 ml (2 h). Temperature setting was carefully adjusted to avoid any boiling². The residue was recovered by 9 ml of 5% nitric acid (suprapur-grade diluted in our purest water, Table II). The solution so obtained (concentration factor 20–50) was then transferred to a polyethylene vial and analysed

TABLE II

METAL CONTENT OF WATER PURIFIED WITH ION-EXCHANGE RESINS AND DOUBLE-DISTILLED IN QUARTZ (CONCENTRATIONS IN p.p.b.)

Na	Mg	K	Ca	Mn	Fe
< 0.1	< 0.2	< 0.5	≤ 0.5	≤ 0.8	≤ 1

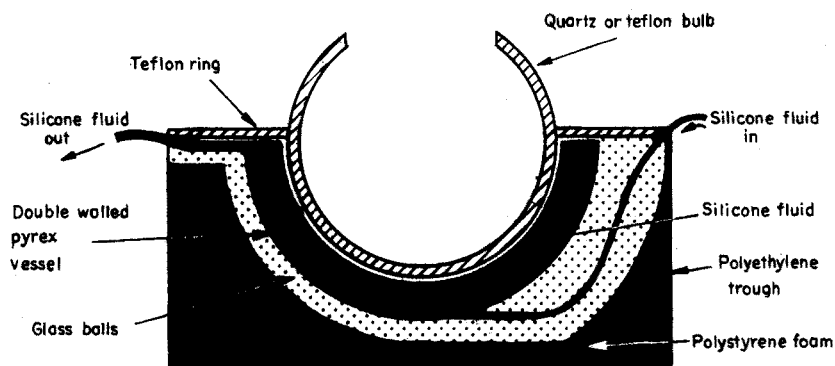


Fig. 1. Contamination-free apparatus for concentration of dilute solutions by non-boiling evaporation.

by atomic absorption (Perkin Elmer 303) for Na, Mg, K, Ca, Mn and Fe.

The calibration of this procedure (Fig. 2) was carefully performed with artificial 200-ml standards prepared from sodium hydrogencarbonate, magnesium metal, potassium chloride, calcium carbonate, manganese metal, and iron metal by dilution in our purest water. Each point in those curves was obtained by the complete concentration process (concentration factor 20). For Mg, Mn, and especially Ca and Fe, the regressions do not fall on the parallel to the diagonal. Apart from the contamination by acids (shown by the zero intercept), losses by, for instance, adsorption on the quartz balloon are probably superimposed. These losses seem to increase with concentration, and are particularly noticeable for calcium and iron. They could also originate from the formation of compounds very difficult to dissolve (*i.e.* colloids).

These complex processes should be studied in the future, *e.g.* by using radioactive tracers.

Concentration in teflon in the presence of aqua regia and hydrofluoric acid

In order to allow dissolution of any silicate particles included in snow, the above procedure was modified to allow the use of 1 ml of concentrated hydrofluoric acid (suprapur material) at the end of the concentration, the beginning of the procedure being unchanged. A teflon (gaflon) bulb (450 ml) was then required.

Table III compares the zero intercepts and slopes of the least square fits of the calibration curves for this new procedure (performed with about 400-ml standards) with those obtained for the quartz aqua regia procedure described above. These values are not directly comparable. However, it is clear that the zero intercepts are lower for the second procedure, except for magnesium, despite rather more difficult conditions: calibration curves are performed with 400-ml samples instead of 200 ml (10 h are then

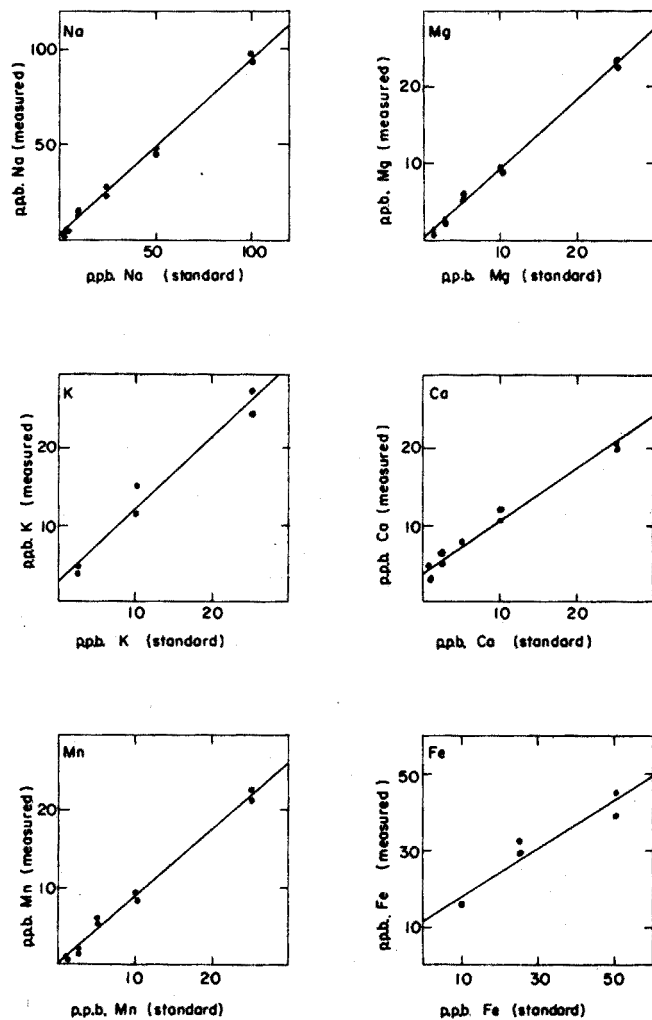


Fig. 2. Concentration in quartz in the presence of aqua regia—calibration curves, p.p.b. (standard): theoretical concentration in the standard, p.p.b. (measured): measured concentration in the concentrated sample divided by the factor of concentration.

TABLE III

CALIBRATION CURVES: ZERO INTERCEPTS AND SLOPES OF THE LEAST SQUARE FITS (IN p.p.b.)

Na	Mg	K	Ca	Mn	Fe	
<i>Zero intercepts</i>						
3.0	0.45	2.7	3.8	0.7	12	"Quartz-aqua regia" procedure
-0.4	1.1	1.7	0.1	-0.4	2.9	"Teflon-aqua regia-HF" procedure
<i>Slopes</i>						
0.93	0.90	0.97	0.69	0.87	0.63	"Quartz-aqua regia" procedure
1.02	0.92	0.96	0.95	1.02	0.57	"Teflon-aqua regia-HF" procedure

required for concentration to 10 ml), and hydrofluoric acid is added (which results in a higher acid blank). The slopes are similar for the two procedures, except for manganese and especially calcium. The iron slope is rather unclear.

Teflon vessels therefore appear more suitable for concentration of very dilute solutions at p.p.b. level.

I thank C. Lorius for his stimulating advice. Analyses were performed at the Service d'Etudes Analytiques, Centre d'Etudes Nucléaires de Fontenay aux Roses. I am grateful to R. Platzer and G. Baudin for their helpful discussions and criticisms during this work.

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SHORT COMMUNICATION

Photometric titration of copper(II) with 8-hydroxyquinoline-5-sulphonic acid

G. J. VAN ROSSUM and G. DEN BOEF

Laboratory for Analytical Chemistry, University of Amsterdam, Amsterdam (The Netherlands)

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In previous papers^{1,2} the possibilities for titrations of metal ions with ligands forming 1:2 complexes have been discussed theoretically, and some practical examples were given. In the present paper the results of a thorough experimental investigation of the photometric titration of copper(II) with 8-hydroxyquinoline-5-sulphonic acid (HQS) are presented. Titrations of 10^{-3} M copper(II) with 8-hydroxyquinoline have been carried out in organic solvents by Boyle and Robinson³, whereas Fujinaga *et al.*⁴ theoretically discussed tensammetric titrations of copper(II) with 8-hydroxyquinoline. HQS has been used for the fluorimetric titration of 10^{-3} M solutions of copper(II) with zinc(II) as indicator ion⁵. HQS was preferred in the present study because of its solubility in water to give stable solutions.

Preliminary considerations

Table I gives the stability constants of the complexes of the ligand with several metal ions, taken from the literature⁶. According to these data an end-point determination at a Cu(II):HQS ratio of 1:1 is impossible. For an accurate determination of the end-point at a 1:2 ratio for Cu(II):HQS, a large difference in molar absorptivity of Cu(HQS)₂ and HQS is desirable. Therefore, the spectra of both compounds were measured in different buffer solutions in the pH range 3–10. At high pH values the spectra of the ligand and of the copper chelate were nearly identical. Best results were obtained at pH 4.5–6.5. The spectra of the different compounds involved in the reaction at pH 5.5 are given in Fig. 1. All titrations were carried out in a 0.1 M acetate-acetic acid buffer pH 5.5 at 380 nm.

TABLE I

STABILITY CONSTANTS OF COMPLEXES OF METAL IONS WITH HQS⁶

<i>Metal ion</i>	$\log \beta_1$	$\log \beta_2$	$\log \beta_3$	<i>Metal ion</i>	$\log \beta_1$	$\log \beta_2$	$\log \beta_3$
Ba ²⁺	1.5			Mn ²⁺	5.7	10.7	
Ca ²⁺	2.7			Ni ²⁺	9.0	16.8	22.9
Cd ²⁺	6.9	13.4		Pb ²⁺	7.7	15.3	
Cu ²⁺	11.9	21.9		Sr ²⁺	2.0		
Co ²⁺	8.1	15.1	20.4	Th ⁴⁺	9.6	18.3	25.9
Fe ²⁺	7.6	14.3		UO ₂ ²⁺	8.5	15.7	
Fe ³⁺	11.6	22.8		Zn ²⁺	7.5	14.3	
Mg ²⁺	4.1	7.6		H ⁺	8.35	12.19	

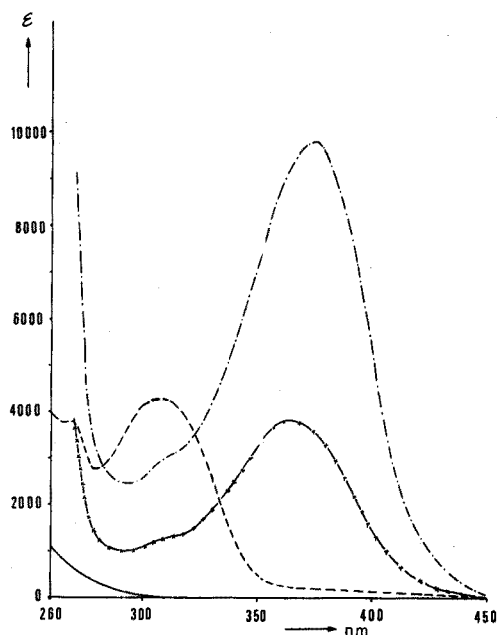


Fig. 1. Spectra of Cu(II) (—), CuHQS (×-×), Cu(HQS)₂ (---) and HQS (-·-) in a 0.1 M acetate-acetic acid buffer pH 5.5.

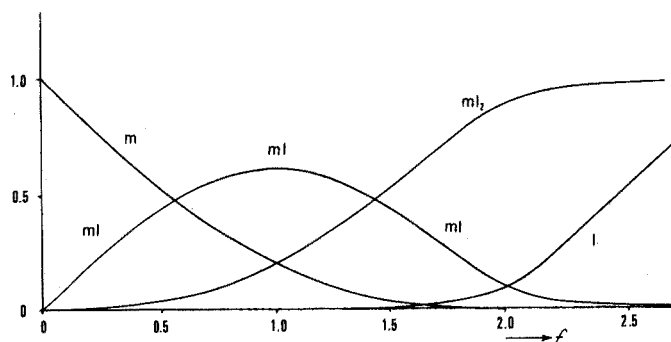


Fig. 2. f -relative concentration relationships for the titration of $1.085 \cdot 10^{-5}$ M copper(II) with HQS. $Z_1 = 10^3$; $Z_2 = 140$.

A further requirement for a suitable end-point determination at $f=2$ is that the values of $Z_1 = K_1 c$ and $Z_2 = K_2 c$ are large enough^{1,2}. From the data mentioned in Table I it can be calculated that in the selected titration medium $\log K'_1 = 8.0$ and $\log K'_2 = 7.1$. These values were calculated with $\log \alpha_{L(H)} = 2.85$ and $\log \alpha_{Cu(ac)} = 1.1$. No ternary complex formation or other possible side-reactions were taken into account.

According to theory^{1,2}, titrations of 10^{-5} M solutions of copper(II) with HQS should be possible in the selected medium with good accuracy at $f=2$, Z_1 being about 10^3 and Z_2 about 100. In Fig. 2 the theoretical relationships of the titration parameter f with the relative concentrations $m = [M]/c$, $ml = [ML]/c$, $ml_2 = [ML_2]/c$ and

$l = [L]/c$ are given for the titration of $1.085 \cdot 10^{-5}$ M copper(II) with HQS in 0.1 M acetate-acetic acid buffer pH 5.5.

From Figs. 1 and 2, the theoretical photometric titration curve can be calculated at any wavelength. Experimental curves appeared to agree with the theoretical curves within experimental error. Figure 3 shows a typical photometric titration curve at 380 nm.

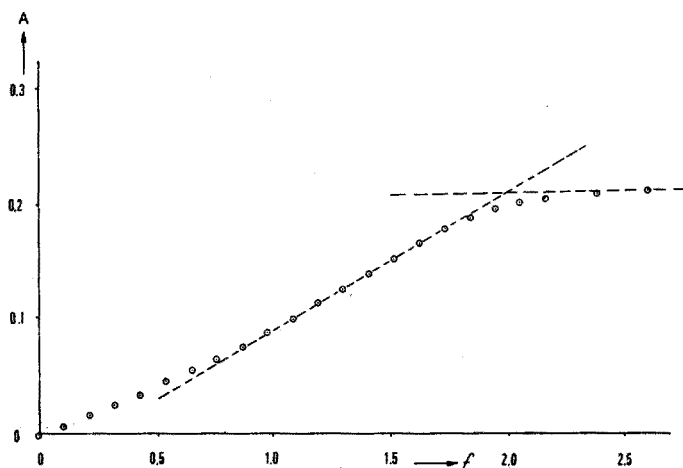


Fig. 3. Photometric titration curve of $1.085 \cdot 10^{-5}$ M copper(II) with HQS in 0.1 M acetate-acetic acid buffer pH 5.5, at 380 nm.

Experimental

Photometric titration curves and spectra were obtained with a Zeiss PMQ II spectrophotometer.

Analytical-grade reagents were used, as well as doubly distilled water.

Procedure. Transfer 8–10 ml of a solution containing 5–100 μg of copper(II) to the titration cell of the photometer. Add 1 ml of a concentrated buffer solution pH 5.5. Set the wavelength at 380 nm. Titrate with $5 \cdot 10^{-3}$ M HQS from a 0.5 ml piston-type buret. The equivalence point is found by the intersection of the two straight parts of the titration curves.

Results

The standard deviation for a single determination was 0.8% for 7 μg of copper (from 20 titrations), 0.5% for 27 μg ($n = 30$) and 0.4% for 70 μg ($n = 15$). No systematic errors were observed. The titrant solution remained stable for about 3 months.

Interferences. Chloride, nitrate, sulphate, fluoride and citrate did not interfere. No interference was observed in the presence of 1000-fold amounts of ammonium ion, alkali metals, alkaline earth metals, Be(II), Cd(II), Mn(II), Hg(II) (when masked with chloride), Ce(III), the lanthanides, U(VI) or Th(IV), or of 100-fold amounts of Ag(I), Pb(II) and Cr(III) (when citrate was added), or 10-fold amounts of Al(III), Bi(III), Zn(II), Co(II) and Ni(II); 10-fold amounts of iron(II) or iron(III) may cause a positive error of 5%. Vanadium(IV) interfered because it reacted with HQS;

this reaction might be useful for the determination of vanadium. Equal amounts of vanadium(V) could be present. Gallium(III) interfered.

The reverse titration. The determination of HQS by photometric titration with copper(II) was found to give very good results in the same concentration region. This reaction might be useful in back-titrations. The results of the reverse titration and the theoretical background of the back-titrations will be presented in other papers.

Discussion

The interference of other metal ions roughly agrees with what can qualitatively be expected from the stability constants. In some cases the interference is not caused by complex formation of the interfering metal ion with the ligand but by the large absorbance at the wavelength used. In some other cases metal ions do not interfere because of a slow reaction with the ligand.

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SHORT COMMUNICATION**Determination of phosphorus in organophosphorus compounds**

R. F. SYMPSON

Clippinger Research Laboratory, Department of Chemistry, Ohio University, Athens, Ohio 45701 (U.S.A.)

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Many methods have been reported for the determination of phosphorus in organophosphorus compounds. Usually the phosphorus is converted to orthophosphate by one of the following methods: closed flask combustion, digestion with $\text{HClO}_4\text{-HNO}_3$ or $\text{H}_2\text{SO}_4\text{-HNO}_3$ mixtures, peroxide fusion, or pyrolysis in a silica tube. The phosphate formed is then determined by one of a number of procedures based on colorimetry, acid-base titrations, volumetric or coulometric precipitation titrations, indirect compleximetric titrations, or gravimetric methods. The review articles of Ma¹ should be consulted for references to specific methods.

The potentiometric titration of phosphoric acid with standard base using a glass pH electrode as the indicating electrode is well-known^{2,3}. Nevertheless, there seems to be no reference in the literature to the application of this method to the determination of phosphorus in organophosphorus compounds. In the method presented here, the organophosphorus compound is burned by the Schöniger method⁴, and the combustion products are absorbed in an alkaline bromine solution. The solution is acidified and boiled to remove carbon dioxide and bromine. The resulting solution of hydrochloric acid and orthophosphoric acid is titrated with electrogenerated hydroxide. The pH is recorded as a function of time. From the time between the H_2PO_4^- equivalence point and the HPO_4^{2-} equivalence point and the value of the electrolysis current, the phosphorus content is calculated.

Experimental

Apparatus. The Beckman Electroscan 30 with potentiostat accessory furnished the constant current and was also used to record the pH continuously with time. A Sargent-Welch combination pH electrode No. S-30072-15 was used to follow the titration. A Beckman 39273 platinum electrode and a larger platinum foil electrode of 6 cm² were both used as the generator electrode. A Beckman 39017 platinum auxiliary electrode was bridged to the solution through a U-type salt bridge. For most titrations described here a current of 10.00 mA and a chart speed of 1.2 in. min⁻¹ were used.

Thomas-Schöniger 500-ml combustion flasks were employed. Although most of the combustions were performed with the conventional platinum mesh sample carrier used with these flasks, the simplest combustion technique was to use a Thomas 6514-F45, Ogg-type sample carrier hooked on a platinum wire extending from the

stopper of the Schöniger flask. The sample was contained in a black wrapper and ignited by a Thomas 6516-S10 infrared igniter.

Chemicals. The triphenylphosphine, triphenylphosphine sulfide, and tributylphosphine were from Eastman Organic Chemicals. The 2-quinolylphosphonic acid, phenylphosphonic acid, and phenyl-*m*-bromophenylphosphinic acid were supplied by Professor R. K. Ingham, and they had been prepared by Sanders⁵ and Denham^{6,7}.

Procedure

Weigh 15–45 mg of the sample onto the filter paper. Add 20–25 ml of water, 0.5 ml of 1 *M* sodium hydroxide and 1–2 ml of saturated bromine water to a 500-ml Schöniger flask. Burn the sample in the usual way. Allow 30 min for all vapors to be absorbed, acidify with 1 *M* hydrochloric acid, and boil to remove carbon dioxide and bromine. Cool the solution to room temperature, add 2 drops of methyl orange and adjust the acidity by adding 1 *M* sodium hydroxide and 1 *M* hydrochloric acid until the solution is just acid to methyl orange. Boil again if much sodium hydroxide had to be added. Transfer to the titration cell containing a magnetic stirring bar. Insert the electrolysis and indicator electrodes. Adjust the pH recorder sensitivity to 7 pH units full scale. Start the magnetic stirrer and the chart drive. Turn on the desired electrolysis current. Adjust the pH calibration control until the recorder pen is at the low pH end of the chart. When the H_2PO_4^- inflection point is passed, adjust the pH calibrate control to position the pen at the low pH end of the chart. Do not interrupt the chart drive while doing this. This prevents the pen from going off-scale at the HPO_4^{2-} equivalence point, and although it makes a discontinuity in the titration curve, the distance between inflection points is the quantity of interest, not the absolute pH values. When the HPO_4^{2-} equivalence point is passed, turn off the electrolysis current and chart drive. Measure the time interval between the H_2PO_4^- and HPO_4^{2-} equivalence points in inches. Calculate the % P by eqn. (1).

$$\% \text{ P} = \frac{i \cdot r \cdot S \cdot 30.97 \cdot 100}{96,494 \cdot w} \quad (1)$$

where i = current (A), r = chart speed (sec in.⁻¹), S = distance between H_2PO_4^- and HPO_4^{2-} equivalence points (in.), and w = weight of the sample (g).

Results and discussion

The method was first applied to the determination of phosphorus in triphenylphosphine and in triphenylphosphine sulfide. The absorption solution used initially contained no bromine and the phosphorus results were slightly low. Belcher and Macdonald⁸ recommended the use of bromine to insure oxidation of phosphorus to phosphate. When bromine was added to the absorption solution, the results improved. The acidity of the solution was adjusted just before titration to a value just on the acidic side of the H_2PO_4^- equivalence point. This is desirable so that time is not wasted titrating a large excess of hydrochloric acid before the H_2PO_4^- break is reached. Methyl orange is a convenient indicator to use for this initial pH adjustment as it changes color slightly on the acidic side of the H_2PO_4^- equivalence point. The excess of bromine and any hypobromite formed by prior hydrolysis of bromine in basic medium must be removed by boiling before addition of methyl orange as they destroy the indicator.

TABLE I

COULOMETRIC TITRATION OF PHOSPHORUS

<i>Compound</i>	<i>Theor. % P</i>	<i>Ave. % P found</i>	<i>No. replicate analyses</i>	<i>Std. dev. (%)</i>
Triphenylphosphine	11.81	11.72	11	0.15
Triphenylphosphine sulfide	10.52	10.57	8	0.22
Phenyl- <i>m</i> -bromophenylphosphinic acid	10.42	10.35	7	0.27
Tributylphosphine ^a	15.31	15.02, 15.59	2	—

^a Results corrected for P in cellulose acetate capsules.

In the first attempts to perform the titration, the auxiliary electrode was immersed in a potassium chloride solution in a straight isolation tube furnished as an accessory with the Beckman Electroscan. High results for phosphorus were always obtained, and it was decided that hydrogen ions liberated at the auxiliary electrode were carried into the titration solution by leakage from the isolation tube. The problem was eliminated by use of a U-type salt bridge.

The results of a series of titrations of various organophosphorus compounds are summarized in Table I.

The determination of phosphorus in organic liquids is complicated by the fact that the cellulose acetate capsules used to weigh out liquids contain a significant amount of phosphorus. An approximate correction for the phosphorus present in the capsules was obtained by burning two empty capsules and titrating the combustion products of the capsules. A phosphorus content of 0.738 and 0.690 mg was found in the two capsules burned. The average value of 0.714 mg P was subtracted from the total phosphorus content calculated from titration of the two tributylphosphine samples.

Several attempts were made to determine phosphorus in 2-quinolylylphosphonic acid by this method. The results were low and scattered over a wide range. It appeared that the phosphonic acids did not burn completely in the combustion step. The reason for this is not apparent, especially in view of the fact that no problems were encountered in the combustion of phenyl-*m*-bromophenylphosphinic acid and subsequent phosphorus determination.

The presence of sulfur and bromine in the compounds did not interfere in the analysis. There is no reason to expect any interference from chlorine in the molecule especially since chloride from hydrochloric acid was present in the solutions titrated.

The method has the advantages usually associated with coulometric titrations. No standard solution is required; and because the titration is followed by recording the pH at a known chart drive rate, little operator attention is required during the titration. Sulfur and halogens do not interfere as they do in many of the other methods for phosphorus. The accuracy is as good as or better than most present methods.

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SHORT COMMUNICATION

Microdetermination of sulfur by the ring-oven technique

RONALD ROWLAND and PHILIP W. WEST

Coates Chemical Laboratories, Louisiana State University, Baton Rouge, La. 70803 (U.S.A.)

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Atmospheric studies have concentrated on the determination of sulfur in the form of sulfur dioxide, hydrogen sulfide, sulfur trioxide, and sulfate. Total sulfur present is approximated by the sum of these four species. Yet in regions where elemental sulfur is being mined and/or naturally present, *e.g.*, Frasch mining regions and Sicilian and other volcanic regions, a simple and economical method should be available for the determination of sulfur in the elemental form.

The method proposed here provides for the identification and determination of elemental sulfur through the use of the Weisz ring-oven technique. This rapid, simple, and reliable method lends itself well to air pollution studies. Sulfur can be collected as particulate matter on an automatic sequential tape sampler. The sampling time can be varied so that the sulfur content on the tape falls within the range of the method. The ring-oven technique then provides an attractive means for the separation, concentration, and determination of sulfur directly on the filter tape containing the sample dust spot.

Mack and Hamilton¹ developed a method for the determination of elemental sulfur in which a solution of copper(I) ammonium sulfate is added to a solution of sulfur in acetone and the resulting colloidal yellow-brown copper(I) sulfide is determined photometrically. Copper(I) ammonium sulfate thus meets the criterion for a ring-oven reagent for sulfur, as it rapidly forms a colored, highly insoluble² (10^{-14} g in 100 ml of water at 20°) precipitate when it is applied to a ring containing sulfur.

Studies presented here show that the reagent is readily adapted to the determination of sulfur by the ring-oven technique.

Reagents and stock solutions

Copper(II) sulfate stock solution. Prepare a copper(II) sulfate pentahydrate solution, 4% in ammonium hydroxide (29.1% ammonia by weight).

Ammoniacal copper(I) sulfate reagent solution. To 5 ml of stock copper(II) solution, add 5 ml aqueous 20% (w/v) hydroxylamine hydrochloride solution, then slowly add water to make 50 ml and shake vigorously. The reagent is unstable and should be freshly prepared from the stock solutions each day. Heat, light, and oxygen tend to decompose the reagent but this is minimized by storing it in a cool, dark place.

Standard stock sulfur solution. Dissolve 0.0100 g of sulfur (dried at 105° for

2 h) in acetone and dilute to 100 ml. Sulfur dissolved in organic solvents undergoes a photochemical reaction³, the product of which reportedly will not react with ammoniacal copper(I) sulfate reagent¹. For this reason, the standard stock solution of sulfur in acetone is stored in the dark and exposed to light only in the preparation of standard rings. When this procedure was adhered to, no problem was encountered from the photochemical reaction.

Apparatus

Trace oven (ring oven) with accessories (Arthur H. Thomas, Co., Philadelphia, Pa.), and a Pandux surface temperature thermometer, range +20–180° (Pacific Transducer Corp., Los Angeles, Calif.). Whatman No. 41 filter paper was used.

Recommended procedure for sampling and determining sulfur

As previously mentioned, sulfur samples (0.1–2.0 μg) can be collected on a low-volume automatic sequential tape sampler. Mark the sample dust spot at its center with a pencil dot and place the filter tape on the ring oven maintained at 50° with the spot centered exactly on the oven surface. Wash the spot with four 30- μl portions of acetone solvent. Allow sufficient time between acetone additions so that the ring is not flooded. Treat the sulfur in the ring with the copper(I) reagent solution applied with a capillary. Allow 3 min for the yellow-brown color to develop fully, and then rinse the filter tape under the tap, blot between sheets of a paper towel, and store moist in a plastic Petri dish until a color intensity comparison is made with a series of standard scale rings.

Prepare a standard scale following the above procedure by making rings with 2-, 4-, 6-, 8-, 10-, 15-, and 20- μl portions of an acetone solution containing 0.1 $\mu\text{g S } \mu\text{l}^{-1}$.

In this procedure, attention must be paid to possible interferences from acetone-soluble species which might be washed to the ring in the acetone washings and give a blank or alter the color intensity of the copper(I) sulfide ring when the reagent solution is applied. Such an interfering stain will be apparent before the addition of the reagent and therefore does not constitute a real source of error.

Reproducibility studies

Test solutions of sulfur in acetone (0.075 $\mu\text{g } \mu\text{l}^{-1}$ and 0.1 $\mu\text{g } \mu\text{l}^{-1}$) were prepared. For each test solution, three rings with different microliter volumes of the solution

TABLE I

DETERMINATION OF SULFUR

Ratio of test to standard solution

<i>Taken</i>	<i>Found^a</i>
0.75	0.776 \pm 0.015 ^b
1.00	1.056 \pm 0.014 ^b

^a Based on averaging 5 values calculated from 3 rings, each by the method of Weisz⁴.

^b Calculated at 95% confidence level.

were developed and the color intensity of each of the three rings was compared visually with that of the standard scale. The quotient obtained by dividing the total number of microliters of the three rings made from the unknown solution, multiplied by the concentration of the standard solution gives the determined concentration of the test solution.

For each test solution, this process was carried out five times and an average value for the ratio of each test solution to the standard solution was calculated⁴. Results are shown in Table I. Standard rings and test solution rings were prepared on Whatman No. 41 filter paper.

Range of the proposed method

The limit of detection for sulfur by the proposed method is 0.1 μg . The range 0.2–2.0 μg is recommended for optimal accuracy for quantitative work. Amounts of sulfur in the ring larger than 2.5 μg tend to give highly diffuse rings which are more susceptible to air oxidation than lesser amounts.

Interferences

The effect of interfering ions was investigated by preparing two rings for each ion. The first ring contained 200 μg of the interfering ion and the second 2 μg of sulfur in the presence of 200 μg of the interfering ion. The ion was established as non-interfering when the first ring was identical to the blank and the second matched with the 2.0- μg sulfur ring of the standard scale.

The possible interfering effects of the following ions were investigated.

Group I Li^+ , Na^+ , K^+ , Rb^+ , Ag^+ , Cs^+ , Au^{3+}

Group II Be^{2+} , Mg^{2+} , Ca^{2+} , Zn^{2+} , Sr^{2+} , Cd^{2+} , Ba^{2+} , Hg_2^{2+} , Hg^{2+}

Group III BO_2^- , $\text{B}_4\text{O}_7^{2-}$, Al^{3+} , Ce^{3+} , Tl^+

Group IV CO_3^{2-} , SiO_3^{2-} , Sn^{2+} , Sn^{4+} , Pb^{2+} , Ac^- , GeO_3^{2-} , Th^{4+} , Zr^{4+}

Group V NH_4^+ , NO_2^- , NO_3^- , HPO_4^{2-} , VO^{2+} , VO_3^- , HAsO_4^{2-} , Sb^{5+} , Bi^{3+}

Group VI S^{2-} , $\text{S}_2\text{O}_3^{2-}$, SO_3^{2-} , SO_4^{2-} , Cr^{3+} , $\text{Cr}_2\text{O}_7^{2-}$, CrO_4^{2-} , SeO_3^{2-} , SeO_4^{2-} , MoO_4^{2-} , TeO_3^{2-} , TeO_4^{2-} , WO_4^{2-} , UO_2^{2+} , UO_4^{2-}

Group VII F^- , Cl^- , ClO_3^- , ClO_4^- , Mn^{2+} , Br^- , BrO_3^- , I^- , IO_3^- , CN^- , SCN^-

Group VIII Fe^{3+} , Co^{2+} , Ni^{2+} , Pd^{2+}

Interferences were observed from Au^{3+} , Ag^+ , Hg_2^{2+} , Hg^{2+} , Al^{3+} , Sn^{2+} , Sn^{4+} , Pb^{2+} , Sb^{5+} , Bi^{3+} , S^{2-} , $\text{S}_2\text{O}_3^{2-}$, $\text{Cr}_2\text{O}_7^{2-}$, SCN^- , and Fe^{3+} . When the quantity of interfering ions was reduced from 200 μg to 20 μg , only Ag^+ , S^{2-} , $\text{S}_2\text{O}_3^{2-}$, $\text{Cr}_2\text{O}_7^{2-}$, and SCN^- interfered.

The interfering ions are water-soluble and could be removed from air sample dust spots by dipping in water or by washing the dust spot with water to the perimeter of a washing ring⁵ which possesses a larger diameter than the 22-mm ring of the standard ring oven. Sulfur is not dissolved or washed to the washing ring with an aqueous rinsing and it would remain in its initial position.

After the paper has dried from the water washing, the sulfur can be washed to the regular ring with acetone and treated with ammoniacal copper(I) sulfate reagent. At this stage, no interfering ions should be present.

Discussion

Attempts to form rings failed when the ring oven was at 105°. Apparently

the high temperature renders the sulfur deposit on the ring unreactive after it has set on the ring for a minute or two. No color results after this time has elapsed when reagent is added.

At 50°, sulfur deposits formed on the ring and allowed to set for 10 min produced the proper color when the developing reagent was added. After 1 h the color intensity was diminished somewhat. As it takes less than 5 min to wash the sulfur to the ring the prescribed number of times, 50° is a satisfactory temperature for carrying out the analysis on the ring oven.

An 80%–20% acetone–water mixture failed to move sulfur from the initial sample introduction site to the ring while 100% acetone readily transported the sulfur spot to the ring. This illustrates the importance of the paper being allowed to dry completely should an aqueous rinsing be used to eliminate interferences. If the paper is not dry, acetone would not move sulfur to the ring zone.

The rings formed on addition of the developing reagent change from yellow-brown to black to a complete disappearance of color if they are allowed to set in the dry state in air. By storing the rings in a moist condition inside a plastic Petri dish, color deterioration is greatly inhibited.

The rings prepared in this study were 22 mm in diameter. This size of ring is satisfactory when eluting materials from 0.5-in. diameter dust spots collected on a tape sampler. When the dust spots are 1 in. in diameter, a 33-mm ring is recommended. The Arthur H. Thomas trace oven attachments provide for the formation of 14, 22, or 33 mm diameter rings.

Whatman No. 41 filter paper proved satisfactory in these studies, as uniform rings were produced on it and the paper gave no blank.

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SHORT COMMUNICATION

Selective extraction of gallium with N-benzylaniline in chloroform from hydrochloric acid media

M. M. L. KHOSLA

Defence Laboratory, Jodhpur (India)

and S. P. RAO

University of Jodhpur, Jodhpur (India)

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Many solvent extraction methods for gallium have been reported in the literature, but none of these is particularly selective for the separation of gallium^{1,2}. Among recently proposed extractants are methyl ethyl ketone^{3,4}, thenoyltrifluoroacetone with tetraphenylarsonium chloride⁵ and the latter reagent alone⁶.

In this communication, N-benzylaniline in chloroform is reported as a new extractant for gallium from hydrochloric acid media. Gallium(III) is readily and quantitatively extracted from 6.5–7.5 M hydrochloric acid; the phase separation is rapid, and gallium can be easily stripped from the organic phase with water and determined by EDTA titration⁷. The extraction is highly selective if thioglycollic acid is added as masking agent.

Experimental

The general equipment and reagents were the same as described previously⁸.

Gallium(III) solution was prepared by dissolving 1.0 g of gallium nitrate octahydrate (99.99%, Fluka) in 100 ml of 0.2 M nitric acid and standardized with EDTA solution⁷.

General procedure. To an aliquot of solution containing up to 10 mg of gallium(III), add enough concentrated hydrochloric acid and water to give 6.5–7.5 M acid in a volume of 30 ml. Shake the solution for 1 min with 15 ml of extractant containing 5 ml of 9% (w/v) N-benzylaniline in chloroform⁸ and 10 ml of chloroform. Swirl the separating funnel slightly and separate the chloroform layer. Re-extract the aqueous layer with 15 ml of the extractant mixture. Combine the organic layers and strip gallium from the organic phase by shaking for 1 min with two 30-ml portions of water. Transfer the back-extract to a 250-ml conical flask. Add dilute ammonia solution until a turbidity appears and then clear it with a few drops of 1 M hydrochloric acid. Add an excess of 0.01 M EDTA, adjust the pH and back-titrate with thorium solution as described previously⁸.

Results and discussion

Interference of diverse ions. Gallium(III) could be selectively and quantitatively

TABLE I

PERMISSIBLE AMOUNTS OF VARIOUS IONS IN THE EXTRACTION OF GALLIUM
(Gallium(III) = 1.72 mg + 4 ml of 80% thioglycolic acid)

Foreign ion	Amount (mg)	Foreign ion	Amount (mg)
Hg(II) ^a	50	Ba(II)	100
Ag(I) ^a	40	Cr(III)	50
Pd(II) ^a	20	Cr(VI) ^a	50
Pt(II, IV) ^a	20	V(V) ^a	50
Ru(III, VII) ^a	30	Mo(VI) ^a	20
Os(VIII) ^a	30	W(VI) ^c	20
Au(III) ^b	10	Ti(IV) ^a	50
Rh(III) ^a	20	Ge(IV)	30
Ir(IV) ^a	15	Y(III)	30
Cd(II) ^a	20	Ce(IV)	50
Sb(III) ^a	60	U(VI)	50
Bi(III)	100	Th(IV)	50
Pb(II) ^a	100	Zr(IV)	23
As(III) ^a	70	Nb(V) ^c	35
Sn(IV) ^a	20	Ta(V) ^c	35
Al(III)	27	Re(VII)	10
In(III)	100	Se(IV)	30
Tl(III) ^a	30	Te(IV) ^a	30
Be(II)	30	La(III)	27
Mn(II)	50	Eu(III)	30
Co(II)	50	Dy(III)	30
Ni(II)	50	Sm(III)	30
Fe(II) ^a	50	Nitrate	150
Fe(III) ^a	50	Phosphate	500
Cu(II) ^a	60	Tartrate	1000
Zn(II)	60	Citrate	1000
Ca(II)	100	Thiourea	1000
Mg(II)	100	Ascorbic acid	1000

^a In the presence of 3–4 ml of 80% thioglycolic acid.

^b In the presence of thiourea without thioglycolic acid.

^c In the presence of tartaric acid.

extracted from most of the cations tested (Table I), provided that the masking agents indicated were used. Gold(III) formed an insoluble white precipitate in the presence of thioglycolic acid in 6.5–7.5 *M* hydrochloric acid, but the interference of gold could be eliminated by thiourea. In the presence of thioglycolic acid, molybdenum(VI) was partially extracted along with gallium, but no interference was found during the recommended titration of gallium. Complete separation of gallium from molybdenum(VI) could be achieved if the former was back-extracted with 1 *M* hydrochloric acid as given under the *General procedure* and the back-extract was re-shaken with a mixture of 3 ml of *N*-benzylaniline solution and 7 ml of chloroform. Gallium was retained in the aqueous phase and determined by titration. Niobium(V), tantalum(V) and tungsten(VI) were kept in solution by tartaric acid. Common anions such as phosphate, citrate, oxalate, tartrate, nitrate, sulphate and borate did not interfere. Thiourea and ascorbic acid also caused no interference.

Several synthetic samples were analysed and the error was $\pm 1.5\%$.

Effect of acidity and reagent concentration. The concentration of hydrochloric acid was varied from 3.5 to 8.0 M while the concentration of gallium(III) and the extractant were kept constant. The ratio of aqueous to organic phase was 2.0. Gallium was quantitatively extracted from 6.5–7.5 M hydrochloric acid; the percentage extraction was only 91.7% from 6 M hydrochloric acid and 96.0% from 8 M hydrochloric acid. Under the conditions given in the procedure, up to 10 mg of gallium could be extracted quantitatively; extraction of 17.0 mg of gallium was 94.6%.

Conclusions

The proposed method is simple and remarkably free from interferences. None of the experimental conditions is highly critical. The high selectivity is achieved by the presence of thioglycollic acid.

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SHORT COMMUNICATION

An electrode selective to the dodecyl sulphate anion

Comments on the application of direct potentiometry to c.m.c. measurements

B. J. BIRCH and D. E. CLARKE

Unilever Research, Port Sunlight Laboratory, Unilever Limited, Port Sunlight, Wirral Cheshire L62 4XN (England)

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In these laboratories work is in progress on the development of a variety of electrodes selective to surfactant ions based on both liquid and solid exchanger membranes. The present communication describes some preliminary data obtained with an electrode system selective to the dodecyl sulphate (DS) anion; some points arising from a recent paper by Gavach and Bertrand¹, who described a similar electrode, are also discussed.

The following cell, connected to a Radiometer pHM 52 digital voltmeter was used for measurement of potential in sodium dodecyl sulphate solutions (SDS):

Ag(s); AgCl(s)	$1.25 \cdot 10^{-3} M$ SDS $2 \cdot 10^{-2} M$ NaCl	Liquid ion exchanger	Test solution	$5 M$ NH_4NO_3	KCl (satd.) Hg_2Cl_2 (s) Hg (l)
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The surfactant selective half-cell was contained within the body of an Orion calcium ion-selective electrode. The original ion-exchanger liquid was replaced by a $10^{-3} M$ solution of cetyltrimethylammonium dodecyl sulphate in nitrobenzene. A Millipore filter disc (pore size 100 nm) was used as an inert porous matrix for the liquid ion exchanger.

A step change in potential was observed with changes in SDS concentration. The potentials reached a steady value (± 0.2 mV) within 30 s. Electrode drift was non-accumulative and was < 1 mV/day. The selectivity coefficients, in the presence of chloride and decylsulphate anions, were 400 and 2, respectively.

With suitable changes in internal reference solution, this cell will also be selective for the cetyltrimethylammonium cation. Electrodes selective to other surfactant ions can be obtained by suitable choice of anionic-cationic complex.

The electrode system exhibited near-Nernstian response, giving a slope of 58.0 ± 0.3 mV per decade change in DS^- activity (a_{DS}) over the range $5 \cdot 10^{-5}$ to $5.6 \cdot 10^{-3} M$ (Fig. 1a). a_{DS} values were calculated from the extended Debye-Hückel expression, taking the ionic diameter of DS^- as 1.2 nm. Since at the experimental

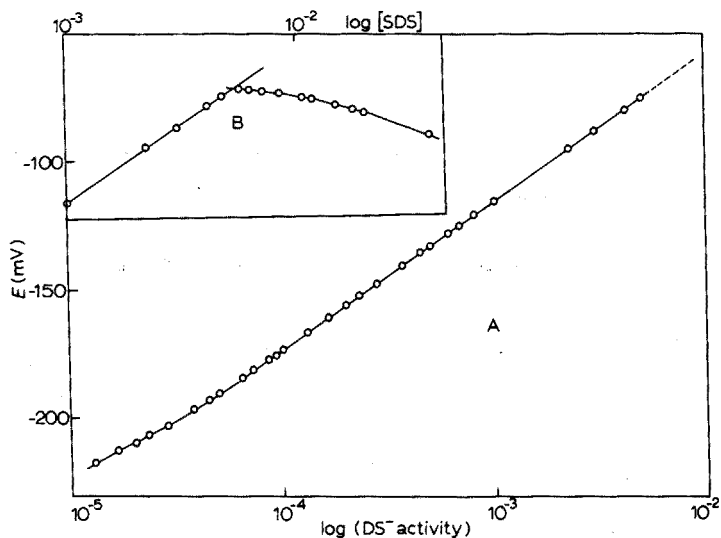


Fig. 1. Response of the DS^- electrode to (A) change in DS^- activity below the c.m.c. and (B) change in DS^- concentration above the c.m.c.

temperature ($294.7 \pm 0.5^\circ K$), a theoretical response of 58.5 mV per decade change in activity is expected, SDS appears to behave as a 1:1 electrolyte, with little or no dimerization occurring. The maximum value of the dimerization constant from our results is 10 l mol^{-1} . This is in good agreement with the work of Van Voorst Vader². The change in response at an activity of $5.6 \cdot 10^{-3} M$, i.e. a concentration of $6.1 \cdot 10^{-3} M$ (Fig. 1b) implies that the critical micelle concentration (c.m.c.) has been reached. This value (or *ca.* $7 \cdot 10^{-3} M$ quoted by Gavach and Bertrand¹) differs significantly from the accepted limits for the c.m.c. of SDS. These limits are³ $8.0\text{--}8.4 \cdot 10^{-3} M$. The lower c.m.c. values reported by earlier workers were due to impure materials or the use of a solubilization method to determine the c.m.c.

We ascribe this present reduced c.m.c. value to solubilization of nitrobenzene at the electrode-test solution interface. It can be shown that for the electrode to respond in the desired manner, the condition $t_{A^+} + t_{DS^-} = 1$ must apply throughout the regions in the cell where there is a gradient in the chemical potential of neutral SDS, t being the transport number of the ionic species. In practice, this means that there should be no such gradient in the aqueous parts of the cell. However, such gradients can be expected to arise when the surfactant concentration exceeds the c.m.c. in a solution saturated with nitrobenzene. As a result, the observed changes in electrode potential are no longer a measure of activity changes in the bulk solution, but are probably an approximate measure of activity changes in the solution immediately adjacent to the liquid membrane interface.

This hypothesis was confirmed by the following experiments.

1. The c.m.c. of the bulk solution was determined by pNa and conductance measurements. The values obtained were within the accepted range ($8.0\text{--}8.4 \cdot 10^{-3} M$) and were independent of the presence of the surfactant-selective electrode.
2. When nitrobenzene was introduced into the bulk solution, the c.m.c. values as determined above (and by viscosity measurements) were reduced to about

$7 \cdot 10^{-3} M$, at approximately half the saturation concentration of nitrobenzene in water.

3. The c.m.c. determined by means of the surfactant-selective electrode was independent of nitrobenzene present in the bulk solution.

It may be noted that saturating the solution with cetyltrimethylammonium dodecyl sulphate did not affect the c.m.c. values, showing that the complex is not solubilized by SDS.

This being so, the statement by Gavach and Bertrand¹ that "these electrodes may be used for the determination of the c.m.c.", with the implication that the electrode can give thermodynamic information at and above the c.m.c., is not correct. In agreement with Gavach and Bertrand, we observe an apparent decrease in a_{DS} values above the c.m.c. Similar results have been obtained for other surfactants, with an anion-exchange membrane cell⁴, electrodes of the second kind⁵ and from e.s.r. measurements on a spin-labelled surfactant⁶. The present results indicate a fall in potential, from the c.m.c. to 0.05 M SDS, of 19 mV (Fig. 1b). The fall obtained by Gavach and Bertrand seems to be, at most, 5 mV (Fig. 1 of ref. 1). The reason for this discrepancy is not clear.

In view of the decrease in monomer activity above the c.m.c. found by these differing techniques, it is most unlikely that the present results can be explained solely by increased solubilization of nitrobenzene. It is proposed that the post-c.m.c. data should be interpreted in terms of micellar properties, with the charged phase model for monomer-micelle equilibria. (This treatment has been successful in predicting thermodynamic properties for a variety of ionic surfactant systems^{7,8}.) Briefly the approach treats micellization by mass-action concepts (which predict a decrease in monomer activity above the c.m.c.⁹) with the micellar molecular weight equal to infinity. This results in a relationship between monomer activity (or electrode potential), total surfactant concentration and the micellar degree of dissociation (α). Use of the present data in the expression gives $\alpha = 0.3$. This is in excellent agreement with values obtained from pNa data obtained on the same SDS solutions, with the same model, and from the effect of sodium chloride upon the c.m.c. of SDS¹⁰. It should be noted that most previous estimates of α from measurement of counter-ion activity¹¹⁻¹⁵, have relied on the assumption that the monomer concentration remains constant above the c.m.c. This assumption leads to lower values of α (0.20 ± 0.05) and indeed the present pNa data give $\alpha = 0.24$.

Work is continuing on the development of electrodes which can be used for unambiguous thermodynamic investigations in post-c.m.c. surfactant solutions. The results are to be reported shortly.

We thank Mr. D. G. Hall for helpful discussion.

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ANNOUNCEMENTS

EUCHEM Conference "Organic Free Radicals" 1972

A EUCHEM Conference on "Organic Free Radicals" will take place on October 15–20, 1972, at Schloss Elmau near Mittenwald, Germany. Professor Dr. Hanns Fischer, Zürich, will be Chairman of the Conference.

The provisional program as well as the preliminary registration forms may be obtained from Dr. W. Fritsche, Gesellschaft Deutscher Chemiker, 6000 Frankfurt (M), Postfach 119075, Germany.

International Symposium on Microchemical Techniques—1973

The next International Symposium on Microchemical Techniques will be held during the period August 26–31, 1973, at Pennsylvania State University, University Park, Pa. 16802, U.S.A. Details will be announced at a later date.

Selective Ion-Sensitive Electrodes

An international symposium on Selective Ion-Sensitive Electrodes will be held under the sponsorship of the International Union of Pure and Applied Chemistry (IUPAC) at the University of Wales Institute of Science and Technology, Cardiff, Wales, U.K., between Monday 9th April and Thursday 12th April 1973. Further details may be obtained from Mr. D. R. Hub, Organiser of Short Courses, UWIST, King Edward VII Avenue, Cardiff, Wales, U.K.

BOOK REVIEWS

Spectrochemical Methods of Analysis—Quantitative Analysis of Atoms and Molecules, Edited by J. D. Winefordner, *Advances in Analytical Chemistry and Instrumentation*, Edited by C. N. Reilley and F. W. McLafferty, Vol. 9, Wiley-Interscience, New York, 1971, xii + 530 pp., price £10.50.

Methods involving measurement of u.v. and visible radiation are undoubtedly the most common means of quantitative analysis. They may involve flame or solution spectroscopy, are applied to species from the simplest ion to complicated macromolecules, and cover a range from below p.p.b. to molar levels. It is convenient, therefore, to have an up-to-date account of the analytical aspects of emission, absorption and luminescence, both in solution and in flames, within the covers of one book, as is the case in the present text. In order to achieve this end, the descriptions of the various techniques have to be concise, and further knowledge must be sought in more detailed specialist texts. The book therefore seems most suited to undergraduate and beginning post-graduate students and analytical chemists who wish to achieve a broad knowledge of analytical spectroscopy.

The flame spectrometry section begins with a very useful discussion of excitation and de-excitation processes in flames (123 pp.) by Alkemade and Zeegers, and is followed by chapters on emission (Ramirez-Muñoz), absorption (Fuwa) and fluorescence methods (R. Smith). The chapter on atomic absorption is not treated in the detail which a method of such importance deserves, but the fluorescence review is especially welcome. It treats the subject clearly and coherently and, as befits its novelty, in rather more depth than its sister techniques. Emission spectrography is not included in the flame section.

The solution spectrometry section is similar in structure to the flame section. An introductory article on excitation and emission, albeit much concerned with solid matrices (McGlynn, Srinivasan and Maria), leads to chapters on absorption (Cheng), fluorescence (van Duuren and Chan) and phosphorescence spectrometry (the late W. J. McCarthy). These are generally comprehensive and readable, although, as is often the case, the examples of fluorescence applications are biochemically biased. The "absorptiometry" chapter curiously restricts its interpretation of structural effects to organic molecules (other than a brief discussion of ligand field theory), and does little more than mention important current developments such as precision spectrophotometry and photon counting. Perhaps the oddest feature of the chapter is the unexpected inclusion of infrared absorbance into the discussion of structural effects on absorbance and the equally abrupt abandonment of the subject eight pages later with the statement "i.r. spectroscopy and gas chromatography complement each other as tools for identifying mixtures". The book concludes with a consideration of signal-to-noise ratios in spectrochemical analysis, also by the late Dr. McCarthy. The development of complete expressions for signal and noise are informative, and the whole chapter should be of interest to those concerned with detection limits.

A. Townshend (Birmingham)

Progress in Separation and Purification, Vol. 4, Edited by E. S. Perry and C. J. Van Oss, Wiley-Interscience, New York, London, Sydney & Toronto, 1971, ix + 414 pp., price £10.55.

The present volume comprises eight chapters by authors who have each made contributions to the fields they review. As in earlier volumes, the plentiful use of diagrams and photographs illustrating techniques will be of particular help to the non-specialists' understanding of the various fields. The topics discussed are: Permeability as a Phenomenological Coefficient, Continuous Column Crystallisation, Endless Belt Electrophoresis, Hydrocarbon Separations with Silver(I) Systems, Parametric Pumping, Use of Liquid Anion Exchangers in Reversed-Phase Extraction Chromatography, Continuous Sample Flow Density Gradient Centrifugation and lastly Continuous Chromatographic Refining. Each chapter is self-contained and deals with relevant theory, in general in considerable detail, experimental parameters and as appropriate, applications.

Unlike Volume 3 in this series which was of particular interest to analytical chemists, the present volume is more directed to chemical engineers. The change to the "cold-type" printing is regretted on grounds of appearance but is offset by the reduction in production time which allows literature coverage to, in most cases, 1970 and in a few instances early 1971. This volume is recommended to libraries with a multidisciplinary readership and to individuals with personal interests in analytical and preparative separation techniques.

D. Thorburn Burns (Loughborough)

N. F. Chamberlain and J. J. R. Reed, *Nuclear Magnetic Resonance Data of Sulfur Compounds. Part III. The Analytical Chemistry of Sulfur and Its Compounds*, Edited by J. H. Karchmer, Wiley-Interscience, New York, 1971, ix + 308 pp., price £8.40.

This book contains a compilation of proton chemical shift values and spin-coupling constants for ca. 1,400 organosulphur compounds covering a wide range of structural type. The data tables appear to be a small-scale reproduction of lineprinter output, with the result that the type is small and somewhat indistinct in places. However, this technique does have the advantage that the material is presented in a very compact book form. It is gratifying to note that the tables indicate whether the coupling constants quoted are precise values or estimates obtained from a first-order analysis. The effects of various sulphur-containing moieties on proton shifts and coupling constants are summarized in correlation tables. It would have been helpful to the casual user if each of these tables had been provided with a caption and footnotes to clarify the symbols used.

This appears to be a very comprehensive compilation of n.m.r. data that should be a useful reference book for those working in the area of organosulphur chemistry.

W. B. Jennings (Birmingham)

Foster Dee Snell and Cornelia T. Snell, *Colorimetric Methods of Analysis, Including Photometric and Fluorometric Methods*, Volume IV AAA, Van Nostrand-Reinhold Co., New York, 1971, xi+351 pp., price £11.25.

This is the last of the three volumes that update Volume IV of this indispensable reference work. It covers Chapters 12–16 of the original text, *i.e.* enzymes (167 pp.), antibiotics (80 pp.), hemoglobin type compounds (31 pp.), organic pigments, such as anthocyanins, chlorophyll, bilirubin (34 pp.), and the colour of liquids (colors of eggs, oranges, Evans blue in blood, oil of basil or rose, and trypan blue in tissues (5 pp.)). The index occupies 33 pages.

The subjects are covered in the competent and comprehensive way that we have come to expect in this series; the sections on enzymes and antibiotics especially are very useful collections of modern methods in rapidly expanding fields.

As the authors say in their introduction, the appearance of further editions of Snell and Snell (the first edition was published in 1921) "will require the enlistment of younger talent". Let us hope that this will be achieved so that the service to analytical chemistry given by Snell and Snell over half-a-century will be continued for further generations of scientists.

A. Townshend (Birmingham)

Paul Kruger, *Principles of Activation Analysis*, Wiley-Interscience, New York, 1971, xi+522 pp., price £11.75.

It is now some years since a definitive text-book was published on the principles of activation analysis. In this rapidly growing field of chemical analysis, a re-statement of the basic principles and techniques in the light of modern developments is therefore more than welcome. The present text is based on an activation analysis course given by the author at Stanford University, and is openly intended as a text-book for this and other similar courses. In this sense, and in view of the title, the emphasis on basic principles and the bringing together of these and other aspects of activation analysis within one volume is perfectly justified. However, *basic* principles do not change very much; as a result, at least half of the book simply repeats or elaborates much of what has been said in other texts on the same general subject.

Principles of Activation Analysis includes nine chapters following a logical pattern from the structure of the atom through to the practices, limitations and applications of activation analysis. Each chapter is provided with an extensive general bibliography (only a few specific references are given in the text itself), and a series of problems based on the subject matter of the chapter. These problems will certainly give the reader food for thought, but whereas they are obviously appropriate to an academic course, the general reader has no direct means of checking that his results and conclusions are correct.

The first six chapters, comprising almost half the book, cover the nuclear characteristics of stable and radioactive nuclides; the activation process with special reference to cross-sections, fluxes and beams; sources of neutrons, charged particles, photons and electrons for irradiation purposes; the decay of radionu-

clides and the interaction of the resulting radiation with matter; gas-filled, scintillation and semi-conductor radiation detectors, and the statistics of radioactivity measurements; and finally radiochemistry and radionuclide analysis. There is a fair amount of duplication of material between these chapters. Again, for an academic course, such repetition is not necessarily a bad thing, but it can be a little trying for the general reader and it certainly detracts from the use of the book as a reference text.

The remaining chapters deal with activation analysis proper and cover the techniques of radiochemical activation analysis, instrumental activation analysis, and related procedures such as prompt-radiation and pulsed-neutron activation analysis; the limitations of activation analysis—chemical, nuclear and spectroscopic; and finally a survey of the uses and applications of the technique and a comparison with some other methods of trace analysis. These chapters are the meat and the most readable part of the book. They bring the reader up to date, even look into the future, and stimulate wider thought.

The book has one major weakness. Although one has to be prepared to tolerate the obvious Americanisms, there are numerous typographical errors, some of which are even perpetuated as separate entries in the index. Fortunately, these errors do not result in any factual mis-statements, but occasionally the reader has to speculate as to what the author really intended, and one would have thought that the price of this volume merited a greater proof-reading effort.

D. Gibbons (Harwell)

H. E. Malone, *The Determination of Hydrazino-Hydrazine Groups*, 1st Ed., 1970, Pergamon Press, Oxford, xv + 393 pp., price £4.50.

This work is Volume 5 in the series *Monographs in Organic Functional Group Analysis*. The author's stated aim was to give a complete digest of essential experimental details of the methods available for the analysis of hydrazine, and in general, the hydrazino-hydrazine functional group. The author must be congratulated on the successful completion of his task and on producing a critical, yet readable, account which cites 330 literature references. As is expected, a major portion is devoted to the numerous oxidation methods, but due regard is paid to gasometric, electrometric, colorimetric and spectrophotometric, chromatographic and selective chemical separative procedures. The last chapter deals with the use of hydrazines and their derivations for the determination of metals, oxidants, carbonyl compounds and of sugars. The monograph is warmly recommended to those who need to determine Hydrazino-Hydrazide Groups and to chemists in general who will find much to stimulate and interest them, in reading a monograph which is problem-, as opposed to technique-, orientated.

D. Thorburn Burns (Loughborough)

Methods of Biochemical Analysis, Vol. 20, Edited by D. Glick, Interscience Publishers—J. Wiley & Sons, Inc., New York, 1971, vi + 393 pp., price £8.25.

The twentieth volume of *Methods in Biochemical Analysis* follows hard on the heels of the nineteenth. It deals with six topics, each of which will as usual be welcomed by numerous workers in various fields of biochemistry.

N. D. Goldberg and Ann G. O'Toole deal with the analysis of cyclic 3',5'-adenosine monophosphate and cyclic 3',5'-guanosine monophosphate, including sampling, extraction and separation from interfering substances followed by conversion of the cyclic phosphates to ATP or GDP which is then measured by "enzymic cycling" methods, ATP being finally determined fluorimetrically in terms of glucose 6-phosphate and GDP in terms of a fluorescent derivative of NAD^+ .

J.-B. le Pecq contributes an article on the use of ethidium bromide for separation and fluorimetric determination of nucleic acids of various conformational forms and measurement of nucleic acid-associated enzymes, *e.g.* nucleases, ligases and polymerases.

The third topic considered (D. Oberleas) is the detection and determination of phytate and inositol phosphates. Qualitative methods such as paper, ion exchange and thin-layer chromatography, and electrophoresis or ionophoresis, are discussed, as well as quantitative procedures, including iron, amperometric, phosphate, inositol and ion exchange chromatographic methods.

M. E. Balis writes on the determination of glutamic and aspartic acids and their amides, chiefly by enzymic methods.

M. Ottesen deals with methods for measurement of hydrogen isotope exchange in globular proteins with particular reference to the infrared spectrophotometric method for hydrogen-deuterium exchange and the gel-filtration method for hydrogen-tritium exchange.

Finally, A. F. Yapel, Jr. and R. Lumry give a practical guide to the temperature-jump method for measuring the rate of fast reactions. This article occupies about half the volume and deals in detail with the mathematical, theoretical and physical bases of the method and with the necessary practical, experimental and technical considerations.

H. G. Bray (Birmingham)

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