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THE DETERMINATION OF SULPHUR AND PHOSPHORUS BY ATOMIC EMISSION SPECTROMETRY WITH AN INDUCTION-COUPLED HIGH-FREQUENCY PLASMA SOURCE

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(Received 11th July 1972)

The application of induction-coupled high-frequency plasma sources for emission spectrometry has been examined by several groups of workers[1–3]. The advantages of this type of source for trace analysis have been described by Fassel *et al.*; for a range of elements detection limits considerably superior to those attainable by flame atomic emission or absorption spectrometry have been recorded[3]. The inert gas atmosphere used to support the plasma, relatively long residence time of sample species in the discharge and the high excitation temperatures attainable provide the potentiality for sensitive emission spectrometry at short wavelengths combined with freedom from solute vaporisation interferences when liquid samples are introduced into the plasma. Current interest in the direct determination of non-metallic elements which exhibit their principal resonance lines at about 200 nm has prompted us to investigate the application of the induction-coupled plasma source for the determination of sulphur and phosphorus. Wendt and Fassel[2] in early work with this type of source recorded a detection limit of 10 p.p.m. for phosphorus in aqueous solution at the phosphorus 253.5-nm line; subsequent work by Dickinson and Fassel[3] with more refined instrumentation and operating conditions led to a detection limit of 0.1 p.p.m. for phosphorus at the 213.62-nm line. Neither of these lines is a gound-state line, however, and the available sensitivity with the phosphorus resonance lines at 177.50, 178.29 and 178.77 nm has not been reported for the plasma source. Similarly, no report of the atomic emission characteristics of sulphur at its resonance lines at 180.7, 182.0 and 182.6 nm has been made although Taylor *et al.*[4] have described the determination of sulphur at the 216.89-nm line, whose origin lies above the ground state, in a low-power microwave plasma source. This was operated at either atmospheric or reduced pressure in helium and provided detection limits of 0.2 and 0.02 μg of sulphur introduced into the plasma as gaseous SO_2 or H_2S. The ability to introduce samples into the high-power induction-coupled plasma source as liquids, and the relative ease with which a conventional plasma source–single channel spectrometer assembly may be modified to extend its range to the detection of radiation between 170 and 200 nm, has led us to investigate the emission spectrometric determination of phosphorus and sulphur introduced into the plasma as aqueous solution of their oxyanions.

EXPERIMENTAL

Apparatus

The plasma power generator employed was the Radyne Model H30/P (Radyne Ltd., Wokingham, Berks.) operating at 36 MHz with a nominal power output of 5 kW. A tangential flow demountable torch similar to that described previously[5] was employed. The actual plasma torch and working coil were as described[5], except that the work coil consisted of only 2 turns of 6.3-nm cylindrical copper tubing.

Aqueous solutions were introduced into the plasma with an indirect nebulizer and spray chamber (Techtron Model AA4, Varian-Techtron, Australia). The fuel inlet of the nebulizer chamber was sealed and the sample was nebulized with the injector gas.

A 0.5-m grating monochromator (Varian Techtron, Melbourne) with a reciprocal linear dispersion of 3.3 nm mm^{-1} was employed. This was bolted onto the body of the plasma generator and positioned to receive radiation from the "tail flame" of the plasma. The monochromator, collection optics and detector were modified, as described below, to permit extension of their operating range to the spectral region between 170 and 200 nm. A rotating sector (1 in Fig. 1), which is used to provide modulation at 285 Hz of the radiation reaching the detector, was sealed from the atmosphere and glass tube extension pieces (3) (22 mm outside diameter) were fitted to its sides. A 25-mm diameter fused silica window (5) was attached to the extension piece nearest the plasma (6) so that the window was 30 mm from the central axis of the plasma tail flame. A 25-mm diameter fused silica lens (2) (62.5 mm focal length) was sealed into the extension piece between the rotating sector and the monochromator to focus the radiation onto its entrance slit. The extension pieces were purged with nitrogen *via* glass side-arms (4). The monochromator housing was purged by passing nitrogen through 6.5-mm diameter copper tubing (7) sealed into the orifice provided for wave-

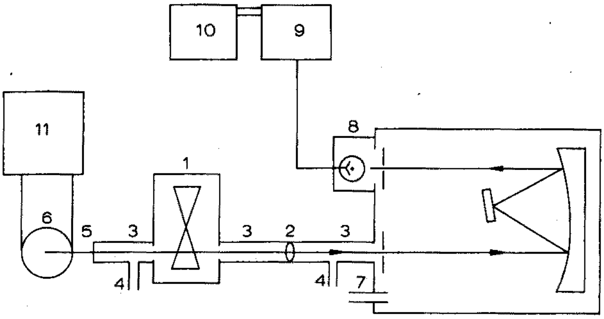


Fig. 1. Instrumental assembly employed. (1) Rotating chopper unit. (2) 62.5-mm focal length silica lens. (3) 25-mm o.d. glass tubes. (4) 8-mm o.d. glass side tube for nitrogen inlet. (5) 25-mm diameter silica window. (6) Plasma torch and work coil. (7) 6.5-mm o.d. copper tube for nitrogen inlet to monochromator. (8) Photomultiplier. (9) Amplifier. (10) Chart recorder. (11) Radiofrequency power supply.

length resetting at the monochromator. The silica cover slip over the monochromator slit mechanism was removed to improve transmission into the monochromator housing.

The standard photomultiplier (Hamamatsu Model R213) of the Techtron Model AA4 spectrometer has poor response characteristics in the short wavelength ultraviolet region examined. In this work a type 9783A photomultiplier (EMI Electronics Ltd., Ruislip), selected for maximum overall gain, was employed. The signal from the photomultiplier (8) was amplified by a phase-sensitive detector (9) (Aim Electronics, Huntingdon; system 5) and displayed either at its meter or on a potentiometric chart recorder (10) (Servoscribe Model RE 511.20).

Reagents

Stock solutions containing 40,000 p.p.m. of sulphur (as sulphate) were prepared by dissolution of analytical reagent-grade ammonium sulphate in distilled water. Solutions containing 1000 p.p.m. P (as phosphate) were prepared from analytical reagent-grade ammonium dihydrogen orthophosphate. These were diluted as required with distilled water. Solutions of diverse ions were prepared from analytical reagent-grade salts.

Analysis of soil extracts for phosphorus

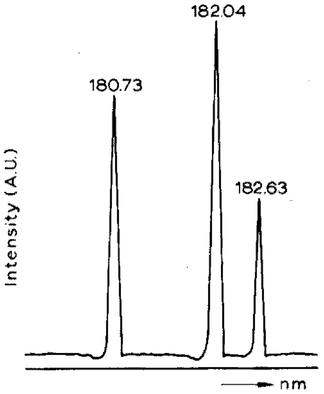
Three 2.5-g samples of each air-dried soil were shaken with 75 ml of 2.5% (v/v) acetic acid for 3 h; 1.0- and 2.0-ml aliquots of an aqueous solution of 50 p.p.m. phosphorus were added to two of the soil samples before shaking. The solutions were filtered through Whatman No. 42 filter paper into 100-ml volumetric flasks. The residue was washed with four 5-ml aliquots of 2.5% acetic acid and the solutions were made to volume with 2.5% (v/v) acetic acid. The solutions were shaken with 1 g of "Amberlite" IR-120(H) ion-exchange resin for 10 min and left to settle for a few minutes. The supernate was then decanted and nebulized into the plasma and the phosphorus emission intensity measured at 213.6 nm relative to a 2.5% acetic acid blank.

RESULTS AND DISCUSSION

Spectral characteristics

Figure 2 shows the emission spectrum between 180 and 183 nm obtained for sulphur obtained on nebulization of an aqueous solution containing 1000 p.p.m. S into the plasma under the optimal operating conditions with the nitrogen-purged monochromator and optical path and viewing the plasma tail flame. The 180.7-, 182.0- and 182.6-nm sulphur lines arise from the triplet ground state in the ^3P–$^3S^0$ transition; the expected intensity ratio for these lines, based on their *gf* values[6], is *ca.* 5:3:1. The relative intensities for these lines shown in Fig. 2 are uncorrected for the significant variation in detection sensitivity with wavelength detailed below for phosphorus.

Figure 3b shows a wavelength scan of the phosphorus line emission observed from an aqueous phosphate solution in the region 185–260 nm. While the background at the 185.92-, 213.62- and 214.91-nm lines is similar, the 213.62-nm line provides the greatest signal intensity with the apparatus employed. The 185.92-



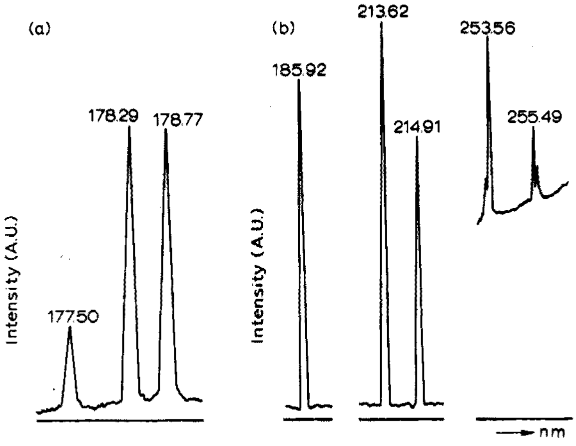


Fig. 2. Emission spectrum for sulphur in region 180–183 nm. 1000 p.p.m. sulphur nebulized as ammonium sulphate. Spectral slit-width 0.08 nm.

Fig. 3. Emission spectra for phosphorus. (a) 175 to 179 nm. 1000 p.p.m. phosphorus nebulized as phosphate. (b) (i) 185.5–186.5 nm. 700 p.p.m. P nebulized as phosphate. (ii) 213–216 nm. 70 p.p.m. P nebulized as phosphate. (iii) 253–256 nm. 70 p.p.m. P nebulized as phosphate. Spectral slit-width 0.08 nm. Amplifier gain unchanged throughout.

nm multiplet line is considerably less intense than the other two lines. Under the conditions used the phosphorus 253.56-nm line, which has been employed by other workers[2], and the 255.49-nm line exhibited poorer signal:background intensity ratios than the 213.62- and 214.91-nm lines. The intensities of the ground-state phosphorus lines in the vacuum ultraviolet at 177.50, 178.29 and 178.77 nm should be greater than, or at least comparable to, those of the lines at 213.62 and 214.91 nm. The three ground-state lines were detected only when the monochromator and optical path were purged with nitrogen and are shown in Fig. 3a. The relative intensities of these lines would be expected to be *ca.* 3:2:1 from the available *gf* values in the literature; but this was not observed, and the intensities of all three lines were less than those observed for the other lines in the ultraviolet region. This is due to (*a*) decreasing photomultiplier sensitivity with decreasing wavelength, (*b*) increasing absorption by the silica windows and lens with decreasing wavelength, (*c*) increased atmospheric absorption at shorter wavelengths, and (*d*) onset of absorption by water vapour below 180 nm. These factors result in attenuation of the signals observed at short wavelengths and do not allow the high sensitivities expected from utilizaton of the ground-state lines with higher transition probabilities.

Operating conditions

The portion of the tailflame being viewed was selected by moving the torch horizontally and vertically to produce the best attainable signal:background intensity ratio for the sulphur 182.04-nm and phosphorus 213.62-nm lines. A viewing height 16 mm above the top of the outer tube of the torch gave the best intensity ratio. The monochromator slit viewed the tailflame between 13 and 19 mm above the top edge of the outer tube with the optical assembly employed.

The effect of variation of the flow rates of the gases supplied to the plasma on the signals obtained for sulphur at 182.04 nm is illustrated in Fig. 4. Optimal signal:background intensity ratios were obtained with the coolant flow rate set to 15 l min^{-1}, an injector flow rate of 3 l min^{-1}, an aqueous sample uptake rate of 4 ml min^{-1}, and with the plasma gas supply switched off. Similar gas flow rates were found to be optimal for the determination of phosphorus at the 213.62-nm line.

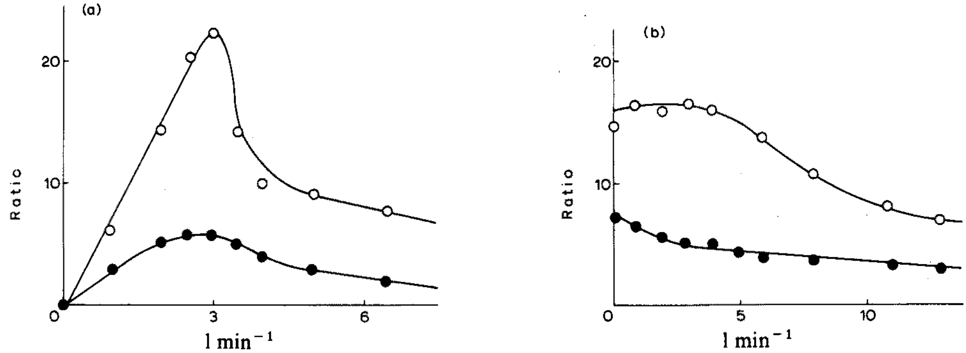


Fig. 4. Effect of gas flow rates on emission of 50 p.p.m. sulphur at 182.04 nm. (a) Effect of injector gas flow rate on signal:background intensity ratio (●) and signal:noise ratio (○). (b) Effect of plasma gas flow rate on signal:background intensity ratio (●) and signal:noise ratio (○).

Little variation of the coolant flow rate was possible as low flow rates led to burning of silica from the walls of the torch and high flow rates tended to extinguish the plasma. Generally the higher the coolant flow rate, the lower the signal for a given combination of plasma and injector flow rates. The minimal coolant flow rate while avoiding possible damage to the walls of the torch was therefore employed.

The flow rates given above were employed for the plasma initiation which was achieved by lowering an ungrounded carbon electrode into the high-frequency field and removing the electrode once the plasma had been established. Fine adjustment was then made to the injector flow rate to maximize the signal at the line of the analyte element.

The maximal signal:noise ratio was observed with the generator supplying full power to the work coil; this did not give the best signal to background ratio however, and this was usually observed at somewhat less than full power. The power to the work coil was adjusted to produce the best signal:background ratio at the sulphur and phosphorus lines chosen.

With the particular Radyne plasma generator used, the power supplied to the work coil is not measured directly but is monitored by ammeters which monitor the high-tension and oscillator valve grid currents. These currents were 1.0 A and 0.41 A, respectively, for the optimal conditions.

Detection limits and calibration curves

With the optimal conditions, the detection limits and relative intensities obtained for the sulphur and phosphorus lines studied are shown in Table I. The detection limits are defined as that concentration of analyte which produces a signal equal to twice the standard deviation of the background noise near the detection limit.

TABLE I

LIMITS OF DETECTION AND RELATIVE INTENSITIES AT ATOMIC LINES STUDIED FOR SULPHUR AND PHOSPHORUS

Wavelength	*Multiplet*	*Limit of detection (p.p.m.)*	*Relative intensity*
Sulphur			
180.73	$^3P-^3S^0$	2.2	78[a]
182.04	$^3P-^3S^0$	1.7	100
182.63	$^3P-^3S^0$	3.7	46[a]
Phosphorus			
177.50	$^4S^0-^4P$	>10	1
178.29	$^4S^0-^4P$	3.0	3.5[b]
178.78	$^4S^0-^4P$	3.0	3.5[b]
–	–	—	—
185.92	$^2D^0-^2D$	0.4	7[c]
213.62	$^2D^0-^2P$	0.08	100
214.91	$^2D^0-^2P$	0.15	65[c]
253.56	$^2P^0-^2P$	2.0	38[c]
255.49	$^2P^0-^2P$	4.0	16[c]

[a] Relative to intensity of 182.04-nm line taken as 100 units. [b] Relative to intensity of 177.50-nm line taken as unity. [c] Relative to intensity of 213.62-nm line taken as 100 units.

Calibration graphs were established for sulphur at the three lines investigated. At each of these lines, the linear region was found to extend to beyond 1000 p.p.m. of sulphur. Deviation from linearity did not occur at 182.0 nm with less than 1750 p.p.m. sulphur introduced into the plasma. Similarly for the phosphorus lines at 178.29, 178.78 and 185.92 nm, the linear range of the calibration graph extended beyond 1000 p.p.m. The calibration graphs at the phosphorus 213.62-nm and 214.91-nm lines were linear to 120 p.p.m. At this phosphorus concentration, full-scale deflection was obtained at the amplifier even when minimal electronic gain and a narrow (25 μm) slit-width were employed.

The most suitable analytical line for the determination of sulphur with our operating conditions is 182.0 nm. This line exhibited the greatest intensity and the best detection limit of the three sulphur lines investigated, while the background intensity remained relatively constant over the region of these lines. All three lines, however, had a large and similar concentration range over which linear calibration graphs could be obtained.

The phosphorus 213.62-nm line was the most intense emission line for this element and gave the best limit of detection of all the lines investigated.

Interferences

As shown in Fig. 5, the introduction of 100 p.p.m. of sulphur into the plasma as aqueous solutions of different sulphur compounds gave the same detection limit and signal per unit concentration of elemental sulphur. No significant chemical or physical interference effects were observed in the emission signal produced at 182.04 nm from an aqueous solution containing 100 p.p.m. sulphur in the presence of fifty-fold (weight) amounts of each of the following ions: Al^{3+}, K^+, Li^+, Mg^{2+}, Na^+, V^{5+}, Zn^{2+}, F^-, Cl^-, I^-, acetate, ammonium, borate, nitrate and phosphate. Freshly prepared solutions containing a fifty-fold amount of calcium show no interference but the signal decreased as calcium sulphate precipitated on standing. The spectral interferences observed in the determinaton of sulphur at 182.04 nm are listed in Table II.

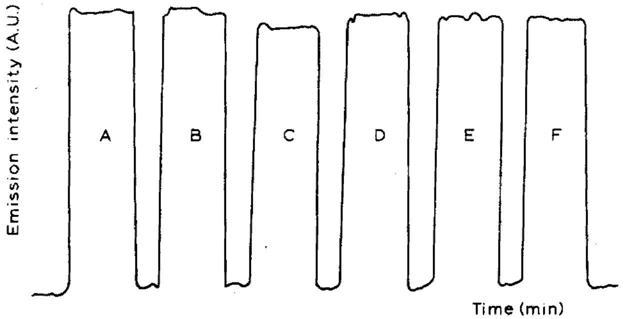


Fig. 5. Emission signals obtained for 100 p.p.m. S at 182.04 nm introduced into plasma as differing anionic forms. (A) Ammonium sulphate, (B) sodium thiosulphate, (C) sodium sulphite, (D) potassium thiocyanate, (E) thiourea, (F) sulphuric acid.

TABLE II

EFFECT OF 50-FOLD AMOUNTS OF DIVERSE IONS ON SIGNAL INTENSITY OBTAINED FOR 100 p.p.m. SULPHUR

Diverse ion	*Wavelength*		
	182.6 nm	*182.0 nm*	*180.7 nm*
Co	+35%	+10%	+25%
Cr	+15%	0	0
Cu	+25%	0	+15%
Fe	+10%	+10%	+15%
Mn	0	0	+10%
Mo	+15%	0	+10%
Ni	+50%	+15%	+50%

No significant chemical or physical interferences at the phosphorus 213.62-, 214.91- and 185.92-nm lines were observed when fifty-fold (weight) amounts of the ions K^+, Mg^{2+}, Na^+, Zn^{2+}, Cl^-, F^-, I^-, acetate, ammonium, borate, nitrate and sulphate were present in a solution containing 100 p.p.m. of phosphorus. Freshly prepared solutions containing molybdenum and vanadium gave no interference, but upon standing the signal decreased, possibly owing to the precipitation of ammonium phosphomolybdate or phosphovanadate.

Copper enhanced the signal observed for phosphorus at the 213.62-nm line owing to spectral interference by the copper ion line at 213.60 nm. Spectral interference at each of the three lines was observed from the aluminium ion line at 185.81 nm and its atomic lines at 213.47 nm and 215.0 nm. Calcium produced a slight enhancement at all three lines. Other interferences observed are shown in Table III.

TABLE III

EFFECT OF 50-FOLD AMOUNTS OF DIVERSE IONS ON SIGNAL INTENSITY OBSERVED FOR 100 p.p.m. PHOSPHORUS

Diverse ion	*Wavelength*		
	214.9 nm	*213.6 nm*	*185.9 nm*
Al	+10%	+35%	+25%
Ca	+10%	+20%	+15%
Co	+15%	+40%	+125%
Cr	+20%	+35%	—
Cu	—	+150%	—
Fe	+20%	+15%	+35%
Ni	+35%	+25%	+10%
Zn	+15%	+10%	+40%

Analysis of soil

Extracts for phosphorus. The accuracy of the determination of phosphorus by plasma excitation was tested in the determination of the phosphate content of soil extracts. The soil samples examined contained 10–80 p.p.m. in the solid. With the detection limit of *ca.* 0.1 p.p.m. at the 213.62-nm line it was necessary to take a 2.5-g sample of soil which, after extraction with acetic acid, provided solutions containing 0.25–2.0 p.p.m. of phosphorus. The soil samples were analysed by the method of standard additions; 50 μg and 100 μg additions of phosphorus were made to the samples before the extraction. Calcium produced an enhancement of the phosphorus emission signal at 213.62 nm. In the soil analysed the calcium content was in some cases as high as 6500 p.p.m. Cobalt, copper, zinc and iron were also present in the soil extracts and these metals also interfered. Most of these interferences were removed by a preliminary batch ion-exchange procedure together with the other metals present, but the iron(III) did not appear to be removed completely, possibly owing to the high stability of the iron(III)–phosphate complex. Emission by iron in the solution after the ion-exchange procedure was detected at 371.99 nm corresponding to a concentration of *ca.* 1 p.p.m. of iron. This concentration of iron(III), however, did not interfere with the emission signal from a 0.5-p.p.m. solution of phosphorus.

The phosphorus content of the soil extracts, calculated from the ratios of the intensities of the emission signals from the soil extracts and soil extracts with addition of known amounts of phosphorus, are shown in Table IV. The results obtained were in good agreement with those obtained by independent analyses.

TABLE IV

DETERMINATION OF EXTRACTABLE PHOSPHORUS IN SOIL EXTRACTS

Soil sample	P_2O_5 *(mg/100 g)*[a]	*Phosphorus content of extract (p.p.m.)*	P_2O_5 *found by plasma emission method (mg/100 g)*	s_r *(%)*
D51023	2.7	0.29	2.66 ± 0.18	± 6.8
D46402	5.1	0.58	5.31 ± 0.19	± 3.1
D44839	8.0	0.88	8.05 ± 0.32	± 3.6
D44189	13	1.44	13.2 ± 0.50	± 3.8
D46755	18	1.99	18.2 ± 0.69	± 3.7

[a] Results obtained by Macaulay Institute for Soil Research.

Conclusion

This investigation of the spectral emission characteristics of sulphur and phosphorus in the high-frequency plasma demonstrates the feasibility of using this source for the determination of traces of these elements in solution. The determination of sulphur requires the use of nitrogen purging in the monochromator and optical path in order to permit the detection of the useful sulphur lines at 180.73, 182.04 and 182.63 nm. The determinaton of sulphur at 182.04 nm is sensitive and relatively free from spectral, physical and chemical interference effects; the plasma source provides equally efficient atomization for sulphur in aqueous solution irrespective of the anionic form of sulphur introduced into it. In the determination of phosphorus no analytical advantage is gained by use of the ground-state phosphorus lines in the far ultraviolet region with the experimental assembly used. The direct determination of phosphorus at the 213.62-nm line, for which nitrogen purging of the optical path and monochromator is unnecessary, is very sensitive. The detection limit obtained is similar to that reported by Dickinson and Fassel[3], and although subject to a greater number of spectral interferences than the determination of sulphur, the determination of phosphorus in soil extracts demonstrates that these interference effects may be readily overcome by a simple preliminary cation-exchange procedure.

In a recent publicaton, Greenfield and Smith[7] stressed the importance of distinguishing between general characteristics of high-frequency plasma discharges and those which are dependent upon the individual system employed. The operating conditions used here will not necessarily produce the best results with other types of plasma generator, but the general principles will be directly applicable. Thus, for example, the height of observation of the analytical signal in the tailflame is an important parameter. Dickinson and Fassel[3] measured the optimal heights of observation for the emission intensity from various elements in a high-frequency plasma, and observed that elements whose excitation energies were high gave the best detection limits at the base of the plasma tailflame (*i.e.* nearer the plasma core).

We have also observed this effect with sulphur and phosphorus; although atomic emission was still observable at heights as great as 50–60 mm above the top of the outer tube of the torch, the signal intensities and detection limits were at least an order of magnitude poorer under these conditions than when measurements were made at the optimal height (16 mm). The effects of optimal gas flow rates, sample uptake rate and power supplied to the work coil are also obviously functions of the particular instrumental arrangement employed, and will vary when different instrumentation is used.

We are grateful to the Science Research Council for the award of a studentship to one of us (A.F.W.), Mr. B. Bach of British Steel Corporation, General Steels Division, Motherwell for the loan of the RF Plasma unit and the Macaulay Institute for Soil Research (Aberdeen) for provision of soil samples for analysis.

SUMMARY

An instrumental assembly is described which permits detection of the atomic emission at their resonance lines below 200 nm from sulphur and phosphorus introduced into a high-frequency induction-coupled plasma source as aqueous solutions of their anions. Optimal conditions for the determination of sulphur at 182.04 nm and phosphorus at 213.62 nm have been established, and detection limits of 1.7 and 0.08 p.p.m. have been obtained for these elements, respectively. The determinations are relatively free from chemical and physical interferences, although spectral interferences from metal ions are observed in both cases. The method established for phosphorus has been applied to its determination in soil extracts.

RÉSUMÉ

On propose une méthode pour le dosage du soufre et du phosphore par spectrométrie d'émission atomique. Les conditions optimales sont obtenues à 182.04 nm pour le soufre et 213.62 nm pour le phosphore, avec limites de détection de 1.7 et 0.08 p.p.m. respectivement. Ces dosages sont relativement exempts d'interférences chimiques et physiques. Cependant on observe des interférences spectrales d'ions métalliques, dans les deux cas. La méthode établie pour le phosphore est appliquée à l'analyse de sols.

ZUSAMMENFASSUNG

Es wird eine instrumentelle Anordnung beschrieben, mit der die Atomemission von Schwefel und Phosphor bei den Resonanzlinien unterhalb 200 nm nachgewiesen werden kann. Wässrige Lösungen der Anionen der beiden Elemente werden einer induktionsgekoppelten Hochfrequenz-Plasmaquelle zugeführt. Die optimalen Bedingungen für den Nachweis von Schwefel bei 182.04 nm und Phosphor bei 213.62 nm wurden ermittelt; die erhaltenen Nachweisgrenzen für diese Elemente sind 1.7 bzw. 0.08 p.p.m. Die Bestimmungen sind relativ frei von chemischen und physikalischen Störungen, obwohl in beiden Fällen spektrale Störungen durch Metallionen beobachtet werden. Die für Phosphor ausgearbeitete Methode wurde auf dessen Bestimmung in Bodenextrakten angewendet.

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INTERFERENCES OF ACIDS IN ATOMIC ABSORPTION SPECTROMETRY WITH A TANTALUM FILAMENT ATOMIZER

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The interferences in atomic absorption spectrometry with flame atomization systems have been reported in previous papers in this series[1,2]. The use of the flame is the most widely accepted means of producing an atomic population. However, flame techniques exhibit some disadvantages as an atomizer, for some interferences result from the flame chemistry. The combustion on fuel gas leads to many kinds of species such as CO, CO_2, NO, OH, etc., which may react with atoms of the element being determined. The formation of refractory compounds in the flame causes some depressing effects on the absorption of certain elements. Mechanisms of interferences in atomic absorption spectrometry in flames are very complex in nature.

Several devices have been reported for the production of free atoms without the use of flames. Nelson and Kuebler[3] atomized solid samples on quartz or graphite strips supported in an enclosed silica chamber by intense flash heating from a capacitor discharge lamp wound round the cell. West and Williams[4] described an efficient carbon filament atomizer, in which the sample in liquid form was placed on a carbon filament supported between two electrodes in a small enclosed pyrex vessel. The sample was atomized by passage of 100 A at 5 V through the filament. Bratzel *et al.*[5] devised a hot wire loop atomizer made from either tungsten or platinum wire; the sample solution was atomized by passing a current through the wire. Bratzel *et al.*[6] reported the enhancing effect of phosphoric acid on cadmium intensity in atomic fluorescence spectrometry with a flameless atomizer. Amos *et al.*[7] reported the depressing effect of phosphoric acid on magnesium absorption with a carbon rod atomizer. Many papers have already described flameless atomic absorption spectrometry, but most of them have been devoted to the development of improved atomizers and more sensitive methods.

In the present work, the interfering effects of various acids on the flameless atomic absorption spectrometry of copper, iron and chromium were investigated. The experimental results were examined in an effort to elucidate the mechanism of the interferences and to provide some information in minimizing their effects.

EXPERIMENTAL

Apparatus

A Nippon-Jarrell-Ash AA-1E atomic and emission absorption spectrophotometer was used with a flameless atomizer system which was of the same type as that reported by Takeuchi *et al.*[8]. A tantalum filament was supported between two electrodes in an enclosed pyrex chamber with optical-quality silica windows. Tantalum was preferred because of its high melting point. The tantalum filament was connected with two copper electrodes by spot fusion. A Yanagimoto Model RA-2511 recorder and a HTV R-106 photomultiplier tube were used. The light sources were hollow-cathode lamps from Westinghouse Electric Corp. for copper, Hitachi Ltd. for iron, and Hamamatsu TV Co., Ltd., for chromium.

The hollow-cathode lamp, two lenses, the atomization chamber and the monochromator were situated in suitable positions for atomic absorption spectrometry, so that the beam of radiation from the hollow-cathode lamp could be focused about midway, immediately above the heated filament via the aperture, and then focused on the slit of the monochromator.

The following resonance lines were used: 324.8 nm for copper, 248.3 nm for iron and 357.9 nm for chromium.

Reagents

Stock solution: copper solution, 1000 μg ml^{-1}; iron solution, 1000 μg ml^{-1}; chromium solution, 1000 μg ml^{-1}. The preparation of the stock solutions was given in the first paper of this series[1]. Weaker solutions were prepared just before use.

All chemicals used were of analytical-reagent grade.

The solutions of copper, iron or chromium containing hydrochloric, perchloric, nitric or phosphoric acid were prepared to give acidities of 0.05, 0.10 or 0.20 M. Each solution was also 0.01 M in hydrochloric acid.

Procedure

The sample solution (2 μl) was placed in the hollow of the filament with a 5-μl micro syringe. The chamber was freed of air by means of argon flowing through it for 2 min. The solvent was completely vaporized without vaporization of the sample by passing a low current (*ca.* 3 A at 0.4 V) through the filament. Heating was discontinued, the filament was allowed to cool for 1 min, and atomization of the sample was effected by passing a high current through the filament. During the measurements, argon was supplied to the chamber at a constant flow rate (2 l min^{-1}).

The power supplied to the filament was estimated from current–voltage measurements as up to 60 W. The temperature attained by the filament was measured with an optical pyrometer.

The atomic absorptions of copper, iron and chromium were measured at various power levels and various acid concentrations.

RESULTS AND DISCUSSION

Hydrochloric acid

The interferences of hydrochloric acid on copper, iron and chromium absorptions are shown in Fig. 1. Hydrochloric acid (0.10 M) had a small depressing effect on copper absorption at low power level, but no effect was observed at higher power levels. The depressing effect may be due to incomplete dissociation of CuCl molecules in the atomizer in the same manner as in the flame[1]. The bands of the CuCl molecule were observed in the flame. The high temperature of the filament in the atomizer may be effective in dissociation of the CuCl molecules.

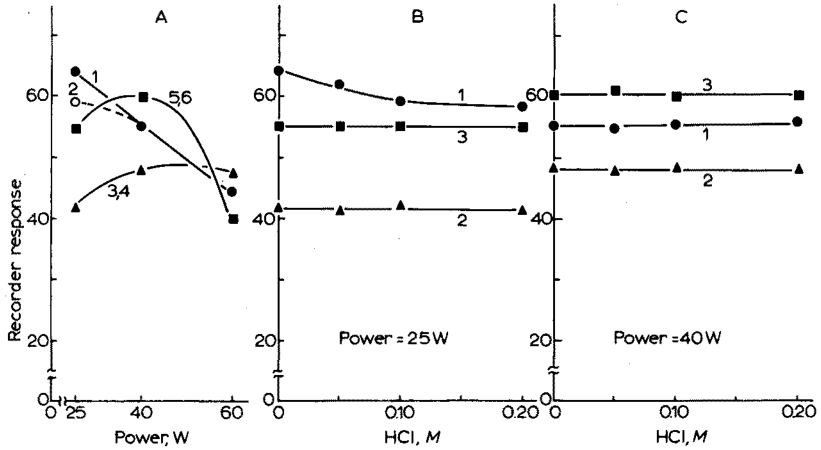

Fig. 1. Interferences of hydrochloric acid on copper, iron and chromium absorptions. (A) Effect of power, (1) 1 ng Cu, 0.01 *M* HCl; (2) 1 ng Cu, 0.11 *M* HCl; (3) 1.5 ng Fe, 0.01 *M* HCl; (4) 1.5 ng Fe, 0.11 *M* HCl; (5) 2 ng Cr, 0.01 *M* HCl; (6) 2 ng Cr, 0.11 *M* HCl. (B) and (C) Effect of concentration of hydrochloric acid, (1) 1 ng Cu; (2) 1.5 ng Fe; (3) 2 ng Cr.

No interference of hydrochloric acid on either iron or chromium absorptions was observed in the atomizer, irrespective both of concentrations of the acid and of power levels supplied to the filament. The effect of the acid on both iron and chromium in the filament atomizer is very different from that observed in the air–acetylene flame in the previous paper[1]. In the present system, the effect of the chlorinating action of hydrochloric acid may be ignored.

Perchloric acid

The effects of perchloric acid on copper, iron and chromium are shown in Fig. 2. No interference of perchloric acid on copper absorption was found, regardless of the acid concentrations and power levels.

Perchloric acid caused a small depressing effect on iron at lower power levels, but no interference was observed at high power level (60 W). Štupar[9] reported a marked depressing effect of perchloric acid on iron absorption. The effect resulted from a greatly increased rate of oxide formation in the presence of perchloric acid. It is assumed that the formation of iron oxides in the presence of perchloric acid which is a powerful oxidizing agent is reponsible for the depressing effect of the acid on iron.

A marked enhancing effect of this acid (0.10 *M*) on chromium was observed at lower power levels; the effect increased with increasing concentration of the acid. The enhancing effect of this acid was also observed in the flame[1]. Iida and Fuwa[10] suggested that the enhancing effect on chromium absorption could result from the oxidation of chromium with perchloric acid. This effect may be attributed

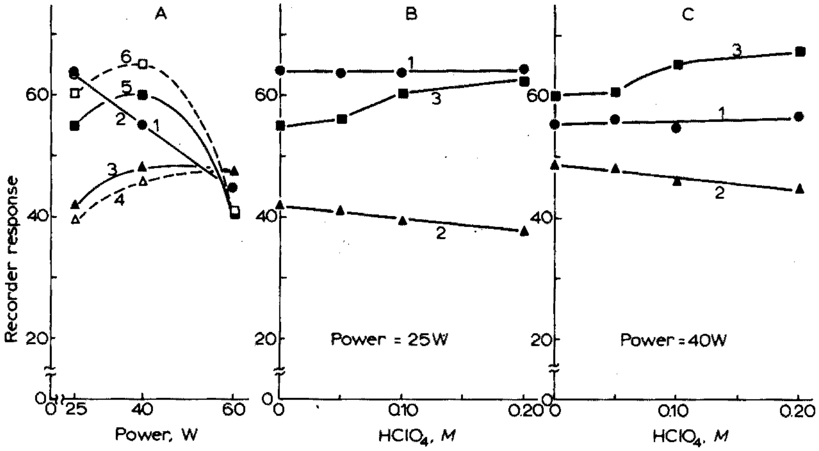

Fig. 2. Interferences of perchloric acid on copper, iron and chromium absorptions. (A) Effect of power, (1) 1 ng Cu, 0.01 *M* HCl; (2) 1 ng Cu, 0.01 *M* HCl+0.10 *M* $HClO_4$; (3) 1.5 ng Fe, 0.01 *M* HCl; (4) 1.5 ng Fe, 0.01 *M* HCl+0.10 *M* $HClO_4$; (5) 2 ng Cr, 0.01 *M* HCl; (6) 2 ng Cr, 0.01 *M* HCl+0.10 *M* $HClO_4$. (B) and (C) Effect of concentration of perchloric acid, (1) 1 ng Cu; (2) 1.5 ng Fe; (3) 2 ng Cr.

to the formation of volatile and readily dissociated chromium compounds, such as oxychloride.

Nitric acid

Figure 3 shows the interferences of nitric acid on copper, iron and chromium absorptions. A very small enhancing effect of nitric acid on copper was found in the present work. Nitric acid caused a depressing effect on copper in the lower

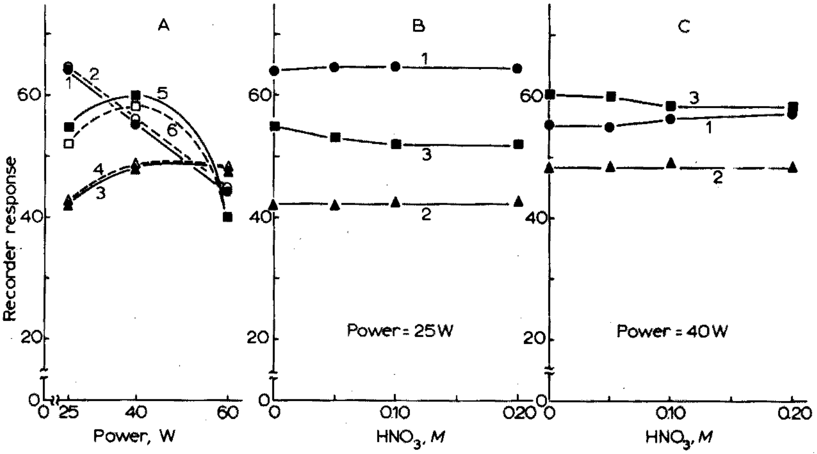

Fig. 3. Interferences of nitric acid on copper, iron and chromium absorptions. (A) Effect of power, (1) 1 ng Cu, 0.01 *M* HCl; (2) 1 ng Cu, 0.01 *M* HCl+0.10 *M* HNO_3; (3) 1.5 ng Fe, 0.01 *M* HCl; (4) 1.5 ng Fe, 0.01 *M* HCl+0.10 *M* HNO_3; (5) 2 ng Cr, 0.01 *M* HCl; (6) 2 ng Cr, 0.01 *M* HCl+0.10 *M* HNO_3. (B) and (C) Effect of concentration of nitric acid, (1) 1 ng Cu; (2) 1.5 ng Fe; (3) 2 ng Cr.

region of the flame, but little effect was observed in the higher region of the flame[1].

Little interference of nitric acid on iron absorption was found, irrespective both of concentrations of the acid and of power levels.

Nitric acid caused a depressing effect on chromium at low power levels, but no interference was observed at high power level (60 W). The effect decreased with increasing power level supplied to the filament. The depressing effect on chromium absorption may be attributed to the formation of the stable chromium oxides in the presence of nitric acid in the atomizer. The high temperature of the filament may be effective in the dissociation of the oxides.

Phosphoric acid

The effect of phosphoric acid on copper, iron and chromium is shown in Fig. 4. Phosphoric acid caused an enhancing effect on copper, especially at high power level. Bratzel *et al.*[6] described the enhancing effect of phosphoric acid on cadmium intensity in the platinum loop atomizer. The effect resulted from a reduced rate of vaporization in the presence of the phosphate. Brodie and Matoušek[11] noted the enhancing effect of phosphoric acid on lead absorption in the carbon rod atomizer, the effect resulting from the formation of the less volatile lead phosphate. The recorder response of copper decreased with increasing power level (Fig. 4-A-1); copper chloride will be partly removed from the filament before dissociation can occur with resultant loss in recorder response. The presence of anions which form a less volatile copper compound will result in an increased recorder response. It is assumed that the enhancing effect of phosphoric acid on copper occurs through an increase of the analyte atom population in the light path by the formation of the phosphate which is less volatile than the chloride.

Phosphoric acid caused a prominent depressing effect on iron at low power level (25 W), but little effect was observed at high power level (60 W). A depressing

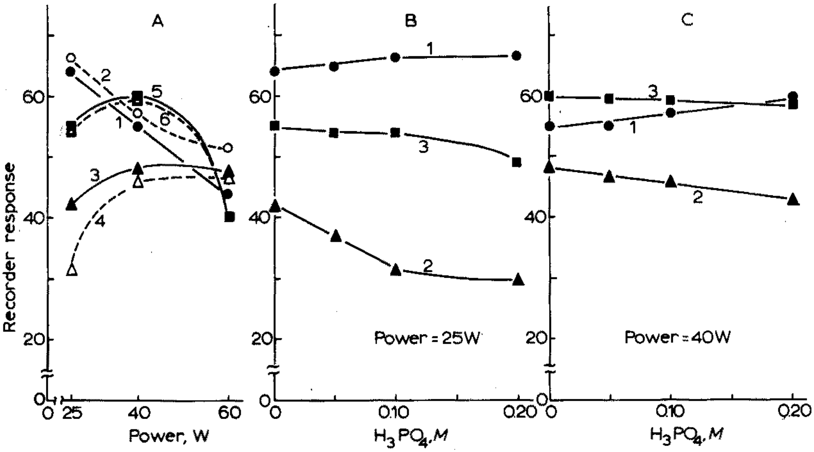

Fig. 4. Interferences of phosphoric acid on copper, iron and chromium absorptions. (A) Effect of power, (1) 1 ng Cu, 0.01 *M* HCl; (2) 1 ng Cu, 0.01 *M* HCl+0.10 *M* H_3PO_4; (3) 1.5 ng Fe, 0.01 *M* HCl; (4) 1.5 ng Fe, 0.01 *M* HCl+0.10 *M* H_3PO_4; (5) 2 ng Cr, 0.01 *M* HCl; (6) 2 ng Cr, 0.01 *M* HCl+0.10 *M* H_3PO_4. (B) and (C) Effect of concentration of phosphoric acid, (1) 1 ng Cu; (2) 1.5 ng Fe; (3) 2 ng Cr.

effect of this acid on iron absorption increased with increasing concentrations of the acid (Fig. 4-B,C).

A small depressing effect of phosphoric acid on chromium was observed at low power levels, but no interference was found at high power level. More concentrated acid (0.20 *M*) gave a depressing effect for chromium at low power level (25 W).

Roos and Price[12] reported that phosphoric acid gave a depressing effect on iron absorption in the lower region of the flame, but no interference was observed in the higher region of the flame. It therefore seems reasonable to consider that the temperature of the atomizer is an important factor for interference of phosphoric acid on both iron and chromium. The depressing effect of this acid on iron may be due to the formation of iron(III) phosphate which is more thermally stable than iron(III) chloride in the relatively low temperature of the atomizer.

The acid interferences observed with the tantalum filament atomizer in the present work were widely different from those with conventional flames[1]. The acid interferences for copper, iron and chromium were minimized at high power level supplied to the filament with the exception of the effect of phosphoric acid on copper absorption. The temperature of the tantalum filament in the atomization chamber plays an important role in determining the pattern of the acid interferences in atomic absorption spectrometry. The interferences varied for different elements and for different acids. The selection of an acid for the analyte is important in minimizing their interference in atomic absorption spectrometry. The acid interferences are complex in nature, and at present cannot be explained by a simple coherent theory.

The authors wish to thank Mr. M. Yanagisawa for his valuable assistance throughout this work.

SUMMARY

The interferences of hydrochloric, perchloric, nitric and phosphoric acids on the flameless atomic absorption spectrometry of copper, iron and chromium have been investigated. The mechanism of the acid interferences is discussed. The interferences depend on the acid used, the elements, and the power levels supplied to the filament. The interferences were minimized at high power supplied to the filament with the exception of the effect of phosphoric acid on copper absorption.

RÉSUMÉ

On examine les interférences des acides chlorhydrique, perchlorique, nitrique et phosphorique, lors de la spectrométrie par absorption atomique sans flamme du cuivre, du fer et du chrome. On en examine également le mécanisme et divers paramètres.

ZUSAMMENFASSUNG

Die Störungen von Salzsäure, Perchlorsäure, Salpetersäure und Phosphorsäure bei der flammenlosen Atomabsorptionsspektrometrie von Kupfer, Eisen und

Chrom wurden untersucht. Der Mechanismus der Säurestörungen wird diskutiert. Die Störungen hängen von der verwendeten Säure, von den Elementen und von der Heizfadenleistung ab. Die Störungen wurden verringert bei hoher Heizfadenleistung, mit Ausnahme des Einflusses von Phosphorsäure auf die Kupferabsorption.

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THE DETERMINATION OF IRON AND COPPER IN HIGH-PURITY SILICA BY FLAMELESS ATOMIC-ABSORPTION SPECTROMETRY

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The increased sensitivity in the determination of many elements by flameless atomic-absorption spectrometry, compared to flame atomic-absorption spectrometry, is well known, and has been used to advantage in the determination of trace elements in organic matrices[1-3] and dilute aqueous solutions[4,5]. The use of this technique for the direct determination of trace elements in inorganic materials has however received little attention.

Production of high-purity silica is necessary for the manufacture of certain types of glass which are required to have low light scattering and absorption properties. Since the presence of trace amounts of iron and copper gives rise to glass of poor quality, it is essential to have a sensitive method of analysis for these two elements in silica.

Colorimetric procedures for the determination of these elements have been in use in these laboratories for several years. They involve the dissolution of the sample initially in hydrofluoric acid with subsequent separation of iron as the bathophenanthroline complex[6] and copper as the dibenzyldithiocarbamate complex[7]. These methods suffer from two disadvantages: (*a*) high blanks (even after reagent purification) compared to the levels being determined in the samples, and (*b*) the time required for the analyses is of the order of 6 h. Both of these factors are important; the first in that it affects the sensitivity of the method and the reliability of the results, and the second in that it gives rise to high analysis costs and also that it takes one working day to show if the silica production is out of specification.

These points led to an investigation into the possibility of flameless atomic-absorption spectrometry providing a quick and accurate method of analysis for iron and copper in silica.

EXPERIMENTAL

Apparatus

All results were obtained with a Perkin-Elmer Model 306 atomic absorption spectrophotometer, equipped with an HGA-70 Graphite Furnace, a deuterium background corrector and a Model 165 recorder. Argon was used to provide the inert atmosphere within the graphite furnace, the operation of which has been described elsewhere[8].

Oxford "Sampler" micropipettes fitted with disposable plastic sampling tips were used for introducing all solutions into the graphite tube.

A simple extraction device was used to remove hydrogen fluoride and silicon tetrafluoride from the graphite tube during the drying stages of analysis. This consisted of a plastic cylinder *ca.* 4–5 cm in length and 3.5 cm in diameter fitted to each end of the graphite furnace. One end of each of two lengths of plastic tubing was fitted through the side wall of each cylinder and the other ends of the two pieces of tubing were joined at a T-junction. One end of a third length of plastic tubing was fitted to the third outlet of the T-junction, and the other end was connected to an absorption tube and from there to a small vacuum pump. The pump was switched on during an analysis and the rate of pumping pre-set by a screw clip on the plastic tubing to ensure that all fumes were extracted from the graphite tube. This device did not affect the atomic absorption signals, since it tends to pull air from the open ends of the plastic cylinders through the vacuum line and only extracts the fumes from the graphite furnace as they emerge from the ends of the graphite tube.

Reagents

Copper and iron standard solutions were prepared by dissolving the pure metals in the minimum quantity of nitric acid and then diluting appropriately with distilled water.

Suprapur 40% (w/w) hydrofluoric acid (E. Merck, Darmstadt, Germany) was used. Each batch of material was analysed for iron and copper by flameless atomic-absorption spectrometry. The iron content was *ca.* 0.01 p.p.m. and the copper content *ca.* 0.005 p.p.m.

Recommended procedure

Pipette 4 ml of hydrofluoric acid into a thoroughly cleaned platinum crucible, which is preferably kept for this type of work, then gradually add 1 g of the silica sample to avoid excessive heat generation, with the possibility of subsequent boiling of the solution. Introduce 10-μl aliquots of this solution into the graphite furnace using a micropipette, having a plastic, or platinum sampling system. Determine iron and copper in turn by atomic absorption. The recommended operating conditions are to use a drying time of 20 s at 100°, an ashing time of 30 s at 490° and an atomization time of 5 s at 2400–2600° (the higher temperature gives slightly better sensitivity for use at the lower concentration levels). These settings correspond to Programme 5 and an atomization voltage of 9–10 V on the Perkin-Elmer HGA-70. Scale expansion (5 ×) is used on the recorder. Compare the readings obtained for this solution with calibration graphs for iron and copper derived from aqueous standards using 10-μl aliquots of each standard solution, under the same conditions as those described above. Measure the iron and copper contents of the hydrofluoric acid to give the blank value and subtract this from the sample concentration. Finally convert the corrected sample readings to give the concentrations of iron and copper in the silica sample.

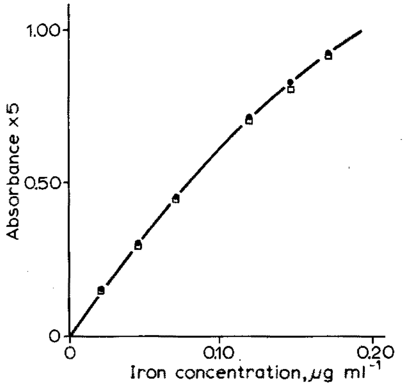
The use of a deuterium background corrector is not necessary, so the analysis can be performed with a single- or double-beam instrument. With a double-beam instrument, where no warm-up period is required for the hollow-cathode lamps, the total analysis time for iron and copper is about 30 min.

RESULTS AND DISCUSSION

The direct determination of iron and copper in finely ground silica was attempted by introducing weighed quantities of material into the graphite tube. This was found to be unsatisfactory; erratic and meaningless results were obtained, owing to sputtering of the silica particles during the atomization stage. The silica was therefore lost from the graphite tube before it had completely vaporized and the particles were not broken down efficiently to allow the complete atomization of the iron and copper impurities.

Separation procedures for the iron and copper were not considered, as these were the cause of the high blank readings in the colorimetric procedures already in use. The approach adopted therefore was to dissolve the silica in a slight excess of hydrofluoric acid to produce silicon tetrafluoride. A volume of 3–3.5 ml of 40% (w/w) hydrofluoric acid was required to convert 1 g of silica. Since silicon tetrafluoride is highly volatile, it was possible to evaporate off this compound together with the water and excess of hydrofluoric acid before the atomization stage.

The effect of hydrofluoric acid on the atomic absorption signals for iron and copper was first investigated to see if the presence of large amounts of fluoride affected the atomization efficiencies of the two elements. No effects were observed, compared to aqueous standards, over the range of concentrations studied (Figs. 1 and 2). Standard hydrofluoric acid solutions of iron and copper were prepared by adding small aliquots (less than 0.1 ml) of standard aqueous solutions of iron and copper to 40% hydrofluoric acid.



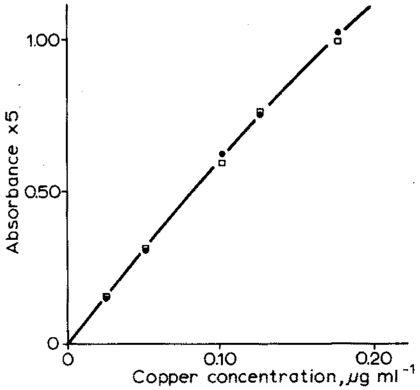


Fig. 1. Calibration graphs for iron. (●) Aqueous solution; (□) hydrofluoric acid solution.

Fig. 2. Calibration graphs for copper. (●) Aqueous solution; (□) hydrofluoric acid solution.

A 10-µl aliquot of a solution resulting from the dissolution of 1 g of finely powdered silica in 4 ml of hydrofluoric acid (in a platinum crucible) was injected into the graphite furnace. Identical readings were obtained during the atomization stages whether the deuterium background corrector was used or not. This indicated that all the silica had been removed during the pre-atomization heating stages, as silicon tetrafluoride, and did not therefore interfere in the determination of iron and copper.

The possible effect of silicon tetrafluoride on the atomic absorption signals for iron and copper was investigated by mixing 4 ml of hydrofluoric acid, containing 1 g of silica, with known amounts of iron and copper. The atomic absorption signals were compared to those signals obtained from aqueous standard. The graphs obtained for iron were found to be linear over a wider range of concentrations than with aqueous solutions, so that the recoveries of iron in the presence of silicon tetrafluoride appeared to be greater. At concentrations less than 0.05 µg Fe ml^{-1} there was little difference, however, between the two calibration graphs. The results for copper were very similar in both cases.

For the accurate determination of iron and copper in silica, the method of standard additions was used, since a volume reduction of *ca.* 5% was observed in the dissolution stage, owing to the high heat of reaction. There will, however, still be a slight error in the reading for the blank (*i.e.* 4 ml of hydrofluoric acid alone), since there is no volume change in this case. Provided that high-purity hydrofluoric acid is used, this error is minimal.

The standard addition graphs for the determination of iron and copper in three samples of silica are shown in Figs. 3 and 4. In Table I these results are compared with those obtained by directly comparing the sample readings with external calibration graphs, together with the results obtained by the colorimetric procetures mentioned earlier. It can be seen that in practical terms little is gained by using the standard additions procedure for these levels of impurities.

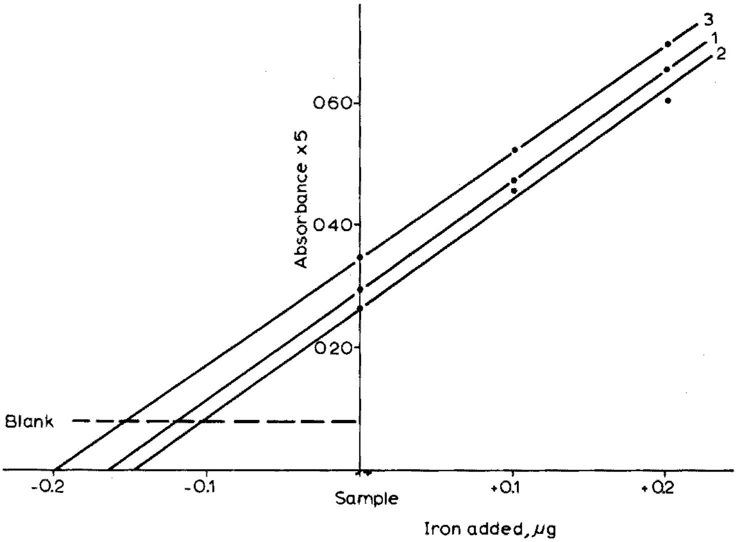


Fig. 3. Standard additions graphs for the determination of iron in three samples of silica.

At the 0.1-p.p.m. level in silica a relative standard deviation of 5% was obtained for both iron and copper.

In the work described here, a limit of 0.01 µg g^{-1} of iron or copper in silica was easily achieved with a 10-µl sample aliquot and 5-times scale expansion. This limit is set by the level of iron and copper in the hydrofluoric acid available,

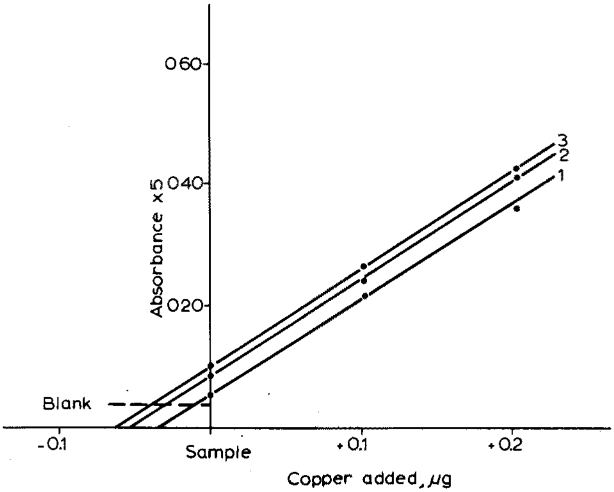


Fig. 4. Standard additions graphs for the determination of copper in three samples of silica.

TABLE I

A COMPARISON OF RESULTS FOR THE DETERMINATION OF IRON AND COPPER IN THREE SAMPLES OF SILICA

Sample	*Iron (µg g⁻¹)*			*Copper (µg g⁻¹)*		
	F.A.A.S.[a]		*Colorimetry*	*F.A.A.S.*[a]		*Colorimetry*
	I	*II*		*I*	*II*	
1	0.12	0.12	0.10	0.01	0.01	< 0.02
2	0.11	0.11	0.14	0.03	0.03	0.02
3	0.15	0.15	0.15	0.04	0.04	0.02

[a] I. Method of standard additions.
II. Direct comparison with a calibration graph.

but could undoubtedly be improved to 0.001 μg g^{-1} by using a 50-μl aliquot and 10-times scale expansion, when a purer reagent becomes available.

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SUMMARY

A simple method for the determination of iron and copper down to the 0.01 μg g^{-1} level in silica by flameless atomic-absorption spectrometry is described. The silica is dissolved in a small excess of hydrofluoric acid and a sample of this solution introduced into a Massmann-type graphite furnace. The silicon tetrafluoride produced in the solution stage is volatilized during a pre-atomization heating period. The results obtained for the determination of iron and copper by direct

and standard additions procedures agree well with those obtained by colorimetric analysis. The total analysis time for iron and copper is about 30 min.

RÉSUMÉ

Une méthode simple est décrite pour le dosage du fer et du cuivre (jusqu'à 0.01 mg g^{-1}) dans la silice, en utilisant la spectrométrie par absorption atomique sans flamme. La silice est dissoute dans l'acide fluorhydrique. Le tétrafluorure de silicium formé est volatilisé au cours de la période de chauffage de pré-atomisation. Les résultats correspondent bien à ceux obtenus par colorimétrie. La durée totale d'une analyse est d'environ 30 min.

ZUSAMMENFASSUNG

Es wird eine einfache Methode für die Bestimmung von Eisen und Kupfer in Siliciumdioxid bis zu etwa 0.01 $\mu g\ g^{-1}$ herab durch flammenlose Atomabsorptionsspektrometrie beschrieben. Das Siliciumdioxid wird in einem kleinen Überschuss Fluorwasserstoff-Säure gelöst und eine Probe dieser Lösung in eine Graphit-Heizvorrichtung des Massmann-Typs überführt. Das in der Lösung gebildete Siliciumtetrafluorid wird während einer Voratomisierungs-Heizperiode verflüchtigt. Die für die Bestimmung von Eisen und Kupfer durch direkte und Standard-Zumischverfahren erhaltenen Ergebnisse stimmen mit denen gut übereind, die durch kolorimetrische Analyse erhalten werden. Die gesamte Analyse für Eisen und Kupfer dauert etwa 30 min.

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ATOMIC-ABSORPTION SPECTROMETRIC DETERMINATION OF TIN IN PREMIXED INERT GAS (ENTRAINED AIR)–HYDROGEN FLAMES

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In atomic-absorption spectrometry, relatively little attention has been given to the determination of tin. Gatehouse and Willis[1] and Allan[2] have obtained a sensitivity of 5.0 p.p.m. for 1% absorption using a very fuel-rich air–acetylene flame and the 286.3-nm resonance line. Agazzi[3] has used the Fuwa–Vallee long-path absorption cell[4] with an oxygen–hydrogen flame at the 286.3-nm line to determine tin in hydrogen peroxide and obtained a sensitivity of 0.025 p.p.m., while Bowman[5] has reported a sensitivity of 1.6 p.p.m. in a nitrous oxide–acetylene flame.

Allan[6] was the first to report that the 224.6-nm resonance line was more sensitive, and that an air–hydrogen flame was more advantageous than an air–acetylene flame for tin, obtaining a 0.4-p.p.m. sensitivity. Capacho-Delgado and Manning[7] have reported that an air–hydrogen flame provided substantially better tin absorption than did an air–acetylene or nitrous oxide–acetylene flame, and obtained a sensitivity of about 0.5 p.p.m. in aqueous solution. Others[8–10] have reported the investigation in the air–hydrogen flame or the air–acetylene flame.

Recently, an inert gas (entrained air)–hydrogen flame has been introduced into atomic fluorescence, atomic absorption or flame emission spectrophotometry. Both argon[11–17] and nitrogen[18–20] have been used as an inert gas. Argon or nitrogen is used to nebulize the sample solution and carry it to the burner port; hydrogen is the fuel, and the flame combustion takes place between the hydrogen and the entrained air. McGee and Winefordner[11] have reported that an argon (entrained air)–hydrogen flame operated in conjunction with a total-consumption nebulizer-burner and a long-path absorption cell was useful in atomic-absorption spectrometry. Furthermore, the low background absorption in the ultraviolet region of a nitrogen (entrained air)–hydrogen flame has been advantageous to absorption measurements. Kahn and Schallis[12] have reported the improvement of detection limits by atomic absorption for arsenic, selenium, and other elements with an argon (entrained air)–hydrogen flame.

This paper describes an investigation of the flame characteristics of the argon (entrained air)– and nitrogen (entrained air)–hydrogen flames produced with a specially designed "multi-flame" burner[21], and of the various interferences with tin absorption in these flames. The detailed study on interferences showed that the presence of iron(III) chloride enhanced about 3-fold the tin atomic absorption in these cool flames, and that in the presence of a large amount of iron(III) chloride the interferences from other elements were completely eliminated. A simple and sensitive method for determining minute amounts of tin in various materials could thus be established. The mechanism of this interference elimination is tentatively explained.

EXPERIMENTAL

Apparatus

A Nippon Jarrell-Ash Model AA-1 atomic absorption/flame emission spectrophotometer was used on a single-pass system to obtain all data. A long-path "multi-flame" burner[21] with a Techtron standard nebulizer-chamber was used. The tin atomic absorptions were measured in the premixed argon (entrained air)– and nitrogen (entrained air)–hydrogen flames, and sometimes in the premixed air–hydrogen flame with the same burner system in an attempt to compare the interferences encountered in measuring the tin absorptions. The height in the flame was taken as zero when the light beam radiated from the hollow-cathode lamp just touched the top of the burner head. The analytical wavelength was 224.6 nm, sometimes 235.4 or 286.3 nm, and the light source was a tin high-spectral-output hollow-cathode lamp (Westinghouse, Type No. 45463), operated at 14 mA. Gas flow rates were carefully regulated and monitored on calibrated flowmeters.

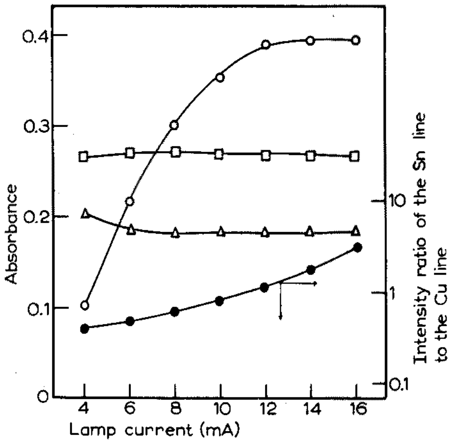
Reagents

A stock solution containing 5000 μg ml^{-1} was prepared by gently heating 5.000 g of high-purity tin metal (99.99%) in 200 ml of 6 *N* hydrochloric acid until dissolved. This solution was diluted to 1 l with distilled water and hydrochloric acid to give a final solution of 2 *N* in hydrochloric acid. Working solutions were prepared by appropriate dilutions. All other reagents were of either reagent grade or the purest grade available and used without further purification. Blanks were run on each solution in the case of interference study.

RESULTS AND DISCUSSION

Effect of lamp current and selection of wavelength

To determine the optimal lamp current, the absorbance for a 50-p.p.m. tin solution was measured at 224.6, 235.4 and 286.3 nm, at lamp currents from 4 to 16 mA. No variation in tin absorbance was observed at the 235.4- and 286.3-nm lines with the change in lamp current value. However, at the 224.6-nm line the absorbance for tin increased with an increase of lamp current from 4 to 12 mA, and reached a limiting value independent of lamp current from 12 to 16 mA, as shown in Fig. 1. This effect of lamp current was found to be due to the presence of a neighboring copper line (224.4-nm copper atomic line), from which the tin line at 224.6 nm could not be isolated by the monochromator employed, resulting in a loss of tin sensitivity at the lower lamp current. This reasoning was confirmed by the fact that the line intensity ratio of the tin line to the copper line observed in the second order spectra increased with lamp current, and at lamp currents higher than 12 mA the tin line became more intense than the copper line. From this result, the most sensitive 224.6-nm resonance line was selected as the analytical line, and the hollow-cathode lamp was operated at 14 mA in further work.



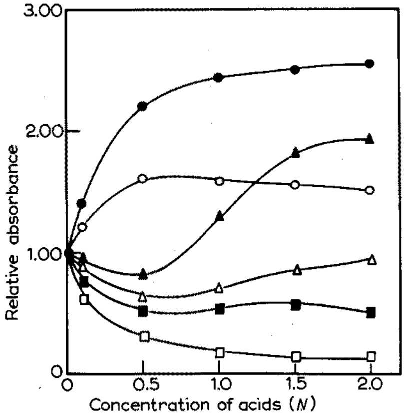


Fig. 1. Effect of lamp current on tin atomic absorption and intensity ratio of the tin line to the copper line. Concentration of tin: 50 p.p.m. Flame: argon (entrained air)–hydrogen flame. (○) At 224.6 nm; (△) at 235.4 nm; (□) at 286.3 nm; (●) line-intensity ratio of tin 224.6 nm to copper 224.4 nm.

Fig. 2. Effect of acids on tin atomic absorption. Concentration of tin: 25 p.p.m. Flame: nitrogen (entrained air)–hydrogen flame. (●) Hydrochloric acid; (▲) perchloric acid; (○) hydrofluoric acid; (△) nitric acid; (■) sulfuric acid; (□) phosphoric acid.

Effect of flame composition and flame height

Determination of tin by atomic-absorption spectrometry has been reported to be more sensitive in fuel-rich flames. Such flames are considered to diminish the formation of tin oxide in the flame by the reducing action of the C_2 species in the acetylene flames or of atomic hydrogen in the hydrogen flames. Hydrogen flames provided a better tin sensitivity and have the advantage of lower background absorption at 224.6 nm than the acetylene flames. The optimal flame conditions used in this study are summarized as follows:

argon (entrained air)–hydrogen flame: hydrogen, 7.2 l min^{-1}; argon, 4.5 l min^{-1}, 1.5 kg cm^{-2}; height in the flame, 2 mm above the top of the burner head;

nitrogen (entrained air)–hydrogen flame: hydrogen, 7.2 l min^{-1}; nitrogen, 5.0 l min^{-1}, 1.5 kg cm^{-2}; height in the flame, 3 mm above the top of the burner head.

Under these conditions, both the hydrogen flames were almost invisible and the sample aspiration rates were 8.9 ml min^{-1} with the former flame and 9.0 ml min^{-1} with the latter flame. Unless otherwise stated, these flame parameters were used in the following study.

Effect of acids

Agazzi[3] has reported that 100 p.p.m. (as P) of phosphate and pyrophosphate depressed the tin absorption by 50 and 25%, respectively, in a long-path absorption cell. Capacho-Delgado and Manning[7] have studied the effect of phosphoric, sulfuric and nitric acids on tin atomic absorption in air–hydrogen and air–acetylene flames; nitric acid produced almost no effect in either flame, while phosphoric and sulfuric acids caused serious depression in an air–hydrogen flame, but phosphoric acid caused absorption enhancement in an air–acetylene flame. Juliano and Harrison[8] have reported that the interference caused by phosphoric acid in an air–hydrogen flame could be negative or positive depending on the fuel-to-oxidant ratio.

In argon (entrained air)– and nitrogen (entrained air)–hydrogen flames, the effects of acids normally used in the dissolution of various samples were examined over the concentration range 0–2.0 *N*.The results obtained in the nitrogen (entrained air)–hydrogen flame (Fig. 2) show that the halogen-containing acids caused large enhancements in the tin atomic absorption, probably owing to the formation of more easily vaporized or dissociated species. A marked depression was caused by phosphoric acid, and smaller depressions by nitric and sulfuric acids, undoubtedly because of the formation of species which were difficult to vaporize or dissociate in the low-temperature flames used. The presence of hydrochloric acid caused the greatest enhancement, *i.e.*, 2.5-fold. The argon (entrained air)–hydrogen flame produced the same results as the nitrogen (entrained air)–hydrogen flame.

TABLE I

EFFECT OF VARIOUS ELEMENTS ON TIN ATOMIC ABSORPTION

(25 p.p.m. Sn; 250 p.p.m. interfering ion. Results are expressed as the ratio of the absorbance for tin in the presence of the interfering ion to the absorbance for tin alone)

Element	*Relative absorbance*			*Element*	*Relative absorbance*		
	N_2(*air*)–H_2	*Ar*(*air*)–H_2	*Air*–H_2		N_2(*air*)–H_2	*Ar*(*air*)–H_2	*Air*–H_2
Al[a]	1.27	1.41	0.86	Mo[d]	0.45	0.95	0.94
Au[a]	0.44	0.56	0.86	Na[a]	1.49	1.68	0.94
Ba[a]	1.43	1.54	0.62	Ni[b]	0.63	0.81	0.91
Be[b]	0.94	1.08	0.42	Pb[c]	2.30	2.20	0.99
Bi[c]	0.54	0.26	0.35	Pd[a]	0.56	0.61	0.67
Ca[c]	0.33	0.57	0.70	Rb[a]	1.25	1.45	0.99
Cd[c]	2.12	2.04	1.00	Sb[a]	0.46	0.61	0.79
Ce[b]	0.42	0.83	0.77	Se[e]	0.24	0.31	0.95
Co[a]	2.86	2.85	1.00	Si[e]	0.34	0.51	0.18
Cr[a]	1.63	2.41	1.00	Sr[c]	0.39	0.40	0.58
Cs[a]	0.84	1.03	1.01	Te[e]	0.55	0.89	0.90
Cu[b]	0.21	0.35	0.98	Th[c]	0.27	0.34	0.20
Fe[a]	2.97	2.83	1.02	Ti[a]	2.81	2.78	1.00
Hg[a]	0.95	0.93	0.95	Tl[c]	1.14	1.07	1.00
In[a]	1.72	1.62	0.97	V[d]	0.31	0.59	0.82
K[a]	1.41	1.45	0.79	W[e]	1.47	1.64	0.96
La[a]	1.20	1.80	1.00	Y[c]	0.40	0.46	0.27
Li[a]	1.31	1.47	0.93	Zn[c]	1.57	1.55	0.98
Mg[a]	2.49	2.72	0.96	Zr[c]	0.47	0.54	0.17
Mn[c]	1.70	1.97	0.93				

[a] Added as chloride.
[b] Added as sulfate.
[c] Added as nitrate.
[d] Added as ammonium salt.
[e] Added as sodium salt.

Effect of various other elements

Capacho-Delgado and Manning[7] have observed that lead, copper, zinc and nickel, at concentrations of 1000 p.p.m., did not interfere by more than 3% in the air–acetylene flame, whether individually or in combination. Amos and Willis[22] have noted that 5000 p.p.m. of sodium (as the hydroxide) depressed tin atomic absorption by 15% in an air–hydrogen flame, whereas no interference was found in an air–acetylene flame. Juliano and Harrison[8] investigated the interference from various elements on tin atomic absorption in a premixed air–hydrogen flame over a wide range of flame conditions.

The experiments in this study were concerned primarily with elucidating the nature and magnitude of interferences in the argon (entrained air)– and nitrogen (entrained air)–hydrogen flames. The effects of various elements on the tin atomic absorption for 25 p.p.m. were first studied at a constant concentration level (250 p.p.m.) in aqueous solutions (Table I). The presence of many elements, such as most of the alkali and transition metals, caused an extraordinary enhancement in the tin atomic absorption, iron having the greatest effect. Other metals, such as alkaline earth metals, produced a considerable depressing interference. The interfertnces from other elements were not linear to their concentration (Fig. 3).

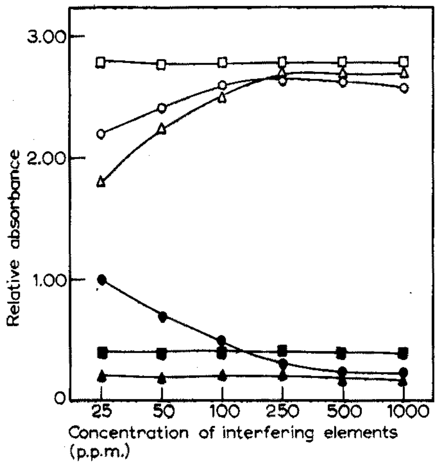


Fig. 3. Effect of various other elements on tin atomic absorption. Concentration of tin: 25 p.p.m. Wavelength: 224.6 nm. Flame: argon (entrained air)–hydrogen flame. (□) Iron; (○) cobalt; (△) titanium; (●) vanadium; (■) silicon; (▲) strontium.

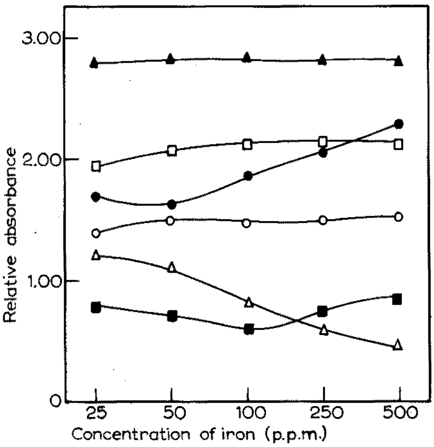


Fig. 4. Effect of some iron compounds on tin atomic absorption. Concentration of tin: 25 p.p.m. Flame: argon (entrained air)–hydrogen flame. Iron added as (▲) iron(III) chloride, (□) iron(III) ammonium sulfate, (●) iron(II) ammonium sulfate, (○) iron(II) sulfate, (△) potassium hexacyanoferrate(II), (■) potassium hexacyanoferrate(III).

Further investigation on the enhancement from some iron compounds was made on a 25-p.p.m. tin solution. The results showed (Fig. 4) that the effect of iron(III) chloride was greatest.

Elements such as bismuth, cerium, copper, strontium, etc., were found to have a strong depressing effect when they were present as nitrate, sulfate or oxy-

TABLE II

EFFECT OF DIVERSE ELEMENTS ON TIN ATOMIC ABSORPTION

(Conditions as in Table I)

Element	*Added as*	*Relative absorbance*	
		N_2(air)–H_2	*Ar(air)–H_2*
Bi	Nitrate	0.54	0.26
	Chloride	1.61	1.51
Ce	Nitrate	0.42	0.83
	Chloride	1.29	1.80
Cu	Sulfate	0.21	0.35
	Chloride	2.50	2.53
Ni	Sulfate	0.63	0.81
	Chloride	1.06	1.41
Sr	Nitrate	0.39	0.40
	Chloride	1.52	1.88
V	Ammonium vanadate	0.31	0.59
	Chloride	1.95	2.44
Zr	Oxynitrate	0.47	0.54
	Chloride	1.54	1.63

nitrate, but a considerable enhancing effect when present as chloride (Table II). This indicates that not only metallic ions but also halide anions can play a significant role in increasing the tin atom population in these flames.

The behavior of interferences at 235.4 and 286.3 nm was the same as at 224.6 nm. But in the premixed air–hydrogen flame produced with the same burner system no enhancement was observed (Table I).

TABLE III

EFFECT OF AMMONIUM HALIDES ON TIN ATOMIC ABSORPTION

Ammonium halide	*Concentration (M)*	*Relative absorbance*[a]		
		N_2(air)–H_2	*Ar(air)–H_2*	*Air–H_2*
NH_4F	0.01	2.01	1.73	0.95
	0.1	2.02	1.73	0.98
	1.0	1.91	1.63	0.94
NH_4Cl	0.01	1.93	1.50	0.96
	0.1	1.83	1.43	0.90
	1.0	1.86	1.56	0.94
NH_4Br	0.01	2.04	1.65	0.97
	0.1	1.95	1.55	0.95
	1.0	1.91	1.56	0.94
NH_4I	0.01	1.97	1.50	0.97
	0.1	1.83	1.47	0.93
	1.0	1.90	1.54	0.90

[a] (Absorbance for 25 p.p.m. Sn plus halides)/(absorbance for 25 p.p.m. Sn).

Effect of ammonium halide

Further experiments on enhancing interferences were made in the presence of ammonium halide, *i.e.*, ammonium fluoride, chloride, bromide and iodide, when their concentrations were 0.01, 0.1 and 1.0 *M* (Table III). The magnitude of the enhancement by the halides was greater in order: fluoride > chloride > bromide > iodide; this order was unexpected from considerations of the order of molecular weight and electronegativity. No enhancing effect was observed in an air–hydrogen flame, thus the halide may contribute to the formation of species which are stable in cool flames, *e.g.* $SnCl_2$, SnCl, and these species favour the formation of SnH which decomposes directly to produce tin atoms.

Effect of iron on the interferences from other elements

In most practical systems, this type of interference has been overcome by using a high-temperature nitrous oxide–acetylene flame. With cool flames, the interference has occasionally been overcome by adding "sacrificial ions" to the test solution or adding complexing agents to the test solution. Figure 5 shows how the addition of iron affects the interaction between strontium and tin.

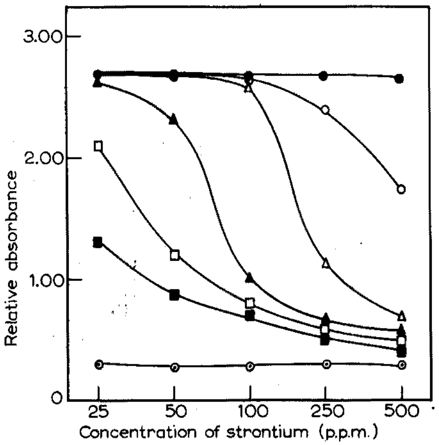


Fig. 5. Effect of iron(III) chloride on the interference from strontium. Concentration of tin: 25 p.p.m. Flame: argon (entrained air)–hydrogen flame. Concentrations of iron added: (⊙) 0 p.p.m.; (■) 25 p.p.m.; (□) 50 p.p.m.; (▲) 100 p.p.m.; (△) 250 p.p.m.; (○) 500 p.p.m.; (●) 1000 p.p.m.

Next, this effect of iron addition was studied on the interferences from the various other elements. Table IV shows that the presence of iron could completely eliminate the interference, enhancing or depressing, of most of the elements, except for bismuth, palladium, cerium, antimony, nickel and vanadium. Such an action of eliminating interferences was not observed for other enhancing elements, *e.g.*, cobalt, titanium, etc.

This finding is clearly favorable for the determination of tin in ferrous samples; if the sample is not ferrous, a sufficient amount of iron (as the chloride) should be added to the test solution.

Further investigation was made on the effect of iron(III) chloride on the tin atomic absorption in the cool flames used. The effect of iron (250 p.p.m.) on tin

TABLE IV

EFFECT OF IRON(III) CHLORIDE ON THE INTERFERENCES FROM VARIOUS OTHER ELEMENTS

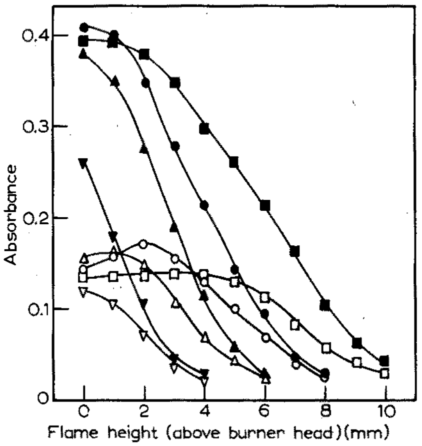
Element	*Relative absorbance*[a]		*Element*	*Relative absorbance*[a]	
	N_2*(air)*-H_2	*Ar(air)*-H_2		N_2*(air)*-H_2	*Ar(air)*-H_2
Al	1.01	1.00	Mo	0.93	0.94
Au	1.02	1.00	Na	1.02	1.01
Ba	1.01	1.01	Ni	0.90	0.93
Be	0.93	0.97	Pb	1.03	1.01
Bi	0.89	0.88	Pd	0.89	0.90
Ca	0.99	1.01	Rb	0.99	1.03
Cd	1.02	1.00	Sb	0.93	0.95
Ce	0.75	0.78	Se	0.98	0.99
Co	0.99	1.01	Si	0.98	0.99
Cr	0.99	1.00	Sr	1.00	1.01
Cs	0.99	1.00	Te	0.94	0.95
Cu	1.00	1.04	Th	0.99	0.98
Hg	0.99	1.00	Ti	1.06	1.03
In	1.03	1.02	Tl	1.00	1.02
K	1.04	1.02	V	0.72	0.80
La	1.00	0.99	W	1.01	0.98
Li	0.95	0.98	Y	0.93	0.96
Mg	0.96	0.99	Zn	1.02	0.99
Mn	0.98	0.99	Zr	0.97	0.99

[a] (Absorbance for 25 p.p.m. Sn plus 1000 p.p.m. Fe plus 250 p.p.m. interferents)/(absorbance for 25 p.p.m. Sn plus 1000 p.p.m. Fe).

(12.5 p.p.m.) absorption at different flame heights in various flame conditions is shown in Fig. 6. In both flames the enhancement increased as lower portions in the flame were monitored, and as the flow rate of hydrogen was increased, *i.e.*, the flame was more reducing. The effect of iron is not only to increase the tin absorbance but also to shift slightly the absorption maximum to a lower portion in the flame. The tin atom population profile in the flame in the presence and absence of iron (Fig. 7) gives a clearer idea of the enhancing effect; the data shown in Fig. 7 were obtained with a pin-hole of 1.0 mm in diameter as described by Rann and Hambly[23].

Mechanism of interference elimination

Tin oxide, one of the species which may be formed in the flame, is relatively stable owing to its high dissociation energy of 5.7 eV[24]. Enhancing elements such as alkali and transition metals may inhibit the formation of tin oxide to release more tin atoms in the flame. The ionization of tin is probably negligible in the low-temperature flames as used in this study, because of its high ionization potential (7.33 eV), and therefore probably does not contribute to the enhancing interference. On the other hand, Dagnall *et al.*[19] have reported that tin hydride emission at 609.5 nm can be used for the flame photometric determination of tin in a nitrogen–hydrogen diffusion flame, and that there was a significant decrease in the emission of tin hydride in an air–acetylene flame. The present authors also observed emission



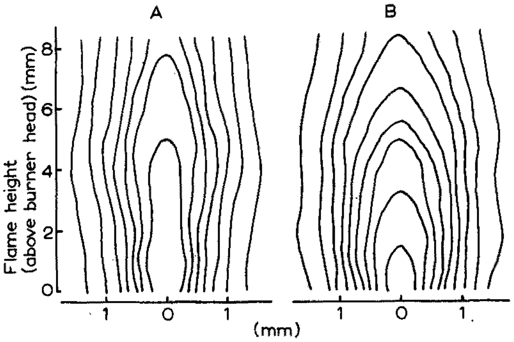
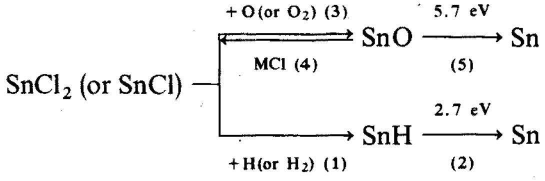


Fig. 6. Effect of flame composition and flame height on tin atomic absorption in the presence and absence of iron(III) chloride. Concentration of tin: 12.5 p.p.m. Flame: argon (entrained air)–hydrogen flame. Hydrogen flow rates in the presence of 125 p.p.m. iron: (▼) 4.3 l min^{-1}; (▲) 5.8 l min^{-1}; (●) 7.2 l min^{-1}; (■) 8.6 l min^{-1}. Hydrogen flow rates in the absence of iron: (▽) 4.3 l min^{-1}; (△) 5.8 l min^{-1}; (○) 7.2 l min^{-1}; (□) 8.6 l min^{-1}.

Fig. 7. Flame profiles of tin atoms in the flame in the presence and absence of iron by the pin-hole method. The maximum absorbance is in the center of the flame and the contours represent decreasing absorbance. Concentration of tin: 25 p.p.m. Flame: nitrogen (entrained air)–hydrogen flame. (A) In the absence of iron; (B) in the presence of 250 p.p.m. iron.

at 609.5 nm with 1000 p.p.m. of tin in the low-temperature flames used in this study. Since dissociation energies are 5.7 and 2.7 eV[25] for tin oxide and tin hydride, respectively, tin hydride decomposes more easily than tin oxide.

The interferences on tin from other elements and the interference-eliminating action of iron(III) chloride may be explained by the following scheme:



where MCl represents hydrogen chloride and/or metallic chloride. Tin is vaporized as $SnCl_2$ or SnCl and the production of tin atoms presumably occurs through the processes (1) and (2), but a larger part of the tin in the air–hydrogen flame is present as SnO. Depressing interference occurs through process (3), oxygen atoms and/or molecules being supplied by air and/or oxygen-containing compounds such as nitrate, sulfate and phosphate. Enhancing interference occurs through process (4), iron(III) chloride being the most effective as MCl. Few tin atoms are produced through process (5), because the flame temperature is too low.

Effect of organic solvents

The effect of organic solvents on the tin atomic absorption in an air–hydrogen flame has been described by Harrison and Juliano[10]. In this study with flames cooler than an air–hydrogen flame, the effect of a series of primary alcohols was studied. As shown in Fig. 8, the depression of tin absorption became more severe as the concentration increased up to 50% by volume. Changes in sample aspiration rates, checked for each solution, were not sufficient to account for these effects. This depressive effect is probably related to the effective removal of active hydrogen atoms which serve to reduce tin oxide directly to tin atoms. The addition of other organic solvents probably also depresses the tin absorption, as Harrison and Juliano[10] have reported in air–hydrogen flames.

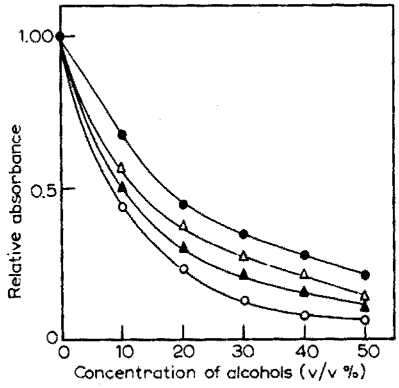


Fig. 8. Effect of organic solvents on tin atomic absorption. Concentration of tin: 25 p.p.m. Flame: nitrogen (entrained air)–hydrogen flame. (●) Ethanol; (△) methanol; (▲) propanol; (○) isopropanol.

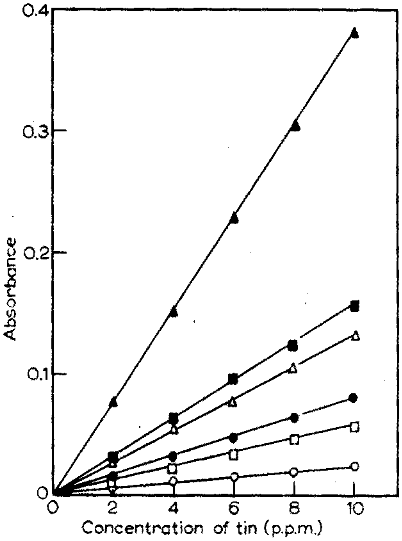


Fig. 9. Calibration graphs for tin in the presence and absence of iron(III) chloride. Flame: argon (entrained air)–hydrogen flame. In the presence of iron (1000 p.p.m.): (▲) at 224.6 nm; (●) at 235.4 nm; (■) at 286.3 nm. In the absence of iron: (△) at 224.6 nm; (○) at 235.4 nm; (□) at 286.3 nm.

Calibration graphs for tin

Calibration graphs for tin are shown in Fig. 9. The tin sensitivities for 1% absorption are 0.33, 1.76 and 0.70 p.p.m. in the absence of iron(III) chloride at 224.6, 235.4 and 286.3 nm, respectively; and 0.12, 0.63 and 0.29 p.p.m. in the presence of iron(III) chloride at 224.6, 235.4 and 286.3 nm, respectively.

Application to the determination of tin in some metallurgical samples

The present method was applied to the determination of tin in copper-base alloy, brass and steel.

The copper-base alloy, NBS 124d, contains an average of 84% Cu, 5% Pb, 5% Zn, 1% Ni, 0.28% Fe and 0.2% Sb. A 0.1-g sample was dissolved in 5 ml of 6 *N* hydrochloric acid and 5 ml of 6 *N* nitric acid by gentle heating on a hot plate. After dissolution, the soluton was diluted to 100 ml. Two 5-ml aliquots were transferred to 50-ml volumetric flasks, and diluted to volume with distilled water with addition of 5 and 10 ml of a 10000-p.p.m. iron solution, respectively. The tin absorbances for the two sample solutions were measured at 224.6 nm in the premixed argon (entrained air)– and nitrogen (entrained air)–hydrogen flames.

The brass, Kansai Bunseki Kenkyukai HK-2, contains an average of 58.17% Cu, 38.14% Zn, 2.55% Pb, 0.288% Fe and 0.138% Ni. A 1.0-g sample was dissolved in 5 ml of 6 *N* hydrochloric acid and 5 ml of 6 *N* nitric acid by gentle heating on a hot plate. Further treatments were exactly the same as for the copper-base alloy.

The steel, Kansai Bunseki Kenkyukai GK-1a, contains an average of 0.364% Mn, 0.137% Cu, 0.105% C and 0.101% Si. A 1.0-g sample was dissolved in 10 ml of 6 *N* hydrochloric acid and 4 ml of 6 *N* nitric acid by gentle heating on a hot plate; the solution was evaporated to dryness, and the residue dissolved in 10 ml of 6 *N* hydrochloric acid by gentle heating. The solution was then transferred to a 100-ml volumetric flask and diluted to volume with distilled water. This sample solution was nebulized and the tin absorbances were measured at 224.6 nm.

All analytical results were obtained by referring to the calibration graphs prepared with 1000 p.p.m. of iron (as the chloride) added to the standard tin solutions. Results of the determination of tin in the above alloys by the proposed method are shown in Table V.

TABLE V

THE DETERMINATION OF TIN IN COPPER-BASE ALLOY, BRASS AND STEEL

Sample	*Tin content (%)*		
	Certificate value	*Atomic absorption*	
		ArQair)–H_2	*N_2(air)–H_2*
Copper-base alloy NBS 124d	4.56	4.43[a] 4.55[b]	4.46[a] 4.57[b]
Brass HK-2	0.568	0.57[a] 0.56[b]	0.56[a] 0.58[b]
Steel GK-1a	0.033	0.032	0.032

[a] Determined with the addition of 1000 p.p.m. iron.
[b] Determined with the addition of 2000 p.p.m. iron.

SUMMARY

Tin can be determined more sensitively in premixed argon (entrained air)– and nitrogen (entrained air)–hydrogen flames than in air–hydrogen or air–acetylene flames. Many foreign elements, however, interfere with the determination, *e.g.*, iron enhances but silicon depresses the tin absorbance. The addition of iron(III) chloride was very effective in eliminating the interferences from other elements with the exception of bismuth, cerium, palladium and vanadium. This finding was satisfactorily applied to the determination of tin in copper-base alloys and steel.

RÉSUMÉ

La sensibilité de l'étain peut être améliorée en remplasant les flammes air–hydrogène ou air–acétylène par des flammes prémélangées argon–azote–hydrogène. On examine l'influence de divers éléments étrangers. On constate qu'une addition de chlorure de fer(III) permet d'éliminer de nombreuses interférences, à l'exception de celles du bismuth, du cérium, du palladium et du vanadium. Cette méthode a été appliquée avec succès au dosage par absorption atomique de l'étain dans des alliages à base de cuivre et dans l'acier.

ZUSAMMENFASSUNG

Zinn kann empfindlicher in vorgemischten Argon (mit Luft)– und Stickstoff (mit Luft)–Wasserstoff-Flammen als in Luft–Wasserstoff- oder Luft–Acetylen-Flammen bestimmt werden. Viele Fremdelemente stören jedoch bei der Bestimmung; die Zinn-Extinktion wird z.B. durch Eisen erhöht, durch Silicium aber vermindert. Die Zugabe von Eisen(III)–chlorid eliminierte sehr wirksam die Störungen durch andere Elemente mit Ausnahme von Wismut, Cer, Palladium und Vanadin. Dieser Befund wurde auf die Bestimmung von Zinn in Kupferlegierungen und Stahl angewendet.

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THE DETERMINATION OF MAJOR AND SOME MINOR CONSTITUENTS IN LEAD ZIRCONATE–TITANATE COMPOSITIONS BY X-RAY FLUORESCENCE AND ATOMIC ABSORPTION SPECTROMETRY

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Compositions of lead zirconate–titanate (PZT) are of great interest for manufacturing piezo-electric ceramics. During manufacture selective volatilization of elements can occur in high-temperature treatments. Therefore, the chemical composition of these materials should be determined after these treatments. Further, the amounts of unreacted oxides must be known for production control. Analytical procedures for this purpose have been described by Goode *et al.*[1] and by Robinson and Joyce[2].

However, relatively accurate determinations of minor additions of elements ("dopes") are also required. Here, emission spectroscopy, as described by Mirti and Shivak[3], lacks the accuracy desired and few other analytical methods have been proposed in the literature to solve this problem.

Moreover, these analytical procedures may run into difficulties, if certain minor constituents are present, and the sophisticated instruments described may not be easily available. X-Ray fluorescence spectrometry carried out with suitable standards and homogeneous samples is very precise, accurate and highly selective. In addition, the application of a borax fusion technique for sample preparation[4] enables sufficient exclusion of matrix effects on determinations of elements. Along these lines, together with analysis by means of atomic absorption, it was possible to achieve satisfactory analysis of PZT composition. This paper describes the development of the X-ray fluorescence spectrometric methods for the determination of lead, zirconium and titanium as major constituents, the determination of minor constituents (K, La, Sm, Yb) and the determination of some of the unreacted oxides (ZrO_2 and TiO_2). Atomic absorption spectrometric methods have also been developed for cases (PbO, Mg) where X-ray fluorescence seemed less appropriate. The methods described are applicable, with obvious modifications, to many types of materials.

Total lead, zirconium and titanium

The above major constituents were determined by X-ray fluorescence spectrometry, consideration being given to the following points*.

For precise results, standards and samples should be matched closely. Where

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* In this section "intensity" means the number of counts per fixed time measured with the X-ray fluorescence spectrometer on the line of the element.

a large variation in sample composition is expected, this is most easily done by a sample pretreatment, *e.g.* dilution in molten borax and addition of a heavy absorber. Here the general method previously described[4] was used; standards are easily prepared from assayed compounds of the elements of interest.

Although a high dilution combined with a large amount of heavy absorber is applied, changes in concentration of a major element (*e.g.* lead) can still influence to some extent the intensity of any other element (*e.g.* zirconium), even when the latter does not change in concentration. The occurrence and degree of mutual influence was tested as follows: standards were prepared containing zirconium and titanium and varying amounts of lead by mixing the appropriate amounts of oxides; next these were analysed as described under the heading procedures.

From the intensities measured it appeared that: (a) the calibration line of zirconium is linear; (b) the variation in lead content has an influence, although small, on the zirconium intensity; and (c) this influence is proportional to the lead content (Fig. 1).

For titanium a similar, but smaller, effect from the lead content was measured. However, there was no perceptible influence from zirconium on titanium or *vice versa*, nor had zirconium or titanium any perceptible influence on the lead intensity.

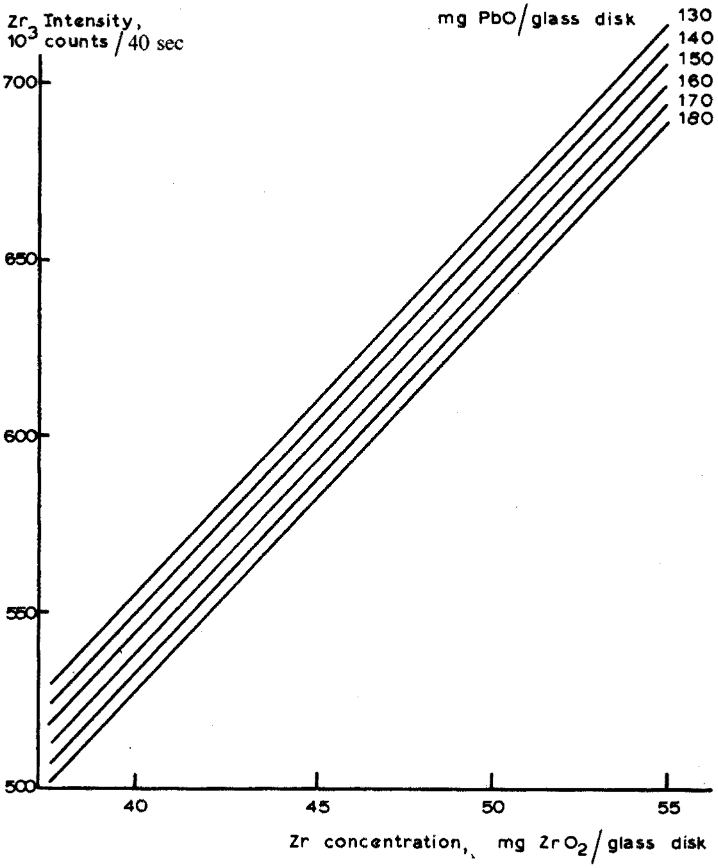

Fig. 1. Zirconium intensity as a function of lead and zirconium concentration.

In the present procedure, the following formulae were applied to calculate the lead, zirconium and titanium concentrations c (element) from the intensities I (element) measured:

$$c(\mathrm{Pb}) = k1 \cdot I(\mathrm{Pb}) + k2$$
$$c(\mathrm{Zr}) = k3 \cdot I(\mathrm{Zr}) + k4 \cdot I(\mathrm{Pb}) + k5$$
$$c(\mathrm{Ti}) = k6 \cdot I(\mathrm{Ti}) + k7 \cdot I(\mathrm{Pb}) + k8$$

where $k1, k2, \ldots, k8$ are constants determined from the standards used to obtain Fig. 1 and similar experiments concerning the mutual influence of other pairs of elements. Once the above linear relationships have been established, only three well chosen standards are needed to calculate the constants $k1$, $k2$, ..., $k8$.

The X-ray fluorescence spectrometer used had a sample changer with 4 positions. To obtain high accuracy it was necessary to consider possible differences between these 4 positions. In the instrument available, adjustment to a difference between positions smaller than 0.1% proved impossible; for most work this is quite acceptable. Measurement in the same position of the sample changer was advisable for the highest accuracy; at the same time sample holders were selected to be as equal as possible.

Occasionally a "burst", probably caused by external electronical interference, gave rise to a high number of counts. In order to detect such interferences, samples and standards were always counted at least twice.

For routine use it was not necessary to establish a calibration line every day. Once a calibration line had been obtained, only one of the standards was measured for each series of samples, in order to correct the sample intensity for daily variations of the spectrometer.

Dope elements

The X-ray fluorescence spectrometer available was unable to determine magnesium; therefore an atomic-absorption spectrophotometric method was developed. Because of the large influence of the major elements on the magnesium absorption, a standard addition method was applied to account for large variations in sample composition.

The other elements were determined by X-ray fluorescence spectrometry, with an internal standard to compensate for the effect of matrix (*i.e.* sample composition) variations. The internal standard element was chosen so that the mass-absorption coefficients of the sample for the wavelength of the element to be determined and for the wavelength of the internal standard were as equal as possible. These wavelengths should not differ much. The amount of the internal standard element was selected so that the count rates of internal standard and dope elements in the concentration region of interest were approximately equal. The choice of the internal standard may be limited for practical reasons, *e.g.* when barium was used as internal standard for lanthanum, it appeared impossible to keep the glass discs intact, whereas cerium proved satisfactory.

Unreacted oxides

The methods described by Robinson and Joyce[2] were used to separate the unreacted oxides from the reaction product PZT. The lead oxide was dissolved in

TABLE I

INSTRUMENTAL CONDITIONS FOR THE DETERMINATION OF ELEMENTS BY X-RAY FLUORESCENCE SPECTROMETRY

Element	*Pb (total)*	*Zr (total)*	*Zr (unreacted)*	*Ti (total)*	*Ti (unreacted)*	*K (dope)*	*Ca (int.st.)*	*La (dope)*	*Ce (int.st.)*	*Sm (dope)*	*Cr (int.st.)*	*Yb (dope)*	*Ni (int.st.)*
X-ray tube	W	W	W	Cr	Cr	Cr	Cr	W	W	W	W	W	W
High tension, kV	50	50	50	40	50	50	50	50	50	50	50	50	50
Current, mA	20	20	20	24	20	20	20	20	20	20	20	20	20
Radiation path	air	air	air	vacuum	vacuum	vacuum	vacuum	vacuum	vacuum	vacuum	vacuum	vacuum	vacuum
Collimator	fine	fine	fine	coarse	coarse	coarse	coarse	coarse	coarse	fine	fine	fine	fine
Analyzing crystal	LiF(200)	LiF(200)	LiF(200)	LiF(200)	LiF(200)	PE	PE	LiF(200)	LiF(200)	LiF(200)	LiF(200)	LiF(220)	LiF(220)
Line	$L\alpha_{1,2}$	$K\alpha_{1,2}$	$K\alpha_{1,2}$	$K\alpha_{1,2}$	$K\alpha_{1,2}$	$K\alpha_{1,2}$	$K\alpha_{1,2}$	$L\alpha_{1,2}$	$L\beta_1$	$L\alpha_{1,2}$	$K\alpha_{1,2}$	$L\alpha_{1,2}$	$K\alpha_{1,2}$
Detector	scint.c	scint.c	scint.c	flow c	flow c	flow c	flow c	flow c	flow c	flow c	flow c	scint.c	scint.c
Voltage (V)	850	825	825	1650	1650	1600	1600	1650	1650	1650	1650	900	900
Attenuator position	2	2	2	4	4	3	3	4	4	4	4	2	2
Pulse height discrimination	no	no	no	no	no	no	no	yes	yes	no	no	no	no
Lower level scale	150	150	150	150	150	150	150	350	350	150	150	150	150
Window scale	—	—	—	—	—	—	—	200	200	—	—	—	—
Counting time, s.	40	40	100	40	100	40	40	40	40	40	40	40	40
Approx. net no. of counts	770,000	650,000	150,000	760,000	70,000	100,000	300,000	80,000	100,000	75,000	150,000	80,000	330,000
For a conc. in the orig. sample, %	63	15	0.6	7.2	0.1	0.3	—	1.5	—	1.5	—	1.5	—
Internal standard used	—	—	—	—	—	Ca	—	Ce	—	Cr	—	Ni	—
Amount (mg) and compound used, respectively	—	—	—	—	—	30	$CaCO_3$	50	CeO_2	80	$K_2Cr_2O_7$	40	NiO
Diam. of sample holder bottom hole, mm	28	28	23	28	23	28	28	20	20	20	20	28	28

EDTA (0.02 M), but a back-titration of the excess of EDTA[2] appeared unattractive. A direct method of determination was applied. Here, X-ray fluorescence spectrometry might have been used, but atomic-absorption spectrometry is much quicker. The 283.3 nm line of lead was chosen, because this line is less prone to interferences and is sufficiently sensitive, that no dilution or concentration of the extracted lead solution was necessary.

The acid-insoluble residue (zirconium oxide and titanium oxide) was taken into a borax melt and determined by X-ray fluorescence spectrometry; sodium chloride was added to prevent cracking of the glass disc.

EXPERIMENTAL

Apparatus

Some of the instrumental conditions applied for the determination of the elements with a Philips PW 1540 XRF spectrometer are shown in Table I; further, use was always made of the sample spinner.

The instrumental conditions applied for the determination of the elements by means of a Jarrell-Ash 82-547 atomic-absorption spectrophotometer are shown in Table II. The instrument was provided with a premix Techtron AB51 laminar burner, and a total consumption Hetco turbulent burner. Westinghouse hollow-cathode lamps were used. A Hamamatsu R213 photomultiplier and a grating blazed for 300 nm were used. Entrance and exit slits of the monochromator were 100 and 150 μm respectively. For the Hetco burner the light was passed 5 times through the flame. For both lead and magnesium determinations, hydrogen and air were the fuel and oxidant gases, respectively.

TABLE II

INSTRUMENTAL CONDITIONS FOR THE DETERMINATION OF THE ELEMENTS BY ATOMIC ABSORPTION SPECTROMETRY

Element	Pb	Mg
Wavelength, nm	283.3	285.2
Burner	Techtron	Hetco
Hollow cathode lamp, current, mA	6	8
Photomultiplier voltage, V	380	380
Gas pressure, kg cm^{-2}	4	4
Gas flow, l h^{-1}	10	13
Oxidant pressure, kg cm^{-2}	4	4
Oxidant flow l h^{-1}	125	96

Reagents

All reagents used were analytical-reagent grade. Either the assay values of the actual batch reported by the manufacturer were accepted, or the chemicals were analysed by wet-chemical methods[5–7].

The preparation of the flux (45 parts of anhydrous sodium tetraborate, 7 parts of lithium hydroxide, and 16 parts of orthoboric acid) has already been described[4]. Solid dilutions of compounds in flux or borax were used in order to weigh any prescribed small amounts of components accurately.

In order to calculate the amount of each component required, assay values and losses resulting from ignition were taken into account.

Procedures

Major constituents. Accurately weigh 250 ± 1 mg of powdered PZT sample into a Degussa II platinum crucible and add 1200 ± 1 mg of tungsten(VI) oxide and 6500 ± 2 mg of flux*. Mix the powders, melt and pour a glass disc as previously described[4]. Measure the intensity of the major elements of the sample and of a standard glass disc, under the conditions shown in Table I. Correct for daily variation. Calculate the content of the major constituents, applying the formulae described above with constants determined from the intensities of standards prepared from assayed compounds.

Magnesium dope. Accurately weigh about 100 mg of powdered PZT sample and dissolve in 2.5 ml of perchloric acid (70%). Add 2.5 ml of concentrated hydrochloric acid and heat until practically all the hydrochloric acid has evaporated, to dissolve the last traces. Transfer the solution to a volumetric flask and dilute with water to 100 ml for expected concentrations of 0.1–0.3% Mg. If a higher concentration is expected, dilute more.

Prepare in 50-ml volumetric flasks, solutions containing 25 ml of the above sample solution, 25 mg of strontium chloride (as a solution) and increasing amounts of magnesium as chloride (*e.g.* 0, 2.5, 5.0, 7.5 etc. mg Mg). Dilute with water to the mark. Measure the absorbance of these solutions under the conditions shown in Table II. Calculate the magnesium content of the sample by the method of standard additions[8].

Other dopes. Accurately weigh 2000 ± 5 mg of powdered PZT into a Degussa II platinum crucible. Add an accurately weighed amount of internal standard (see Table I) as a solid dilution (*e.g.* 1:10) in borax. Add powdered borax to give a total weight of 5000 ± 2 mg. Mix the powder, melt and pour a glass disc as previously described[4]. Measure the ratio of intensities of dope element and internal standard, under the conditions shown in Table I. Calculate the dope content from a calibration line, determined from the ratios of intensities in standards, prepared from assayed compounds.

Unreacted lead oxide. Accurately weigh about 250 mg of powdered PZT sample into a dry stoppered flask and add 50.0 ml (or 100.0 ml for high concentrations of unreacted lead) of 0.02 *M* EDTA solution. Shake the flask for 30 min. Allow the insoluble matter to settle and filter the solution through a dry fine-porosity filter. Discard the first 5 ml. The filtrate should be clear. Determine the absorbance of the filtrate by atomic absorption, under the conditions described in Table II. Calculate the lead content from a calibration line determined from the absorbances of standards prepared from lead nitrate and EDTA.

Unreacted zirconium and titanium oxide. Accurately weigh about 250 mg of powdered PZT sample. Dissolve in 50 ml of hot concentrated hydrochloric acid. Add 50 ml of hot water and filter through a fine-porosity filter. Wash with hot water. Ash the filter in a Degussa II platinum crucible. Add 500 ± 2 mg of a solid mixture of

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* If standards and samples are not prepared with the same batch of flux, the amount of flux is: 6500 y/y', where y and y' are the residues on ignition of standard batch and new batch of flux respectively.

lead(II) oxide and sodium chloride (6:1 by weight). Add 7500±2 mg of flux, mix the powders, melt and pour a glass disc as previously described[4]. Measure the intensity of zirconium and/or titanium under the conditions shown in Table I. Calculate the zirconium and titanium contents from calibration lines, determined from the intensities of standards prepared from assayed compounds.

DISCUSSION AND RESULTS

The relative standard deviation found[9] for the determinations of the major elements was about 0.2%. This standard deviation includes sample inhomogeneity, sample changer dissimilarity, etc.

The absolute standard deviation found for determination of the unreacted oxides is reported in Table III. It was not investigated whether 0.02 *M* EDTA indeed dissolves only free lead oxide. Robinson and Joyce[2] do not exclude the possibility of dissolving lead from lead-rich titanium compounds. However, in that case one would expect the measured amount of dissolved lead to depend on the EDTA concentration, and this was not observed. Further, no significant amounts of titanium were found in the EDTA extracts.

TABLE III
COMPARISON OF ANALYSES

	Sample identification	*Classical methods*	*Proposed method*
Unreacted lead	1	1.25±0.05	1.22±0.02
Unreacted zirconium	1	0.60±0.1	0.65±0.1
Unreacted titanium	1	0.02±0.01	0.03±0.01
Total lead	1	63.7±0.1	63.6±0.1
	4	63.4	63.3
Total zirconium	1	14.78±0.1	14.88±0.04
	2	14.58	14.53
	3	13.80	13.86
	4	13.71	13.69
Total titanium	1	6.97±0.05	6.95±0.02
	2	6.77	6.80
	3	7.50	7.48
	4	7.35	7.30

Not enough samples were analysed for dope content to calculate a standard deviation. From the results so far obtained for magnesium, this deviation is expected to be about 5%; for the other dope elements a standard deviation of less than 2% appeared. In both cases not too low concentrations were present.

The time necessary for the analyses compares very favourably with that of many other methods. The following time requirements do not include the preparation of standards and depend on the length of the series, but include the time necessary for cleaning, calculation and reporting. The simultaneous determination of the three major constituents can be made in about 3 h. Unreacted lead requires about 1.5 h, unreacted zirconium and titanium simultaneously require 3 h. A dope element can be determined in about 1 h, but magnesium requires more time.

Some representative samples were also analysed by chemical methods[5,6] (dissolution in hydrochloric acid and fusion of the insoluble residue with pyrosulphate). From the results (Table III) a good precision is apparent. The dopes were not analysed by wet chemistry, because of the difficulties encountered.

We thank Mrs. A. van Veen-Blaauw for the development of the magnesium determination and Mr. H. Weber for much help in preparing standards and analysing samples.

SUMMARY

An accurate X-ray fluorescence spectrometric method is described for the determination of lead, zirconium and titanium in lead zirconate–titanate ceramics. Careful matching of samples and standards by a borax fusion method resulted in a relative standard deviation of about 0.2% for the major constituents. The determination, after separation, of the unreacted oxide of lead by atomic absorption spectrometry, and of the unreacted oxides of zirconium and titanium by X-ray fluorescence spectrometry is also described. An X-ray fluorescence spectrometric method is proposed for the determination of dope elements (K, La, Sm, Yb) with internal standards (Ca, Ce, Cr, Ni respectively). The magnesium dope is determined by atomic-absorption spectrometry with standard addition.

RÉSUMÉ

On décrit une méthode spectrométrique de fluorescence aux rayons-X pour le dosage du plomb, du zirconium et du titane dans des céramiques. Un essayage précautionneux d'échantillons et d'étalons par voie de la méthode de fusion à borax fournissait une déviation standard relative d'environ 0.2% pour les composés principaux. Après séparation, des dosages ont été effectués pour la partie non-convertie de l'oxyde de plomb à l'aide d'absorption atomique et pour celle respectivement des oxydes de zirconium et de titanium à l'aide de spectrométrie de fluorescence aux rayons-X. On propose également une méthode pour le dosage des éléments de base (K, La, Sm, Yb) au moyen d'étalons internes (respectivement Ca, Ce, Cr et Ni). Le magnésium est dosé spectrophotométriquement par absorption atomique, avec addition d'étalon.

ZUSAMMENFASSUNG

Es wird eine genaue Röntgenfluoreszenz-Methode beschrieben für die Bestimmung von Blei, Zirkonium und Titan in keramischen Werkstoffen auf Blei–Zirkonat–Titanat-Basis. Durch sorgfältige Angleichung der Analysen- und Vergleichsproben mittels eines Borax-Schmelzverfahrens wurde für die Hauptbestandteile eine relative Standardabweichung von etwa 0.2% erzielt. Nach Abtrennung wurden die Oxide bestimmt, die bei der Herstellung nicht reagiert hatten, und zwar Bleioxid durch Atomabsorptionsspektrometrie und die Oxide von Zirkonium und Titan durch Röntgenfluoreszenzanalyse. Für die Bestimmung der zugesetzten Elemente (K, La, Sm, Yb) wird ebenfalls eine röntgenfluoreszenzspektrometrische Methode mit

inneren Standards (resp. Ca, Ce, Cr, Ni) vorgeschlagen. Der Magnesium-Zusatz wird durch Atomabsorptionsspektrometrie nach einer Standard-Zumischmethode bestimmt.

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A KINETIC METHOD FOR THE DETERMINATION OF AMMONIA BY ITS CATALYTIC EFFECT ON THE LIGAND SUBSTITUTION REACTION OF THE MERCURY(II)–*o*-CRESOLPHTHALEIN COMPLEXONE COMPLEX WITH *trans*-1,2-DIAMINO-CYCLOHEXANE-N,N,N′,N′-TETRAACETIC ACID

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Kinetic methods of analysis which utilize reactions based on metal complexes have been discussed by several authors[1–3]. The effect of metal ions and various ligands on the rate of ligand substitution reactions of metal complexes provides a basis for the determination of these species[4–8]. In an earlier paper[9], it has been reported that halide ions and hydroxide ions accelerate the rate of the ligand substitution reaction of the mercury(II)–4-(2-pyridylazo)resorcinol complex with *trans*-1,2-diaminocyclohexane-N,N,N′,N′-tetraacetic acid (CyDTA), and that the reactivities of these ions are quantitatively accounted for in terms of their electron-donating property. The reaction has been utilized for the determination of very small amounts of iodide[8]. From values of the electron-donor constant[10], it was expected that ammonia could be determined similarly.

In the present paper, a new kinetic method of analysis is proposed for determining microgram amounts of ammonia. The method is based on the catalytic effect of ammonia on the following ligand substitution reaction:

$$\mathrm{Hg(II)\text{-}CPC + CyDTA \rightarrow Hg(II)\text{-}CyDTA + CPC} \qquad (1)$$

where CPC denotes 3,3′-*bis*-N,N-di(carboxymethyl)aminomethyl-*o*-cresolphthalein. This reaction is accelerated by a small amount of ammonia.

PRINCIPLE OF THE DETERMINATION

Mercury(II) ion forms a 1:1 complex with CPC under the present experimental conditions[11]. The rate equation of the ligand substitution reaction of the mercury(II)–CPC complex with CyDTA in the presence of ammonia is expressed as follows:

$$-(\mathrm{d}[\mathrm{Hg(II)\text{-}CPC}])/\mathrm{d}t = k_{0(\mathrm{CyDTA,CPC,H,NH_3})}[\mathrm{Hg(II)\text{-}CPC}] \qquad (2)$$

where $k_{0(\mathrm{CyDTA,CPC,H,NH_3})}$ is a conditional first-order rate constant which depends on

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the experimental conditions such as the concentrations of CyDTA, CPC, hydrogen ion and ammonia. Careful study of the kinetics of the substitution reaction showed the following relationship[12]:

$$k_{0(\mathrm{CyDTA,CPC,H,NH_3})} = \{(k_1 + k_2[\mathrm{H^+}] + k_3[\mathrm{H^+}][\mathrm{NH_3}])/[\mathrm{CPC}]\}[\mathrm{CyDTA}] \quad (3)$$

where $k_1 = 1.06 \cdot 10^{-3}$ s^{-1}, $k_2 = 7.17 \cdot 10^6$ M^{-1} s^{-1}, and $k_3 = 4.19 \cdot 10^{11}$ M^{-2} s^{-1} at 25° and 0.1 M ionic strength ($NaClO_4$). It is obvious from eqn. (3) that, under conditions where CPC and CyDTA are present in large excess relative to mercury(II) and the pH is kept constant, the conditional rate constant $k_{0(\mathrm{CyDTA,CPC,H,NH_3})}$ is a linear function of the concentration of ammonia. This provides the basis of the determination of ammonia by means of the ligand substitution reaction of the mercury(II)–CPC complex with CyDTA.

The reaction path corresponding to the third term on the right-hand side of eqn. (3) is expressed as follows:

$$\mathrm{Hg\text{–}CPC + NH_3 \rightleftarrows HgNH_3 + CPC} \quad (4)$$

$$\mathrm{HgNH_3 + CyDTA \rightarrow Hg\text{–}CyDTA + NH_3} \quad (5)$$

Equilibrium (4) precedes the rate-determining step (5). Ammonia released in reaction (5) is repeatedly involved in reaction (4) and accelerates the substitution reaction. Details of the kinetics and mechanism of this reaction will be reported elsewhere[12].

RESULTS AND DISCUSSION

Effect of pH

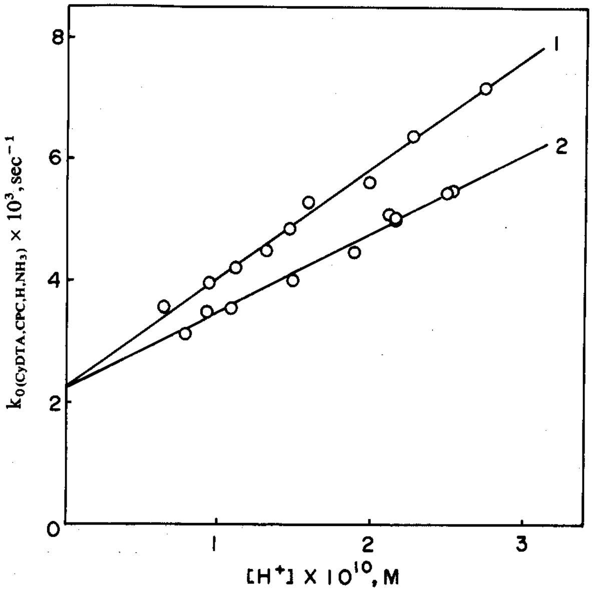
Conditional rate constants for reaction (1) in the presence and in the absence of ammonia are plotted against the concentration of hydrogen ion in Fig. 1. The difference between the conditional rate constants in the presence and in the absence of ammonia increases with increasing concentration of hydrogen ion. Therefore, a low pH value is preferable for sensitivity. On the other hand, the substitution reaction at too low a pH is too fast to be followed by any conventional method. Accordingly, a pH value of 9.5 is recommended.

Effect of reactants

A relatively high concentration of mercury(II) leads to improved sensitivity. For the optimal sensitivity and precision, a mercury(II) concentration of $1 \cdot 10^{-5}$ M is preferable. The rate of the ligand substitution reaction is of first order with respect to the concentration of CyDTA and the reciprocal concentration of CPC, respectively (see eqn. 3). Concentrations of $2 \cdot 10^{-4}$ M CPC and of $4 \cdot 10^{-4}$ M CyDTA are recommended.

Calibration curve

The change in the absorbance of the mercury(II)–CPC complex is shown as a function of reaction time in Fig. 2. The rate of decrease of the absorbance increases with increasing concentration of ammonia. Accordingly, the concentration of ammonia can be determined from the absorbance at a certain reaction time. A calibration curve can be constructed for concentration of ammonia against, for example, $A_{75,0} - A_{75,\mathrm{NH_3}}$, where $A_{75,0}$ and $A_{75,\mathrm{NH_3}}$ denote the absorbances at 75 s



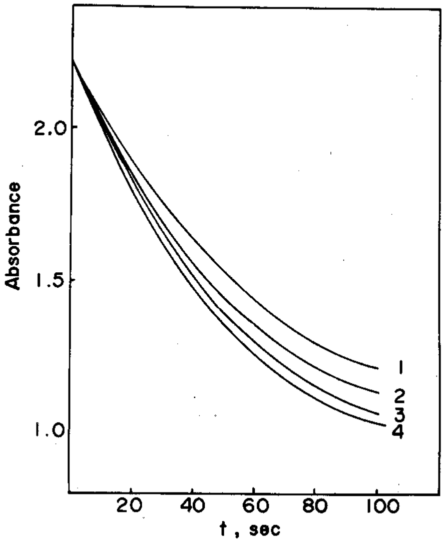


Fig. 1. Plot of $k_{0(\mathrm{CyDTA,CPC,H,NH_3})}$ *vs.* $[H^+]$. $C_{Hg}=4.18\cdot10^{-6}$ *M*; $C_{CPC}=2.00\cdot10^{-4}$ *M*; $C_{CyDTA}=3.87\cdot10^{-4}$ *M*; 25°. Straight line 1: in the presence of $6.00\cdot10^{-6}$ *M* ammonia; straight line 2: in the absence of ammonia.

Fig. 2. Change in the absorbance of the reaction system at 583 nm *vs.* reaction time for the reaction of the Hg(II)–CPC complex with CyDTA. $C_{Hg}=1.04\cdot10^{-5}$ *M*; $C_{CPC}=2.00\cdot10^{-4}$ *M*; $C_{CyDTA}=3.87\cdot10^{-4}$ *M*; pH=9.56, 25°. C_{NH_3}: (1) 0, (2) 22.4, (3) 39.2, (4) 51.8 μg NH_3-N l^{-1}

in the absence and in the presence of ammonia, respectively. Such a calibration curve was found to be linear over the range 0–55 μg NH_3-N l^{-1} with $(A_{75,0}-A_{75,NH_3})$ values of *ca.* 0.04–0.18.

Distillation of ammonia

With a thorough knowledge of the kinetics of the reaction system, the following elements are expected to interfere with the determination of ammonia: complexing agents for mercury(II), and metals forming complexes with CyDTA and/or CPC. In order to avoid interference of these species, ammonia was distilled in the apparatus shown in Fig. 3 before its determination by the proposed method. In the distillation flask, 25 ml of the sample solution was mixed with 10 ml of 10^{-2} *M* ethylenediamine-N,N,N′,N′-tetraacetic acid (EDTA) solution, and 25 ml of a saturated potassium carbonate solution was added. The receiver contained 1 ml of a solution which was 10^{-4} *M* in mercury(II) perchlorate and 10^{-2} *M* in perchloric acid. A gentle stream of washed air was passed through the system with an aspirator. EDTA was used to prevent the precipitation of metal hydroxides which reduced the quantitative recovery of ammonia in some cases, for instance in the presence of manganese. To avoid the decomposition of unstable organic nitrogen compounds, distillation was carried out at 25°.

In order to determine the time necessary for the quantitative recovery of ammonia, distillation was carried out over various periods (Table I). These results

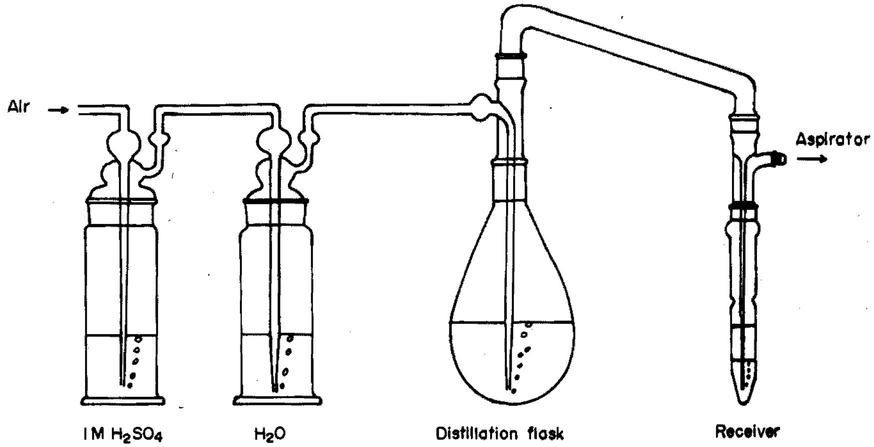


Fig. 3. Apparatus for distillation of ammonia.

indicate that, under conditions described, the recovery of ammonia is practically quantitative after about 50 min. This distillation time was adopted in all subsequent work.

TABLE I RATE OF DISTILLATION OF AMMONIA AT 25°

(Conditions: $C_{NH_3}=39.2$ μg NH_3-N l^{-1}, $C_{EDTA}=1.66\cdot10^{-3}$ M, $C_{Hg}=1.04\cdot10^{-5}$ M, $C_{CPC}=2.00\cdot10^{-4}$ M, $C_{CyDTA}=3.87\cdot10^{-4}$ M, pH$=9.56$, 25°)

Distillation time (min)	*Found NH_3-N (μg l^{-1})*	*Recovery (%)*
30	36.4	93
45	40.8	104
45[a]	39.6	101
60	39.6	101

[a] In the absence of EDTA.

TABLE II EFFECT OF FOREIGN IONS ON THE DETERMINATION OF AMMONIA

Foreign ions	*Concentration (M)*	*NH_3 taken (μg NH_3-N l^{-1})*	*NH_3 found (μg NH_3-N l^{-1})*	*Recovery (%)*
Ca^{2+} 103	10^{-4}	39.2	40.4	
Mg^{2+}	10^{-4}	39.2	38.5	98
Mn^{2+}	10^{-5}	39.2	38.8	99
Cu^{2+}	10^{-5}	39.2	38.7	99
Zn^{2+}	10^{-5}	39.2	40.6	104
Al^{3+}	10^{-5}	39.2	41.0	105
Fe^{3+}	10^{-5}	39.2	39.2	100
SO_4^{2-}	10^{-3}	39.2	36.8	94
NO_3^-	10^{-3}	39.2	37.2	95
I^-	10^{-3}	39.2	40.0	102
Br^-	10^{-3}	39.2	39.6	101
Cl^-	10^{-3}	39.2	40.0	102

Effect of foreign ions

The recovery of ammonia in the presence of various cations and anions was tested. Table II shows that ions supposed to be present in natural waters are eliminated by distillation and do not interfere with the determination.

Determination of ammonia in natural waters

This kinetic method was applied to the determination of ammonia in natural waters. Ammonia concentrations even at the micromolar level can be determined (Table III). An extract of dead pine leaves was used to examine the recovery of ammonia in the presence of many organic compounds.

TABLE III

DETERMINATION OF AMMONIA IN NATURAL WATERS

Sample (*μg* NH_3-*N* l^{-1})	NH_3 *added* (*μg* NH_3-*N* l^{-1})	NH_3 *found* (*μg* NH_3-*N* l^{-1})	*Recovery* (*%*)
Underground water			
26.7	0		—
26.7	0	av. 26.3	—
25.6	0		—
26.3	33.6	59.2	98
26.3	22.4	48.6	100
Rain water			
36.7	0		—
37.3	0	av. 36.9	—
36.7	0		—
36.9	11.2	48.4	103
Extract of dead pine leaves[a]			
19.2	0		—
19.9	0	av. 19.4	—
19.2	0		—
19.4	22.4	39.8	91
19.4	11.2	30.8	102
19.4	11.2	30.6	100

[a] Dead pine leaves were soaked in distilled water for about one month.

EXPERIMENTAL

Reagents

Ammonium perchlorate. Gaseous ammonia was led to a perchloric acid solution; the precipitated ammonium perchlorate was recrystallized twice from distilled water, and dried *in vacuo* over P_2O_5 at 100°. The concentration of ammonium perchlorate was determined as perchloric acid by using a cation-exchange resin (Amberlite IR 120-B exchanger). The value agreed with the theoretical value within 0.2%. The solution should be freshly prepared.

o-Cresolphthalein complexone. The acid form (Dojindo Chemical Co., Kumamoto, Japan) was purified as described by Schwarzenbach *et al.*[13]. Purity was checked by paper chromatography and non-aqueous titration of the imino group in acetic acid[14]. The water content of the crystals was determined by the Karl Fischer method. A CPC solution was freshly prepared with 2 equivalents of sodium hydroxide.

The preparations of all other reagents (sodium hydroxide, sodium borate, mercury perchlorate) have been described previously[9,15].

Apparatus

The following instruments were used: a photoelectric spectrophotometer Type 6 (Hirama Rikakenkyujo, Japan); a Hitachi Model QPD-53 recorder; a Yokokawa Type LER-10 A recorder; a Radiometer-PHM-4d (Copenhagen) with a Type G 202 glass electrode and K 401 calomel electrode; a Coolnics Model CTR-1 B thermoelectric circulator (Komatsu Solidate Co., Japan).

Recommended procedure

Place 1 ml of a mercury(II) perchlorate solution ($[Hg^{2+}]=10^{-4}$ *M*, $[HClO_4]=10^{-2}$ *M*) in the receiver. Mix 25 ml of a sample solution with 10 ml of 10^{-2} *M* EDTA solution in the distillation flask, and add 25 ml of a saturated potassium carbonate solution. Pass a gentle stream of washed air for 50 min at 25° (see Fig. 3). Rinse out the receiver with water and add water to the mark (about 6 ml). Take 5 ml of the solution in a quartz reaction vessel with a light path of 3 cm placed in a cell compartment thermostated at 25°. Add 2 ml of a borax–sodium hydroxide buffer solution to maintain the pH at 9.5 and 2 ml of 10^{-3} *M* CPC solution. Start the reaction by mixing 1 ml of $4\cdot10^{-3}$ *M* CyDTA solution into the reaction vessel. Follow the reaction automatically, recording the absorbance at 583 nm as a function of time. Determine the concentration of ammonia from the calibration curve previously constructed.

SUMMARY

A kinetic method for the determination of microgram amounts of ammonia is described. The method is based on the catalytic effect of ammonia on the ligand substitution reaction of the mercury(II) complex of *o*-cresolphthalein complexone with *trans*-1,2-diaminocyclohexane-N,N,N′,N′-tetraacetic acid. Ammonia concentrations at micromolar level can be determined. Cationic and anionic interferences can be avoided by simple distillation of ammonia at room temperature.

RÉSUMÉ

On décrit une méthode cinétique pour le microdosage de l'ammoniaque. Elle est basée sur l'effet catalytique de l'ammoniaque sur la réaction de substitution du complexe mercure(II)–*o*-crésolphtaléinecomplexone par l'acide *trans*-diamino-1,2-cyclohexane-N,N,N′,N′-tétracétique. Des interférences cationiques et anioniques peuvent être évitées par simple distillation de l'ammoniaque à la température ambiante.

ZUSAMMENFASSUNG

Eine kinetische Methode für die Bestimmung von Mikrogramm-Mengen Ammoniak wird beschrieben. Die Methode beruht auf dem katalytischen Effekt von Ammoniak auf die Ligandensubstitutionsreaktion des Quecksilber(II)-Komplexes von *o*-Kresolphthalein-Komplexon mit *trans*-1,2-Diaminocyclohexan-N,N,N',N'-tetraessigsäure. Ammoniakkonzentrationen im mikromolaren Bereich können bestimmt werden. Kationische und anionische Störungen können durch einfache Destillation des Ammoniaks bei Raumtemperatur vermieden werden.

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DOSAGE DE TRACES D'URANIUM, DE THORIUM ET DE PLOMB PAR FLUORESCENCE-X. ÉTUDE SUR DES "ZIRCONS" SYNTHÉTIQUES ET APPLICATION À QUELQUES ZIRCONS NATURELS DU GROENLAND

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(Reçu le 13 juin 1972)

Le dosage de l'uranium, du thorium et du plomb à des concentrations de l'ordre de quelques dizaines ou centaines de p.p.m. revêt une importance particulière dans le cas de la géochronométrie des zircons, minéraux dont la composition chimique moyenne est de 65% de ZrO_2 et 35% de SiO_2. Ces trois éléments (U, Th et Pb) permettent en effet de calculer l'âge des zircons soit par la méthode dite du "plomb total" décrite plus loin, soit par la méthode des âges isotopiques. Dans ce dernier cas, on détermine les isotopes par spectrométrie de masse.

La fluorescence-X a été choisie car elle permet une analyse non destructive des zircons, avec un minimum de préparations. La méthode décrite est dérivée des travaux de Buchs[1] et Laurent *et al.*[2]; les modifications apportées ont eu pour but principal d'améliorer la reproductibilité et la précision des résultats.

Le dosage est basé sur la mesure, au spectromètre à rayons-X, de l'intensité des raies $L\alpha^{I}_{1,2}$ de l'uranium et du thorium, et $L\beta^{I}_{1,2}$ du plomb. Un cristal LiF 220 a été préféré au cristal LiF 200 employé généralement car son pouvoir séparateur est meilleur. Les échantillons ont été soumis au rayonnement-X primaire sous forme de pastilles; une matrice commune, en l'occurence un mélange de 65% ZrO_2 et 35% SiO_2 (dit "zircon" synthétique), a été utilisée afin de normaliser l'effet de matrice qui exprime l'influence de la composition chimique générale de l'échantillon et qui nécessite souvent bien des calculs de correction.

PARTIE EXPÉRIMENTALE

Appareillage et conditions de mesures

Les mesures ont été faites au moyen d'un ensemble de spectrométrie à rayons-X Philips, muni d'un tube à anticathode de molybdène (alimentation: 50 kV et 20 mA) et d'un discriminateur à hauteur d'impulsions. Un cristal LiF 220, de distance réticulaire 2d = 2.848 Å, a permis la séparation des pics dus aux trois éléments étudiés. L'intensité de ces pics a été mesurée par une sonde à scintillation et les impulsions transmises par le système enregistreur à une machine à calculer Précisa. Les raies analytiques suivantes ont été utilisées:

	2θ pic	*2θ fond continu*
uranium $L\alpha^{I}_{1,2}$	37°27 (th. 37°31)	38°40
thorium $L\alpha^{I}_{1,2}$	39°15 (th. 39°23)	38°60 et 39°70
plomb $L\beta^{I}_{1,2}$	40°29 (th. 40°34)	39°79 et 41°50

Pour chaque élément, les mesures ont été faites dans l'ordre: fond continu inférieur—pic—fond continu supérieur. Chaque mesure est la moyenne de 10 mesures de 10 s chacune; on répète trois fois cette opération pour une pastille.

Préparation des standards

A $(1-x)$ g d'un mélange ZrO_2–SiO_2 (65%–35%) on incorpore x g d'un mélange analogue contenant en outre des quantités d'uranium, de thorium et de plomb telles que les concentrations finales s'échelonnent de 100 à 2000 p.p.m. pour l'uranium, 50 à 300 p.p.m. pour le thorium et 50 à 400 p.p.m. pour le plomb. Le mélange, additionné d'acétone, est homogénéisé dans un mortier en agathe, puis séché dans une étuve à 110°. On procède ensuite au pastillage de la manière suivante: à 100 mg de mélange, on ajoute 200 mg d'un mélange MoO_3–cellulose (50%–50%). Ce nouveau mélange est homogénéisé comme ci-dessus, par addition d'acétone, puis comprimé sous forme d'une pastille de 31 mm de diamètre au moyen d'une presse hydrolique atteignant une pression de 30 tonnes (l'épaisseur de la pastille s'obtient par adjonction de cellulose).

Pour ces préparations, les produits suivants ont été utilisés: ZrO_2; SiO_2; PbO; ThO_2 (tous "specpure" Johnson-Matthey, Londres); U_3O_8 (standard No. 950 du National Bureau of Standards, Washington); MoO_3 (Merck p.a.); cellulose pour chromatographie (Roth); acétone (Merck p.a.).

Préparation des mélanges dits "zircons" synthétiques

Même procédé que pour les standards, mais avec des mélanges contenant (U + Th), (U + Pb), (Th + Pb) et (U + Th + Pb). Ces éléments ont été ajoutés dans les proportions telles qu'on les trouve dans les zircons naturels.

TABLEAU I

ZIRCONS EXAMINÉS
(Provenance: Söndre Strömfjord, Groenland)

Zircon	*Roche*
Zr-445 Gd 16	Granulite à hypersthène
Zr-446 Gd 17	Gneiss à biotite
Zr-447 Gd 18	Charnockite
Zr-448 Gd 19	Gneiss à biotite
Zr-449 Gd 20	Granulite à hypersthène
Zr-450 Gd 21	Gneiss à biotite

Préparation des échantillons des zircons naturels

Zircons (100 mg), extraits de la roche par purification et broyage[3], sont broyés à moins de 400 mesh. On procède au pastillage comme décrit ci-dessus.

Les zircons mentionnés dans le Tableau I ont été analysés.

ÉTUDE ANALYTIQUE

Dosage de l'uranium

Tout d'abord des courbes d'étalonnage ont été établies, d'une part entre 0 et

1000 p.p.m., par bonds de 100 en 100 p.p.m., et d'autre part de 1000 à 2000 p.p.m., par bonds de 200 en 200 p.p.m. Les mesures ont été faites dans les conditions indiquées ci-dessus. Ces courbes d'étalonnage ne peuvent que donner un ordre de grandeur de la teneur en uranium d'un échantillon inconnu car les valeurs de l'intensité pour une même concentration changent quelque peu en quelques heures; elles permettent de choisir les standards adéquats. Pour une détermination précise il faut donc entourer l'échantillon à analyser de trois standards (un plus faible et deux plus forts ou *vice-versa*). Les mesures se font alors dans l'ordre: standard—échantillon—standard—standard. On répète trois fois chaque mesure et l'on en calcule la moyenne. La durée est d'environ une heure. On calcule alors la droite de régression entre les trois standards, on corrige la valeur de chaque standard au moyen de cette droite et on détermine la teneur en uranium de l'échantillon à partir des standards corrigés. Seule cette méthode de calcul a donné des résultats reproductibles et plus précis que ceux obtenus en traçant sur papier millimétré une courbe (nombre d'impulsions en fonction de la teneur en uranium) entre deux standards[2].

L'étude du dosage de l'uranium a été faite sur des "zircons" synthétiques préparés selon la méthode décrite ci-dessus. Elle a eu pour but d'une part de déterminer la précision du dosage et d'autre part d'étudier l'influence du thorium et du plomb.

TABLEAU II

DOSAGE DE L'URANIUM DANS DES "ZIRCONS" SYNTHÉTIQUES

Mélanges préparés (p.p.m.)			*U trouvé (p.p.m.)*	*Erreur relative (%)*
U	*Th*	*Pb*		
200	100	—	200	0.00
200	200	—	189	5.50
200	300	—	189	5.50
500	100	—	480	4.00
500	200	—	524	4.80
500	300	—	490	2.00
500	—	25	477	4.60
500	—	200	487	2.60
500	—	400	484	3.20
1000	100	—	996	0.40
1000	200	—	956	4.40
1000	300	—	954	4.60
1000	—	25	1055	5.50
1000	—	75	1055	5.50
1000	50	25	1037	3.70
1000	100	100	959	4.10
1000	300	25	982	1.80
1500	50	300	1570	4.66
1500	100	250	1531	2.06
1500	150	50	1500	0.00
2000	100	—	2048	2.40
2000	200	—	1992	0.40
2000	300	—	2016	0.80
2000	—	25	1909	4.55
2000	—	75	1955	2.55
2000	—	200	1992	0.40

Les interférences dues à d'autres éléments présents à l'état de traces dans les zircons n'ont pas été recherchées, cette étude ayant déjà été faite par Buchs[1]. Les résultats sont consignés dans le Tableau II.

On remarque que pour des teneurs en uranium comprises entre 200 et 2000 p.p.m., il n'y a pas d'influence marquée du thorium ou du plomb. La tendance est plutôt une diminution de la teneur effective en uranium, mais elle n'est pas assez forte pour pouvoir en tirer des conclusions et affirmer une interaction des autres éléments.

Les erreurs relatives sont comprises entre 0.50 et 5.50%, valeurs qui sont bonnes dans le domaine de l'analyse des traces. Dans les conditions indiquées, la limite de dosage est située vers 100 p.p.m.

Dosage du thorium

La mise au point du dosage du thorium a été beaucoup plus délicate; en effet cet élément est situé entre l'uranium et le plomb et l'influence de ces éléments sur les fonds continus du thorium se fait sentir. Laurent *et al.*[2] ont déterminé le thorium au moyen du rapport U/Th obtenu sur des spectres, avec LiF 200; mais ce procédé n'est pas entièrement satisfaisant car il nécessite la recherche d'un facteur de correction et n'est pas toujours précis suivant l'allure du spectre. Par contre, avec le cristal LiF 220, qui sépare mieux les pics, on procède plus facilement au comptage des

TABLEAU III

DOSAGE DU THORIUM DANS DES "ZIRCONS" SYNTHÉTIQUES

Mélanges préparés (p.p.m.)			*Th trouvé (p.p.m.)*	*Erreur relative (%)*
Th	*U*	*Pb*		
50	100	25	72	44.00
50	500	25	73	46.00
50	1000	25	53	6.00
50	1500	300	46	8.00
100	500	—	107	7.00
100	1000	—	104	4.00
100	—	25	101	1.00
100	—	100	100	0.00
100	—	200	97	3.00
100	—	300	101	1.00
100	500	300	103	3.00
100	1000	100	97	3.00
200	—	100	190	5.00
200	—	300	207	3.50
200	200	—	200	0.00
200	500	—	185	7.00
300	—	25	296	1.33
300	—	100	306	2.00
300	200	—	296	1.33
300	500	—	283	5.66
300	1000	—	296	1.33
300	2000	—	306	2.00

impulsions et il est reconnu que les méthodes de comptage sont plus précises que les méthodes graphiques. Les mesures ont été faites dans les conditions indiquées ci-dessus. Une courbe d'étalonnage a été établie entre 50 et 300 p.p.m., par bonds de 50 en 50 p.p.m. Les résultats obtenus ont été satisfaisants aussi bien en ne considérant qu'un fond continu, à 39°70, qu'en en considérant deux. Comme dans le cas de l'uranium, la courbe d'étalonnage ne sert qu'à donner un ordre de grandeur de la teneur en thorium d'un échantillon inconnu. Pour une détermination précise, on procède comme indiqué pour l'uranium. L'étude du dosage du thorium a également été faite sur des mélanges dits "zircons" synthétiques. Dans ce cas il faut considérer les deux fonds continus pour obtenir des résultats satisfaisants. Les résultats sont consignés dans le Tableau III.

On remarque que pour 50 p.p.m. de thorium, les résultats peuvent être complètement aberrants et les valeurs obtenues très irrégulières. Il faut d'ailleurs signaler que jusqu'à 150 p.p.m., la valeur du fond continu à 38°60 (en présence d'uranium) est supérieure à celle du pic; mais étant donné que l'on considère pour les calculs la moyenne des deux fonds continus, on obtient toujours une valeur positive pour le "pic-fonds continus".

De nombreux essais ont permis de fixer la limite de dosage vers 100 p.p.m. Les erreurs relatives sont généralement comprises entre 1.00% et 5.00%, ce qui est à nouveau satisfaisant.

TABLEAU IV

DOSAGE DU PLOMB DANS DES "ZIRCONS" SYNTHÉTIQUES

Mélanges préparés (p.p.m.)			*Pb trouvé (p.p.m.)*	*Erreur relative (%)*
Pb	*U*	*Th*		
25	—	200	31	24.00
25	—	300	36	44.00
25	100	50	31	24.00
25	1000	50	17	32.00
50	1500	150	51	2.00
75	500	—	73	2.73
75	2000	—	75	0.00
100	—	100	95	5.00
100	—	200	102	2.00
100	—	300	105	5.00
100	1000	100	97	3.00
200	500	—	200	0.00
200	1000	—	201	0.50
200	2000	—	201	0.50
200	—	100	200	0.00
200	—	300	207	3.50
250	1500	100	240	4.00
300	—	100	290	3.33
300	—	200	300	0.00
300	500	100	301	0.33
400	500	—	400	0.00
400	1000	—	406	1.50

Dosage du plomb

Comme précédemment, des courbes d'étalonnage ont été établies entre 25 et 400 p.p.m., par bonds de 25 en 25 p.p.m. jusqu'à 100 p.p.m. et 50 en 50 p.p.m. pour des teneurs de 100 à 400 p.p.m., d'une part en ne considérant que le fond continu supérieur à 41° 50 et d'autre part en tenant compte des deux fonds continus.

A nouveau les déterminations précises de la teneur en plomb des échantillons ont été faites selon la méthode indiquée pour l'uranium. Les "zircons" synthétiques ont permis de constater que les résultats étaient plus précis avec un fond continu qu'avec deux fonds continus: aucune explication n'a été trouvée pour justifier ce phénomène. Lors de l'application de la méthode à des zircons naturels, des résultats identiques ont été obtenus par les deux moyens de comptage. Les résultats sont consignés dans le Tableau IV.

Les résultats obtenus avec 25 p.p.m. sont complètement aberrants. Comme pour l'uranium et le thorium, la limite de dosage se situe vers 100 p.p.m. Les erreurs relatives sont comprises entre 0.50 et 5.00%. Aucune influence prépondérante de l'uranium ou du thorium n'a été remarquée.

APPLICATION

La méthode décrite a été appliquée au dosage de traces d'uranium, de thorium et de plomb dans des zircons naturels provenant du Groenland (voir Tableau I). Les résultats obtenus (Tableau V) ont été comparés à des résultats obtenus précédemment par la méthode des spectres[2].

L'âge "plomb total" des zircons a été calculé au moyen des formules de Keevil[4] données ci-dessous:

$$\text{activité } \alpha = 0.366\text{U} + 0.0869\text{Th}\ [\text{c mg}^{-1}\ \text{h}^{-1}]\ \text{U et Th en p.p.m.} \quad (1)$$

$$\text{âge} = t_0 = E - \tfrac{1}{2}K(E^2) \quad [\text{m.a.}] \quad (2)$$

$$\text{où } E = \left[\frac{2632 + 624\text{Th/U}}{1 + 0.312\text{Th/U}}\right]\frac{\text{Pb}}{\alpha} \quad (3)$$

$$\text{et } K = \left[\frac{77.2 + 6.20\text{Th/U}}{4.06(1 + 0.312\text{Th/U})}\right]10^{-5} \quad (4)$$

TABLEAU V

DOSAGE DE L'URANIUM, DU THORIUM ET DU PLOMB DANS DES ZIRCONS NATURELS ET CALCUL DE L'ÂGE "PLOMB TOTAL"

Zircon	*Méthode de comptage*				*Méthode des spectres*			
	U (p.p.m.)	*Th (p.p.m.)*	*Pb (p.p.m.)*	*Age (m.a.)*	*U (p.p.m.)*	*Th (p.p.m.)*	*Pb (p.p.m.)*	*Age (m.a.)*
Zr-445	437	118	253	2568	438	118	306	2784
Zr-446	565	142	290	2424	559	128	327	2595
Zr-447	332	150	167	2296	316	136	207	2714
Zr-448	284	118	133	2246	288	110	171	2593
Zr-449	394	150	136	1760	402	152	177	2166
Zr-450	610	145	311	2420	563	149	331	2590

Pour des âges supérieurs à 1700 millions d'années (m.a.), ce qui est précisément le cas des zircons du Groenland, la formule (2) subit la modification suivante:

$$\text{âge} = t_0 = [E - \tfrac{1}{2}K(E^2)] + 3.4 \cdot 10^{-9}[E - \tfrac{1}{2}K(E^2)]^3 \qquad (5)$$

Les résultats obtenus sont consignés dans le Tableau V.

Les résultats obtenus pour l'uranium concordent entre les deux méthodes. Ceci est normal car dans la méthode des spectres, l'uranium se fait également par comptage. Par contre, pour le thorium et le plomb, les valeurs obtenues sont plus faibles par la méthode de comptage que par celle des spectres qui considère les rapports U/Th et U/Pb des hauteurs des pics. La méthode de comptage est certainement plus précise car elle tient plus strictement compte des éventuelles interférences dues aux autres éléments par un choix plus judicieux des fonds continus. Par conséquent, les âges sont également plus faibles par comptage. Des considérations géologiques permettent de penser que ces derniers résultats sont meilleurs que ceux donnés par la méthode des spectres.

Pour chaque zircon, plusieurs déterminations ont été faites et les erreurs relatives entre les résultats ont toujours été comprises entre 0.50% et 5.00%, valeurs obtenues avec les mélanges synthétiques.

CONCLUSION

Le dosage de traces d'uranium, de thorium et de plomb par fluorescence-X dans les zircons a été mis au point pour des teneurs en ces éléments comprises dans les limites suivantes: 100–2000 p.p.m. pour l'uranium, 100–300 p.p.m. pour le thorium, et 100–400 p.p.m. pour le plomb. Les résultats sont entachés d'une erreur relative comprise entre 0.50% et 5.00%.

L'application de cette méthode est limitée aux zircons de plus de 1700 millions d'années qui contiennent, en règle générale, plus de 100 p.p.m. de plomb, valeur représentant la limite de dosage de la méthode.

La durée de l'analyse d'un zircon est d'environ 4 h; soit préparation de l'échantillon (à partir du zircon purifié et broyé) 30 min; mesures au spectromètre à rayons-X, 1 h par élément (mesures de l'échantillon et de trois standards); interprétation des résultats, 30 min. La durée de préparation des standards n'est pas comprise dans ce temps; elle est d'environ 30 min par standard à partir des mélanges enrichis en uranium, thorium ou plomb.

Je remercie les professeurs A. Buchs et M. Delaloye pour leurs conseils, et le Fonds National Suisse pour la Recherche Scientifique qui a bien voulu mettre à ma disposition l'appareillage nécessaire.

RÉSUMÉ

Une méthode de dosage de l'uranium, du thorium et du plomb dans les zircons, basée sur la mesure au spectromètre à rayons-X de l'intensité des raies $L\alpha^{I}_{1,2}$ de l'uranium et du thorium et $L\beta^{I}_{1,2}$ du plomb, est proposée. A partir de 100 mg de zircon, mis sous forme de pastille, on a déterminé les teneurs suivantes: 100–2000 p.p.m. d'uranium, 100–300 p.p.m. de thorium et 100–400 p.p.m. de plomb, avec une erreur

relative comprise entre 0.50% et 5.00%. La méthode est applicable aux zircons ayant un âge supérieur à 1700 millions d'années.

SUMMARY

A method is proposed for evaluating uranium, thorium and lead in zircons by means of X-ray fluorescence, based on the measurement of the intensities of the $L\alpha^{I}_{1,2}$ line for uranium and thorium and the $L\beta^{I}_{1,2}$ line for lead. With 100 mg of zircon as a compressed tablet, the following contents have been determined: 100–2000 p.p.m. of uranium, 100–300 p.p.m. of thorium and 100–400 p.p.m. of lead. The relative error lies between 0.50% and 5.00%. This method is applicable to zircons older than 1700 million years.

ZUSAMMENFASSUNG

Eine Methode zur Dosierung von Uran, Thorium und Blei in Zirkonen mit Röntgenspektrometer wird vorgeschlagen. Diese Methode basiert auf der Messung der Intensitäten der Linien $L\alpha^{I}_{1,2}$ für Uran und Thorium und $L\beta^{I}_{1,2}$ für Blei. Ab 100 mg Zirkon, in Tablett gepresst, hat man folgende Gehalte bestimmt: 100–2000 p.p.m. Uran, 100–300 p.p.m. Thorium und 100–400 p.p.m. Blei. Der relative Fehler liegt zwischen 0.50% und 5.00%. Diese Methode ist auf Zirkone anwendbar, die ein höheres Alter als 1700 Millionen Jahre haben.

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DUAL-WAVELENGTH SPECTROPHOTOMETRY

PART III. DETERMINATION OF ARSENAZO I IN ARSENAZO III

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In a previous paper[1], a general method of dual-wavelength spectrophotometry for analytical applications was described. This new method is not very familiar in analytical chemistry, therefore, the principle is briefly described here. In this method, light from a highly stabilized tungsten iodide lamp or deuterium lamp is divided into two beams with wavelengths of $\lambda 1$ and $\lambda 2$ in two grating monochromators. The two light beams of different wavelength from the two gratings are time-shared through a single cell by means of a chopper and the difference between the absorbances at wavelengths $\lambda 1$ and $\lambda 2$ is measured.

Instruments of this new type can be easily used as the classical double-beam recording spectrophotometer by self-rocking of two gratings so that $\lambda 1 = \lambda 2$. A detailed description of the apparatus is available in the previous paper[1].

Spectrophotometric analysis for two components generally requires the solution of simultaneous equations. Many schemes have been proposed to simplify the calculations and to lessen the amount of time.

When the dual-wavelength measurement is applied, the simultaneous determination of mixtures, or masking of diverse components can be done very easily and accurately without any calculations[2]. Suppose that a two-component sample contains X and Y. If it is desired to determine Y by eliminating the influence of X, two wavelengths at which X shows the same absorbance are selected from its absorption spectrum. At these wavelengths, the baseline in the dual-wavelength measurement remains level in spite of variations in the concentration of X because $\Delta A_{\lambda 1-\lambda 2}$ equals zero. The wavelengths $\lambda 1$ and $\lambda 2$ are selected according to the shapes of the absorption spectra of the two components. The wavelengths chosen must satisfy the following two fundamental conditions:

1. the coexisting component must show the same absorbance at those wavelengths ($\Delta A_{\lambda 1-\lambda 2} = 0$), so that variations in its concentration have no influence on the measurement;

2. the differential absorbance of the other component to be determined between those wavelengths must show an adequate value. An alternative simple method is also described in this paper.

Recently, the analytical application of mono and bisazo compounds of chromotropic acid has been studied extensively[3]. Two representatives of this group, *o*-arsonophenylazochromotropic acid (arsenazo I) and 2,7-bis-(azo-2)-arsonophenyl-1,8-dihydroxynaphthalene-3,6-disulfonic acid (arsenazo III)[4] have proved to be very useful chromogenic reagents for metals, especially for thorium, uranium, zirconium and rare-earth metals. Generally the synthesis and purification of bisazo compounds, *e.g.* arsenazo III, is very difficult because the preparation reactions are always accompanied by the monoazo compound, *i.e.* arsenazo I. Therefore, purity must be checked.

Although the simultaneous determination of arsenazo I and III by classical spectrophotometric methods has been reported by Nemodruk[5], the method requires the calculation of some mathematical equations. However, although the absorption spectra of arsenazo I and III overlap almost completely (Fig. 1), the spectrophotometric determination of arsenazo I in the presence of large amounts of arsenazo III can be done very easily and accurately without calculations by utilizing dual-wavelength spectrophotometry.[1]

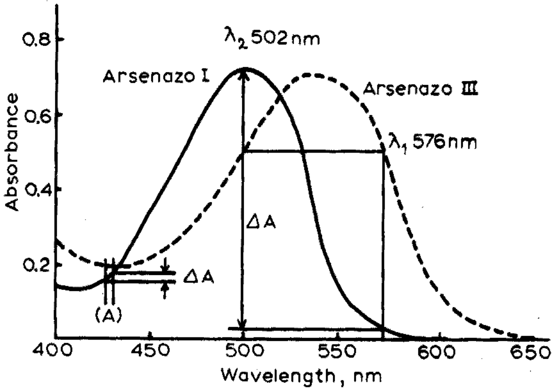


Fig. 1. Selection of $\lambda 1$ and $\lambda 2$ by drawing figures. Determination of arsenazo I in the presence of arsenazo III. pH 2.0, $\lambda 1 = \lambda 2$, 2.0 mg/100 ml of each component.

EXPERIMENTAL

Reagents

Arsenazo I and III solutions. Both reagents (Dotite analytical grade) were purified by recrystallization from water and passage through an alumina column[6]. Aqueous 0.1% (w/v) stock solutions were prepared.

Sulfuric acid of analytical grade (95%) was used. All other reagents were made from high-purity materials or purified reagents, and all solutions were prepared with redistilled water.

Apparatus

A Hitachi 356 two-wavelength spectrophotometer was used with 1-cm quartz cells. This instrument can be used for both dual-wavelength and classical double-beam recording spectrophotometry. A Hitachi M5 type pH meter was used.

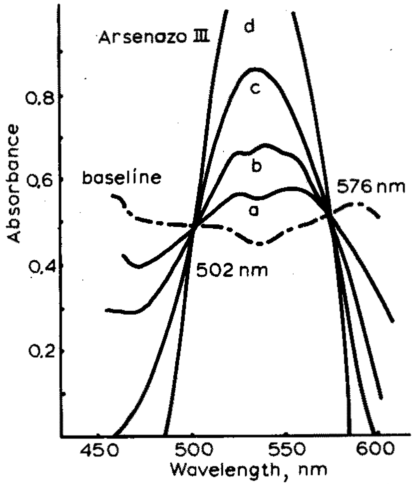
RESULTS AND DISCUSSION

The most important feature of the determination of mixtures is the selection of the optimal wavelengths for $\lambda 1$ and $\lambda 2$ and this procedure is quite simple.

Initial selection of approximate values for $\lambda 1$ and $\lambda 2$

This can be done either by drawing figures or by scanning the diverse component with one wavelength fixed. Figure 1 shows the absorption spectra of arsenazo I and III in aqueous solution at pH 2.0. If the wavelength of maximum absorbance for arsenazo I at 502 nm is chosen as the analytical wavelength, $\lambda 2$, a line is drawn from this peak to the x-axis. A point of intersection is then obtained on the absorption spectrum of arsenazo III, and from this point, a line horizontal to the x-axis is drawn. Another absorption point $\lambda 1$ is thus obtained. At the combination $\lambda 1$–$\lambda 2$, the baseline does not change when the concentration of arsenazo III is altered, *i.e.* $A_{\lambda 1} - A_{\lambda 2} = \Delta A = 0$. Accordingly, any variation in the concentration of the arsenazo III has no influence on the determination of arsenazo I. Of course, at the combination of $\lambda 1$ and $\lambda 2$ selected, the ΔA value for arsenazo I should be sufficiently large. From Fig. 1, the combination 502–576 nm would be selected for this system. Generally, the selection of the combination of $\lambda 1$ and $\lambda 2$ depends on the shape of each spectrum. If the maximum absorbance wavelength cannot be used as the analytical wavelength, any other suitable wavelength on the absorption spectra can be selected.

Although in the above description, $\lambda 1$ and $\lambda 2$ are determined from a single concentration of arsenazo III, it is also possible to use several samples of different concentration. This method then enables any changes in the soluble species, caused by polymerization, dissociation or other chemical or physical effects, to be easily checked from the shapes of the spectra. Initially, it is necessary to choose an analytical wavelength from the normal absorption spectrum of arsenazo I; as mentioned above 502 nm was selected. The fixed wavelength $\lambda 2$ is then dialed at 502 nm, and absorption spectra of various concentrations of arsenazo III are measured, $\lambda 1$ being the scanning wavelength. If any changes in the soluble species have occurred, an isosbestic point can then be observed on the baseline, *i.e.*, the differential absorbance ΔA between 502 nm and this point is zero. Spectra obtained in this way for arsenazo III are shown in Fig. 2.



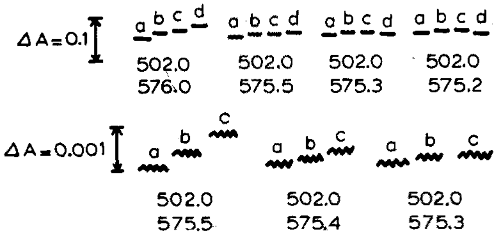


Fig. 2. Selection of $\lambda 1$ and $\lambda 2$ from absorption spectra with $\lambda 2$ fixed (502.0 nm) and $\lambda 1$ as the scanning wavelength. Arsenazo III (mg/100 ml): (a) 1.0, (b) 2.0, (c) 4.0, (d) 8.0.

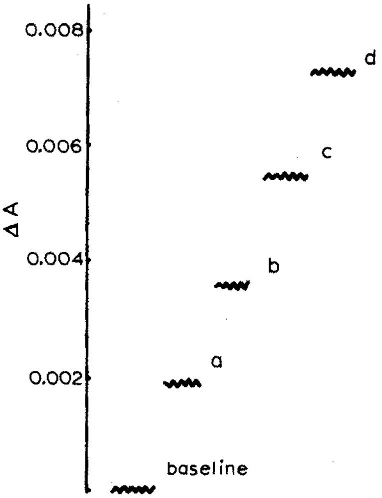
Fig. 3. Precise method for selection of $\lambda 1$ and $\lambda 2$. Arsenazo III (mg/ml): (a) 0.25, (b) 0.50, (c) 1.00, (d) 2.00.

Precise method of selecting suitable wavelengths

Here, the changes in the differential absorbance in response to some variation in the concentration of arsenazo III are measured 5 or 6 times in the vicinity of the temporary wavelength settings, so that $\lambda 1$ and $\lambda 2$ can be finally set at wavelengths which minimize changes in the difference of absorbance.

Advantageously, wavelength $\lambda 1$ is first altered forward or backward by about 1 nm so that the direction and size of the change in the differential absorbance ΔA can be observed. Then both wavelengths are finally adjusted successively until the differential absorbance becomes zero despite variations in the concentration of arsenazo III. An example of the procedure for selecting $\lambda 1$ and $\lambda 2$ is shown in Fig. 3. With a scale range of 0.1 absorbance unit, this procedure presents few problems. But when the range is 0.01 absorbance unit for full scale, great prudence is needed^2.

By this procedure, suitable combination of $\lambda 1$–$\lambda 2$ was established as 502.0–575.3 nm for the determination of arsenazo I in the presence of arsenazo III at pH 2. In the case of determinations of arsenazo III, the optimal selection of $\lambda 1$–$\lambda 2$ can be established by a similar procedure. Figure 4 shows some calibration data for the determination of arsenazo I in the presence of arsenazo III.



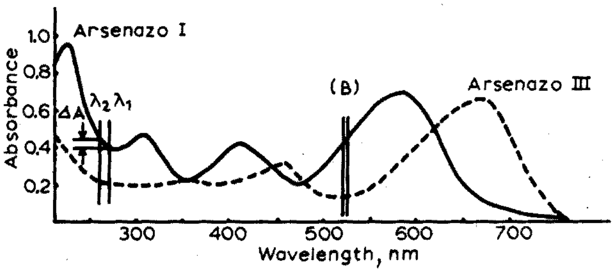


Fig. 4. Determination of arsenazo I in the presence of arsenazo III. pH 2.00, $\lambda 1 = 502.0$ nm, $\lambda 2 = 575.3$ nm. (a) Arsenazo I 0.006 mg/25 ml + arsenazo III 1.0 mg/25 ml. (b) Arsenazo I 0.012 mg/25 ml + arsenazo III 0.25 mg/25 ml. (c) Arsenazo I 0.018 mg/25 ml + arsenazo III 0.50 mg/25 ml. (d) Arsenazo I 0.024 mg/25 ml + arsenazo III 1.50 mg/25 ml.

Fig. 5. Absorption spectra of arsenazo I and III in 92% (v/v) sulfuric acid solution. Arsenazo I, 0.5 mg/25 ml; arsenazo III 0.3 mg/25 ml. $\lambda 1 = \lambda 2$.

Alternative more rapid method

As already described, this dual-wavelength spectrophotometry is useful for the measurement of very small amounts of samples and for observation of the behavior of substances in very low absorbance ranges. Generally, it is possible to find several plateaux between some very narrow wavelengths (1–2 nm) on the absorption spectrum (see Fig. 5); that is, at these wavelengths the baseline in the dual-wavelength measurement remains level in spite of variations in the concentration of the substances because $\Delta A = 0$. Figure 5 shows the absorption spectra of arsenazo I and III in 92% (v/v) sulfuric acid solution. Arsenazo I can be detected qualitatively from the characteristic absorption at 215, 308 and 415 nm,

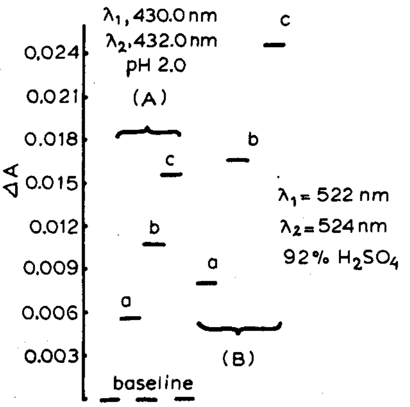


Fig. 6. Determination of arsenazo I in the presence of arsenazo III at various combinations of wavelengths.
(A) pH 2.0, $\lambda 1 = 430.0$ nm, $\lambda 2 = 432.0$ nm.
(a) Arsenazo I 0.8 mg/25 ml + arsenazo III 1.0 mg/25 ml. (b) Arsenazo I 1.6 mg/25 ml + arsenazo III 0.5 mg/25 ml. (c) Arsenazo I 2.4 mg/25 ml + arsenazo III 2.0 mg/25 ml.
(B) 92% (v/v) sulfuric acid solution. $\lambda 1 = 522.0$ nm, $\lambda 2 = 524.0$ nm.
(a) Arsenazo I 0.8 mg/25 ml + arsenazo III 1.0 mg/25 ml. (b) Arsenazo I 1.6 mg/25 ml + arsenazo III 0.5 mg/25 ml. (c) Arsenazo I 2.4 mg/25 ml + arsenazo III 2.0 mg/25 ml.

TABLE I

DETERMINATION OF ARSENAZO I IN THE PRESENCE OF ARSENAZO III

(502.0–575.3 nm)

Arsenazo III (mg/25 ml)	*Arsenazo I (mg/25 ml)*	*Wt.%*	*Arsenazo I found*			
			ΔA	*mg/25 ml*	*Wt.%*	*Error (%)*
—	0.160	—	0.235	—	—	—
0.25	0.160	39.0	0.232	0.158	38.5	−0.5
0.50	0.160	24.2	0.241	0.164	24.8	+0.6
1.00	0.160	13.8	0.233	0.158	13.6	−0.2
1.50	0.160	9.6	0.233	0.158	9.5	−0.1
2.00	0.160	7.4	0.230	0.156	7.2	−0.2
—[a]	0.012	—	0.0041	—	—	—
0.25	0.012	4.5	0.0040	0.011	4.4_6	−0.04
0.50	0.012	2.3	0.0041	0.012	2.3_0	±0.00
1.00	0.012	1.1	0.0039	0.011	1.1_0	±0.00
1.50	0.012	0.79	0.0044	0.012	0.84	+0.05
2.00	0.012	0.59	0.0043	0.012	0.6_2	+0.03

[a] Full scale $\Delta A = 0.01$.

and it can be determined directly at the wavelength combinations of 273.0–262.0, 522.0–524.0 or 430.0–432.0 nm (see Fig. 1).

Figure 6 shows some calibration data at various combinations of $\lambda 1$ and $\lambda 2$, and some typical results by this new measurement are shown in Table I.

SUMMARY

A simple rapid spectrophotometric method for the determination of arsenazo I in the presence of large amounts of arsenazo III by means of a dual-wavelength method is discussed. By proper selection of the combination of two wavelengths, $\lambda 1 = 502.0$ nm and $\lambda 2 = 575.3$ nm, arsenazo III can be masked instrumentally even when its concentration varies. By this method about 0.5–40% of arsenazo I in arsenazo III can be determined very easily and accurately.

RÉSUMÉ

Une méthode spectrophotométrique, simple et rapide est proposée pour le dosage d'arsénazo I, en présence de fortes quantités d'arsénazo III. Elle est basée sur le procédé à double longueur d'onde: $\lambda_1 = 502.0$ nm et $\lambda_2 = 575.3$ nm. L'arsénazo III peut ainsi être masqué instrumentalement même lorsque sa concentration varie. On peut alors dosé environ 0.5 à 40% d'arsénazo I dans l'arsénazo III, très facilement et avec précision.

ZUSAMMENFASSUNG

Eine einfache und schnelle spektrophotometrische Methode für die Bestimmung von Arsenazo I in Gegenwart von grossen Mengen Arsenazo III mit Hilfe einer Zweiwellenlängenmethode wird diskutiert. Durch sorgfältige Auswahl der Kombination zweier Wellenlängen, $\lambda_1 = 502.0$ nm und $\lambda_2 = 575.3$ nm, kann Arsenazo III instrumentell maskiert werden, auch wenn dessen Konzentration variiert. Nach dieser Methode können etwa 0.5–40% Arsenazo I in Arsenazo III sehr leicht und genau bestimmt werden.

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THE DETERMINATION OF TRACE AMOUNTS OF BISMUTH IN STEELS BY SOLVENT EXTRACTION AND ATOMIC ABSORPTION OR ATOMIC FLUORESCENCE SPECTROMETRY

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Headridge and Richardson[1], in a method for the determination of 0.0001–0.01% of bismuth in steels, have shown the need to employ solvent extraction to concentrate the bismuth before its determination by atomic absorption spectrometry. The bismuth was extracted as the iodide complex into isobutyl methyl ketone (MIBK). Good results for the determination of 2–130 μg Bi g^{-1} in cast irons and stainless steels were obtained. The method, however, involves the addition of ascorbic acid to reduce iron(III) and this makes it necessary to add iron to the standard calibration solutions. In addition, a distillation step, to concentrate the organic phase, is incorporated, which is rather time-consuming. More recently, Burke[2] has described a method for the determination of microgram amounts of antimony, bismuth, lead and tin in aluminium, iron and nickel-base alloys by non-aqueous atomic absorption spectrometry. This method involves the quantitative extraction of these elements from a solution which is 10% in hydrochloric acid, 6% in potassium iodide and 2% in ascorbic acid into a 5% solution of trioctyl phosphine oxide (TOPO) in MIBK. Excellent results have been obtained and this procedure promises to be a very useful one.

Ammonium 1-pyrrolidinedithiocarbamate (APDC) has received increasing attention for the extraction of metals before their determination by atomic absorption spectrometry (a.a.s.)[3–5]. Lau *et al.*[6] have made a detailed study of APDC as a reagent for bismuth and have shown the feasibility of both spectrophotometric and atomic absorption spectrometric determination of bismuth in the presence of a large number of diverse ions. The possibility of applying their procedure to the determination of bismuth in highly-alloyed steels has therefore been examined.

In view of the current interest in the potential usefulness of atomic fluorescence spectroscopy (a.f.s.), it was decided to examine the possibility of determining bismuth in steels by a.f.s. in addition to a.a.s. Several workers[7–9] have investigated the fluorescence characteristics of bismuth under a variety of conditions. Bismuth fluorescence has been excited with an iodine electrodeless discharge tube[7] and in later work[8] with an electronically modulated bismuth electrodeless discharge tube. In this latter work a method was described for the determination of bismuth in aluminium alloys by a.f.s. No problem was encountered from scattered radiation and the results obtained were in good agreement with those obtained by a solution spectrophotometric method.

In the present work, it was established that the method of Lau *et al.*[6], with only minor modification, can be applied to the determination of bismuth in highly-alloyed steels and that perfectly satisfactory results are obtained whether the organic phase after extraction is subjected to a.a.s. or a.f.s.

EXPERIMENTAL

Apparatus

A Unicam SP90 atomic absorption spectrophotometer and a bismuth hollow-cathode lamp were used for the atomic absorption measurements.

Standard instrumental conditions

Wavelength	223.1 nm	Air pressure	30 p.s.i.
		flow	5 l min^{-1}
Slit width	0.05 mm		
Burner height	0.4 cm	Acetylene pressure	15 p.s.i.
		flow	0.3 l min^{-1}
Lamp current	12 mA		

For the atomic fluorescence measurements a Jarrell-Ash 82-529 Maximum Versatility Flame Spectrometer was used. Some modification to this instrument was required. It was found that the major contribution to noise came from the photomultiplier tube. The zero control was not capable of completely backing off this noise when the P.M. was operated at high voltages. A 10 kΩ variable resistor was incorporated into the zero control circuit to enable this "backing off" to be effectively carried out at high P.M. voltages.

An argon–hydrogen–oxygen flame, burning on a Hetco total-consumption burner was used for the fluorescence measurements. This flame was selected because of its low background[10] and low quenching characteristics[10,11]. A bismuth electrodeless discharge tube (E.M.I.) was operated in an E.M.S. 214L $\frac{1}{4}$ wave cavity (Electro-Medical Supplies Ltd.) and powered by a Microton 200 Mk II microwave generator (2450 MHz, Electro-Medical Supplies Ltd.). The tube, which was operated at 55 W in the unmodulated mode, was placed at right angles to the optical axis of the spectrometer as in the normally accepted position for fluorescence studies. No mirrors or lenses were used and the cavity was placed near the flame (*ca.* 5 cm). An asbestos shield effectively prevented stray light from the tube from falling on the entrance slit of the monochromator.

Standard instrumental conditions

Wavelength	306.8 nm	Argon pressure	20 p.s.i.
		flow	8 l min^{-1}
E.D.T. power	55 W		
Entrance slit	0.1 mm	Oxygen pressure	10 p.s.i.
		flow	0.5 l min^{-1}
Exit slit	0.15 mm	Hydrogen pressure	10 p.s.i.
		flow	2 l min^{-1}
Burner height	6.5 cm		

Reagents

All reagents used were of analytical-reagent grade.

Bismuth solution A (100 μg ml^{-1}). Dissolve 0.10 g of pure bismuth in 25 ml of water and 40 ml of concentrated nitric acid, and dilute to 1 l with water.

Bismuth solution B (10 μg ml^{-1}). Dilute 10.0 ml of bismuth solution A to 100 ml with water.

APDC solution. Dissolve 0.4108 g of APDC in 100 ml of water. Filter before use. (A fresh solution should be prepared weekly.)

Masking agent. Dissolve 50 g of disodium EDTA and 294 g of trisodium citrate in 267 ml of concentrated ammonia solution and dilute to 1 l with water.

Sodium citrate solution (30% w/v). Dissolve 300 g of trisodium citrate in 250 ml of water. Dilute to 1 l with water.

All solutions were stored in polythene bottles.

Analysis of steels

Dissolve 1.00 g of the steel in 20 ml of concentrated hydrochloric acid and 10 ml of concentrated nitric acid. Evaporate the solution down to *ca.* 5 ml and add 20 ml of water followed by 10 ml of 30% trisodium citrate solution. Add concentrated ammonia until the solution is alkaline and then add a solution of 7 g of disodium EDTA in 70 ml of hot water. Evaporate the solution to *ca.* 30 ml. Transfer to a 125-ml separating funnel, add 10 ml of masking agent solution, and 10 ml of APDC solution. Dilute to 60 ml with distilled water and add 10 ml of MIBK (Note). Shake for 2 min and allow the layers to separate. Discard the aqueous layer and filter the MIBK layer through a Whatman 540 filter paper containing 1 g of anhydrous sodium sulphate into a stoppered polythene bottle. Spray into the flame and read off the bismuth content from the calibration graph.

Note. It may prove more satisfactory to extract with 20 ml of MIBK if an atomic fluorescence measurement is taken. Longer spray times are required for the a.f.s. determination, hence a volume of 10 ml is sometimes inadequate for duplicate readings. This in no way detracts from the a.f.s. method.

Preparation of calibration graph

From a burette transfer 0, 2, 4, 6, 8 and 10 ml of bismuth solution B into separate 125-ml separating funnels. Add 10 ml of masking solution and 10 ml of APDC solution to each. Dilute to 60 ml with distilled water and continue as described above. The calibration graphs, both in atomic absorption and atomic fluorescence, are linear from 0 to 10 μg ml^{-1} bismuth in the MIBK layer. If extraction of bismuth into 20 ml of MIBK is carried out for a.f.s., the calibration graph is linear from 0 to 5 μg ml^{-1}.

RESULTS AND DISCUSSION

Extraction of bismuth–APDC complex and interferences

Lau *et al.*[6] have shown that the bismuth–APDC complex can be quantitatively extracted into chloroform or MIBK from solutions of pH 0 to 12. Since the dithiocarbamates are generally unselective reagents, these authors made a detailed study of the reactions of a large number of ions with APDC in the presence and absence of EDTA and cyanide as masking agents. In the presence of EDTA, citrate and cyanide, no ion in up to at least 40-fold amounts interfered with the atomic absorption determination of bismuth on spraying the MIBK layer into the flame.

In view of the large amounts of chromium, nickel and particularly iron present in a steel sample, it was thought necessary to increase the amount of EDTA present in the aqueous phase to complex all the iron. In addition, it was hoped to perform the determination in the absence of cyanide if possible. If cyanide is absent, copper will form an APDC complex which might interfere. The amount of APDC used in the extraction was therefore increased from that used by Lau *et al.* to ensure complete complexing of bismuth and copper. If a 1-g sample weight is taken, a steel containing 0.005% bismuth extracted into 10 ml of MIBK gives a solution containing 5 μg Bi ml^{-1}. A number of elements, commonly found in steels, in amounts corresponding to their maximum possible concentration in steel, were added to an aqueous solution containing 50 μg of bismuth and the bismuth was extracted into MIBK. The concentration (equivalent percentage in steel) of each element studied is given in parenthesis after each element. There was no interference from iron (100%), chromium (25%), nickel (25%), manganese (10%), molybdenum (5%), vanadium (2%), copper (0.5%), tin (0.5%), aluminium (10%) and cobalt (2%).

Atomic fluorescence of bismuth

It is well known that the bismuth resonance line at 306.8 nm is the most intense fluorescence line[7] but it is generally not used because of the proximity of the hydroxyl band emission which might prove troublesome in an unseparated flame with an unmodulated source. On modulation at 50 Hz, the stability and intensity of the output from the bismuth source was found to decrease and generally proved troublesome. This is in agreement with the findings of Hobbs *et al.*[8]. In view of the low background of the argon–hydrogen–oxygen flame[10], it was hoped that complications caused by variations in the flame background would be minimal and indeed this was found to be the case. Maximum intensity of the source was obtained at a power of 50–55 W in the unmodulated mode. Maximal bismuth fluorescence and minimal background were obtained with a low flow rate of oxygen. Increasing the flow rate of hydrogen increased the fluorescence marginally but also increased the background. It was hoped that since a solvent extraction stage had been incorporated into the procedure, little or no interference from matrix elements would result. This was found to be the case and no interference from elements commonly found in steels was observed. The interference study was carried out in an identical way to that described above for a.a.s. It seems likely that if bismuth is to be determined directly in an aqueous phase with large amounts of other elements present, then a hotter flame may well be required.

Detection limits and linearity of calibration curves

The atomic absorption curve was found to be linear in the range 0–10 μg Bi ml^{-1} in the organic phase with a 1% absorption value of 0.18 μg ml^{-1}. The detection limit, defined as that concentration of bismuth in the organic solution which produces a signal:noise ratio of 1:1, was found to be 0.06 μg ml^{-1} in a.a.s.

In atomic fluorescence the curve was again linear in the range 0–10 μg ml^{-1} with a detection limit, defined as before, of 0.012 μg ml^{-1}. A comparison of the detection limits of the two techniques shows that atomic fluorescence is approximately five times more sensitive than atomic absorption for bismuth in organic solutions.

Recoveries of bismuth by the proposed methods

Bismuth was added to seven steels known not to contain bismuth and the steels were analysed by the proposed method. The results obtained by both atomic absorption and atomic fluorescence are shown in Table I.

TABLE I

RECOVERY OF BISMUTH ADDED TO STEELS

Sample	*Steel*					*Bismuth added (μg)*	*Bismuth found (μg)*	
	% Element						*A.a.s.*	*A.f.s.*
	Ni	*Cr*	*Mo*	*Cu*	*Mn*			
1	12	17	2	0.15	1.5	30	31	31
2	—	1	–	0.10	0.5	10	9	11
3	10	18	0.5	0.25	1	5	5	5
4	—	1	–	0.20	1	30	30	31
5	10	18	1	0.30	1	10	9	10
6	10	18	1	0.20	1	5	5	5
7	10	18	1	0.20	1	10	9	10

TABLE II

THE DETERMINATION OF BISMUTH IN STEELS

Alloy		*Bismuth content*[a] *(μg g^{-1})*	*Proposed methods (μg g^{-1})*	
			A.a.s.	*A.f.s.*
1	18% Cr, 4% Ni	1	1, 1	1.5, 1.5
2		50	51, 51	50, 51
3		68	70, 70	68, 70
4		105	107, 106	104, 106

[a] Values quoted by the British Steel Corporation which represented the average of analyses by other methods, including square-wave polarography, and dithizone and iodide extraction-spectrophotometry.

Application to high-alloy steels

Results for the determination of bismuth in four high-alloy steels by the two methods are shown in Table II. These results are considered perfectly satisfactory.

In conclusion it is considered that this method is an attractive alternative to previously published methods for bismuth in steels. There is very little to choose between the two methods described here. However, for the determination of even lower amounts of bismuth in alloys, *e.g.* at the 0.1 μg g^{-1} level, the a.f.s. method, which is more sensitive, offers more scope and is likely to be the method of choice.

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SUMMARY

A method is described for the determination of 0.0001–0.01% bismuth in high-alloy steels by either atomic absorption spectrometry or atomic fluorescence spectrometry after solvent extraction. After sample dissolution, the bismuth is extracted by ammonium pyrrolidine dithiocarbamate into MIBK and the organic phase is sprayed into an air–acetylene flame (atomic absorption) or an argon–hydrogen–oxygen flame (atomic fluorescence). Extraction of possible interfering elements is prevented by the addition of EDTA and citrate ion. Results for the analysis of four stainless steels are presented.

RÉSUMÉ

Une méthode est proposée pour le dosage du bismuth (de 0.0001 à 0.01%) dans des aciers. On procède soit par spectroscopie d'absorption atomique, soit par spectrométrie de fluorescence atomique. Après dissolution de l'échantillon, le bismuth est extrait par le pyrrolidinedithiocarbamate d'ammonium dans la méthylisobutylcétone. La phase organique est vaporisée dans une flamme air–acétylène (absorption atomique) ou dans une flamme argon–hydrogène–oxygène (fluorescence atomique). Des interférences peuvent être évitées par addition d'EDTA et de citrate.

ZUSAMMENFASSUNG

Es wird eine Methode für die Bestimmung von 0.0001–0.01% Wismut in hochlegierten Stählen durch Atomabsorptionsspektroskopie oder Atomfluoreszenzspektrometrie beschrieben. Nach Auflösung der Probe wird das Wismut durch Ammoniumpyrrolidindithiocarbamat in MIBK extrahiert und die organische Phase in eine Luft–Acetylen-Flamme (Atomabsorption) oder eine Argon–Wasserstoff–Sauerstoff-Flamme (Atomfluoreszenz) gesprüht. Die Extraktion von möglicherweise störenden Elementen wird durch Zugabe von EDTA und Citrat verhindert. Die Ergebnisse der Analyse von vier rostfreien Stählen werden vorgelegt.

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STUDIES ON SOLVENT EXTRACTION TECHNIQUES FOR ACTIVATION ANALYSIS OF SERUM

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Neutron activation analysis (n.a.a.) possesses considerable sensitivity, versatility, and accuracy for the measurement of trace metals in biological materials. A comprehensive review of this field recently has been published[1]. Employment of n.a.a. for measurements on biological materials is complicated considerably by the relatively high concentrations of sodium, potassium, and bromine which, because of their quantity, half-lives and cross-sections, become much more active than the trace metals present in the sample. As a result, the spectra of the trace metals are masked and lost in the Compton radiation and spectra of sodium, potassium and bromine.

A common technique employed in biological studies is post-irradiation radiochemical separation and isolation. Girardi[2] has reviewed the full range of these methods. Ion-exchange resins have been used extensively in this work[3-8], as have non-radioactive carriers[9-11]. Although these methods provide acceptable results, the extensive handling and exposure required have made them undesirable in trace metal screening procedures. Fritze and Robertson[12] reported a unique attempt to separate protein-bound metals by gel filtration before irradiation. These workers accomplished the separation of Cu, Fe, Zn, Al, and Mn with the elimination of sodium. However, post-irradiation separations were still necessary for the determination of As, Ag, Au, Cr, Sb, Co, Cd, Mo, and Sn.

A recent report[13] describes a procedure involving a combination of chemical group separation and high-resolution γ-spectrometry for the quantitative analysis of orchard leaves with some qualitative data on kidney and heart tissue. Sodium was selectively removed on a column of hydrated antimony pentoxide. Solvent extraction methods are often preferred procedures for separations because they are rapid, easy to use, and require little in the way of special equipment. Morrison[14] and Freiser[15] have reviewed separation techniques based on solvent extraction and give many references to specific extraction procedures for individual elements. The use of multiple element extraction, however, has been very limited and is used primarily in gas-chromatographic analyses[16-19]. In recent work by Armitage and Zeitlin[20], solvent extraction was used to extract and concentrate several elements for X-ray fluorescence analysis.

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The present investigation was undertaken to develop procedures for the simultaneous measurement of several trace metals in biological samples by using pre-irradiation, solvent extraction, and neutron activation analysis. The purpose of this study was to examine several established selective extraction procedures and determine their applicability to multiple element extraction. In addition, the use of pre-irradiation solvent extraction was examined with respect to interferences and advantages in analyzing biological samples for trace metals. Four chelating systems, ammonium pyrrolidinedithiocarbamate (APDC), diethyldithiocarbamate (DDTC), acetylacetone, and dithizone, were selected as worthy of study after a review of existing extraction systems. These systems showed similar extraction conditions for the elements of interest as well as the potential of modification for multiple element extraction. Significant work with APDC systems in aqueous solutions has been reported[21-24] and the application of APDC to biological material has been summarized by Christian[25]. Sandell[26] and Morrison and Freiser[27] have reviewed the application to biological material of the other three extraction systems.

EXPERIMENTAL

Apparatus

The central vertical port of the University of Florida Training Reactor (UFTR) was used exclusively for this work. The pulse-height spectra were measured with a 55-cm^3 nominal active volume Ge(Li) detector (Model LGCC-8.0–2.7, Nuclear Diodes, Inc., Prairie View, Ill. 60069) and stored in a 400-channel pulse-height analyzer (Model 34–27, Nuclear Chicago Corp., Gainesville, Fla. 32601). Readout was obtained through an ASR Model 33 Teletype and/or a Model 850 x–y plotter (Data Equipment Co., Santa Ana, Calif. 92705). A PDP-8/L laboratory computer (Digital Equipment Co., Maynard, Ma. 01754) was used for calculations and data reduction.

A Model LTA-600 five-chamber radiofrequency low-temperature dry asher (Tracerlab, Richmond, Calif. 94802) was used to ash serum samples. The oxidation chambers were redesigned to permit the use of a single container for drying, ashing, and extracting samples up to about a 5-ml volume. The predrying step was carried out in a heated vacuum desiccator. A Model 450 gas purifier (Matheson Gas Products, Morrow, Ga. 30260) was used to filter the oxygen before its introduction into the oxidation chamber.

Pyrex glassware was used whenever possible. Disposable Pasteur pipets were used in transferring liquid samples. The ashing and extraction vessels were 6-dram screw cap vials (Kimble, Toledo, Ohio 43601, Cat. No. 60910-L) whose caps were fitted with Teflon laminated discs after the cardboard seals had been removed. The glassware was thoroughly washed in nitric acid before use. Pipets were stored in acid-washed covered containers while the other glassware was kept covered to prevent contamination.

Reagents

All reagents used were of analytical-grade purity (>99%) and were used without any further purification. Reagent-grade ethyl acetate and methyl isobutyl ketone were redistilled before use. Commercially prepared ionic buffer solutions of pH 3.0, 4.0, 7.4, 8.0, and 10.0 (Hartman-Leddon Co., Philadelphia, Pa. 19143) were obtained and purified by extraction with methyl isobutyl ketone.

Extraction solutions

The following solutions were prepared: APDC, 2% (w/v) in methyl isobutyl ketone (MIBK); DDTC, 2% (w/v) in ethyl acetate; dithizone, 0.01% (w/v) in MIBK; acetylacetone, 20% (w/v) in MIBK.

Acid digestion mixture

Three volumes of concentrated nitric acid were mixed with 3 volumes of 60% perchloric acid and 1 volume of concentrated sulfuric acid. All concentrated acids used were of ultrahigh purity (Aristar, B.D.H., Ltd., Poole, England).

Serum

A serum pool from hospital patients was obtained; only nonicteric and non-lipemic specimens were used.

Radioactive tracer solution

Ultrapure chromium (1.0 mg), selenium (10 mg), silver foil (1 mg), zinc foil (300 mg), iron foil (50 mg), rubidium wire (100 mg) and cadmium carbonate (0.3 mg) (Alpha Inorganics, Beverly, Ma. 01915) were irradiated for 16 h in the UFTR. The irradiated materials were dissolved in the minimal volume of appropriate mineral acids and a mixture of these metal solutions was diluted to 500 ml with pH 7.4 phosphate buffer.

Serum radioactive tracer solutions

Two tracer-spiked serum samples were prepared during the present investigation. One solution did not contain chromium tracer (direct extraction studies) and the other solution did not contain cadmium tracer (dry-ash extraction studies).

The radioactive tracer solution (5 ml) was diluted to 500 ml with the pooled serum. Final concentrations of radioactive tracer solutions in the serum were selenium 20 μg/100 ml, silver 2 μg/100 ml, rubidium 200 μg/100 ml, and either chromium 2 μg/100 ml or cadmium 0.4 μg/100 ml. These concentrations are approximately those encountered in physiological serum samples. Obviously, the actual concentrations present in the spiked serum pool were greater than those listed above owing to the endogenous levels of the metals already present in these pooled samples.

Irradiation and counting

Samples were irradiated in a neutron flux of *ca.* $3.2 \cdot 10^{12}$ n cm^{-2} s^{-1} for 16 h to produce satisfactory activities. Wide-mouth polyethylene screw-cap sample bottles of 5-ml and 10-ml volumes (Cole-Parmer Instrument Co., Chicago, Ill. 60648) were found to be satisfactory for the irradiation of solid and aqueous solutions. The bottles were cleaned before use by soaking for 48 h in chloroform followed by rinsing in acid and distilled-deionized water. The samples were sealed in the containers by melting the caps to the bottles with a soldering iron. Quartz breakseal vials were drawn from 12-mm clear fused quartz (Amersil, Inc., Hillside, N.J. 07205) and used to irradiate the organic solutions. The acid-washed quartz vials were filled by means of disposable Pasteur pipets cooled in liquid nitrogen and sealed with an oxygen–natural gas torch. The contents were refrozen after irradiation and the necks of the vials broken. After thawing, the solutions were transferred with disposable pipets to 60 × 15-mm Petri dish bottoms and sealed with silicon sealer (General Electric Co.) and 2-in watch glasses. The PDP-8/L computer was programmed to calculate the activities of a number of elements for a series of irradiation and decay times using the activation equation. From this study it was determined that an irradiation time of 16 h was necessary to obtain a satisfactory activity for the elements of interest.

Photopeaks were positively identified by spectra comparison with standard samples. Portions of the pure metals and compounds were irradiated and sealed in plastic 60 × 15-mm Petri dishes. Spectra of these samples were then obtained and compared with those of the samples for the positive identification of spectral components. All samples obtained from the solvent extraction experiments were counted for a period of 10 h.

In the extraction experiments, both the radioactive tracer-spiked serum and the nonirradiated serum pool were used. In the tracer studies the serum and the organic extracts were counted to determine the extraction efficiencies of the various metals used as tracers. In the nontracer serum studies the organic extracts of the serum were irradiated in the UFTR and then counted at 24-h intervals over a 1 week period to determine the extent of sodium, potassium, and bromine extraction. Distilled water blanks were also extracted and the organic layers irradiated to determine reagent contamination.

Extraction directly from serum

A method similar to that developed by Hwang *et al.*[28] for the atomic absorption spectrometric measurement of lead in blood was used. To 2.5 ml of serum was added 5.0 ml of formamide, 2.5 ml of extraction solution and 10 ml of MIBK or ethyl acetate, depending on the solvent used in the extraction solution. Thorough mixing was carried out after the addition of each reagent, and the aqueous and organic layers were allowed to separate.

Low-temperature ashing

Before ashing all samples were dried in a desiccator at 60° for 12 h. Samples were then ashed for 10 h at a radiofrequency power of 250 W, an oxygen flow of 0.7 gauge units, and a chamber pressure of 0.7–1.0 mm Hg. The ash was dissolved in 4 ml of buffer (pH 4.0 for APDC extractions; pH 3.0 for DDTC; pH 8.0 for acetylacetone; and pH 10.0 for dithizone), with vigorous mixing for 2 min. The dissolved ash solutions were extracted with 4 ml of the respective extraction solutions by mixing on a Vortex mixer for 30 s and separating the aqueous and organic layers by centrifugation.

Extraction following acid digestion

Acid digestion coupled with extraction in APDC and MIBK was evaluated by the following procedure:

Serum (5 ml) and 5 ml of distilled deionized water were transferred in duplicate to separate 50-ml centrifuge tubes. Aliquots (5 ml) of the acid digestion mixture were added to each of the tubes which were then heated in an oil bath at 135° for 1 h. These tubes were allowed to cool to room temperature (23°) and placed in an ice bath. The solutions were adjusted to pH 4.0 with concentrated ammonia solution. Buffer pH 4.0 solution (10 ml) and 2 ml of APDC in MIBK were added to each tube and mixed vigorously. MIBK (10 ml) was added to each tube, mixed on a Vortex mixer for 1 min and centrifuged for 5 min at 2000 r.p.m. to separate the organic and aqueous layers. The organic layers were transferred to quartz snap-neck vials with Pasteur pipets.

RESULTS

Direct extraction

The direct extraction of metals from serum was greatly complicated by the formation of precipitates and the coagulation of serum proteins. Immediate coagulation occurred with APDC and dithizone, while with acetylacetone and DDTC a white flocculent precipitate appeared about 5 min before the serum fully coagulated. All four systems lost much of the organic solvent in the agglutination process yielding only 5–8 ml of the original 10-ml volumes in separation. It was felt that this loss was due to the trapping of the solvent in the gelatinous mass. The degree of solvent recovery was found to be DDTC > dithizone > acetylacetone > APDC.

TABLE I

DIRECT EXTRACTION OF TRACE METALS FROM SERUM

Element	*Extraction efficiency (%)*							
	APDC–MIBK		*DDTC–ethyl acetate*		*Acetylacetone–MIBK*		*Dithizone–MIBK*	
	Mean	s_r	*Mean*	s_r	*Mean*	s_r	*Mean*	s_r
Cd	8.8	±2.38	8.5	±5.76	8.6	±5.67	12.3	±6.63
Se	11.8	±1.73	3.8	±1.78	1.6	±1.05	12.5	±7.13
Ag	42.8	±5.71	10.8	±3.66	9.0	±4.00	55.8	±8.46
Rb	9.4	±5.92	1.5	±0.90	2.5	±1.01	12.5	±7.24
Zn	78.4	±3.70	32.4	±4.42	8.9	±0.88	90.3	±9.94
Fe	4.5	±2.57	6.9	±5.67	8.7	±3.44	9.6	±7.09

The results of the extraction of tracer-spiked serum are summarized in Table I. Five aliquots of spiked serum were extracted and the percentage proportions of Cd, Se, Ag, Rb, Zn, and Fe which were extracted are given. The extraction of zinc and silver was good but not quantitative. The other metals, Cd, Se, Rb, and Fe, gave poor extractions. The results of extraction of the pooled serum followed by irradiation of the organic phase showed that very small amounts of interfering sodium, potassium, and bromine were extracted. The distilled water blanks were free of metal contamination.

Low-temperature dry ashing

In order to check the loss of trace metals, serum spiked with radioactive

TABLE II

EXTRACTION OF TRACE METALS FROM A DRY ASH OF SERUM

Element	*Extraction efficiency (%)*							
	APDC–MIBK		*DDTC–ethyl acetate*		*Acetylacetone–MIBK*		*Dithizone–MIBK*	
	Mean	s_r	*Mean*	s_r	*Mean*	s_r	*Mean*	s_r
Se	12.5	±10.92	12.1	± 5.84	0.7	±0.45	1.7	±1.02
Cr	16.7	± 6.65	17.0	± 5.00	3.8	±2.54	15.6	±8.47
Ag	27.4	±13.57	55.5	±27.04	2.5	±1.69	31.9	±3.21
Rb	1.3	± 0.82	12.0	± 5.60	0.7	±0.38	1.7	±0.93
Zn	51.5	±23.31	23.0	± 9.45	5.8	±0.49	4.9	±2.64
Fe	52.5	±23.14	39.5	±12.72	12.1	±2.96	4.9	±3.61

tracers was carried through the entire procedure and the activity of each tracer was measured before and after drying or ashing. Quantitative recoveries of each metal were obtained after the drying step and after the serum at 100, 150, 200, and 250 W of radiofrequency power.

The extraction efficiencies of the four chelation–extraction systems for Se, Cr, Ag, Rb, Zn, and Fe are given in Table II. As with the direct extraction experiment, extractions were carried out on five aliquots of serum, and the proportion of metals extracted is presented. The best results were obtained with the APDC–MIBK and DDTC–ethyl acetate systems although extraction efficiencies were far from quantitative. Irradiation of extracts from pooled serum not containing radioactive tracers showed that very little sodium was extracted; the activated sodium decaying to tolerable levels within one week. Some bromine was extracted with the acetylacetone–MIBK system but not with the other systems. Distilled water blanks extracted under the same conditions as the serum were free of metal contamination.

Acid digestion

Pre-extraction acid digestion of the serum proteins was attempted. Even with ultrapure reagents, the blank extracts generally were found to contain quantities of metals and other contaminants comparable to those in the serum extracts. The total volume of the extraction mixture often reached 40–50 ml, and the volume of ammonia solution needed to neutralize the acid was not constant, thus leading to different volumes of solution to be extracted. The neutralization of the acid also was often violent and posed a safety problem. The major γ-ray energy peaks that were identified by this method were bromine, sodium, and potassium. The activities of the remaining metals, if present in the extract, were too low to be detected.

DISCUSSION

The purpose of the present investigation was to obtain good separations of trace metals from serum, retaining sodium, potassium, and bromine in the aqueous phase. In this laboratory, direct analysis of serum showed sodium as a dominant species in the γ-ray spectra until about 39 days after irradiation. Bromine and potassium disappeared from the spectra after 7 days.

Solvent extraction was the separation technique investigated since minimal technical manipulations should be required and reagents could be purified from trace metal contaminants. Direct extraction of metals from serum should provide the simplest approach but in the present study recoveries of activated Cd, Se, Rb, and Fe were very low, probably because of competitive binding of these metals to proteins, amino acids, and other serum constituents. Silver and zinc gave better extraction recoveries but only with the APDC–MIBK and DDTC–ethyl acetate systems. Attempts to remove all organic material from the serum before extraction involved acid digestion and low-temperature dry ashing. The former technique introduced contaminants and was unsatisfactory. Low-temperature dry ashing provided some promising results with the APDC–MIBK and DDTC–ethyl acetate systems with most of the interfering sodium, potassium, and bromine being eliminated during the extractions.

Results from all of these studies indicate the considerable problems associated with the chelation–solvent extraction of trace metals from serum samples. In no instance could quantitative recoveries of any metal be obtained and, thus, none of the chelation systems investigated could be applied to the routine analysis of serum by neutron activation.

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SUMMARY

Studies on the possible use in neutron activation analysis of serum of solvent extraction before irradiation, are presented. Various chelating solvent extraction systems were studied with and without prior ashing or acid digestion of the serum sample. Solvent extraction eliminates most of the interfering sodium, potassium, and bromine in the extract, but extraction efficiencies of a variety of trace metals were variable and never quantitative.

RÉSUMÉ

Une étude est effectueé pour examiner les possibilités d'utilisation d'extraction en solvant pour l'analyse par activation neutronique du sérum. Divers systèmes de chélates sont étudiés, avec et sans incinération préalable ou digestion acide de l'échantillon de sérum. L'extraction dans un solvant élimine une grande partie du sodium, du potassium et du brome; cependant les rendements sont généralement variables et jamais quantitatifs.

ZUSAMMENFASSUNG

Untersuchungen über die mögliche Verwendung der Solventextraktion vor der Bestrahlung bei der Neutronenaktivierungsanalyse von Serum werden vorgelegt. Verschiedene chelatisierende Solventextraktionssysteme wurden teils mit vorhergehender Veraschung oder Säurebehandlung der Serumprobe, teils ohne dieselben untersucht.

Die Solventextraktion schaltet die grössten Anteile von störendem Natrium, Kalium und Brom im Extrakt aus, jedoch war die Extraktion bei einer Anzahl Spurenmetalle unterschiedlich wirksam und niemals quantitativ.

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RADIOCHEMICAL STUDIES ON THE LIQUID–LIQUID EXTRACTION OF SEVERAL ELEMENTS IN FUSED MANGANESE NITRATE HEXAHYDRATE–TRI-*n*-BUTYL PHOSPHATE IN VARIOUS DILUENTS

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Several attempts have been made to obtain higher distribution ratios than those obtained in the usual liquid–liquid extraction systems consisting of organic and simple aqueous phases. One of them is the extraction system to which a salting-out agent was added, and another is that consisting of organic and anhydrous molten salt phases at temperatures above 150°. However, there are a few disadvantages in these liquid–liquid extraction systems[1]. Therefore, Akatsu and Asano[1] suggested the use of a fused salt hydrate with a melting point near room temperature as the inorganic phase in place of the aqueous or the anhydrous molten salt phase. The inorganic phase studied was manganese nitrate hexahydrate (m.p. 25.8) or calcium chloride hexahydrate (m.p. 29.9), and the organic phase was tri-*n*-butyl phosphate in dodecane. The distribution ratios of some metal ions were determined at 30°, and were higher than those measured in the system of tri-*n*-butyl phosphate *vs.* nitric or hydrochloric acid. In this work, the use of other diluents, *i.e.*, xylene, chloroform and 1-hexanol, was examined for the manganese nitrate hexahydrate tri-*n*-butyl phosphate system at 30°. Distribution ratios of several elements were radiochemically determined in these systems.

EXPERIMENTAL

Materials

The reagents and the radioactive tracers were the same as reported previously[1], except for diluents. Xylene, chloroform and 1-hexanol (JIS special grade) were used as received.

Determination of distribution ratios

Distribution ratios were determined by the batch extraction method, where solutions containing 1.0, 2.0, 5.0, 7.5, 10, 20, 50, 75 and 100% (v/v) tri-*n*-butyl phosphate (TBP) in each of the diluents were used as the organic phases, and manganese nitrate hexahydrate fused at 30° was used as the inorganic phase. The organic phases were used after pre-equilibration with the inorganic phase. Two kinds of determination (Method I and Method II) were made by the experimental procedure described previously[1]. In Method I, a radioactive tracer was used and its gross γ-ray activity was measured above the γ-ray energy of 0.060 MeV with a conventional NaI(Tl) scintillation counter. A mixture of fission products was used as tracers and γ-ray spectrometry was done in Method II. When high distribution ratios of thorium and uranium(VI) were determined, the γ-ray activity of tracers was made high enough to reduce statistical errors in the count rate.

Measurement of γ-ray absorption

Ethanol (99.5%), distilled water and fused manganese nitrate hexahydrate were selected as solvents. The radioactive tracers used were cesium–barium-137 and cerium–praseodymium-144; the γ-rays emitted have, for the most part, energies of 0.662 and 0.133 MeV, respectively[2]. Each tracer was dissolved in distilled water; 1-ml aliquots of the solution were poured into 63 measuring bottles. The solutions in 42 bottles were evaporated to near dryness; 1-ml aliquots of ethanol and fused manganese nitrate hexahydrate were poured into the other 21 bottles. The γ-ray activity of the 63 samples was measured by scintillation counting. The measuring bottles and the scintillation counters were the same as those used in the determination of distribution ratios.

RESULTS AND DISCUSSION

Deviation and experimental error of distribution ratios

Table I shows the known specific gravity of the various solvents. The value for the solvent of the measured samples was considered to be between 1.82 (manganese nitrate hexahydrate) and 0.7511 (dodecane). Solvents with various specific gravities were found to result in different count rates for the same γ-ray activity; the measured count rate depended on the solvent and also on γ-ray energy of the nuclide (Table II), hence corrections were necessary. For this purpose, many different samples, containing the same γ-activity in a wide variety of solvents and nuclides, would have to be prepared in order to clarify all the necessary values of the γ-ray absorption rate; for the specific gravity of the solvent has no simple relation to the γ-ray absorption rate. Instead of this, it was considered that the

TABLE I

SPECIFIC GRAVITIES OF REAGENTS

Solvents			*Temp. (°)*	*Specific gravity (d_4^T)*
Components of organic phase	Diluent	Dodecane	20	0.7511
		Xylene[a]	Room temp.	0.86–0.87
		Chloroform	20	1.4890
		1-Hexanol	25	0.8158
	Extractant	TBP	20	0.9766
Inorganic phase		Manganese nitrate hexahydrate	21	
			30	1.72 (liquid)[b]
Another solvent		Ethanol	20	0.7893

[a] A mixture of *o*-, *m*- and *p*-xylene. [b] Measured value.

TABLE II

COUNT RATES FOR DIFFERENT SOLUTION MEDIA

γ-Ray emitter		*^{137}Cs–Ba*	*^{144}Ce–Pr*	*^{144}Ce–Pr*
NaI(Tl) scintillation counter		*A*	*A*	*B*
Average count rate (counts min^{-1})^a in	ethanol	7110 ± 91	40300 ± 350	50600 ± 440
	water	6830 ± 71	38900 ± 450	49000 ± 320
	$Mn(NO_3)_2 \cdot 6\,H_2O$	6720 ± 90	36000 ± 240	45000 ± 370
Average of the three^a		6900 ± 410	38000 ± 2200	48000 ± 2900
Number of samples		21 × 3	21 × 3	21 × 3
Ratio of count rate for	$\frac{\text{Ethanol}}{\text{Mn salt}}$	1.06 ± 0.020	1.12 ± 0.012	1.12 ± 0.013
	$\frac{\text{Water}}{\text{Mn salt}}$	1.02 ± 0.017	1.08 ± 0.014	1.09 ± 0.011
s_r (%)		12.0	11.6	12.0

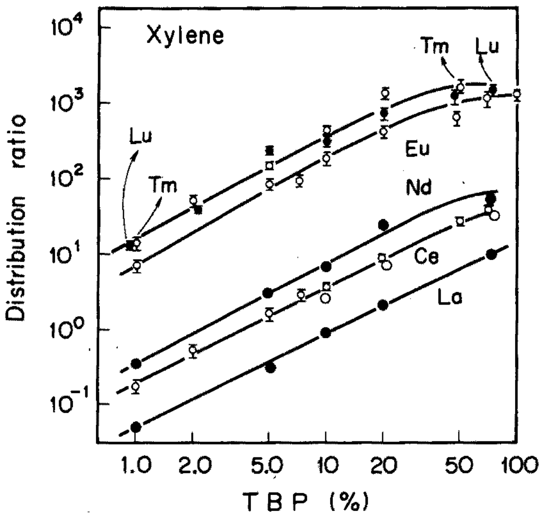
[a] With standard deviation.

measured count rates, with a wide variety of deviations from the real count rates, could be regarded as possessing "experimental error". In order to estimate the "experimental error", the count rates measured for samples of the same radioactivity in three different solvents, were assumed to show a normal distribution, and the relative standard deviation was calculated. The relative standard deviation, with 95% confidence, was calculated by using 63 values, which are not shown in Table II; in Table II, only three values of the average count rate are shown.

There were further experimental errors such as sampling errors, statistical errors of counting, etc. Experiments involving γ-ray absorption were done in the same manner as the liquid–liquid extraction, so that errors, except for statistical counting errors, were included in the determined relative standard deviation, S_r. The results are shown in Table II, where it can be seen that the relative standard deviation depends neither on the γ-ray energy nor on the scintillation counter used. Thus a value of 12% was adopted as the relative standard deviation for all the count rates measured in this study. However, statistical counting errors arising from radioactive decay, could not be contained in the value of 12%, and so were calculated for each count rate with 95% confidence. In practice, the statistical counting error was found to be twice the standard deviation, Δn_s. Then a total counting error, Δn, was computed by the use of

$$\Delta n = \pm\{(0.12n)^2 + (2\Delta n_s)^2\}^{\frac{1}{2}}$$

where n is a value of the count rate. The Δn values were used to calculate the errors in the distribution ratios. In some cases, especially thorium, determinations were repeated several times, and an average Δn value was computed. The errors thus obtained are shown in the Figures for all the distribution ratios determined by Method I.



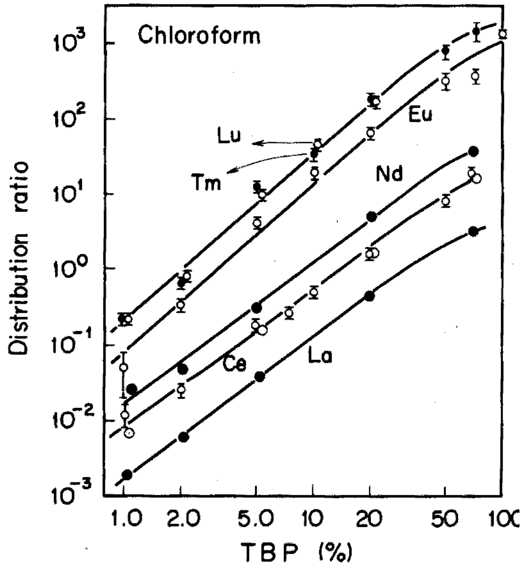


Fig. 1. Distribution ratios of some elements of the lanthanum series with postulated errors. ($\overline{\underline{\circ}}$, $\overline{\underline{\bullet}}$) Method I. (○, ●) Method II.

Fig. 2. Distribution ratios of some elements of the lanthanum series with postulated errors. Symbols as in Fig. 1.

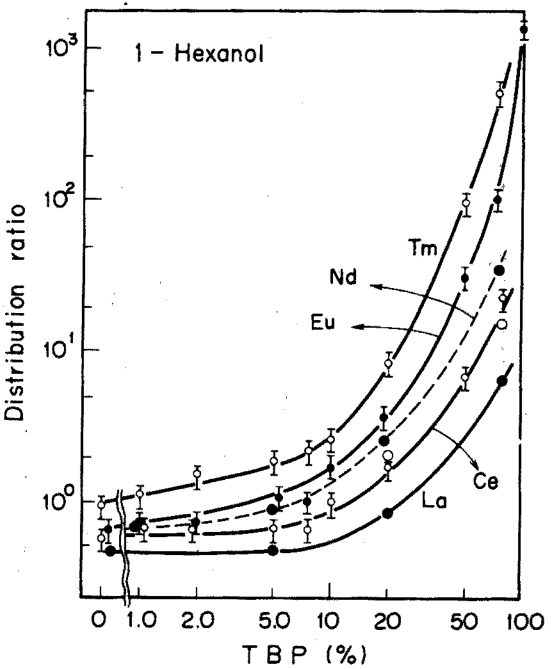


Fig. 3. Distribution ratios of some elements of the lanthanum series with postulated errors. Symbols as in Fig. 1.

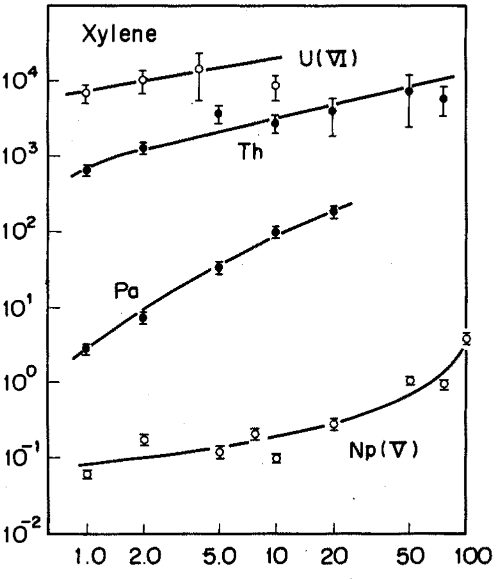


Fig. 4. Distribution ratios of some actinide elements with postulated errors. Symbols as in Fig. 1.

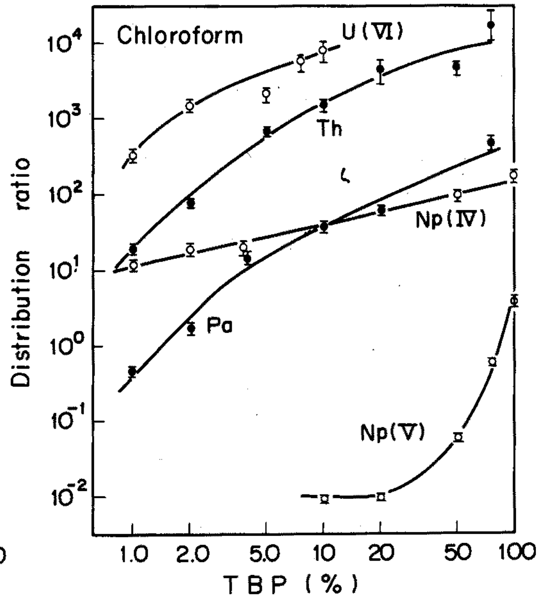


Fig. 5. Distribution ratios of some actinide elements with postulated errors. Symbols as in Fig. 1.

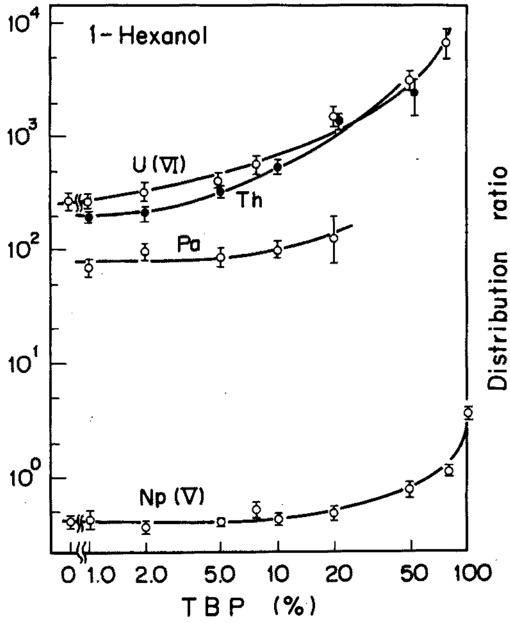


Fig. 6. Distribution ratios of some actinide elements with postulated errors. Symbols as in Fig. 1.

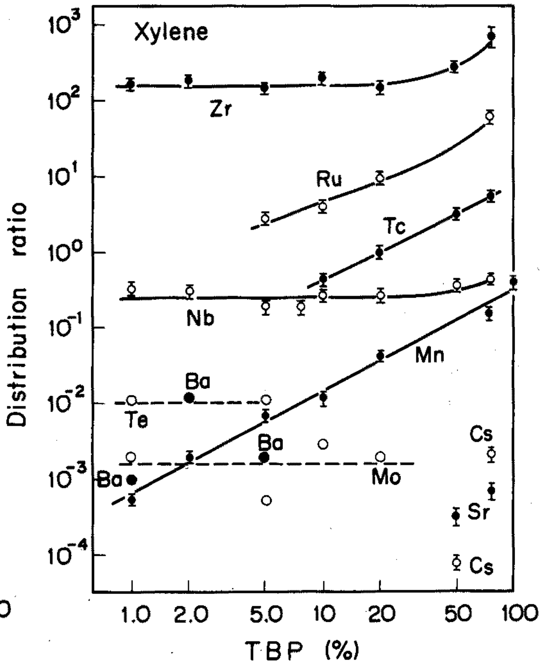


Fig. 7. Distribution ratios of some elements of fission products with postulated errors. Symbols as in Fig. 1.

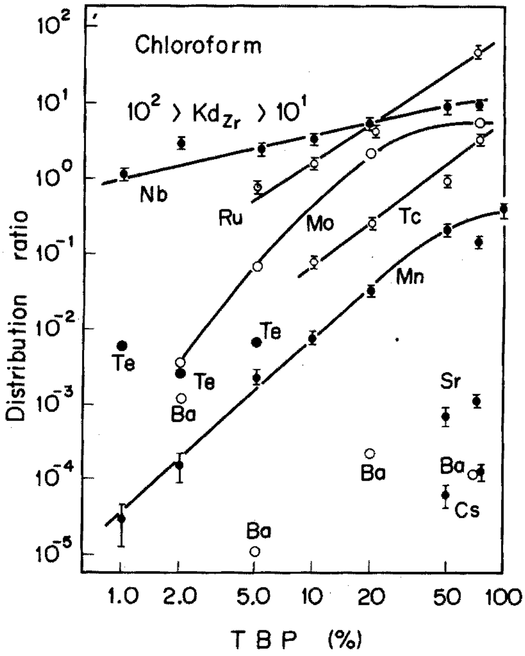
Distribution ratios of elements

The distribution ratios of some elements of the lanthanum series are shown in Figs. 1–3. The ordinate shows the distribution ratios and the abscissa the initial concentration of TBP in logarithmic scale.

McKay *et al.*[3,4] and Peppard *et al.*[5] have shown that the distribution ratios of the lanthanon elements increase with increasing atomic number in the 100% TBP–nitric acid system. Although the behavior of all the lanthanon elements was not studied, a similar tendency is seen in the TBP–manganese nitrate hexahydrate system, when xylene or chloroform was used as a diluent; but the dependence was small when 1-hexanol was used as diluent.

The distribution ratio of some actinide elements are shown in Figs. 4–6. Uranium(VI) and thorium showed distribution ratios more than 10^2, except for those of thorium at TBP concentrations below 2% in chloroform.

The distribution ratios of some fission products are shown in Figs. 7–9. When xylene was used as diluent, the distribution ratios of niobium did not depend on the concentration of TBP in the range 1–75% (about $3 \cdot 10^{-1}$), although the organic phases were scrubbed two times with fresh inorganic phase. This value was lower than those obtained with dodecane[1], chloroform and 1-hexanol as



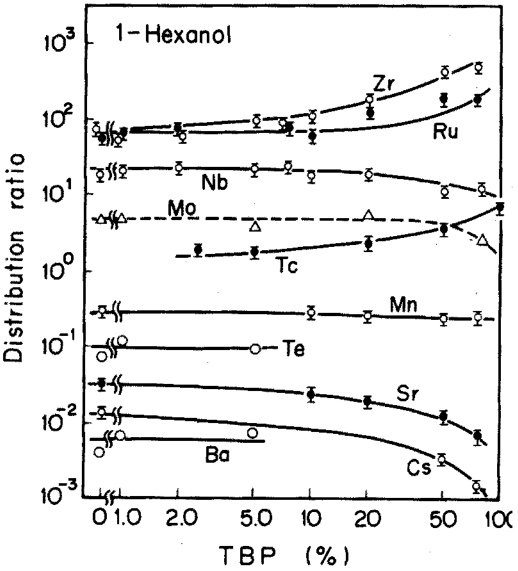
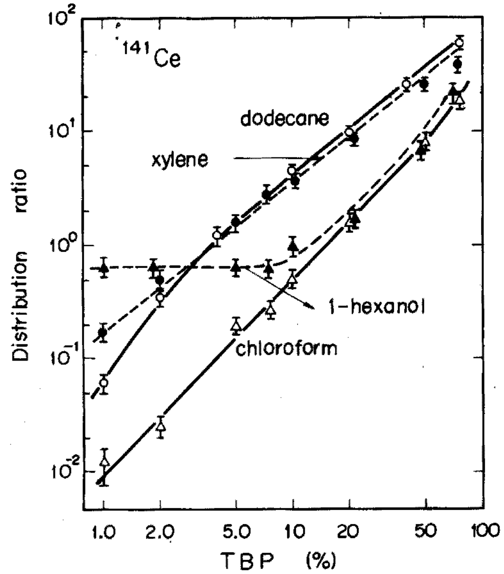


Fig. 8. Distribution ratios of some elements of fission products with postulated errors. Symbols as in Fig. 1.

Fig. 9. Distribution ratios of some elements of fission products with postulated errors. Symbols as in Fig. 1.



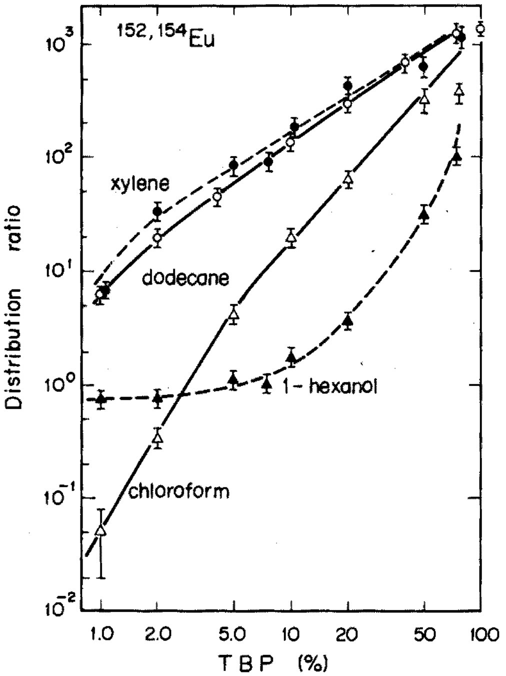
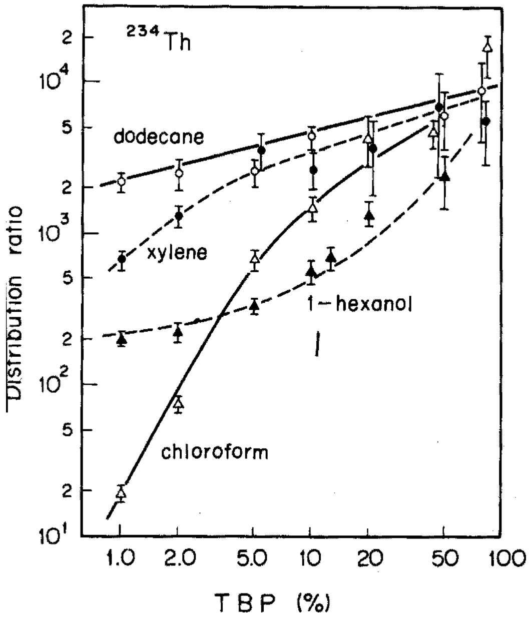


Fig. 10. Distribution ratios of ^{141}Ce with various diluents.

Fig. 11. Distribution ratios of ^{152,154}Eu with various diluents.



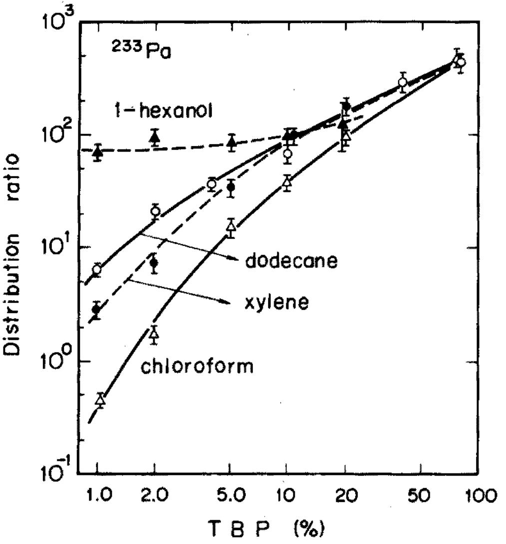


Fig. 12. Distribution ratios of ^{234}Th with various diluents.

Fig. 13. Distribution ratios of ^{233}Pa with various diluents.

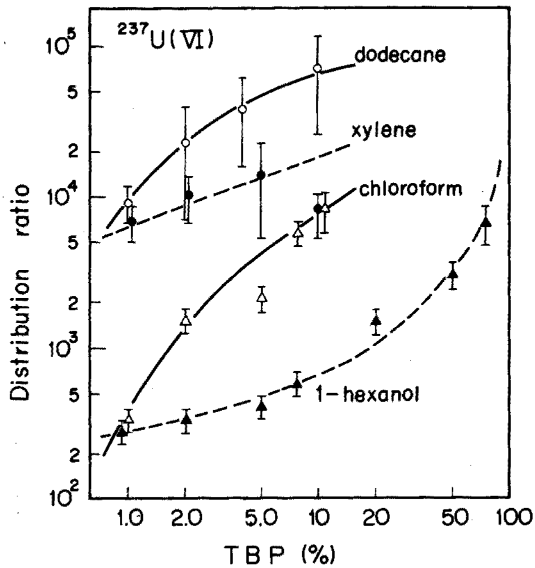


Fig. 14. Distribution ratios of ^{237}U with various diluents.

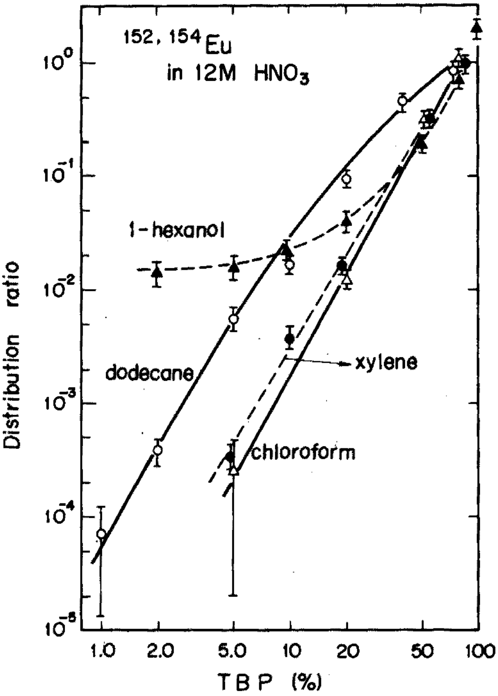


Fig. 15. Distribution ratios of ^{152,154}Eu in 12 M nitric acid with various diluents.

diluents. Repeated experiments showed the same values. Molybdenum showed a similar behavior in the xylene diluent system. Its distribution ratios were about $2 \cdot 10^{-3}$ in 1–20% TBP in xylene. Distribution ratios below $3 \cdot 10^{-2}$ were obtained for cesium, strontium and barium. The distribution ratios of manganese, which was a component of the inorganic phase, are also shown in Figs. 7–9.

Effect of diluents

The effect of the diluents for TBP on the distribution ratios is shown in Figs. 10–14 for cerium(III), europium, thorium, protactinium and uranium(VI). The Figures show TBP concentration dependence curves for each element with various diluents. It was found that the distribution ratios measured with dodecane diluent were approximately the same as those with xylene diluent but were higher than those with chloroform diluent in dilute TBP regions. A similar phenomenon was found in the TBP–nitric acid extraction system (Fig. 15) and has also been reported by other investigators[6, 7]. This may be due to the strong polarity of chloroform compared with dodecane and xylene[8].

The distribution ratios in 1-hexanol below 5% TBP showed a slight dependence on the concentration of TBP and were practically the same as those measured without TBP. Thus pure 1-hexanol must play a prominent role in the extraction of metal ions at low TBP concentrations in TBP–1-hexanol systems.

TABLE III

COMPARISON OF DISTRIBUTION RATIOS IN THE CONCENTRATED NITRIC ACID OR MANGANESE NITRATE HEXAHYDRATE–20% TBP SYSTEMS IN VARIOUS DILUENTS

Inorganic phase		*Conc.* HNO_3				$Mn(NO_3)_2\cdot 6\,H_2O$			
Temperature		*Room*				*30°*			
Organic phase		*20% TBP in*				*20% TBP in*			
		Dodecane	*Xylene*	*Chloroform*	*1-Hexanol*[a]	*Dodecane*	*Xylene*	*Chloroform*	*1-Hexanol*
Distribution ratio of	U(VI)	9.4	7.7	5.9	—	$6\cdot10^4$	$3\cdot10^3$	$1\cdot10^4$	$1.5\cdot10^3$
	Th	7.7	1.6	$8.9\cdot10^{-1}$	$6.0\cdot10^{-1}$	$5\cdot10^3$	$3\cdot10^3$	$2\cdot10^3$	$1.4\cdot10^3$
	Tm	2.3	$2.3\cdot10^{-1}$	$1.7\cdot10^{-1}$	$2\cdot10^{-2}$	$5.5\cdot10^2$	$1.3\cdot10^3$	$1.5\cdot10^2$	8.2
	Eu	$3.8\cdot10^{-1}$	$6.8\cdot10^{-2}$	$3.3\cdot10^{-2}$	$4.0\cdot10^{-2}$	$3.1\cdot10^2$	$4.2\cdot10^2$	$6.4\cdot10$	3.7
	Ce(III)	$5.1\cdot10^{-2}$	$5.2\cdot10^{-2}$	$1.7\cdot10^{-2}$	—	9.9	8.6	1.6	1.7

[a] 12 *M* HNO_3 was used as an aqueous phase because NO_2 gas was evolved when the concentrated acid was used.

The comparison of distribution ratios with those in aqueous nitrate systems

In the previous work[1], it was found that the distribution ratios of some elements were higher in the manganese nitrate hexahydrate–TBP–dodecane system at 30° than in concentrated nitric acid system at room temperature. Similar phenomena were found when xylene, chloroform and 1-hexanol were used as the diluents (Table III). The values for uranium(VI) in Table III are not the highest possible in the nitric acid system, since a maximum is shown in the acidity-dependence curve of the distribution ratios of uranium(VI)[9,10]. The maximum values were not determined with the same diluents, but they are about 30 in a 5 *M* nitric acid–19% TBP–kerosene system at 25° [9] and about 50 in a 7 *M* nitric acid–25% TBP–carbon tetrachloride system at room temperature[10]. However, the values in the manganese nitrate hexahydrate–20% TBP system are still considered to be higher than the maximum values in the nitric acid system.

Distribution ratios for uranium(VI) and thorium have been reported in the TBP–nitric acid system with a salting-out agent[11,12]. In these cases the distribution ratios seemed to be lower than those in the manganese nitrate hexahydrate system.

The authors wish to express their thanks to Dr. K. Ueno, Japan Atomic Energy Research Institute, for his advice.

SUMMARY

The liquid–liquid extraction of several elements was radiochemically studied in several fused manganese nitrate hexahydrate (m.p. 25.8°)–tri-*n*-butyl phosphate–diluent systems at 30°; the diluents were xylene, chloroform and 1-hexanol. The distribution ratios of several elements were higher than those in nitric acid systems with each diluent. The dependence of the distribution ratios on various diluents was almost similar to that in nitric acid systems.

RÉSUMÉ

Une étude radiochimique est effectuée sur l'extraction liquide–liquide de plusieurs éléments dans divers systèmes: nitrate de manganèse hexahydrate fondu (p.f. 25.8°)–tri-n-butylphosphate–diluant; xylène, chloroforme et hexanol-1 ont été choisis comme diluants. Les coefficients de partage sont plus élevés que ceux obtenus dans un système acide nitrique correspondant.

ZUSAMMENFASSUNG

Die Verteilung verschiedener Elemente zwischen Mangannitrat–Hexahydrat-Schmelze (Fp. 25.8°) und verdünntem Tri-n-butylphosphat wurde bei 30° radiochemisch untersucht. Die Verdünnungsmittel waren Xylol, Chloroform und 1-Hexanol. Die Verteilungsverhältnisse verschiedener Elemente waren grösser als jene in den Salpetersäuresystemen bei allen Verdünnungsmitteln. Die Abhängigkeit der Verteilungsverhältnisse von den verschiedenen Verdünnungsmitteln war etwa die gleiche wie in Salpetersäuresystemen.

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UTILISATION DES CHELATES DE DICETONES-β POUR L'ANALYSE QUANTITATIVE DE L'URANIUM ET DU THORIUM

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L'heptafluoro-1,1,1,2,2,3,3 diméthyl-7,7 octanedione-4,6 [H(fod)] forme avec les métaux uranium et thorium les chélates U(fod)$_4$ et Th(fod)$_4$[1]7[2].

Ces chélates sont suffisamment volatils pour être élués en chromatographie en phase gazeuse et une étude qualitative de leur séparation a déjà été mentionnée[2]. Dans le présent travail, nous avons étudié les possibilités d'utilisation de la dicétone H(fod) pour effectuer l'extraction par solvant et l'analyse quantitative du thorium(IV) et de l'uranium à ses deux degrés d'oxydation (IV) et (VI). D'autre part, nous avons défini les conditions permettant une telle analyse par chromatographie en phase gazeuse.

TECHNIQUES EXPÉRIMENTALES

Extraction par solvant de l'uranium

Nous avons étudié l'extraction de l'uranium sous ses deux degrés d'oxydation. En général, les solutions aqueuses d'uranium contiennent le métal à son degré d'oxydation +6; cependant, nous savons[2] que le complexe le plus stable formé avec la dicétone H(fod) correspond au chélate U(fod)$_4$ dans lequel l'uranium est au degré d'oxydation +4.

Extraction de l'uranium(IV). Une solution contenant environ 5 g d'uranium par litre est préparée en dissolvant du chlorure d'uranyle (K and K Lab. Inc, Hollywood, Calif.) dans 500 ml d'acide chlorhydrique 0.8 *M*. La réduction totale de l'uranium en U(IV) est obtenue en faisant passer cette solution sur une colonne en verre de 30 cm de longueur et 15 mm de diamètre remplie de grenaille de plomb[3] de granulométrie 20–100 mesh (Mallinckrodt Chemical Works, St. Louis, U.S.A.). On recueille à la sortie de la colonne la fraction contenant U(IV) et on y détermine la teneur en uranium sur une partie aliquote. Pour cela, on réoxyde l'uranium en U(VI) par l'acide nitrique et on procède à un dosage spectrométrique, à 400 nm, du complexe uranium–dibenzoylméthane[4].

Les extractions par solvant sont effectuées à différents pH sur cette solution selon le processus suivant.

A une fraction de 1 ml de solution, on ajoute 15 mg de citrate trisodique afin d'éviter toute précipitation à des pH supérieurs à 2. Le pH est fixé à la valeur choisie par addition d'acide chlorhydrique ou de soude. On complète à 10 ml avec de l'eau distillée et on ajoute 10 ml d'une solution benzénique à 5% en masse de H(fod). On agite le mélange pendant 10 min dans une ampoule à décanter et on sépare les deux phases.

La phase aqueuse est amenée lentement à sec en présence d'acide nitrique et d'acide sulfurique pour détruire toute trace éventuelle de matière organique et oxyder l'uranium sous la forme U(VI). Après remise en solution, l'uranium est dosé selon la méthode déjà mentionnée[4].

Il est très difficile de déterminer avec précision la quantité de métal présente dans l'autre phase: la nature organique du solvant gêne l'analyse spectrométrique. On peut cependant étudier le comportement de cette solution en chromatographie en phase gazeuse.

Extraction de l'uranium(VI). L'extraction par une solution benzénique de H(fod) est possible et la solution organique est stable, bien que le complexe extrait, isolé sous forme solide, présente une décomposition très rapide.

Nous avons préparé une solution aqueuse d'uranium(VI) contenant environ 5 g d'uranium par litre à partir de sulfate d'uranyle cristallisé ($UO_2SO_4 \cdot 3.5\ H_2O$, British Drug Houses Ltd). Les extractions sont effectuées sur des fractions de 1 ml de solution auxquelles on ajoute 20 mg d'acétate de sodium afin d'éviter la précipitation à des pH supérieurs à 2. Le pH est fixé par addition d'acide sulfurique ou de soude et on complète à 10 ml avec de l'eau.

L'extraction et le dosage de l'uranium restant dans la phase aqueuse sont conduits selon le processus décrit précédemment.

Extraction par solvant du thorium

Les extractions ont été effectuées à partir d'une solution de nitrate de thorium ($Th(NO_3)_4 \cdot 4\ H_2O$; Nobel Bozel, Cuise la Motte, Oise) contenant *ca.* 1 g Th l^{-1}.

A 1 ml de cette solution, on ajoute 5 ml d'une solution d'acétate d'ammonium à 250 g l^{-1}. On fixe alors le pH par l'acide nitrique ou la soude et on complète à 10 ml par de l'eau distillée. Après addition de 10 ml d'une solution benzénique de H(fod) à 5‰, on agite pendant 10 min, puis on sépare les deux phases. La phase aqueuse est amenée à sec en présence d'acide sulfurique. Après remise en solution dans un mélange acide perchlorique acide tartrique, le thorium est dosé par spectrométrie du complexe formé avec le thorin, à 545 nm.

Chromatographie en phase gazeuse

L'appareil utilisé est un chromatographe "Microtek" modèle 2500 R II équipé d'un détecteur à ionisation de flamme.

La colonne est constituée d'un tube en verre "Pyrex" de 1.5 m de long et 4 mm de diamètre intérieur rempli de billes de verre (60–80 mesh) imprégnées à 0.5% en masse de graisse DC/QF (Applied Science Laboratories, State College, Pa.).

Le gaz vecteur est l'hélium à un débit de 65 $cm^3\ min^{-1}$.

Les chélates sont injectés en solution benzénique à l'intérieur d'un tube en verre "Pyrex" placé dans l'injecteur en acier inoxydable afin de protéger ce dernier d'une attaque chimique éventuelle.

La température du détecteur est fixée à 200°.

Pour les déterminations quantitatives un étalonnage préalable nous a permis d'exprimer la réponse du détecteur en quantité d'électricité par gramme de métal injecté à partir de la mesure de la surface des pics.

RÉSULTATS ET DISCUSSION

Extraction

Les rendements d'extraction des chélates d'uranium(IV) et (VI) et de thorium, par une solution benzénique de H(fod), sont présentés en fonction du pH sur la Fig. 1.

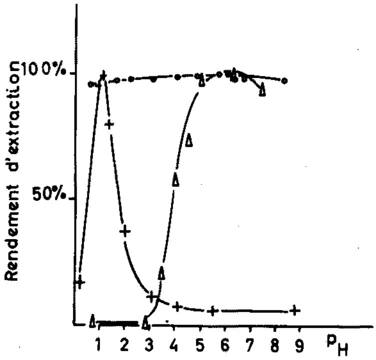

Fig. 1. Variation du rendement d'extraction de l'uranium et du thorium par une solution benzénique de H(fod) en fonction du pH. (○) Th(IV), (+) U(IV), (≂) U(VI).

On y voit qu'en choisissant convenablement la valeur du pH, il est possible de procéder à une séparation quasi-complète de ces métaux.

Chromatographie en phase gazeuse

Détermination quantitative du thorium. Les températures d'injecteur et de colonne sont fixées respectivement à 175° et 170°. Plusieurs injections successives de 0.5 μl d'une solution benzénique de $Th(fod)_4$ à 10 g Th l^{-1} donnent des pics asymétriques présentant une traînée importante, de surface et de hauteur non reproductibles. On peut observer alors, sur le tube en verre "Pyrex" placé dans l'injecteur, un dépôt noir. Ce dépôt est localisé dans la région proche de l'extrêmité de l'aiguille au moment de l'injection; il se dissous facilement dans le mélange sulfochromique. Après nettoyage et remontage du tube on obtient des pics symétriques et reproductibles. Après une quinzaine d'injections, la dissymétrie et le manque de reproductibilité réapparaissent et s'amplifient rapidement avec les injections suivantes. Ces difficultés sont vraisemblablement dues à une destruction partielle du chélate dans l'injecteur et il semble que les produits de décomposition favorisent cette réaction.

Si l'on essaie de réduire ce phénomène en abaissant la température de l'injecteur à 150°, on n'observe plus l'élution du chélate. La température minimale d'injection compatible avec la volatilité du complexe est de 160°. Dans ces conditions, le phénomène de décomposition intervient encore notablement.

Une diminution de la température de colonne à une valeur inférieure à 170° ne permet pas une élution correcte du chélate et conduit à un chromatogramme difficilement exploitable.

Afin de concilier les impératifs résultant de ces observations, la température de l'injecteur a été fixée à 160° et celle de la colonne à 170°. Toutefois, pour obtenir des résultats reproductibles, il est indispensable de nettoyer le tube en verre "Pyrex" placé dans l'injecteur après un nombre maximum de 10 injections.

Dans ces conditions, il est possible de procéder à des déterminations quantitatives. La méthode a été testée par des injections de 1 μl de solutions connues en $Th(fod)_4$. La reproductibilité sur les mesures des aires des pics est de $\pm 4\%$.

La courbe d'étalonnage est une droite passant par l'origine ainsi que le montre la droite de regression $y=ax+b$ déterminée à partir de cinq points expérimentaux. Les valeurs de a/σ_k et b/σ_l sont respectivement 24 et -1.92. Le facteur de réponse du détecteur à ionisation de flamme vis-à-vis de ce chélate est de $2.7 \cdot 10^{-3}$ C g^{-1} de thorium et la limite de détection d'environ 1 μg de métal.

Détermination quantitative de l'uranium. Là encore, il est très difficile d'obtenir des résultats reproductibles: on observe une décomposition du chélate $U(fod)_4$, en particulier au niveau de l'injecteur. Toutes les tentatives faites pour supprimer ou limiter cette décomposition se sont soldées par un échec (variation des températures d'injecteur et de colonne; nettoyage du tube en verre de l'injecteur entre chaque injection; injection de solvant pur entre chaque injection de solution de chélate).

Cependant, la détermination quantitative de l'uranium a pu être effectuée à partir des solutions benzéniques résultant de l'extraction de U(VI) décrite précédemment. Les températures de l'injecteur et de la colonne étant fixées à 150°, l'injection de 1 μl de cette solution donne, en plus du pic du solvant, un second pic dû à la présence du chélate.

Comme dans les expériences précédentes, on constate un manque de reproductibilité des résultats que l'on peut là aussi attribuer à une décomposition du complexe ainsi qu'en témoigne la présence de résidus solides sur la surface du tube en verre "Pyrex" placé dans l'injecteur. Un abaissement de la température de l'injecteur n'apporte pratiquement pas d'amélioration. Par contre, un nettoyage systématique du tube en verre après chaque essai et l'introduction de 1 μl de benzène pur entre chaque injection d'une solution de chélate permet d'obtenir une bonne reproductibilité.

On a pu, en prenant ces précautions, effectuer des déterminations quantitatives du complexe d'uranium(VI), c'est-à-dire du chélate instable à l'état solide, alors que le composé $U(fod)_4$ ne peut être analysé quantitativement par chromatographie en phase gazeuse. L'étalonnage de la méthode est réalisé à partir de solutions de chélate obtenues par dilution d'une solution à 37.5 g U l^{-1}, concentration déterminée par spectrométrie. Pour ces essais, les températures d'injecteur et de colonne sont fixées respectivement à 140° et 150°; l'injection de 1 μl de solution donne un pic dont la surface est reproductible à $\pm 4\%$.

La courbe d'étalonnage est une droite passant par l'origine ainsi que le montre la droite de regression $y=ax+b$ déterminée à partir de cinq points expérimentaux. Les valeurs de a/σ_k et b/σ_l sont respectivement de 32 et -0.38.

Le facteur de réponse du détecteur à ionisation de flamme vis-à-vis de ce chélate est de $2.4 \cdot 10^{-2}$ C g^{-1} d'uranium et la limite de détection d'environ 1 μg de métal. Cette limite est du même ordre de grandeur que celle relative au thorium bien que le facteur de réponse du détecteur soit environ dix fois plus grand car la résolution des pics du solvant et du chélate d'uranium est incomplète.

Analyse d'un mélange uranium–thorium

Nous avons montré[2] que l'on peut séparer par chromatographie en phase gazeuse les complexes de H(fod) et des métaux Th et U(IV). Cependant, nous venons de voir que dans les conditions de la chromatographie la détermination quantitative de U(IV) n'est pas possible. Une analyse simultanée du thorium et de l'uranium par cette méthode doit donc être effectuée sur la forme U(VI).

L'analyse des deux chélates à une température isotherme de 170° montre que le complexe d'uranium(VI) n'est pas séparé du solvant. Il est inutile d'envisager une analyse à température plus basse puisque nous avons vu que la détermination quantitative du thorium est alors impossible. Une programmation de la température de la colonne permet d'une part une séparation satisfaisante du solvant et du chélate de U(VI) et d'autre part l'exploitation quantitative du chromatogramme. La température de la colonne est maintenue à 145° pendant 6 min, c'est-à-dire jusqu'à élution du complexe d'uranium(VI), puis portée à 175° à une vitesse de 10° min^{-1}. Le chélate de thorium est élué au bout de 10 min (Fig. 2).

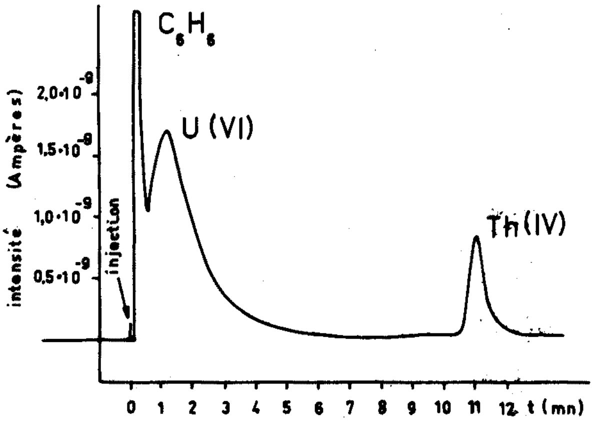

Fig. 2. Analyse chromatographique d'un mélange Th–U(VI). Colonne: température isotherme de 145° pendant 6 min puis programmée jusqu'à 175° à 10° min^{-1}. Injecteur 155°. Détecteur 200°. Débit d'hélium 65 $\text{cm}^3\ \text{min}^{-1}$.

CONCLUSION

Les résultats précédents montrent qu'il est possible d'extraire le thorium et l'uranium {sous la forme U(IV) et sous la forme U(VI)} par une solution benzénique de H(fod). Le domaine de pH pour lequel le rendement d'extraction du thorium est voisin de 100% est très étendu. Au contraire, pour l'uranium(IV) et (VI) ces domaines sont restreints et très différents. Il en résulte une méthode immédiate de séparation de ces métaux.

On a pu montrer par ailleurs que la séparation chromatographique du thorium et de l'uranium(VI) était possible. De plus des conditions opératoires très strictes ont été établies qui permettent leurs déterminations quantitatives. Les précisions obtenues sont ici légèrement inférieures à celles données par l'analyse spectrométrique. Cependant, la méthode est plus rapide et l'emploi d'un détecteur à capture d'électrons, ayant un facteur de réponse vis-à-vis des composés fluorés plus grand que celui du détecteur à ionisation de flamme, permettrait d'améliorer les performances de l'analyse chromatographique.

RÉSUMÉ

Les extractions du thorium, de l'uranium(IV) et de l'uranium(VI) ont été effectuées par une solution benzénique d'une dicétone β fluorée. Ces extractions sont quantitatives dans des domaines de pH très différents. Les conditions expérimentales de l'analyse quantitative de ces deux métaux par chromatographie en phase gazeuse des chélates extraits ont été définies.

SUMMARY

Thorium and uranium(IV, VI) can be extracted with a solution of 1,1,1,2,2,3,3-heptafluoro-7,7-dimethyloctane-4,6-dione [H(fod)]. Extraction of thorium is quantitative in the pH range 3–7, but the pH ranges for quantitative extraction of uranium are very narrow {pH 1.2±0.1 for U(IV) and pH 6–7 for U(VI)}. Thorium and uranium(VI) can be determined by gas–liquid chromatography of their extracted H(fod) chelates, the limit of detection being *ca.* 1 μg of metal with a flame ionisation detector; strict experimental conditions are essential to avoid errors from decomposition of the chelates. The thorium and uranium(VI) chelates can be readily separated by temperature programming.

ZUSAMMENFASSUNG

Thorium und Uran(IV, VI) können mit einer Lösung von 1,1,1,2,2,3,3-Heptafluor-7,7-dimethyloktan-4,6-dion [H(fod)] extrahiert werden. Die Extraktion von Thorium ist im pH-Bereich 3–7 quantitativ, jedoch sind die pH-Bereiche für die quantitative Extraktion von Uran sehr eng (pH 1.2±0.1 für U(IV) und pH 6–7 für U(VI)). Thorium und Uran(VI) können durch Gas–Flüssig-Chromatographie ihrer extrahierten H(fod)-Chelate bestimmt werden; die Nachweisgrenze ist *ca.* 1 μg Metall bei einem Flammenionisationsdetektor; genaue experimentelle Bedingungen sind wesentlich zur Vermeidung von Fehlern durch Zersetzung der Chelate. Die Chelate von Thorium und Uran(VI) können durch Temperatur-Programmierung leicht getrennt werden.

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ADSORPTION BEHAVIOR OF VARIOUS METALS ON A WEAKLY BASIC ANION-EXCHANGE RESIN IN SULFURIC ACID MEDIA

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Systematic studies on the behavior and separation of metals on anion-exchange resins in sulfuric acid or sulfate media are comparatively few. Bunney *et al.*[1] have determined the distribution coefficients for 11 radioactive traces with Dowex 2 in sulfuric acid solutions. Danielsson[2] has reported the anion-exchange characteristics of 26 metals on Dowex 1 in sulfuric acid solutions of varying concentration. Strelow and Bothma[3] have presented the anion-exchange distribution coefficients with Bio-Rad AG 1 for as many as 52 metals in sulfuric acid media and have shown several elution curves for multicomponent systems. Scattered pieces of information on the adsorption and separation of metals in sulfuric acid or sulfate media are also available[4–6] and have been reviewed[7].

Less information has been published about the inorganic analytical use of weakly basic resins. Recently Fritz and Kaminski[8] have investigated the analytical potential of a weakly basic macroreticular resin for the quantitative separation of metals in thiocyanate media. In a previous paper[9], the present authors have described the adsorption behavior of some 40 metals with a phenol condensation type of anion-exchange resin, Amberlite CG-4B, in hydrochloric acid media, demonstrating many useful analytical separations. The work was extended in this paper to examine the adsorption characteristics of some 20 metals on CG-4B in sulfuric acid solutions of varying concentration. Many separations of analytical interest were also conducted to demonstrate some possibilities inherent in this anion-exchange system.

EXPERIMENTAL

Reagents and apparatus

The resin used was a condensed phenol type, the weakly basic anion-exchange resin, Amberlite CG-4B, Type 1, of 100–200 mesh, in the chloride form. After a preliminary wash with 3 *M* hydrochloric acid and deionized water to remove fines, the resin was placed in a large column and a sufficient volume of 1 *M* hydrochloric acid and 1 *M* sodium hydroxide was passed alternately through the column until the effluent became colorless. The resin was converted to the sulfate form by 0.5 *M* sulfuric acid and then washed thoroughly with deionized water until the pH of the effluent reached about 2.3. The resin was dried at 40° for 24 h and stored in a desiccator containing saturated potassium bromide solution.

Conventional ion-exchange columns of i.d. 1.0 or 1.2 cm, pulled to a tip and plugged with glass wool at the outlet, were used. Portions (5 g) of the dried resin were slurried with deionized water and poured into the columns. The beds were 14.5 or 9.5 cm long depending on the bore.

Stock solutions of metals were prepared by dissolving the appropriate amounts of their sulfate or oxyacid salt in sulfuric acid of varying concentration to yield usually 1–10 mg of metal per ml of the solution. Each stock solution was standardized by a conventional analytical method.

Analytical reagent-grade chemicals were used whenever possible.

Measurement of distribution coefficient

Measured amounts of the resin (0.5 g) and a definite volume of sulfuric acid (20 ml) of varying concentration, which contained *ca.* 0.2 mequiv. of each metal, were mixed and agitated for 20 h at 25.0±0.1°. The distribution coefficient was computed according to the formula: K_d = amount of metal per gram resin/amount of metal per ml solution.

Column separation procedure

The column was pretreated before use with sufficient of the sulfuric acid to be used as eluent. A sample solution of 10–20 ml was adjusted to the desired concentration of sulfuric acid, which varied according to the metal ion pair to be separated. The sample was allowed to pass down the column at a flow rate of 1 ml min^{-1}. The less adsorbable metal then was eluted with sulfuric acid, the concentration of which was the same as used for sample preparation. Metal remaining on the column was then removed by elution with an appropriate eluent. Procedures for individual separations will be given later. Analytical methods used for effluent analysis are summarized in Table I.

TABLE I

ANALYTICAL METHODS USED

Metal	*Method*
Al(III), Ga(III)	Titration with EDTA to Cu–PAN indicator.
Be(II)	Colorimetrically with 8-hydroxyquinaldine.
Cr(III)	Colorimetrically with diphenylcarbazide.
Cu(II)	Titration with EDTA to 1-(2-pyridylazo)-2-naphthol indicator.
Hf(IV), U(VI)	Colorimetrically with arsenazo III.
In(III)	Colorimetrically with 1-(2-pyridylazo)-2-naphthol.
Fe(III), Mo(VI)	Colorimetrically with thiocyanate.
Mg(II)	Titration with EDTA to eriochrome black T indicator.
Sc(III), Y(III), rare earths(III), Th(IV)	Titration with EDTA to xylenol orange indicator. Traces determined colorimetrically with arsenazo III.
Ti(IV)	Colorimetrically with hydrogen peroxide.
V(IV, V)	Colorimetrically with 4-(2-pyridylazo)resorcinol.
W(VI)	Colorimetrically with dithiol.
Zr(IV)	Colorimetrically with quercetin.

RESULTS AND DISCUSSION

In Table II are listed the distribution coefficients obtained for metals as a function of sulfuric acid concentration. The metals are arranged in the decreasing order of their distribution coefficients in 0.5 *M* sulfuric acid medium. Aluminum(III), beryllium(II), copper(II), gallium(III), magnesium(II), the rare earth metals(III) and yttrium(III) were found not to adsorb on Amberlite CG-4B to any great extent from 0.1 *M* sulfuric acid and were not included in Table II.

TABLE II

DISTRIBUTION COEFFICIENTS OF METALS ON AMBERLITE CG-4B IN SULFURIC ACID SOLUTIONS

Ion	*Concentration of H_2SO_4 (M)*								
	0.005	0.015	0.05	0.1	0.25	0.5	1	1.5	2
W(VI)[a]	>3000	>3000	>3000	2910	1780	1570	1560	1600	1310
Zr(IV)		15300	14700	5930	1340	380	62	25	16
Mo(VI)	98100	4310	1650	801	410	180	89	74	52
Mo(VI)[a]			3810	1950	236	128	55	42	36
U(VI)	3120	1700	791	493	240	120	58	34	24
Hf(IV)		>10000	25200	2490	350	100	29	27	16
Cr(III)	12	5.1	10	20	29	23	14	7.5	13
Ti(IV)[a]			45	46	24	18	6.9	11	8.5
Th(IV)	900	258	81	40	19	11	6.6	3.7	3.1
V(IV)[a]	121		44		33	6.0		3.0	
Sc(III)	44	32	17	12	7.6	3.2	3.5	1.2	<0.5
V(IV)	65	28	13	6.1	3.4	1.7	0.7	<0.5	<0.5
V(V)	300	44	12	5.0	2.6	1.4	0.9	<0.5	<0.5
In(III)	7.5	4.6	2.9	1.8	1.3	1.0	0.8	<0.5	<0.5
Fe(III)	5.7	4.2		1.1				<0.5	<0.5
La(III)	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5

[a] 0.15% H_2O_2 present.

The valence states given in Table II are those of the metals when contacted with the resin. A couple of metals afforded evidence of reactions other than simple exchange. Thus chromium(VI) was reduced almost quantitatively to the trivalent state in contact with resin in 0.5 *M* sulfuric acid; when fed on to the top of a small column, the upper layer of the resin bed turned black and deteriorated, and a green solution, which gave no reaction with diphenylcarbazide, was eluted from the column. Iron(III) was also reduced, so that the K_d values for iron(III) in Table II are only tentative.

Distribution coefficients in the region from 0.005 *M* to 2 *M* decreased generally with increasing concentration of sulfuric acid. An exception was chromium(III), which showed a possible maximum at about 0.25 *M* sulfuric acid concentration. The metals showing high adsorption on CG-4B also exhibited high adsorption on Dowex 1 and the like, except those such as titanium(IV) and vanadium(IV). However, there are considerable differences in the magnitude of the distribution coefficients and the adsorption sequence between the two types of the resin. Generally the distribution coefficients are appreciably higher on CG-4B than on the strongly basic resins. As far as the metals studied are concerned, this is the case for tungsten(VI) and titanium(IV) (peroxide present), zirconium(IV) and hafnium(IV), uranium(VI), chromium(III), thorium(IV) and vanadium(IV). Thus, at 0.1 *M* sulfuric acid solution the ratios of the distribution coefficients (CG-4B to Bio-Rad AG-1) are as high as 92 for titanium(IV) (peroxide present), 29 for chromium(III), >12 for vanadium(IV), 8.4 for zirconium(IV), 6.4 for tungsten(VI) (peroxide present), 3.6 for hafnium(IV), 2.0 for uranium(VI) and 1.9 for thorium(IV); all ratios were calculated from the distribution coefficient data reported by Strelow and Bothma[3].

Non-retention of titanium(IV) on the strongly basic anion-exchange resin from sulfuric acid containing hydrogen peroxide has been reported by Strelow and Bothma. Danielsson[2] found $K_d \geqslant 1$ below *ca.* 0.2 *M* sulfuric acid, and also found that hydrogen peroxide increased the adsorption of titanium(IV) only to a small extent. On the other hand, titanium(IV) was adsorbed on CG-4B from the sulfuric acid solution containing hydrogen peroxide, to a sufficient extent to allow its column separation from many other metals (Table III).

TABLE III

SEPARATION OF TITANIUM(IV) FROM OTHER METALS

(A 1.0 × 14.5-cm column (50°) was used throughout. Foreign metals were first eluted with 150–180 ml of 0.1 *M* H_2SO_4–0.15% H_2O_2, then Ti(IV) with 200 ml of 2 *M* H_2SO_4)

Ti(IV)		*Foreign metals*		
Added (mg)	*Found (mg)*	*Metal*	*Added (mg)*	*Found (mg)*
12.4	12.2	Mg(II)	11.3	11.2
12.4	12.4	Al(III)	5.85	5.84
12.4	12.1	Cr(III)	12.9	12.7
12.4	12.1	Cu(II)	9.65	9.76
12.4	12.3	Ga(III)	11.0	11.4
12.4	12.5	Mixed R.E.	12.3	12.3
	av. 12.3±0.2	(La+Sm+Y)		

Another feature of the present system is that an appreciable uptake of vanadium(IV) takes place on CG-4B from dilute sulfuric acid solution. Strelow and Bothma[3] reported a distribution coefficient of 3.4 for vanadium(IV) in 0.005 *M* acid, which decreased with increasing acid concentration down to <0.5 at 0.5 *M* sulfuric acid.

In contrast to the metals mentioned, vanadium(V) is adsorbed less markedly on CG-4B than on AG-1: in the acidity range from 0.005–0.015 *M*, a 3–4-fold decrease in the distribution coefficients is involved. This is also the case for scandium(III), although the difference is less marked.

Irrespective of the presence or absence of peroxide, molybdenum(VI) seems to be adsorbed on the two types of resin to a similar extent over the acid concentration range tested, even though there is partial disagreement about the distribution coefficient in the absence of peroxide. Actually, molybdenum(VI) has been found to break through the column of Dowex 1 to a great extent despite its high distribution coefficient, when adsorbed from sulfuric acid solution containing no peroxide[6]. Therefore, the distribution coefficients obtained batchwise in the absence of peroxide may not be due entirely to ion-exchange and may be erratic in nature.

Indium(III), iron(III) and lanthanum(III) behave similarly on CG-4B and Bio-Rad AG-1 in sulfuric acid media, although their distribution coefficients are very low.

Separations

The adsorption data listed in Table II clearly indicate many possible separations for the metals studied. Strelow and Bothma[3] stated that exchange rates for reasonably strongly adsorbed metals are considerably slower than those found for anion-exchange in hydrochloric acid or cation-exchange in hydrochloric, nitric and sulfuric acid. In the present work, it was also found that the kinetics of the ion-exchange reaction in the CG-4B–sulfuric acid system is low, causing slight tailing in most cases. However, if a flow rate of *ca.* 1 ml min^{-1}, and an elevated temperature column (*ca.* 50°) are used, the utility of the system in practical separations is not hampered. The following separations of two component mixtures have been found quantitative at *ca.* 50°: Be(II)–Th(IV) (0.1 *M* H_2SO_4, 2 *M* H_2SO_4); Be(II)–U(VI) (0.1 *M* H_2SO_4, 2 *M* $HClO_4$); Al(III)–Sc(III) (0.005 *M* H_2SO_4, 3 *M* HCl); Sc(III)–U(VI) (2 *M* H_2SO_4, 2 *M* H_2SO_4); Cr(III)–W(VI) (0.05 *M* H_2SO_4–0.15% H_2O_2, 0.5 *M* NaCl–0.5 *M* NaOH); Y(III)–Th(IV) (0.1 *M* H_2SO_4, 2 *M* H_2SO_4); La(III) or Sm(III)–Th(IV) (0.1 *M* H_2SO_4, 2 *M* H_2SO_4); Sm(III)–U(VI) (0.1 *M* H_2SO_4, 2 *M* $HClO_4$); and mixed rare earths–Sc(III) (0.05 *M* H_2SO_4, 3 *M* HCl). Reagents in parentheses are the eluents used for the separations; the first metal of each pair was first eluted by the first-mentioned eluent. Total amounts loaded were mostly 10–100 mg in varying proportions. In the chromium(III)–tungsten(VI) pair, the separation of 1 mg of chromium and 9.5 mg of tungsten was successful, but a partial retention of chromium was found when an increased amount of chromium (7 mg) was taken.

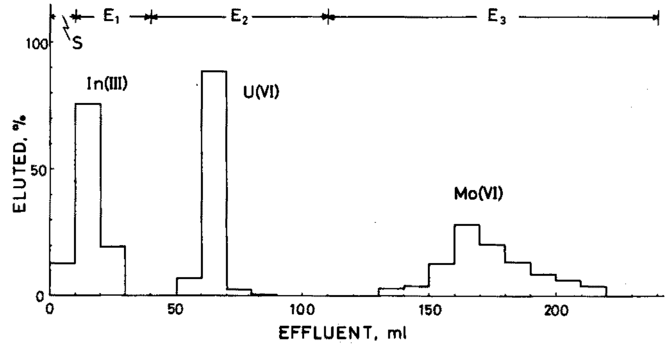

Fig. 1. Procedure for the separation of In(III), U(VI) and Mo(VI). S = sample, E_1 = 0.5 *M* H_2SO_4–0.15% H_2O_2, E_2 = 3 *M* HCl–0.15% H_2O_2, E_3 = 0.5 *M* NaCl–0.5 *M* NaOH. A 1.2×9.5 cm column containing 5 g of Amberlite CG-4B was used. In(III), 19.1 mg added and 20.2 mg found; U(VI), 28.5 mg added and 29.0 mg found; Mo(VI), 19.8 mg added and 19.6 mg found.

An example of triplicate separations involving the samarium(III)–uranium(VI) pair (1:5,000) may provide some idea about the precision of the procedures. Values of 20.6, 20.8 and 20.9 (av. 20.8 ± 0.2) μg of samarium and 98.6, 99.5 and 99.7 (av. 99.3 ± 0.6) mg of uranium, respectively, were found when 21.7 μg of samarium and 99.3 mg of uranium were used; the errors indicated are standard deviation.

Results for quantitative separations of titanium(IV) from several metals are given in Table III. Titanium(IV) is retained on the column as a discernible orange band, while the other metals pass through the column.

A consecutive chromatographic separation of indium(III), molybdenum(VI) and uranium(VI) gave quantitative yields as illustrated in Fig. 1, and no cross-contamination was observed. A somewhat slow flow rate of 0.3 ml min^{-1} was used here at room temperature.

SUMMARY

A systematic study is presented on the adsorption behavior of some 20 metals on a weakly basic condensed phenol resin, Amberlite CG-4B, in sulfuric acid media. The distribution coefficients were determined over a sulfuric acid concentration range of 0.005 *M* to 2 *M*. The metals adsorbed are similar to those which exhibit strong adsorption on a strongly basic resin, but the magnitudes of the distribution coefficients and the adsorption sequences differ considerably between the two types of the resin. Several two- and three-component separations of analytical interest are possible. A new method for the separation of titanium(IV) is described; this is based on its high adsorption on CG-4B from sulfuric acid media containing hydrogen peroxide.

RÉSUMÉ

Une étude systématique est effectuée sur le comportement d'environ 20 métaux, adsorbés sur résine phénol légèrement basique, Amberlite CG-4B, en milieu acide sulfurique. Les coefficients de partage et les séquences d'adsorption diffèrent considérablement d'avec ceux d'une résine fortement basique. On propose une méthode pour la séparation du titane(IV).

ZUSAMMENFASSUNG

Eine systematische Untersuchung über das Adsorptionsverhalten von etwa 20 Metallen an einem schwach basischen kondensierten Phenolharz, Amberlite CG-4B, in Schwefelsäuremedium wird vorgelegt. Die Verteilungskoeffizienten wurden über einen Schwefelsäurekonzentrationsbereich von 0.005–2 *M* bestimmt. Die adsorbierten Metalle sind ähnlich jenen, die an einem stark basischen Harz eine starke Adsorption zeigen, jedoch unterscheiden sich die Grössen der Verteilungskoeffizienten und die Adsorptionsreihenfolge bei den beiden Harztypenbeträchtlich. Verschiedene Zwei- und Drei-komponententrennungen von analytischem Interesse sind möglich. Eine neue Methode für die Abtrennung von Titan(IV) wird beschrieben; sie beruht auf der starken Adsorption an CG-4B in wasserstoffperoxidhaltigem Schwefelsäuremedium.

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SELECTIVE SEPARATION OF THORIUM FROM RARE EARTHS, ZIRCONIUM AND OTHER ELEMENTS BY CATION-EXCHANGE CHROMATOGRAPHY IN HYDROBROMIC ACID MEDIA

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Separation of thorium from other elements by means of ion-exchange chromatography has received considerable attention during the last twenty years. A good summary of the available methods is given by Korkisch[1]. The most attractive anion-exchange procedure is probably that developed by Korkisch and Ahluwalia[2] who used 0.6 *M* nitric acid in 55% acetone to elute all other elements except bismuth, lead, gold and palladium which accompany thorium being retained on the column. Even more selective is cation exchange in 4 *M* hydrochloric acid with AG50W-X12, Dowex 50W-X12 or an equivalent resin[3–6]. Only those elements which form precipitates in 4 *M* hydrochloric acid cannot be separated directly, but can be eluted before the elution with 4 *M* hydrochloric acid by using appropriate eluting reagents. The method can therefore provide separation of thorium from all other elements. Its drawback is the fact that it is impossible to obtain quantitative elution ($\geqslant$99.9%) of thorium from an 8% or 12% cross-linked resin with an easily volatile eluting reagent. The most effective eluting reagent, 3 *M* sulphuric acid[7], introduces complications for determinations and further separations. For accurate work the resin has preferably to be ashed.

In order to obtain a more efficient elution of thorium, one would tend to use a resin of lower cross-linkage. Unfortunately, the separation of the Th–Zr pair in hydrochloric acid becomes difficult already with resin of 8% cross-linkage and impossible with 4%, when large amounts of zirconium are present. Distribution coefficients published by Nelson and Michelson[8] and a recent systematic study carried out in this laboratory indicate that hydrobromic acid should have very definite advantages over hydrochloric acid as eluting agent for rare earths, zirconium, etc. in their separation from thorium. Relevant distribution coefficients of thorium and separation factors are considerably higher in hydrobromic than in hydrochloric acid, especially with resins of low cross-linkage. Furthermore, a study of distribution coefficients in nitric acid showed that 5 *M* nitric acid should be a promising eluting agent for thorium from AG50W-X4 resin. The merits of an accurate separation procedure for thorium from rare earths, zirconium and other elements based on these facts were therefore investigated in more detail.

EXPERIMENTAL

Reagents and apparatus

Only analytical reagent-grade chemicals were used. The resins were AG50W-

X4, AG50W-X8 and AG50W-X12 sulphonated polystyrene cation exchangers (Bio-Rad, Richmond, Calif.). Resin of 100–200 mesh particle size was used for batch equilibrium and of 200–400 mesh for column experiments. Borosilicate glass tubes of 2.1-cm inner diameter fitted with B19 ground-glass joints at the top, and glass sinter plates of No. 2 porosity and burette taps at the bottom, were used as columns.

Equilibrium distribution coefficients

Dry resin (2.500 g) in the H^+-form was equilibrated with 1.25 mmole of thorium, 1.67 mmole of rare earths, or 2.50 mmole of zirconium in 250 ml of aqueous hydrochloric or hydrobromic acid of the designed concentration by shaking for 24 h at 25°. After separation of the resin from the aqueous phase, the amounts of the elements in both phases were determined by suitable analytical methods. From the results, the equilibrium distribution coefficients

$$D = \frac{\text{moles on resin}}{\text{moles in solution}} \times \frac{\text{ml solution}}{\text{g dry resin}}$$

were calculated. They are presented in Tables I and II. Coefficients in hydrochloric acid with 8% crosslinked resin have been published before[9], but were redetermined and are included for comparative purposes. Table III shows coefficients for thorium in nitric acid under the same conditions as outlined above.

Elution curves

From the distribution coefficients in the Tables and the known fact that thorium tails very strongly with resins of 8 or more percentage cross-linkage, it appeared that favourable conditions for the separation of thorium from lanthanum and zirconium could be obtained by using a resin of 4% cross-linkage and

TABLE I

CATION-EXCHANGE DISTRIBUTION COEFFICIENTS IN HYDROCHLORIC ACID WITH RESINS OF VARIOUS CROSS-LINKAGES

Molarity HCl	*AG50W-X4*			*AG50W-X8*			*AG50W-X12*		
	La	*Zr*	*Th*	*La*	*Zr*	*Th*	*La*	*Zr*	*Th*
0.1	$>10^4$	$>10^4$	$>10^4$	$>10^4$	$>10^4$	$>10^4$	$>10^4$	$>10^4$	$>10^4$
0.2	3820	$>10^4$	$>10^4$	$>10^4$	$>10^4$	$>10^4$	$>10^4$	$>10^4$	$>10^4$
0.5	491	6590	5470	1880	$>10^4$	$>10^4$	4200	$>10^4$	$>10^4$
1.0	100	2710	492	277	9200	2220	527	8620	4560
2.0	23.2	221	80	57	521	230	96	500	499
3.0	10.4	32.2	35.5	23.8	85	97	38.4	85	171
4.0	6.6	10.7	26.1	11.4	15.8	60	21.8	21.2	98
5.0	7.0	7.1	25.0	10.1	6.0	48.7	17.3	8.4	74
6.0	7.5	6.2	26.4	9.8	3.9	46.3	13.7	4.9	60
7.0	8.1	5.4	28.3	10.4	3.2	45.4	13.8	3.9	50
8.0	9.0	5.1	30.6	11.3	3.1	45.0	14.7	4.0	41.7
9.0	11.1	6.2	30.9	13.6	4.3	43.7	17.5	5.8	33.5
10.0	15.1	7.9	31.2	18.0	8.6	40.9	22.8	9.5	24.8

TABLE II

CATION-EXCHANGE DISTRIBUTION COEFFICIENTS IN HYDROBROMIC ACID WITH RESINS OF VARIOUS CROSS-LINKAGES

Molarity HBr	*AG50W-X4*			*AG50W-X8*			*AG50W-X12*		
	La	*Zr*	*Th*	*La*	*Zr*	*Th*	*La*	*Zr*	*Th*
0.1	$>10^4$	$>10^4$	$>10^4$	$>10^4$	$>10^4$	$>10^4$	$>10^4$	$>10^4$	$>10^4$
0.2	4330	$>10^4$	$>10^4$	$>10^4$	$>10^4$	$>10^4$	$>10^4$	$>10^4$	$>10^4$
0.5	558	$>10^4$	2950	1950	$>10^4$	$>10^4$	5000	$>10^4$	$>10^4$
1.0	115	5570	405	284	$>10^4$	2410	641	9710	8170
2.0	28.7	364	145	55	661	341	102	662	641
3.0	13.6	56	80	22.4	159	151	43.4	116	234
4.0	9.9	14.7	60	14.2	31.6	115	25.1	31.3	157
5.0	8.3	7.8	77	11.0	12.6	145	19.2	12.7	147
6.0	9.0	6.0	126	11.4	8.5	197	18.1	7.9	153
7.0	12.0	6.8	229	13.6	9.6	295	20.8	7.6	143
8.0	19.0	9.8	638	21.3	14.1	349	27.7	10.5	101

TABLE III

CATION-EXCHANGE DISTRIBUTION COEFFICIENTS FOR THORIUM IN NITRIC ACID WITH RESINS OF VARIOUS CROSS-LINKAGES

Molarity HNO_3	*X4*	*X8*	*X12*	*X16*
0.1	$>10^4$	$>10^4$	$>10^4$	$>10^4$
0.2	$>10^4$	$>10^4$	$>10^4$	$>10^4$
0.5	2070	$>10^4$	$>10^4$	$>10^4$
1.0	327	1180	3380	3670
2.0	52	123	271	332
3.0	21.4	43.0	90	122
4.0	14.8	24.8	55	68
5.0	12.6	19.7	39.4	49.6
6.0	12.8	21.3	41.2	52

eluting lanthanum and zirconium with about 5.5 *M* hydrobromic acid. At this concentration both elements have low distribution coefficients, while the respective separation factors $\alpha_{\mathrm{La}}^{\mathrm{Th}}$ and $\alpha_{\mathrm{Zr}}^{\mathrm{Th}}$ are both larger than 10. Elution curves were therefore prepared for the ion pairs, Th–La, Th–Zr and also for Th–Ba, because barium is the most strongly adsorbed of the divalent elements (except radium) and has a distribution coefficient of about 14 in 5.5 *M* hydrobromic acid. Figure 1 shows an elution curve for the Th–La pair. About 2 mmole of lanthanum and 1 mmole of thorium in 50 ml of 1 *M* hydrobromic acid were adsorbed on a column containing 65 ml (15 g) of AG50W-X4 cation-exchange resin of 200–400 mesh particle size in the hydrogen form. The column was 20 cm in length and 2.1 cm in diameter and had been equilibrated by passing through 50 ml of 1 *M* hydrobromic acid. The lanthanum was eluted with 5.5 *M* hydrobromic acid at a flow rate of 3.0±0.5 ml $\min^{-1}$. After 400 ml the elution was stopped and thorium was eluted

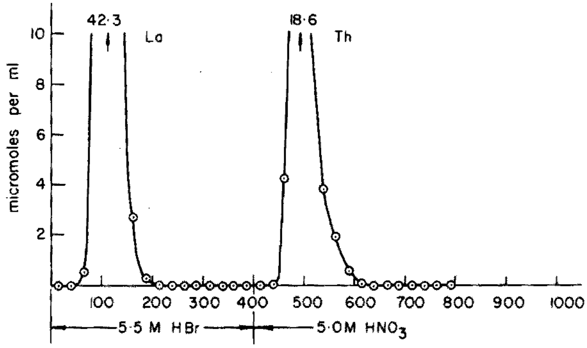

Fig. 1. Elution curve for La–Th with 5.5 *M* HBr and 5.0 *M* HNO_3. Column of 65 ml (volume in H_2O) AG50W-X4, 200–400 mesh, resin (20 × 2.1 cm). Flow rate 3.0 ± 0.5 ml min^{-1}.

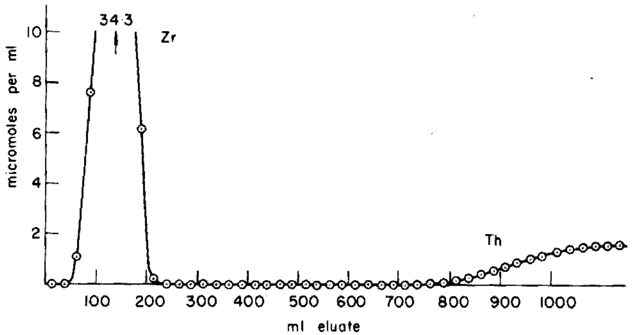

Fig. 2. Elution curve for Zr–Th with 5.5 *M* HBr. Column of 65 ml (volume in H_2O) AG50W-X4, 200–400 mesh, resin (20 × 2.1 cm). Flow rate 3.0 ± 0.5 ml min^{-1}.

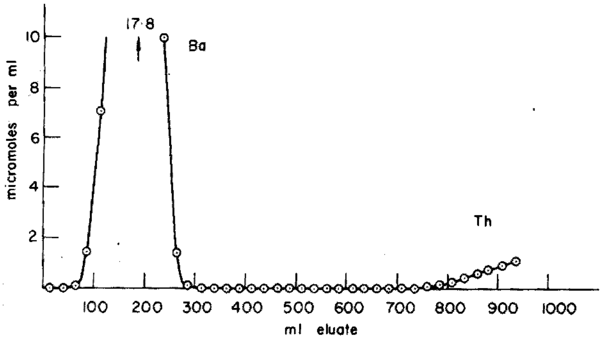

Fig. 3. Elution curve for Ba–Th with 5.5 *M* HBr. Column of 65 ml (volume in H_2O) AG50W-X4, 200–400 mesh, resin (20 × 2.1 cm). Flow rate 3.0 ± 0.5 ml min^{-1}.

with 5.0 *M* nitric acid. All elutions were carried out at room temperature between 20° and 25°. Fractions of 25-ml volume were taken with an automatic fractionator and the amounts of the elements in the fractions were determined by a suitable analytical method. Figures 2 and 3 show curves for the Th–Zr and Th–Ba pairs. In these cases the elution with 5.5 *M* hydrobromic acid was continued until thorium appeared in the eluate to show the gap between the peaks and demonstrate the quality of the separation. Other elements such as Sc, Y, Ce, the other rare earths, Sr, Ca, Mg, Be, Ti(IV), Hf, Al, Cr(III), Fe(III), Fe(II), Co(II), Ni(II), Mn(II), Cu(II), Zn, Cd, Ga, In, Hg(II), Li, Na, K, Rb, Cs, Sn(IV), Pb(II), Ge(IV), Se(IV), Te(IV), V(V), As(III), Sb(III), Bi(III), Pd(II), Pt(IV), Ir(III), Ir(IV), Rh(III) and U(VI) are eluted together with or ahead of lanthanum, zirconium and barium. Radium was not investigated, but should be eluted together with barium according to the distribution curve published by Nelson and Michelson[8]. Gold has a relatively high distribution coefficient in 5.5 *M* hydrobromic acid. This element can be eluted with 3 *M* hydrobromic acid or even better with 0.5 *M* hydrobromic acid in 90% acetone before elution of the other elements. Elements such as Ga, In, Cd, Fe(III) and many others will then accompany gold. Figure 4 shows an elution curve for the Th–La pair with 3 *M* hydrochloric acid as eluting agent from a 43-ml (10 g) column of AG50W-X4 resin of 200–400 mesh particle size. Only zirconium and hafnium of the elements named above are not eluted together with lanthanum, but can be eluted with 5.5 *M* hydrobromic acid subsequently.

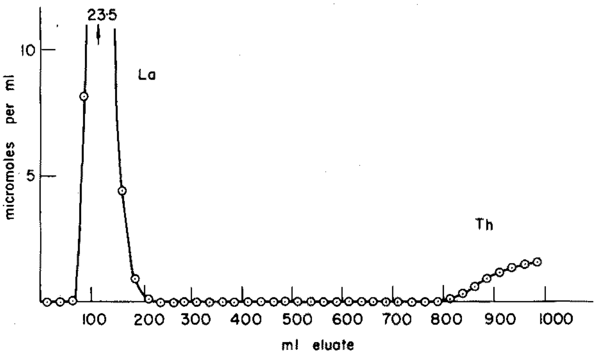

Fig. 4. Elution curve for La–Th with 3.0 *M* HBr. Column of 65 ml (volume in H_2O) AG50W-X4, 200–400 mesh, resin (20 × 2.1 cm). Flow rate 3.0 ± 0.5 ml min^{-1}.

Quantitative separations of synthetic mixtures

Amounts of standard solutions of thorium and one other element in 1 *M* hydrobromic acid were measured out, mixed and passed on to a column containing 65 ml (15 g) of AG50W-X4 resin of 200–400 mesh particle size. The resin column was 20 cm in length and 2.1 cm in diameter after it had settled in water. It was equilibrated with 50 ml of 1 *M* hydrobromic acid. The elements were washed on to the column with 5.5 *M* hydrobromic acid, and the "other elements" were then eluted with 350 ml of this acid (including wash solution). In the case of gold(III) 350 ml of 0.5 *M* hydrobromic acid in 90% acetone was used for elution. The eluate was taken from the beginning of the adsorption step. After elution with 5.5 *M* hydrobromic acid, 20 ml of 2 *M* hydrobromic acid followed by 30 ml of 2 *M* nitric acid, and after elution with 0.5 *M* hydrobromic acid in 90% acetone, 30 ml of

TABLE IV

QUANTITATIVE RESULTS FOR SEPARATIONS OF SYNTHETIC MIXTURES

Taken		*Found*	
mg Th	*mg other element*	*mg Th*	*mg other element*
219.6	277.2 La[a]	219.6 ±0.1	277.3 ±0.1
457.8	11.32 La[a]	457.9 ±0.1	11.32 ±0.02
22.52	277.2 La[a]	22.53 ±0.03	277.2 ±0.1
0.220	1384.1 La[a]	0.221 ±0.002	1384.1 ±0.2
457.8	0.226 La[a]	457.8 ±0.1	0.225 ±0.002
219.6	44.77 Sc	219.6 ±0.1	44.75 ±0.02
219.6	182.1 Zr	219.6 ±0.1	182.2 ±0.2
219.6	94.8 Ti	219.5 ±0.2	94.8 ±0.1
219.6	267.9 Ba	219.6 ±0.1	267.8 ±0.2
219.6	81.6 Ca	219.6 ±0.1	81.6 ±0.1
219.6	48.94 Mg	219.7 ±0.1	48.95 ±0.04
219.6	54.31 Al	219.6 ±0.2	54.32 ±0.05
219.6	110.2 Mn(II)	219.6 ±0.1	110.2 ±0.1
219.6	111.8 Fe(III)	219.6 ±0.1	111.9 ±0.1
219.6	208.5 Bi(III)	219.7 ±0.1	208.4 ±0.2
219.6	207.8 Pb(II)	219.6 ±0.1	207.8 ±0.1
219.6	196.5 Au(III)[b]	219.6 ±0.1	196.4 ±0.2
219.6	105.4 Pd(II)	219.6 ±0.1	105.4 ±0.1
219.6	131.6 Zn	219.5 ±0.1	131.6 ±0.1
219.6	126.8 Cu(II)	219.6 ±0.1	126.7 ±0.1
219.6	128.0 Ni(II)	219.6 ±0.1	128.0 ±0.1
219.6	475.4 U(VI)	219.6 ±0.1	475.5 ±0.1
219.6	102.4 V(V)	219.7 ±0.1	102.4 ±0.1
219.6	139.1 Ga	219.6 ±0.1	139.1 ±0.1

[a] The results are means of triplicate determination except those marked which are means of 6 determinations. [b] Eluted with 0.5 *M* HBr in 90% acetone.

0.5 *M* nitric acid were passed through the column before thorium was finally eluted with 500 ml of 5.0 *M* nitric acid. A flow rate of 3.0±0.5 ml $\min^{-1}$ was used throughout, and all elutions were carried out at room temperature. The excess of acid was removed from the eluates by evaporation, and the amounts of the elements were determined by suitable analytical methods. The results of the quantitative separations are presented in Table IV, and the analytical methods used are summarized in Table V.

DISCUSSION

The described method provides an excellent means for the selective separation of thorium from other elements. La, Sc, Zr, Ti(IV), Ba, Ca, Mg, Al, Ga, Mn(II), Fe(III), Bi(III), Pb(II), Pd(II), Zn, Cu(II), Ni(II), U(VI) and V(V) can be eluted with 350 ml of 5.5 *M* hydrobromic acid from a column of 65 ml of AG50W-X4 resin of 200–400 mesh particle size. Thorium can then be eluted with 500 ml of 5 *M* nitric acid. Separations are sharp and quantitative. When separating six synthetic mixtures containing 219.6 mg of thorium and 277.2 mg of lanthanum,

TABLE V

ANALYTICAL METHODS USED

Element	*Method*
Th, La	Gravimetrically as the oxide after precipitation as the oxalate from 0.1 *M* HCl. Complexmetric titration at pH 2.5 with xylenol orange indicator for small amounts. Traces of thorium spectrophotometrically with thorin.
Ti, Zr, U	Gravimetrically as the oxide after precipitation with ammonia.
Ba	Gravimetrically as sulphate.
Cd, Mn	Complexmetric titration in excess ammonia with methylthymol blue indicator.
Mg	Complexmetric titration at pH 10 with eriochrome black T indicator.
Pb, Zn	Complexmetric titration at pH 5.5 with xylenol orange indicator.
Al, Fe(III), Ga, Bi(III)	Addition of excess EDTA; back-titration with zinc sulphate at pH 5.5 with xylenol orange indicator.
Au(III)	Gravimetrically as the metal.
Pd(II)	Gravimetrically with dimethylglyoxime.
Cu	Complexmetric titration with naphthylazoxime indicator.
Ni	Complexmetric titration with murexide indicator.
V(V)	Titration with iron(II), with barium diphenylaminesulphonate indicator.
Sc	Complexmetric titration with EDTA at pH 4 with xylenol orange indicator.

average results of 219.6 mg and 277.3 mg, respectively, were obtained, both results with a standard deviation of 0.04%. Thorium (220 μg) could be separated from 1.384 g of lanthanum and determined with an error of about $\pm 1\%$. Gold(III), which has a rather high distribution coefficient in 5.5 *M* hydrobromic acid, can be eluted with 0.5 *M* hydrobromic acid in 90% acetone before the elution with 5.5 *M* hydrobromic acid. Y, Ce, the other rare earth metals, Sr, Be, Hf, Cr(III), Co(II), Cd, In, Hg(II), Li, Na, K, Rb, Cs, Sn(IV), Ge(IV), Se(IV), Te(IV), As(III), Sb(III), Pt(IV), Ir(III), Ir(IV) and Rh(III) have not been investigated quantitatively; but all these elements should be separated together with lanthanum according to their elution curves and distribution coefficients. Elements such as Mo(VI), W(VI) and Nb(V) can be eluted with 0.5 *M* nitric or hydrochloric acid containing hydrogen peroxide before the other elements are eluted. Bi(III), Pb(II), Au(III) and Pd(II), which are not separated by anion exchange in nitric acid–acetone[2], are included in the separation.

Hydrobromic acid has definite advantages over hydrochloric acid as an eluting agent for the selective separation of thorium from other elements by cation-exchange chromatography. The fact that it provides considerably higher distribution coefficients and separation factors for thorium than hydrochloric acid makes it possible that a resin with 4% cross-linkage can be used, while the separation factors in 5.5 *M* hydrobromic acid are still about 12 for the Th–La and Th–Zr pairs, compared with about 5 in 4 *M* hydrochloric acid with the 12% cross-linked resin[3]. From the 4% cross-linked resin thorium can be eluted by 5 *M* nitric acid with recoveries better than 99.9%, while the recoveries from 8% cross-linked resin with 3 *M* sulphuric acid, the most favourable concentration, are claimed to be about 98%[10, 11]. Nitric acid of any concentration is even less effective on the latter resin. The eluting agents used are readily volatilized and the samples are easily prepared for further work. The method seems to be suited for the accurate determination of thorium in complex mixtures of elements.

SUMMARY

Thorium can be separated from La, Sc, Zr, Ti(IV), Ba, Ca, Mg, Al, Mn(II), Fe(III), Bi(III), Pb(II), Pd(II), Zn, Cu(II), Ni(II), U(VI) and V(V) by eluting these elements with 5.5 *M* hydrobromic acid from a column of AG50W-X4 cation-exchange resin. Thorium is retained and can be eluted with 5 *M* nitric acid with recoveries of better than 99.9% for amounts from about 200 μg to more than 400 mg. Au(III) and Ga(III) can be eluted with 0.5 *M* hydrobromic acid in 90% acetone before the elution with 5.5 *M* hydrobromic acid. Y, Ce, the other rare earths, Sr, Be, Hf, Cr(III), Co(II), Cd, In, Hg(II), Li, Na, K, Rb, Cs, Sn(IV), Ge(IV), Se(IV), Te(IV), As(III), Sb(III), Pt(IV), Ir(III), Ir(IV), and Rh(III) have not been investigated quantitatively, but should also be separated according to their distribution coefficients and elution curves. Some relevant distribution coefficients, elution curves and results for the analysis of synthetic mixtures are presented.

RÉSUMÉ

On propose une séparation sélective du thorium d'avec terres rares, zirconium et autres éléments, à l'aide d'un échangeur de cations, résine AG50W-X4 et élution avec acide bromhydrique. Le thorium est retenu et élué ensuite par l'acide nitrique 5 *M*. Quelques coefficients de partage, des courbes d'élution et des résultats d'analyse de mélanges synthétiques sont donnés.

ZUSAMMENFASSUNG

Thorium kann von La, Sc, Zr, Ti(IV), Ba, Ca, Mg, Al, Mn(II), Fe(III), Bi(III), Pb(II), Pd(II), Zn, Cu(II), Ni(II), U(VI) und V(V) abgetrennt werden, indem diese Elemente mit 5.5 *M* Bromwasserstoffsäure aus einer Säule mit dem Kationenaustauscher AG50W-X4 eluiert werden. Thorium wird zurückgehalten und kann mit 5 *M* Salpetersäure in Mengen von etwa 200 μg bis mehr als 400 mg mit Ausbeuten besser als 99.9% eluiert werden. Au(III) und Ga(III) können mit 0.5 *M* Bromwasserstoffsäure in 90% Aceton vor der Elution mit 5.5 *M* Bromwasserstoffsäure eluiert werden. Y, Ce, die anderen Seltenen Erden, Sr, Be, Hf, Cr(III), Co(II), Cd, In, Hg(II), Li, Na, K, Rb, Cs, Sn(IV), Ge(IV), Se(IV), Te(IV), As(III), Sb(III), Pt(IV), Ir(III), Ir(IV) und Rh(III) wurden nicht quantitativ untersucht, sollten aber entsprechend ihren Verteilungskoeffizienten und Elutionskurven ebenfalls getrennt werden. Einige wichtige Verteilungskoeffizienten, Elutionskurven und Ergebnisse der Analyse synthetischer Gemische werden vorgelegt.

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SOME NEWER EXAMPLES OF THE APPLICATION OF CATALYZED INDICATOR REACTIONS IN TITRIMETRIC ANALYSIS

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The application of catalytic reactions for the indication of the end-point in titrimetric analysis has led to the development of numerous new methods during recent years[1–9]. In contrast to the other kinetic catalytic analytical methods a quantitative interpretation of the catalyzed reaction is not necessary; the mere qualitative ascertainment suffices, that the catalyst is present in just an amount to cause an observable acceleration of the indicator reaction.

In the application of the above-mentioned method of indication for volumetric determinations in a classical sense, the solution of the titrant which has catalytic activity on a certain reagent mixture is added from a burette to this reagent mixture. A substance can be titrated which can inhibit distinctly or even reduce practically to zero this catalytic activity of the titrant through either precipitation or complex formation. It might also be possible to achieve this inhibition of the catalyst by reduction or oxidation but so far no suitable example has been described.

After all the inhibitor has been consumed (end-point of the titration) the first drop in excess of the titrant (catalyst) will immediately accelerate the indicator reaction. Either the disappearance of one of the reactants or the appearance of a reaction product of the catalyzed indicator reaction may be observed. This can be followed simply visually or by any suitable instrumental technique (photometry, potentiometry, thermometry, dead stop). In Table I several examples of such titri-

TABLE I

SOME EXAMPLES OF TITRATIONS WITH CATALYZED INDICATOR REACTIONS

A[a]	*B*[a]	*C*[b]	*Titrant*[c]	*Titrand*	*Ref.*
Ce(IV)	As(III)	Ce(III)/As(V)	I^-	Ag^+, Hg^+	2, 4, 5, 10
$S_2O_8^{2-}$	Methyl orange	Colourl. ox. prod.	Ag^+	Cl^-, Br^-, I^-	2
H_2O_2	Hydroquinone	Yellow ox. prod.	Cu^{2+}	Oxine	11, 12
H_2O_2	Diphenols	Col. ox. prod.	Co^{2+}	EDTA	2, 13, 14
Perborate	Tiron	Gold-yell. ox. prod.	Co^{2+}	EDTA	2, 3
H_2O_2	Resorcinol	Red ox. prod.	Mn^{2+}	EDTA	7
Acetone	—	Polymerizate	OH^-	H^+	1
H_2O_2	—	$O_2+\ldots$	Mn^{2+}	EDTA	6
JO_4^-	Malachite green	Colourl. ox. prod.	Mn^{2+}	EDTA a.o.	9

[a] Participants in the catalyzed indicator reaction.
[b] Product of the indicator reaction.
[c] The titrant reacts stoichiometrically with the titrand, and then catalyzes the indicator reaction.

metric determinations are listed. In these examples, the ion to be determined always acts as an inhibitor and is titrated with a standard solution of the catalyst ("direct titration"). Obviously, the catalyst can likewise be determined by "reversed titration": a known volume of a standard solution of a suitable inhibitor is titrated with the unknown sample solution (catalyst). Ions which do not have catalytic activity on the indicator reaction can nevertheless be determined by "back-titration", if they form a stronger complex or a more stable compound with the inhibitor than does the catalyst; in this case, a known excess of the standard solution of the inhibitor is added to the sample solution and the unconsumed excess of the inhibitor is back-titrated with a standard solution of the catalyst.

In all the examples so far mentioned here, the catalyst is used as a titrant. It is also possible to add the catalyst in an inhibited blocked form together with the indicator reagent mixture to the solution to be titrated (inhibitor); as soon as the end-point is reached, the catalyst is demasked, liberated, reactivated and starts the indicator reaction ("substitution titration")[7,8].

For titrations in nonaqueous media (DMSO), catalytic indicator reactions have likewise been applied[8].

The great advantage of such catalytic titration end-points is that the excess of titrant at the end-point is not used for a stoichiometric reaction with the indicator, but only as a catalyst. Consequently, a very small excess of the titration reagent suffices to catalyze large amounts of the indicator reagent mixture. Such catalytic end-points are therefore remarkably sensitive and very readily recognizable.

In this paper some new examples of such catalytic indicator reactions in titrimetric analysis are described.

DIRECT PRECIPITATION TITRATION WITH VISUAL OBSERVATION OF THE INDICATOR REACTION

The silver-catalyzed oxidation of leuco malachite green with potassium peroxydisulphate

Silver-catalyzed oxidation reactions with peroxydisulphate are well known and have been extensively examined[15-18]. Because the reaction rate of the oxidation of leuco malachite green with potassium peroxydisulphate in presence of 2,2′-bipyridine serving as an activator[19], is very high at room temperature, this system can be used as an indicator reaction for argentimetric titrations. Chloride, bromide and iodide are inhibitors and can consequently be determined in this way. At the end-point of the titration an intense green or blue-green colour occurs, which can be seen without difficulty even in the presence of larger amounts of silver halides. The titration error amounts to about one drop of silver nitrate solution or even less.

Direct titration of chloride, bromide and iodide with silver nitrate solution

The sample solution (neutralized with 0.25 *M* sulphuric acid) is mixed with 0.5 ml of 2,2′-bipyridine (2% in 0.1 *M* sulphuric acid), 0.5 ml of leuco malachite green solution (2% in 0.1 *M* sulphuric acid), and 1 ml (for chloride and bromide) or 0.25 ml (for iodide) of a 0.02 *M* solution of potassium peroxydisulphate. For the determination of chloride and bromide, 2 ml of 0.25 *M* sulphuric acid are added. The solution is made up with water to about 25 ml and immediately titrated with 0.1 *M* silver nitrate solution whilst vigorously mixing (magnetic stirrer). The speed of titration should be about 1 drop per second at the beginning and slower near the equivalence point.

At the end-point a change of the colour from light-green to dark-green or blue-green is observed. In the presence of higher concentrations of halide ions, it is recommended to add the activator and leuco malachite green only 1 or 2 ml before the end of the titration.

Some results are given in Table II.

TABLE II

DETERMINATION OF CHLORIDE, BROMIDE AND IODIDE BY DIRECT TITRATION WITH 0.1 M $AgNO_3$

mg Cl⁻		*mg Br⁻*		*mg I⁻*	
Given	*Found*	*Given*	*Found*	*Given*	*Found*
7.71	7.68	16.45	16.45	11.02	11.16
14.45	14.50	32.91	33.01	23.50	23.85
15.79	15.90	41.10	40.75	34.50	34.30
23.13	23.27	49.37	49.75	43.70	43.40
32.80	32.55	65.80	65.80	47.90	48.90

COMPLEXIMETRIC TITRATION WITH PHOTOMETRIC OBSERVATION OF THE INDICATOR REACTION

The manganese(II)-catalyzed oxidation of dyestuffs with hydrogen peroxide

Several manganese-catalyzed oxidation reactions have already been used for end-point indication in volumetric analysis[3,6,7,9]. Here, the application of thorin and carminic acid is described for this purpose.

Determination of manganese(II) by reversed titration against EDTA

Into a round cuvette (30 mm diameter) the following solutions are added: a known suitable volume of 0.05 M EDTA, 3.5 ml of 1 M ammonium carbonate solution, 1.5 ml of hydrogen peroxide solution (1 mg H_2O_2 ml^{-1}), 0.2 ml of an aqueous solution of thorin (6 mg ml^{-1}) and water to about 25 ml. The cuvette is placed into the photometer (Kolorimeter Typ J, Lange, Berlin), with a blue filter, and titrated (about 1 drop per second) whilst thoroughly mixing (magnetic stirrer) with the unknown solution of manganese(II). During the course of the titration, the absorbance decreases slightly (*ca.* 8 scale units per 100) but after adding the last drop it is reduced within about 30 s to 60–65 units per 100.

Table III gives some results.

The same titration can also be carried out with carminic acid instead of thorin. In this case the following conditions have proved best: 1.5 ml of 1 M ammonium carbonate solution, 0.5 ml of the above peroxide solution and 0.1 ml of carminic acid (4 mg ml^{-1} in 0.1 M sodium hydroxide) are diluted with water to about 25 ml. The absorbance is measured with a green filter.

These titrations can also be graphically recorded if a motor syringe burette is used and the photoelement of the colorimeter is connected to a suitable recorder. Figure 1 shows a typical titration curve.

TABLE III

DETERMINATION OF MANGANESE(II) BY REVERSED TITRATION AGAINST EDTA; PHOTOMETRIC INDICATION

(5.00 ml 0.05 *M* EDTA (equivalent to 13.735 mg Mn) applied)

Sample solution (Mn) consumed (ml)	*Mn conc. calc. (mg ml^{-1})*	*Mn conc. given (mg ml^{-1})*
13.85	0.99	1.002
4.60	2.99	3.005
2.76	4.98	5.008
1.96	7.01	7.011
1.38	9.96	10.015

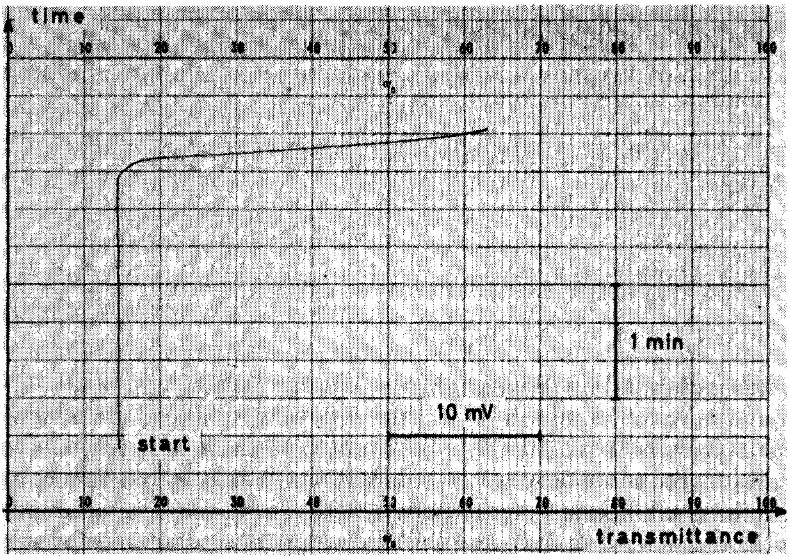

Fig. 1. Determination of manganese(II) by reversed titration against EDTA. 0.70 ml 0.05 *M* EDTA (equivalent to 1.923 mg Mn) applied. Titrant, solution of manganese(II) with 2.97 mg Mn(II) ml^{-1}; speed of recorder, 30 mm min^{-1}; measuring range, 50 mV; speed of burette, 0.277 ml min^{-1}.

COMPLEXIMETRIC TITRATION WITH BIAMPEROMETRIC OBSERVATION OF THE INDICATOR REACTION

The manganese(II)-catalyzed auto-decomposition of hydrogen peroxide

Hydrogen peroxide, which can be oxidized or reduced, can be detected biamperometrically[20]. The presence of free manganese(II) can therefore be noticed by the occurrence of a dead-stop effect, which is due to the catalytic decomposition of hydrogen peroxide.

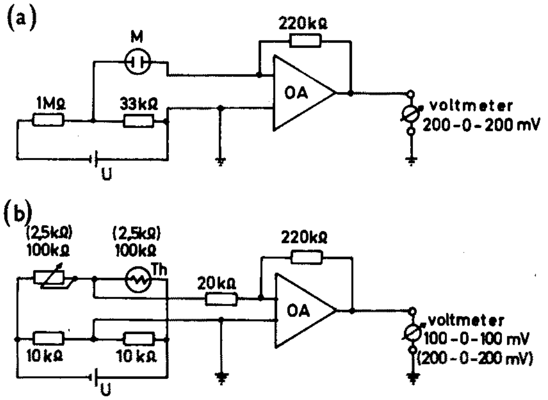

Fig. 2. Schematic representation of the measuring devices for (a) biamperometry and (b) thermometry. (OA) Philbrick/Nexus Q 200; (U) Mallory RM 42 R (1.35 V): (M) measuring cell; (Th) Siemens K 17.

Determination of manganese(II) by reversed titration against EDTA

Figure 2a is a schematic representation of the measuring device. A double-platinum electrode for dead-stop titrations is used. The following solutions are added to a 50-ml beaker: a suitable known volume of 0.05 *M* EDTA, 2.0 ml of 1 *M* ammonium carbonate solution, 0.5 ml of hydrogen peroxide (1 mg H_2O_2 ml^{-1}) and water up to about 25 ml. One or two minutes after dipping in the electrode, a constant potential (resulting from a current to voltage conversion in the measuring device, Fig. 2a) is reached. The solution in the beaker is titrated (about 1 drop per s) with the unknown solution of manganese(II) whilst thoroughly mixing (magnetic stirrer). During the titration the potential already decreases slightly (by *ca.* 10% of full scale), but after adding the last drop it falls within 30 s by another 30% or so.

Some results are given in Table IV.

TABLE IV

DETERMINATION OF MANGANESE(II) BY REVERSED TITRATION AGAINST EDTA; BI-AMPEROMETRIC INDICATION

(5.00 ml 0.05 *M* EDTA (equivalent to 13.735 mg Mn) applied)

Sample solution (Mn) consumed (ml)	*Mn conc. calc. (mg ml^{-1})*	*Mn conc. given (mg ml^{-1})*
13.91	0.99	1.002
6.90	1.99	2.003
4.65	2.96	3.005
3.44	4.00	4.006
1.53	9.00	9.014

This titration can likewise be graphically recorded by use of a motor syringe burette and a suitable recorder.

The electrodes must be cleaned after each determination with concentrated nitric acid, followed by 1 *M* ascorbic acid and water.

COMPLEXIMETRIC TITRATION WITH THERMOMETRIC OBSERVATION OF THE INDICATOR REACTION

The copper(II)-catalyzed oxidation of hydrazine with hydrogen peroxide

The metal ion-catalyzed decomposition of hydrogen peroxide has already been used as an indicator reaction for compleximetric titrations[6]. But its calorific effect was not sufficient for thermal exchanges with the surroundings of the measuring cell to be neglected. Therefore rather cumbersome precautions had to be taken in order to prevent this exchange.

The copper(II)-catalyzed oxidation of hydrazine with hydrogen peroxide[21] is a coupled system of two exothermic reactions, their reaction products being mainly elemental oxygen and nitrogen; its heat of reaction is so high that titration can be performed in a simple reaction vessel (a 50-ml beaker, fitted into a styropore cylinder of about 70 mm outer diameter). The temperature is measured with a thermistor with 2.5 or 100 kohms cold resistance and a resistance decade, wired with an operational amplifier as shown in Fig. 2b.

Determination of copper(II) by reversed titration against EDTA

Into the measuring cell described above, the following solutions are added: a suitable known amount of 0.01 *M* EDTA, 5 ml of aqueous 2 *M* ammonia solution, 1 ml hydrazine hydrate solution (50 mg N_2H_4 ml^{-1}), 0.5 ml of hydrogen peroxide (30%) and water up to about 25 ml. The thermistor is put into the solution and after 1–2 min the measuring bridge is levelled to zero. The EDTA solution is titrated (about 1 drop per s) with the unknown solution of copper(II) whilst thoroughly mixing (magnetic stirrer). During the titration the pointer deflection increases only slightly (10–15% of full scale), but after the last drop of titrant has been added, it goes up within about 30 s by another 30% or so. If necessary, the measuring bridge may be levelled for a second time during the titration.

Some results are given in Table V.

TABLE V

DETERMINATION OF COPPER(II) BY REVERSED TITRATION AGAINST EDTA; THERMOMETRIC INDICATION

(10.00 ml 0.01 *M* EDTA (equivalent to 6.354 mg Cu) applied)

Sample solution (Cu) consumed (ml)	*Cu conc. calc. (mg ml^{-1})*	*Cu conc. given (mg ml^{-1})*
12.71	0.50	0.50
7.08	0.90	0.90
6.37	0.99	1.00
3.19	1.99	2.00
1.60	3.97	4.00

SUMMARY

The principles of the application of catalyzed reactions for the indication of end-points in titrimetric analysis are discussed. Some newer examples are given for this type of titration. An argentimetric titration (Cl^-, Br^-, I^-), in which the indicator reaction is followed visually, and three compleximetric titrations in which the indicator reactions are observed photometrically (Mn), biamperometrically (Mn) and thermometrically (Cu), are described.

RÉSUMÉ

On examine les possibilités d'application des réactions catalysées pour l'indication du point final, lors d'analyse titrimétriques. Quelques exemples nouveaux de ce type de titrage sont décrits: Un titrage argentimétrique (Cl^-, Br^-, I^-), avec détermination visuelle du point final, et trois titrages compleximétriques avec détermination du point final photométrique (Mn), biampérométrique (Mn) et thermométrique (Cu).

ZUSAMMENFASSUNG

Die Anwendung katalysierter Reaktionen zur Endpunktserkennung in der Massanalyse wird kurz diskutiert. Einige neuere Beispiele hierzu werden angegeben. Eine argentometrische Titration von Cl^-, Br^- und J^-, bei der die Indikatorreaktion visuell beobachtet wird und drei komplexometrische Bestimmungen, bei denen die Indikatorreaktion photometrisch (Mn), biamperometrisch (Mn) und thermometrisch (Cu) verfolgt wird, werden beschrieben.

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NEPHELOMETRIC AND TURBIDIMETRIC END-POINTS FOR TITRATION OF SILVER(I) WITH PHOTOGENERATED CHLORIDE ION USING A SINGLE-SOURCE APPARATUS

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Previous work has demonstrated the use of photochemical reactions for generation of titrants[1]. In the only previously reported precipitation titration[2], the precipitate was not photoactive and incremental turbidimetric measurements were used. The present paper describes the photochemical precipitation titration of silver(I). Chloride ion was generated *in situ* at constant rate by photolysis of both monochloroacetic and trichloroacetic acids. The titration product, solid silver chloride, is photoactive[3], and turbidimetric or nephelometric measurements to the point at which precipitation is complete cannot be used. Instead, the first appearance of precipitate is taken as the end-point; the photolysis time to this end-point is inversely proportional to the original silver(I) concentration.

The photolysis of aqueous monochloroacetic acid solutions has been the subject of many past studies[4–8]. The quantum yield of photolysis products, glycolic acid and chloride ion, is temperature-dependent and has been measured only at 254 nm. Previous studies of trichloroacetic acid[7–10] do not report chloride ion as a photoproduct; although such was found in the present study. A novel coulometric method of indirect *in situ* generation of chloride is reported by Hanselman and Rogers[11]. Fifty micromoles of silver(I) could be conveniently titrated by their method.

EXPERIMENTAL

Reagents

Water was doubly distilled and then deionized to assure removal of all chloride. Standard (0.500 *M*) solutions of reagent-grade silver nitrate were prepared in the usual way[12]. Solutions of lesser concentration were prepared by dilution as required.

Monochloroacetic and trichloroacetic acids (Baker and Adamson) met the ACS standard of less than 0.001% free chloride (0.28 micromoles of chloride per g of compound); this amount does not contribute significant chloride for the recommended procedure. In aqueous solutions the chloroacetic acids decomposed to yield significant chloride even when stored at 4° in the dark; therefore use of the

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solid reagent is advised. Both acids were dried for at least 24 h under vacuum before use, and stored under vacuum over Drierite.

Apparatus

The apparatus used was specially constructed for photochemical titrations with a turbidimetric or nephelometric end-point. Construction details have been given[1]. A similar single-source apparatus has been used previously in titrations with fluorimetric end-points[13].

In the nephelometric mode, the first increase in signal from the photocell was taken as the first formation of precipitate. Thus, the sample container and photocell must be carefully shielded from extraneous sources of light. In the turbidimetric mode of operation a decrease in light transmission is measured and the beaker and photocell need be only partially shielded from direct room light; this is an added convenience.

An ultraviolet-transmitting, visible-absorbing filter (C.S. No. 7-54, Corning Glass Works, Corning, N.Y.)[13] was used to attenuate the intensity of photolytic radiation in the turbidimetric configuration, with a 436-nm interference filter (No. 44-79-43, Bausch and Lomb) in the photometric beam. A wide bandpass (350–470 nm) filter was used in the nephelometric configuration; whenever possible the photolytic beam was unfiltered so as to maximize the intensity of scattered radiation.

Procedures

Turbidimetric end-point. Combine about 2 g of trichloroacetic acid with 1–50 μmole of silver ion and dilute to 150 ml. Place a magnetic stirring bar in the titration cell, insert in the apparatus, and stir for 30–60 s. For samples containing 1–5 μmole, no filters or screens are used in the photolysis beam (rapid generation of chloride). For samples containing 5–50 μmole, a neutral-desity screen and 7-54 filter are used (slow generation of chloride). The recorder is started which simultaneously opens the shutter[13]. The recorder is operated in the logarithmic mode for turbidimetric titrations. The solution turbidity, $\log(I_0/I_T)$, is recorded for at least 2 min beyond the first increase in turbidity. The extrapolated intersection of the two straight-line segments (point EP, Fig. 1) is taken as the end-point. Monochloroacetic

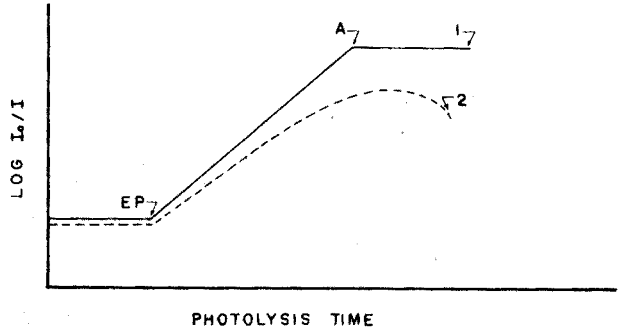

Fig. 1. Titration curves for turbidimetric end-point determination. (1) Theoretical titration curve (no photodecomposition of AgCl). (2) Experimental titration curve (with photodecomposition). (EP) End-point for time to first formation of precipitate. (A) End-point for time to complete precipitation of silver (not obtainable experimentally). Turbidimetric wavelength 436 nm.

acid may be substituted for trichloroacetic acid by using 7 g of the dry reagent. With the 7-54 filter in the photolytic beam, 10–100 μmole can be titrated. Trichloroacetic acid is recommended for reasons to be discussed.

Nephelometric end-point. The trichloroacetic acid reagent and silver(I) are prepared as in the turbidimetric method. For samples containing 1–20 μmole, a neutral density screen is used. For 0.5–2.0 μmole the screen is removed. With the recorder operated in the 0–10%T linear mode, the 0%T is set initially with a bucking voltage[13]. The intensity of scattered light is recorded for at least 2 min past the end-point, which is taken as the first increase in light scattering (formation of silver chloride)

RESULTS AND DISCUSSION

Selection of the end-point

Titration of silver with chloride should result in a plot of turbidity *vs.* time such as Curve 1 of Fig. 1, if silver chloride were not photoactive[3]. The turbidity would remain constant until the solubility product of silver chloride is exceeded, followed by a linear increase in turbidity as the amount of precipitate increases. (See the treatment of Meehan and Chiu[14] for a thorough discussion.) The turbidity should then remain constant after all the silver has been precipitated. Two end-points would then be available in this system: the point where precipitation begins, EP in Fig. 1, and the point where precipitation of silver is completed, point A in Fig. 1. The experimentally obtained curve is shown by Curve 2, Fig. 1. Therefore, all titration data were obtained with the point of first precipitation as the end-point.

The relationship between the time of first precipitation and silver ion concentration is as follows. The chloride concentration required to yield the first precipitate is:

$$[\mathrm{Cl}^-]_{\mathrm{minimum}} = K_{\mathrm{sp}}[\mathrm{Ag}^+]^{-1} \tag{1}$$

The amount of chloride generated at any time, t, is given by:

$$[\mathrm{Cl}^-]_t = (\mathrm{Rate})\cdot t \tag{2}$$

where the rate of chloride generation is the product of the quantum yield, the intensity of radiation, and fraction of incident radiation absorbed[1]. From eqns. (1) and (2) it follows that:

$$t_{\mathrm{ep}} = K_{\mathrm{sp}}(\mathrm{Rate}\cdot[\mathrm{Ag}^+])^{-1} \tag{3}$$

where t_{ep} is the photolysis time required to reach the end-point. Thus a plot of t_{ep} *vs.* $[\mathrm{Ag}^+]^{-1}$ is linear, with a slope of K_{sp}/Rate. Typical working curves are shown in Fig. 2. The fact that an equilibrium model provides an adequate description of the experimental results summarized in Fig. 2 means that the nucleation of silver chloride must occur rapidly as soon as the K_{sp} is exceeded[15]. Other workers have observed that colloidal silver chloride precipitates without supersaturation[15], and photochemical precipitations in which equilibration is rapid, are also known[2].

The precision obtained depends on the precision in measuring the time to the end-point. Very short photolysis times, corresponding to large silver concentrations,

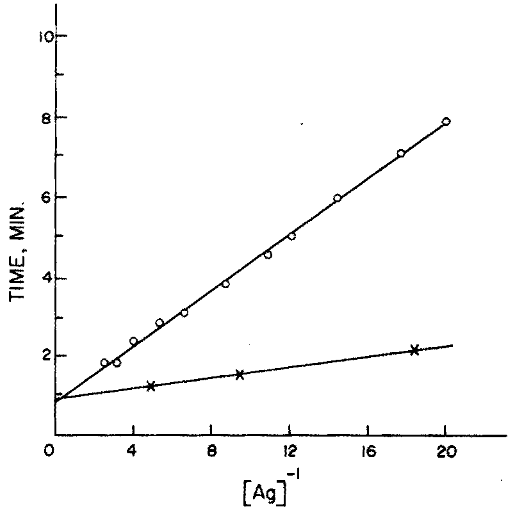

Fig. 2. Working line for titrations of silver(I). (○) Experimental points with turbidimetric end-points. (×) Experimental points with nephelometric end-points. (Solid lines) Least-squares fit of data points. $[Ag^+]^{-1}$ = concentration of silver, in μmole/150 ml. Time = minutes of photolysis to reach point EP in Fig. 1.

result in large relative errors. In order to minimize the error, the generation rate should be adjusted *via* filters in the photolysis beam so that titration times are long enough. For example, titration of 5 μmole of silver required photolysis for 0.75 min with fast generation; with slower generation the time was extended to 7.30 min. The relative errors, given in Tables I and II, are 4.17% with the fast rate and 0.2% for the slower rate.

TABLE I

TITRATION OF SILVER WITH SLOW GENERATION FROM TRICHLOROACETIC ACID AND TURBIDIMETRIC END-POINT

Silver taken (μmole)	*Time to end-point found (min)*	*Time to end-point calcd.[a] (min)*	*Error[b] (%)*
5.0	7.30	7.28	+0.27
6.0	6.10	6.11	−0.16
8.0	4.80	4.70	+2.13
9.0	4.10	4.22	−2.84
12.5	3.15	3.15	0.00
16.0	2.50	2.55	−1.96
20.0	2.05	2.12	−3.30
25.0	1.87	1.78	+5.06
40.0	1.15	1.26	−8.73
50.0	1.14	1.09	+4.59

[a] Calculated from least-squares fit of data points: time to end-point = slope·$[Ag^+]^{-1}$ + intercept.
[b] Percentage difference between observed and calculated values.

TABLE II

TITRATION OF SILVER WITH FAST GENERATION FROM TRICHLOROACETIC ACID AND TURBIDIMETRIC END-POINT

Silver taken (μmole)	*Time to end-point found (min)*	*Time to end-point calcd.[a] (min)*	*Error[b] (%)*
1.0	2.80	2.78	+0.72
2.0	1.45	1.50	−3.33
3.0	1.17	1.24	−5.65
3.5	0.90	0.94	−4.26
4.0	0.82	0.85	−4.17
5.0	0.75	0.72	+4.17

[a] Calculated from least-squares fit of data points. See Table I.

[b] Percentage difference between observed and calculated values.

Tables I and II give the turbidimetric end-point data obtained with trichloroacetic acid as the generator. Over the range of 5–50 μmole an average relative error of 2.9% was obtained. The 1–5 μmole range yielded a relative error of 3.7%. Table III lists some turbidimetric end-point data obtained with monochloroacetic acid as the generator. Over the 10–100 μmole range an average relative error of 3.4% was realized. Data from nephelometric end-points are given in Table IV; these were carried out with trichloroacetic acid, although the monochloroacetic acid would serve as well. Note the larger errors at short titration times. Typical working curves are shown in Fig. 2. In both cases the least-squares line is shown relative to the experimentally obtained points.

The preference for trichloroacetic acid as the photochemical chloride generator is based on the following considerations. From the absorption spectra of the acids, the molar absorptivities at 254 nm were estimated to be about 1 for monochloroacetic acid and 4 for trichloroacetic acid. The ratio of quantum yields,

TABLE III

TITRATION OF SILVER WITH SLOW GENERATION FROM MONOCHLOROACETIC ACID AND TURBIDIMETRIC END-POINT

Silver taken (μmoles)	*Time to end-point found (min)*	*Time to end-point calcd.[a] (min)*	*Error[b] (%)*
10.0	6.80	6.77	+0.44
15.0	4.50	4.52	−0.44
20.0	3.35	3.40	−1.47
25.0	2.80	2.72	+2.94
35.0	1.78	1.95	−8.72
50.0	1.50	1.37	+9.49
100.0	0.70	0.70	0.00

[a] Calculated from least-squares fit of data points. See Table I.

[b] Percentage difference between observed and calculated values.

TABLE IV

TITRATION OF SILVER WITH SLOW GENERATION FROM TRICHLOROACETIC ACID AND NEPHELOMETRIC END-POINT

Silver taken (μmole)	*Time to end-point found (min)*	*Time to end-point calcd.[a] (min)*	*Error[b] (%)*
1.0	9.70	9.73	−1.35
2.0	5.34	5.05	+5.43
5.0	2.18	2.24	−2.75
10.0	1.14	1.30	−14.04
20.0	0.88	0.84	+4.55

[a] Calculated from least-squares fit of data points. See Table I.

[b] Percentage difference between observed and calculated values.

Φ TCA/Φ MCA, was found to be about 2.5. If the literature value of 0.32[16] is used for the quantum yield of monochloroacetic acid, that for trichloroacetic acid is calculated as 0.80 at 254 nm and 25°. The higher molar absorptivity[7] and quantum yield of trichloroacetic acid thus make it the more efficient chloride generator.

Temperature effects

The turbidimetric titration of silver(I) with trichloroacetic acid was studied at three different temperatures. The neutral density screen and 7-54 filter were used in the photolysis beam. Dry trichloroacetic acid (2 g) was added to 100 ml of water at the desired temperature. An aliquot of silver nitrate solution also at the desired temperature, and containing 5–75 μmoles of silver(I), was added to the reaction cell and the whole was diluted to 150 ml. The temperature of the solution was measured and the solution titrated to a turbidimetric end-point. No attempt was made to maintain constant temperature during photolysis. The temperature was measured again after the titration and the elapsed time noted. The temperature at the time of the end-point was calculated, a linear temperature change throughout the titration being assumed. The arithmetic mean of the initial and end-point temperatures was taken as the average individual titration temperature. Several different silver(I) concentrations were titrated at each temperature. The average temperature and standard deviation of the temperature for a series were computed from the individual determinations. The same procedure was followed with monochloroacetic acid, except that only the 7-54 filter was used in the photolysis beam, and 7 g of the acid were required to absorb all the incident light[1].

Equation (3) shows that the photolysis time required to titrate any concentration of silver is directly proportional to K_{sp} and inversely proportional to the chloride generation rate. Both the K_{sp}[17] and quantum yield[16] have been shown to increase with an increase in temperature. Since K_{sp} and rate have opposite effects on the photolysis time to the end-point, the effect of temperature on photolysis time was studied. The necessary data are summarized in Table V. After the solubilities found in the literature[17] had been corrected for ionic strengths, the rate was calculated from the experimentally observed slopes of plots of t_{ep} *vs.* $[Ag^+]^{-1}$ at the various temperatures studied. These data illustrate that the effect of temperature on K_{sp} is the major factor in determining the time to the end-point for these titrations. Effects of temperature on chloride generation rate (quantum yield) are much less. Arrhenius plots of log rate *vs.* $1/T$ (°K) were made and energies of activation of about 3.5 kcal mole^{-1} were obtained for both trichloro- and monochloroacetic acids. The value for monochloroacetic acid agrees well with the value obtained from previously published data[16] and is in accord with a solvent-cage-effect recombination following heterolytic cleavage of the C–Cl bond.

TABLE V

EFFECT OF TEMPERATURE ON K_{sp} OF AgCl AND CHLORIDE GENERATION RATE FROM TRICHLOROACETIC ACID AND MONOCHLOROACETIC ACID

Acid used	*Temperature (°) ± std. dev.*	*Slope of t_{ep} vs. $[Ag^+]^{-1}$*	*Rel. K_{sp} of AgCl*	*Rel. chloride generation rate*
TCA	4.58±0.94	16.73	1.00[a]	1.00[c]
TCA	25.80±0.52	73.00	5.98	1.37
TCA	38.72±0.46	156.82	18.15	1.95
MCA	4.20±0.61	11.71	1.00[b]	1.00[d]
MCA	22.92±0.02	14.50	4.92	1.30
MCA	37.55±0.13	100.81	17.01	1.98

[a] K_{sp} at 4.58° is 1.31 (micromoles/150 ml)^2 (ref. 17).
[b] K_{sp} at 4.20° is 1.02 (micromoles/150 ml)^2 (ref. 17).
[c] Rate at 4.58° is 0.211 (micromoles/min·150 ml) (this work).
[d] Rate at 4.20° is 0.087 (micromoles/min·150 ml) (this work).

Since the mercury source used in this study transfers considerable heat to the surroundings, the temperature rise of the sample during titration was checked. With trichloroacetic acid as the generator, samples of silver were titrated at ambient temperature. Under the conditions used to obtain the data in Table I, a rise of 0.1° min^{-1} was found. At 25° a 1° temperature rise during a 10-min titration would cause a relative error of about 2.5% in determining concentration. The errors presented in Tables I to IV reflect this order of magnitude effect of temperature.

SUMMARY

Nephelometric and turbidimetric titrations of silver(I) have been carried out with chloride ion photochemically generated *in situ* from monochloroacetic and trichloroacetic acids. Trichloroacetic acid is the preferred photogenerator because of larger molar absorptivities and quantum yields at 254 nm. Samples containing 1–100 μmoles of silver can be titrated in less than 10 min with an average error of 3%. Owing to photolysis of silver chloride, end-points were taken as the first appearance of a precipitate; the photolysis time to the end-point is thus inversely proportional to the silver concentration of the sample. A mercury vapor arc is used as the source for both photolysis and end-point measurements. Errors from temperature changes caused by heating of the sample by the arc were studied.

RÉSUMÉ

On propose des titrages néphélométrique et turbidimétrique de l'argent(I), au moyen d'ion chlorure photochimiquement formé à partir des acides monochloracétique et trichloracétique. Des échantillons contenant 1–100 μmoles d'argent peuvent être analysés en moins de 100 min, avec une erreur moyenne de 3%. Le temps de photolyse au point équivalent est inversément proportionnel à la concentration en argent de l'échantillon. Un arc à vapeur de mercure est utilisé comme source soit pour la photolyse, soit pour les mesures du point final. On examine l'influence des variations de température due au chauffage de l'échantillon par l'arc.

ZUSAMMENFASSUNG

Nephelometrische und turbidimetrische Titrationen von Silber(I) wurden mit Chloridionen durchgeführt, die aus Monochloressigsäure und Trichloressigsäure photochemisch *in situ* erzeugt wurden. Trichloressigsäure wird als Photogenerator wegen der grösseren molaren Extinktionskoeffizienten und Quantenausbeuten bei 254 nm bevorzugt. Proben, die 1–100 μmol Silber enthalten, können in weniger als 10 min mit einem mittleren Fehler von 3% titriert werden. Wegen der Photolyse von Silberchlorid wurde als Endpunkt das erste Auftreten eines Niederschlages genommen; die Photolysezeit bis zum Endpunkt ist so umgekehrt proportional der Silberkonzentration der Probe. Ein Quecksilberdampfbogen wird sowohl für die Photolyse als auch für die Endpunktsmessungen verwendet. Fehler aufgrund von Temperaturänderungen, die durch Erwärmung der Probe durch den Lichtbogen hervorgerufen werden, wurden untersucht.

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ACID–BASE DETERMINATION OF ALUMINIUM IN BAUXITE AND RED MUD WITH POTENTIOMETRIC END-POINT DETECTION

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There are several different methods for the determination of the aluminium content of bauxite and red mud. For a suitable choice of method, the most important factors are time consumption, reproducibility and accuracy; the simplicity of the methods may also be important. The automation of the Bayer process demands an automatic quality control of bauxite, and so an objective instrumental analytical procedure seems most appropriate.

As a basic method, the potentiometric potassium fluoride procedure was selected, because of its excellent reproducibility, accuracy, and rapidity. This method was recommended by Watts[1]. However, experiments carried out in this laboratory showed that reproducible and accurate results could be obtained only for pure aluminium solutions. The presence of impurities originating from bauxite and red mud caused serious interferences.

PRINCIPLE OF THE METHOD

Because of its high charge and relatively small size, the aluminium ion generally exists in hydrated form in aqueous solutions; since its coordination number is 6, the following coordination complexes may be formed depending on the concentration of hydrogen ions[2,3]:

pH 4	$Al(H_2O)_6^{3+}$
pH 4–10	$Al(OH)(H_2O)_5^{2+}$, $Al(OH)_2(H_2O)_4^{+}$, $Al(OH)_3(H_2O)_3 \cdot xH_2O$
pH >10	$Al(OH)_4(H_2O)_2^{-}$

The aluminium ion forms different complexes with fluoride ions AlF_n^{3-n} ($n = 1$–6) with different stability constants ($K_1 = 10^{-6}$ and $K_6 = 10^{-20}$). Aluminium may also form polynuclear species. Accordingly, the aluminium–fluoride–hydroxide system is very complicated and the equilibrium depends on the concentration of both hydrogen and fluoride ions. This equilibrium can be stabilized by a large excess of fluoride and hydroxide ions.

In this case, the following reaction can be written:

$$Al(OH)_4(H_2O)_2^- + 6\,F^- \rightleftharpoons AlF_6^{3-} + 4\,OH^- + 2\,H_2O$$

The aluminium is precipitated as an insoluble cryolite-type compound. If the reaction is carried out at pH 10, and the liberated hydroxide ions are titrated back to pH 10, only 3.9 mole of hydroxide can be measured instead of 4 mole of hydroxide per mole of aluminium, *i.e.* the reaction is not stoichiometric. The missing hydroxide may be involved in the formation of a polynuclear species in which an aluminium ion combines with less than four hydroxyl ligands. Therefore, the hydrochloric acid solution applied for back-titration must be standardized against aluminium.

The starting and end points of the titration are adjusted between pH 10 and 11. In more acidic solution, aluminium hydroxide starts to form—even at pH 9.9—and at higher pH, the slope of titration curve is unfavourable from the point of view of back-titration. The change of hydrogen ion concentration during the titration is illustrated in Fig. 1. It can be seen from this Figure and the above-mentioned facts, that the pH must be adjusted and followed with an accuracy of ±0.05, which would require a high quality glass-electrode, pH meter and calibrating buffer system[4].

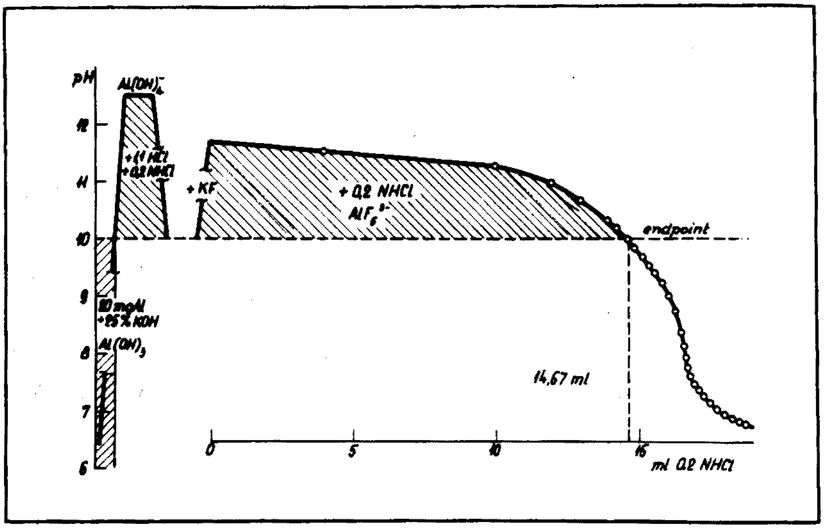

Fig. 1. The change of pH during aluminium determination.

EXPERIMENTAL

Apparatus

A precision pH meter (Radelkis OP 205), and a Radiometer TTT1 Titrator were used with glass electrodes (Metrohm EA-120 U). The electrodes were standardized against 0.01 *M* sodium tetraborate decahydrate solution (pH = 9.18 ± 0.01 at 25°).

Reagents

All chemicals employed were of analytical grade. In solutions of pH 10, corresponding to 10^{-4} *M* hydroxide concentrations, the interference of atmospheric carbon dioxide had to be eliminated. It was found that pentane or other protective layers were unnecessary for the titration, but the 50% potassium fluoride dihydrate reagent at pH 10 stored in a polyethylene flask had to be protected from carbon dioxide by means of an absorber tube containing potassium hydroxide. The pH of the potassium fluoride solution was adjusted to 10.5 (glass electrode). The final adjustment was made as a blank titration; 40 ml of reagent should not change the pH of 300 ml of sodium hydroxide solution at pH 10.1 more than ±0.02 pH.

Because of two contrary factors—the dilution effect and the better reproducibility with large volumes of titrant—the concentration of the titrant had to be selected carefully. The back-titration was done with 0.2 *M* hydrochloric acid as titrant. The hydrochloric acid solution must be standardized by titration against a standard aluminium solution containing an amount of iron equal to the expected Fe_2O_3 content of bauxite or red mud (see Table I).

TABLE I

AMOUNT OF STANDARD IRON SOLUTION ADDED IN STANDARDIZATION

(Standard iron solution (1 g l^{-1}) added to 25 ml of standard aluminium solution (1 g l^{-1}) for standardization of 0.2 *M* hydrochloric acid, depending on the composition of the sample)

Fe_2O_3(%)	Al_2O_3 (%)					
	10	20	30	40	50	60
10	25	10	10	10	10	10
20	50	25	20	10	10	10
30	75	50	25	25	20	20
40	100	50	50	25	20	—
50	100	75	50	25	—	—
60	100	75	50	—	—	—

Procedure for the determination of the Al_2O_3 content of bauxite and red mud

Weigh 1 g of bauxite or 2–3 g of red mud with a precision of 0.1 mg and prepare a solution by high-temperature fusion with sodium hydroxide or by dissolution in acid mixture (sulphuric, hydrochloric and nitric acids). For the separation of silicic acid, dehydrate the solution with sulphuric acid, and after dilution to about 200 ml, filter off the precipitate. Dilute the filtrate to 250 ml in a volumetric flask. Transfer an aliquot containing 20–50 mg of alumina to a 400-ml beaker and dilute to about 200 ml with distilled water. Add 10 ml of a 5% solution of sodium oxalate and adjust the pH to above 12 with 25% potassium hydroxide. Then adjust to pH 10 (exactly the pH of the potassium fluoride reagent) with 1 *M* and 0.2 *M* hydrochloric acid, using the glass electrode. After addition of 40 ml of a 50% (w/v) solution of potassium fluoride dihydrate, titrate the solution with 0.2 *M* hydrochloric acid exactly to the starting pH. The fine adjustment of pH and the titration may be carried out by an autotitrator. The Al_2O_3 content can be calculated from the consumption of standard 0.2 *M* hydrochloric acid solution.

RESULTS AND DISCUSSION

The results of several aluminium determinations are summarized in Table II.

TABLE II

ACCURACY AND REPRODUCIBILITY OF THE METHOD FOR PURE ALUMINIUM SOLUTIONS

(20.00 mg of aluminium was taken in each case)

0.2 M HCl (ml)	*Found Al (mg)*	*Deviation (mg)*
14.65	19.99	−0.01
14.70	20.06	0.06
14.62	19.94	−0.06
14.65	19.99	−0.01
14.67	20.01	0.01
14.65	19.99	−0.01
	Standard deviation (rel.%) 0.24	

These solutions contained aluminium only. The standard deviation calculated was ±0.24 rel.%[5]. The accuracy and reproducibility of the method were the same as those of an acid–base titration.

The application of the method to the analysis of bauxite and red mud

In the case of bauxite and red mud, the method is less simple, because of the other constituents in these materials. The interferences of the other constituents of bauxite and red mud must be known, for an exact and rapid method to be possible. As the alumina content of bauxite is about 50%, interferences are expected primarily from iron, silicon and titanium, which are present in considerable amounts in the solutions, as shown in Table III. In the analysis of red mud, the amount of calcium and sodium may also be important. If the samples are dissolved by mixed acids (H_2SO_4–HCl–HNO_3), or the silica is dehydrated by sulphuric acid, a large amount of sulphate ion will be present in the solution; the effect of sulphate ion must therefore also be considered.

TABLE III

THE COMPOSITION OF SOLUTIONS OF DISSOLVED BAUXITE AND RED MUD

Element or ion	*Concn. unit*	*Bauxite*	*Red mud*
Al	$mg\ l^{-1}$	60–80	60–80
Fe	$mg\ l^{-1}$	40–50	150–300
Si	$mg\ l^{-1}$	5–10	50–100
Ti	$mg\ l^{-1}$	5	40
SO_4^{2-} [a]	$g\ l^{-1}$	10	10
Na	$mg\ l^{-1}$	0.5	60–80
Ca	$mg\ l^{-1}$	1	2 (50)[b]
Mg, V, F, Mn, Cr	$mg\ l^{-1}$	0.5	0.5

[a] If the samples are dissolved by triacid mixture or dehydration of silica is carried out with sulphuric acid. [b] Only from red mud treated with alkali.

Interferences caused by the iron content of bauxite and red mud

The iron oxide content of bauxite is about 10–20%, which is approximately half of the aluminium oxide content. The iron oxide amounts about 50% in red mud but the aluminium oxide content is only 10–20%. Consequently, the red mud analysis presents a more unfavourable case from the point of view of iron–aluminium ratio.

The interference of iron may be explained as follows. Iron(III) forms a complex with fluoride ions, and this process can liberate some hydroxide ions causing an increase of titrant volume. Moreover, during the titration, iron(III) precipitates as hydrated iron(III) oxide and aluminate ions can be adsorbed on the surface of the voluminous precipitate, again causing an increase in titrant consumption. A similar effect is obtained if the precipitated aluminium hydroxide cannot be redissolved as a result of occlusion or adsorption effects of the iron(III) hydroxide.

The stability constant of the fluoroferrate(III) complex is only about 10^{-5} whereas the solubility product of hydrated iron(III) oxide is about 10^{-36}. Measurements proved that the following reaction does not occur under the conditions of the titration:

$$\mathrm{Fe(OH)_3 \cdot x\,H_2O + 6\,F^- = FeF_6^{3-} + 3\,OH^- + x\,H_2O}$$

Only 0.05 ml of 0.2 *M* hydrochloric acid was consumed by titrating 100 mg of iron(III) in the absence of aluminium.

To investigate the absorption and occlusion effect of hydrated iron(III) oxide, the interferences of 1–10 mg and 1–100 mg of iron were measured. The results are shown in Fig. 2. The negative bias is about 1–2 rel.% for bauxite and can reach 10 rel.% for red mud.

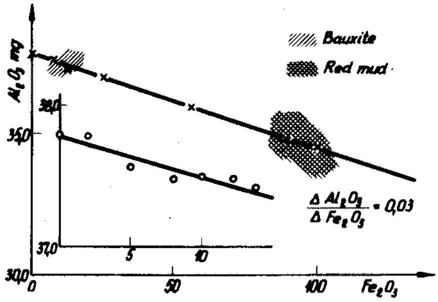

Fig. 2. Adsorption effect of $\mathrm{Fe(OH)_3 \cdot x\,H_2O}$.

Titrations were carried out to identify the process or processes causing the negative error depending on iron content. The results of these experiments proved that hydroxide ions were not absorbed so strongly by hydrated iron oxide in the presence of either fluoride or $\mathrm{AlF_6^{3-}}$ ions that they could not be titrated with hydrochloric acid. These results suggested that the negative bias could be explained by the loss of $\mathrm{Al(OH)_4(H_2O)^-}$ ions only. This could be caused by incomplete redissolution of aluminium hydroxide at pH 12.

The negative bias caused by the iron content of bauxite and red mud is very reproducible; therefore, it can be compensated by a correction factor or during the standardization of the titrant. The standardization can be carried out against a standard aluminium solution containing an amount of iron equal to the expected Fe_2O_3 content, as indicated in Table I (standardization against "standard bauxite or red mud"). It was proved that if the iron content of bauxite was known with an accuracy of ±2%, the bias did not exceed ±0.5% relative.

The interference of the silica content of bauxite and red mud

The silica content of bauxite and red mud solutions is roughly one order of magnitude lower than the aluminium content, but its interference is serious. Under the conditions of the titration at pH 10 or above, the silicon exists in the form of $Si(OH)_4$ or polymeric silicic acid, and fluoride ions can react to form hexafluorosilicate ions:

$$Si(OH)_4 + 6\,F^- \rightleftharpoons 4\,OH^- + SiF_6^{2-}$$

If this reaction occurs, a positive bias would be expected in the titrations. However, the reaction goes quantitatively to the left in the pH range involved in the titration[6]. As was expected, it was found that the hydroxide concentration was not increased by fluoride addition in a solution of pH 10 containing only $Si(OH)_4$. The hydroxide concentration was, however, higher than expected from the aluminium content, when the solution contained both $Si(OH)_4$ and aluminium. As shown in Fig. 3, the situation is similar to that caused by iron in the solutions.

The formation of an excess of hydroxide can be explained by the formation of compounds behaving like ion-exchangers; the hydroxide ions are exchanged by fluoride owing to the high fluoride concentration. It was found that the bias caused by the silica content of bauxites did not exceed ±1% relative. In the case of bauxites and red muds containing extremely large amounts of silica, or if more accurate results are required, the solutions must be freed from silica before the titration.

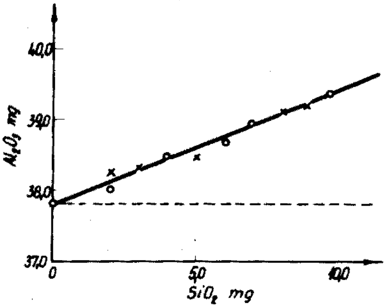

Fig. 3. Interference effect of SiO_2, (○) 0 mg Fe_2O_3 and (×) 12 mg Fe_2O_3.

The effects of the titanium, calcium and sulphate contents of bauxite and red mud

The titanium content of bauxite and red mud solutions is about 5–50 mg l^{-1} (Table III). Under the conditions of the titrations, the titanium precipitates quantitatively because of the high concentration of hydroxide ions, and this process is completed by the coprecipitation effect of iron. The precipitate contains neither aluminate nor aluminium hydroxide[7].

The calcium content of solutions to be titrated amounts only a few mg per l, but may be higher in alkaline red mud. As the calcium reacts with fluoride to form calcium fluoride, releasing hydroxide to the solution, it must be eliminated by the addition of oxalate to form the sparingly soluble calcium oxalate[1].

A large amount of sulphate ion can be present in the solution to be titrated, as a result of the preliminary dissolution or separation process. However, no interferences in the concentration range of 1–50 g of sulphate ions per litre were observed.

Reproducibility of the potentiometric method

The alumina content of a bauxite sample and a red mud sample determined by the proposed method are presented in Table IV. The model sample of bauxite contained 17% Fe_2O_3 and 6% SiO_2. The model sample of red mud contained 40% Fe_2O_3 and 10% TiO_2. The solutions were prepared by fusion with alkali.

The bauxite and red mud samples were also analysed by two independent departments of this Institute. The alumina contents found are also given in Table IV. It can be seen that the accuracy and reproducibility of the results may be considered satisfactory.

TABLE IV

REPRODUCIBILITY OF THE POTENTIOMETRIC METHOD FOR BAUXITE AND RED MUD

Sample	*Measured Al_2O_3 (%)*		*Deviation (rel.%)*	*s_r (%)*	*Al_2O_3 by independent method (%)*
	47.99		0.63		47.55
	47.35		−0.70		47.42
Bauxite	47.51	*47.69*	−0.36	0.53	
	47.83		0.29		
	47.60		−0.18		
	47.88		0.37		
	9.84		0.11		9.90
	9.81		−0.22		9.60
Red mud	9.83	*9.83*	0.00	0.64	
	9.91		0.88		
	9.75		−0.88		

SUMMARY

A method is described for the determination of the alumina content of bauxite and red mud, based on the formation of the aluminium fluoride complex and titration of the liberated hydroxide with 0.2 *M* hydrochloric acid to a potentiometric end-point. The standard deviation is better than ±1% relative. The interference caused by other elements in bauxite and red mud, particularly iron, silicon, calcium and titanium, have been investigated thoroughly.

RÉSUMÉ

On décrit une méthode pour le dosage de l'alumine dans ses minerais; elle consiste à former le complexe fluoré de l'aluminium et à titrer potentiométriquement l'hydroxyde libéré au moyen d'acide chlorhydrique 0.2 *M*. On examine les interférences causées par d'autres éléments, en particulier fer, silicium, calcium et titane.

ZUSAMMENFASSUNG

Es wird eine Methode beschrieben für die Bestimmung des Aluminiumoxidgehalts von Bauxit und Rotschlamm. Sie beruht auf der Bildung des Aluminium–Fluorid-Komplexes und Titration des freigesetzten Hydroxids mit 0.2 *M* Salzsäure bis zu einem potentiometrischen Endpunkt. Die relative Standardabweichung ist besser als ±1%. Die Störungen, die durch andere Elemente in Bauxit und Rotschlamm, insbesondere durch Eisen, Silicium, Calcium und Titan hervorgerufen werden, wurden gründlich untersucht.

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AN IMPROVED SOLID-STATE PERCHLORATE-SELECTIVE ELECTRODE

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In a recent article it was shown that anion-sensitive electrodes may be constructed which employ organic radical-ion salts as electrochemical sensing materials[1]. Solid-state electrodes sensitive to perchlorate ions were chosen for initial examination mainly because of the relative ease with which suitable sparingly soluble perchlorate salts of several Wurster radical-cations could be prepared. The results of that earlier investigation were encouraging because the response towards changes in perchlorate ion activity in the aqueous test solutions approached ideal Nernstian behaviour, even if over only a limited activity range, typically 10^{-1}–$10^{-3.5}$ *M* perchlorate. Furthermore, a certain degree of selectivity towards perchlorate ion was observed. The sensitivity of the electrode potential to variations in pH and the narrow range of pH in which the radical-cation was stable (*e.g.*, $3 < \mathrm{pH} < 5$ for *o*-tolidine radical-cation) were serious limitations to electrode function. As a consequence of these studies certain directions for further efforts became clear and the results of one such investigation are reported below. The general performance observed in this exploratory examination suggests that use of the radical-ion salt chosen as sensing material in solid-state constructions yields electrodes selective for perchlorate ion which have properties comparable with, or better than, existing liquid-membrane types.

The azaviolenes constitute a group of radical-ions which is closely related to the Wurster radicals of the earlier study. Hünig *et al.*[2,3] have shown that azaviolenes derived from the symmetrical 2,2′-azines of several heterocyclic aromatic molecules, *e.g.*, quinoline or benzoimidazole, exhibit extremely high stabilities and may be readily isolated as perchlorate or tetrafluoroborate salts. The original papers may be consulted for further details of preparative methods and properties. A useful brief review has also been published[4].

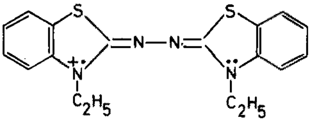
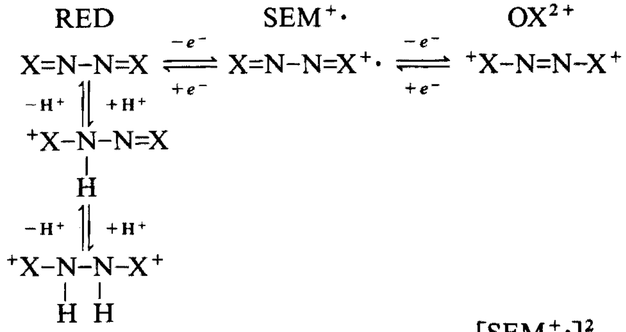


Fig. 1. Structure of the azaviolene form of N-ethylbenzothiazole-2,2′-azine.

As for the Wurster radical, the azaviolene forms part of a two-stage redox system which includes the corresponding azine, RED, the semiquinone or radical-cation (azaviolene), $\mathrm{SEM}^{+\cdot}$, and the azo-dication, OX^{2+}. In solution, additional acid–base equilibria may be established through protonation of the nitrogen atoms in the azo-bridge of the azine species, RED[4]. Both types of equilibrium are represented below in terms of the general formula, the substituent, X, denoting the heterocyclic π-system.



$$\begin{array}{ccccc} \text{RED} & & \text{SEM}^{+\cdot} & & \text{OX}^{2+} \\ X{=}N{-}N{=}X & \underset{+e^-}{\overset{-e^-}{\rightleftharpoons}} & X{=}N{-}N{=}X^{+\cdot} & \underset{+e^-}{\overset{-e^-}{\rightleftharpoons}} & {}^{+}X{-}N{=}N{-}X^{+} \\ {\scriptstyle -H^+}\upharpoonleft\downharpoonright{\scriptstyle +H^+} & & & & \\ {}^{+}X{-}\underset{\underset{H}{|}}{N}{-}N{=}X & & & & \\ {\scriptstyle -H^+}\upharpoonleft\downharpoonright{\scriptstyle +H^+} & & & & \\ {}^{+}X{-}\underset{\underset{H}{|}}{N}{-}\underset{\underset{H}{|}}{N}{-}X^{+} & & & & \end{array}$$

The semiquinone formation constant, $K = \dfrac{[\text{SEM}^{+}\cdot]^2}{[\text{RED}]\,[\text{OX}^{2+}]}$

attains values typically in the range $10^5 < K < 10^{10}$ and these reflect the great stability which results from extensive charge delocalization within the π-electronic system of the radical-cation[4]. It can be clearly seen from the above equilibria, however, that the stability of the azaviolene in solution depends upon the extent to which the parent azine, RED, becomes protonated. Appreciable protonation of RED will cause K to become apparently pH-dependent and it follows that in such instances the observed potential of an electrode which incorporates a salt of the azaviolene as sensor will also depend upon pH. An assessment of the basic properties of the RED species is therefore relevant. Closer consideration of the azine structure suggests that the basicities of the nitrogen atoms forming the azo-bridge will be low (sp^2-hybridization) and that the inductive and mesomeric effects of the substituents, X, will play an important role in either increasing or decreasing these basicities. Thus by a suitable choice of X the tendency of RED to undergo protonation may be decreased to a level where K, and hence the electrode potential, will become effectively independent of pH. Among the compounds investigated by Hünig *et al.*, the azine derived from N-ethylbenzothiazole was found to be so weakly basic that the redox potential corresponding to the reaction

$$\text{RED} \rightleftharpoons \text{SEM}^{+\cdot} + e^-$$

remained constant[3] over the range $2 < \text{pH} < 11$. The azaviolene formed from this particular azine and whose structure is shown in Fig. 1 was therefore considered appropriate for use as electrode sensor in the form of its perchlorate salt.

EXPERIMENTAL

Materials

The perchlorate salt of the azaviolene of N-ethylbenzothiazole-2,2′-azine was prepared by the method of Hünig *et al.* with similar reactant proportions and reaction conditions[2]. A brief summary, covering only the principal stages of the synthesis, is therefore given below.

2-Chlorobenzothiazole (Eastman Kodak) was N-alkylated by treating it with the stoichiometrically required amount of freshly prepared triethyloxonium tetrafluoroborate[5] in refluxing 1,2-dichloroethane. After cooling and allowing to stand overnight, the reaction mixture was filtered to give colourless crystals of N-ethyl-2-chlorobenzothiazolonium tetrafluoroborate. These crystals were washed with 1,2-dichloroethane and dry ether and dried *in vacuo* over anhydrous calcium sulphate.

The symmetrical 2,2′-azine of N-ethylbenzothiazole was then prepared from the above quaternary salt by reaction with hydrazine hydrate in methanol solution in the presence of triethylamine. Colourless crystals with m.p. 206° (lit. m.p. 204–208°)[2] were obtained after filtering, washing with methanol, and drying. Ultraviolet–visible spectra in acetonitrile confirmed the identity of the product; the shape and position of the major absorption peak at 335 nm agreed fully with the observations of Hünig *et al.*[2].

N-ethylbenzothiazole-2,2′-azine was finally dissolved in dimethylformamide and oxidized to the corresponding azaviolene with the appropriate quantity of lead tetraacetate (saturated solution in acetic acid). The intensely blue solution was filtered and the filtrate added to a solution of sodium perchlorate in dimethylformamide. The resulting blue precipitate was filtered off, washed with water and dry ether, and dried *in vacuo* over anhydrous calcium sulphate. The absorption spectrum of the azaviolene perchlorate in acetonitrile showed a major absorption centred at 396 nm, the position and shape of which agreed with that observed by Hünig *et al.*[2].

No additional examination of the azaviolene perchlorate salt was undertaken; information relevant to the stability, radical-ion content, and stoichiometry may be found in the literature[2–4].

Electrode construction

A "Selectrode" body was used throughout the present investigation. The details of its construction have appeared elsewhere[6]. A small amount (*ca.* 0.5 mg) of the azaviolene perchlorate salt was pressed into the pre-roughened sensing surface (fine-grained sandpaper) and the surface was manually polished with a rounded glass rod. Electrode regeneration comprised the cutting-away of *ca.* 0.5 mm of electrode stem followed by application of the radical-ion salt to the newly exposed sensing surface as above.

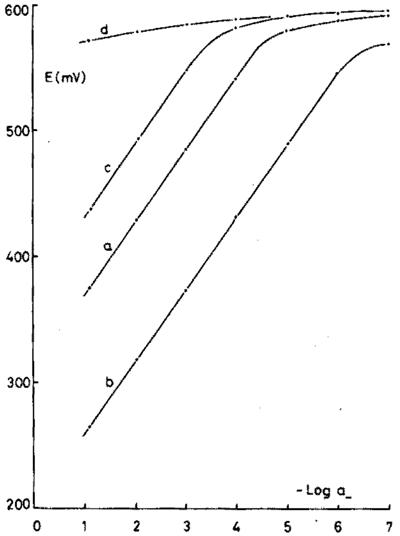
Measuring procedure

Cell potentials were measured at 25° with an Orion model 701 digital pH-meter which was connected to an Orion model 751 digital printer. The printer facilitated preliminary studies of the stabilities of the observed potentials. The reference was an Orion model 90-02 double liquid-junction electrode with an outer-chamber filling of aqueous 10% (1.87 *M*) ammonium chloride. No corrections for variations in liquid-junction potential were applied to the cell potentials observed. Calibration and interference response curves were established from measurements carried out in separate aqueous solutions of single sodium salts (for pH-response, mixtures of hydrochloric acid and sodium perchlorate solutions were used). After immersing the electrodes in a given test solution, readings were taken at 30-s intervals until a steady potential was attained. Such data provided an estimate of the rapidity of electrode response. Single ion activities were calculated from the extended Debye–Hückel relation[7] with the ion-size parameters of Kielland[8].

Absorption spectra were recorded at room temperature with a Unicam SP 1800 spectrophotometer.

RESULTS

Figure 2 illustrates the response behaviour of the N-ethylbenzothiazole-2,2′-azaviolene perchlorate electrode towards the reference ion, perchlorate, and the major interfering anions, iodide and tetrafluoroborate. The linear region of the perchlorate calibration curve between 10^{-1} and $10^{-4.5}$ M corresponded to a slope



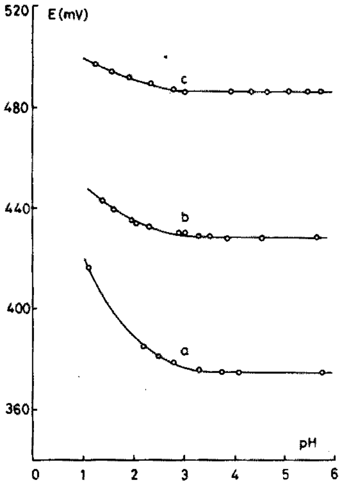


Fig. 2. Response of the N-ethylbenzothiazole-2,2′-azaviolene perchlorate electrode towards the following ions: (a) ClO_4^-, (b) I^-, (c) BF_4^-, (d) F^-.

Fig. 3. Dependence of cell potential on pH at different activity levels of perchlorate ion: (a) 10^{-1} M ClO_4^-, (b) 10^{-2} M ClO_4^-, (c) 10^{-3} M ClO_4^-. The contributions from liquid-junction potential changes are estimated to amount to *ca.* +5 mV at pH 1 (Henderson equation).

TABLE I

APPARENT SELECTIVITY COEFFICIENTS FOR $a_{ClO_4^-} = 10^{-1}$ M IN UNBUFFERED AQUEOUS SOLUTIONS[a]

Anion(X)	$K_{ClO_4^-/X}$	*Anion (X)*	$K_{ClO_4^-/X}$
ClO_4^-	1.0		
F^-	$4.2 \cdot 10^{-4}$	CH_3COO^-	$3.2 \cdot 10^{-4}$
Cl^-	$7.8 \cdot 10^{-4}$	OH^-	$6.3 \cdot 10^{-3}$
Br^-	$6.5 \cdot 10^{-4}$	ClO_3^-	$8.7 \cdot 10^{-4}$
I^-	75	BF_4^-	0.12
NO_3^-	$1.1 \cdot 10^{-3}$	SO_4^{2-}	$2.3 \cdot 10^{-4}$

[a] Maximum uncertainty in $K_{ClO_4^-/X}$ values estimated to be ±7%.

of 58 ± 1 mV decade^{-1}. The response curve for fluoride, also shown in the Figure, was typical of those observed for all the remaining anions studied, namely, OH^-, Cl^-, Br^-, NO_3^-, CH_3COO^-, ClO_3^-, and SO_4^{2-}. (The plots for the last-mentioned anions have been omitted to preserve clarity.) These data showed that, with the exception of iodide, the electrode responded selectively to perchlorate ions. Apparent selectivity coefficients, which are collected in Table I, were evaluated from the cell potentials corresponding to reference ion and interference ion activities of 10^{-1} *M* (10^{-2} *M* for sulphate) according to

$$\log K_{\text{ref/interf}} = (E_{\text{ref}} - E_{\text{interf}})/59.2$$

where the potentials E_{ref} and E_{interf} are expressed in mV. Selectivity for the reference ion is reflected by values of $K_{\text{ref/interf}}$ less than unity. The coefficients thus obtained remain valid only for 10^{-1} *M* ClO_4^-; poorer selectivity results at lower perchlorate activities.

Figure 3 shows the variation of cell potential with pH observed at different activity levels of perchlorate ion; pH values were measured *in situ* with a combination glass-electrode, Metrohm type EA 147X. Interference from hydrogen ion occurs only for $\text{pH} \leqslant 3$. For the alkaline regions, the interference of hydroxide may be estimated from the value of the selectivity coefficient appropriate to a given activity of perchlorate. Such data, shown in Table II, indicate that 10^{-1} *M* perchlorate may be measured in solutions of pH 13, and 10^{-3} *M* perchlorate in solutions of pH 11 without significant interference from hydroxide.

TABLE II

APPARENT SELECTIVITY COEFFICIENT $K_{ClO_4^-/OH^-}$ AS A FUNCTION OF PERCHLORATE ION ACTIVITY

$a_{ClO_4^-}$ (*M*)	$K_{ClO_4^-/OH^-}$
10^{-1}	$6.3 \cdot 10^{-3}$
10^{-2}	$1.1 \cdot 10^{-2}$
10^{-3}	$4.0 \cdot 10^{-2}$
10^{-4}	$2.1 \cdot 10^{-1}$

Calibration checks were performed after each series of solutions containing a particular interfering ion had been measured. These showed that in all cases, except that of iodide, the original calibration plot was reproduced within 1 mV over its entire range. After the electrodes had been immersed in iodide solutions, however, measurement in 10^{-1} *M* perchlorate gave a cell potential which was *ca.* 70 mV too high. This potential remained constant within 1 mV for a period exceeding 18 h, *i.e.*, no drift of the potential towards the calibration curve was discernible. The probable cause of this permanent "poisoning" by iodide ion is considered in the discussion.

Response times in perchlorate solutions were estimated to be less than 1 min at all activities. In the interfering ion solutions stable potentials were reached within 3–4 min. The stabilities of the potentials were extremely good. For 10^{-1} *M* sodium perchlorate the cell potential remained constant within 1 mV for *ca.* 72 h;

for 10^{-4} *M* perchlorate the stable (± 1 mV) period exceeded 19 h.

The lifetime of an individual electrode based upon the "Selectrode" construction becomes a question of secondary importance provided that acceptably reproducible examples can be obtained. If this condition is met, a simple regeneration procedure is all that is required when the electrode ceases to function because of insufficient sensing material at the surface or because of "poisoning". The purity and stability of the sensing material itself and the reproducibility of its preparation become the major factors affecting the electrode performance in this respect. Different electrode examples were prepared from a single batch of the azaviolene salt over a period of 2 months. These gave calibration curves which differed by at most ± 2 mV from a mean curve over the activity range studied, *i.e.*, 10^{-1}–10^{-6} *M* ClO_4^-. Comparisons between electrodes derived from separate syntheses have not, as yet, been performed.

DISCUSSION

The preliminary results summarized above show that a practical solid-state perchlorate selective electrode may be obtained by employing N-ethylbenzothiazole-2,2′-azaviolene perchlorate as sensing material. The operational activity range (10^{-1}–$10^{-4.5}$ *M* perchlorate), the effectively Nernstian response (58 ± 1 mV decade^{-1}), the speed of response, the stabilities of the potentials observed and the selectivity over commonly encountered anions compare favourably with similar parameters for liquid-membrane electrodes. In addition, the sensitivity of the electrode potential towards both hydrogen ions and hydroxyl ions is reduced in comparison with that shown by the liquid-membrane types currently available. Determinations of perchlorate ion activity are thus permitted over a much wider range of pH-values without the occurrence of interference.

Among the anions studied, only iodide interfered so seriously as to affect the reproducibilities of the potentials observed in perchlorate solutions (see Results). The cause of this irreversible "poisoning" probably arises from the reduction, by iodide ions, of a significant proportion of the azaviolene molecules which occupy the surface layers of the sensor salt. (The redox potential for the system RED/SEM$^{+\cdot}$ is *ca.* $+690$ mV *vs.* N.H.E.[3]). Qualitative confirmation of such a reduction was readily obtained by spectral analyses of solutions of the azaviolene perchlorate salt in 2-ethoxyethanol/water mixtures (1:1 v/v). The addition of a few drops of a solution of lithium iodide in the same solvent produced a marked decrease in the absorption peak at 396 nm (azaviolene) and the introduction of a strong absorption at 335 nm (parent azine, RED). If it is assumed that the electrode potential is determined by the ratio of the activities of azaviolene in the solution and crystalline phases and further that the activity in solution is controlled by a solubility equilibrium, then

$$E = \text{const.} + (RT/F) \ln (a_{\text{SEM}^{+\cdot}})_{\text{aq.}} / (a_{\text{SEM}^{+\cdot}})_{\text{cryst.}}$$

or equivalently,

$$E = \{\text{const.} - (RT/F) \ln (a_{\text{SEM}^{+\cdot}})_{\text{cryst.}} + (RT/F) \ln K_{\text{so}}\} - RT \ln (a_{\text{ClO}_4^-})_{\text{aq.}}$$

where K_{so} is the solubility product of the azaviolene perchlorate. The standard electrode potential, denoted by the bracketed term, thus depends on the activity of azaviolene molecules in the solid phase. A decrease in $(a_{\mathrm{SEM}^{+\cdot}})_{\mathrm{cryst.}}$ through reduction by iodide should thus lead to an increase in the standard potential. Such a change is consistent with observation. Further quantitative studies are needed to verify this explanation.

The response curve obtained from measurements in iodide solutions, which was linear over the activity range 10^{-1}–10^{-6} M I$^-$ and of slope 58 ± 1 mV decade^{-1}, suggested that the electrode might provide a sensor selective towards iodide ions. At present, a detailed assessment of this possibility has not been made.

As a general conclusion it may be stated that, on the basis of the behaviour observed, the solid-state perchlorate electrode described in this report represents a significant improvement over the radical-ion salt electrodes of the previous study. Furthermore, it offers a practical alternative to sensors which involve the use of liquid ion-exchange systems.

The author wishes to thank Dr. J. Ruzicka for gifts of "Selectrode" bodies and Prof. G. Johansson for his continued interest in this work. Financial support by the Swedish Board for Technical Development is gratefully acknowledged.

SUMMARY

A solid-state perchlorate sensitive electrode, based upon a radical-ion salt derived from N-ethylbenzothiazole-2,2′-azine, has been prepared. Its response characteristics and high apparent selectivity for perchlorate over many common anions show marked improvements with respect to similar systems which were studied earlier. The general electrode properties observed suggest that it may be considered an acceptable practical alternative to existing liquid-membrane sensors for perchlorate.

RESUME

On a préparé une électrode sélective au perchlorate, basée sur un sel à radical ionique dérivant du N-éthylbenzothiazole-2,2′-azine. Ses caractéristiques de réponse et sa sélectivité montrent qu'elle offre une nette amelioration par rapport aux systèmes similaires précédemment étudiés.

ZUSAMMENFASSUNG

Es wurde eine für Perchlorat empfindliche Festkörper-Elektrode hergestellt, die auf einem von N-Äthylbenzothiazol-2,2′-azin abgeleiteten Radikalionsalz beruht. Ansprecheigenschaften und hohe scheinbare Selektivität für Perchlorat gegenüber vielen üblichen Anionen zeigen merkliche Verbesserungen gegenüber ähnlichen, früher untersuchten Systemen. Aufgrund der beobachteten allgemeinen Elektrodeneigenschaften kann die Elektrode als angenehme, praktische Alternative zu bekannten Flüssig-Membran-Sensoren für Perchlorat angesehen werden.

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DETERMINATION OF TRACE AMOUNTS OF SILVER(I) BY POLAROGRAPHIC, ANODIC STRIPPING AND CHRONOPOTENTIOMETRIC METHODS AT A MERCURY ELECTRODE

STUDIES IN AQUEOUS AND NONAQUEOUS MEDIA

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Polarographic methods are not widely used for the determination of silver for several reasons. Use of a classical mercury dropping electrode in a non-complexing aqueous medium is not possible. The normal potential of the Ag^+/Ag couple (0.799 V) is so close to those of the Hg^{2+}/Hg (0.854 V) and Hg_2^{2+}/Hg (0.789 V) couples that the polarographic wave is masked by the oxidation wave of mercury. In order to overcome this limitation some authors have experimented with solid electrodes, principally platinum[1-4] and to a lesser degree, carbon paste[5], graphite[6] and silver[7] electrodes. Nevertheless, because of the poor reproducibility of the results obtained with such electrodes[8], several authors have preferred to use indirect methods[9-11]. The advantage of the indirect methods which use mercury electrodes is that results are reproducible, whereas the disadvantage, inherent in all indirect methods, is the poor selectivity.

The aim of this work was to find a direct method for the determination of

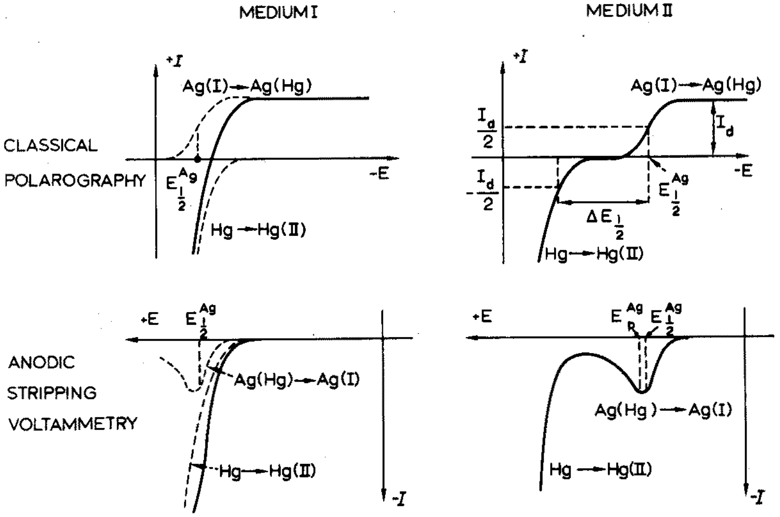

Fig. 1. Schematic representation of current–potential curves for Ag(I)/Ag(Hg) and Hg(II)/Hg couples in 2 different media.

silver(I), with a mercury electrode. The techniques of dissolution of silver after accumulation by pre-electrolysis on the electrode were mainly studied as they enabled higher sensitivity to be attained. They require media in which the half-wave potential ($E_{\frac{1}{2}}$) of silver is sufficiently negative compared to the oxidation potential of mercury.

Figure 1 shows that an accurate determination of silver by d.c. polarography in medium I is impossible, because the capacitance and residual currents cannot be subtracted from the silver reduction current. Moreover, determinations by anodic stripping are impossible in this medium. On the other hand, in medium II an accurate determination is possible by both d.c. polarography and anodic stripping.

For quantitative work, it is usually assumed that $\Delta E_{\frac{1}{2}}$ must be greater than or equal to 100 mV. In order to obtain this result, the degree of complexation (or solvation) must be higher for silver than for mercury. It has been shown by Baumgartner[12] that the potential of the Ag(I)/Ag(Hg) couple can be sufficiently reduced by complexation to enable the oxidation of the amalgamated silver by an oxidizing agent present in the solution. However, there is a simultaneous oxidation of mercury. In polarographic methods, this oxidation must be avoided in order to obtain accurate results. Hence the choice of the complexing agent is made more difficult.

POLAROGRAPHIC REDUCTION OF SILVER(I) IN AQUEOUS MEDIA

Choice of ligand

Although Hg(I) is relatively stable in noncomplexing medium[13], it is generally unstable in the presence of ligands; in the latter case, the Hg(II)/Hg couple determines the potential of the mercury electrode in polarography[13,14].

When the two redox reactions

$$\mathrm{Hg} + \mathrm{Me}^{n+} + ne^- \rightleftarrows \mathrm{Me(Hg)}$$

and

$$\mathrm{Hg}^{2+} + 2e^- \rightleftarrows \mathrm{Hg}$$

are reversible and if the ligands present are in large excess in comparison with Me^{n+}, then for the two polarographic curves we have[14]:

$$E = E_{\frac{1}{2}}^{\mathrm{Me}} - \frac{RT}{nF} \ln \alpha_{\mathrm{Me}} + \frac{RT}{nF} \ln \frac{I_{\mathrm{d}} - I}{i} \tag{1}$$

and

$$E = E_{\mathrm{o}}^{\mathrm{Hg}} - \frac{RT}{2F} \ln \alpha_{\mathrm{Hg}} + \frac{RT}{2F} \ln \frac{-I}{K_{\mathrm{Hg}}} \tag{2}$$

respectively, where the current I is negative for oxidation and positive for reduction; $\mathrm{K_{Hg}}$ is the Ilkovič constant for mercury(II), and α_{Me} and α_{Hg} are the complexation degrees of Me(n) and mercury(II), respectively.

$$\begin{aligned}\alpha_{\mathrm{Me}} = 1 &+ \beta_1^1[\mathrm{L}_1] + \beta_2^1[\mathrm{L}_1]^2 + \ldots + \beta_i^1[\mathrm{L}_1]^i \\ &+ \beta_1^2[\mathrm{L}_2] + \beta_2^2[\mathrm{L}_2]^2 + \ldots + \beta_j^2[\mathrm{L}_2]^j \\ &\vdots \\ &+ \beta_1^m[\mathrm{L}_m] + \beta_2^m[\mathrm{L}_m]^2 + \ldots + \beta_k^m[\mathrm{L}_m]^k\end{aligned}$$

where $[\mathrm{L}_p]$ = total concentration of ligand L_p (when in excess over Me(n)), Me(n) = metallic ion in the oxidation state $+n$, β_q^p = overall stability constant of the q^{th}

complex of Me(n) with the ligand L_p, at the ionic strength of the medium under consideration.

The other terms have their usual meaning.

From eqns. (1) and (2) it is possible to show that:

$$\Delta E_{\frac{1}{2}} = E_o^{Hg} - E_{\frac{1}{2}}^{Me} + \frac{RT}{2F}\ln\left[\frac{n}{4}\left(\frac{\bar{D}_{Me}}{\bar{D}_{Hg}}\right)^{\frac{1}{2}}\right] + \frac{RT}{2F}\ln[Me] + \frac{RT}{F}\ln\left(\frac{(\alpha_{Me})^{1/n}}{\alpha_{Hg}^{\frac{1}{2}}}\right) \quad (3)$$

where $\bar{D}_{Me}$ and $\bar{D}_{Hg}$ are the mean diffusion coefficients of complexed Me(n) and Hg(II), respectively, and [Me] is the total concentration of Me(n) in the solution.

For a constant value of [Me], it can be assumed that only the last term in eqn. (3) depends on the nature and concentration of the ligands.

In the present case, Me(n)=Ag(I).

When only one ligand is present in the solution, the expression

$$\frac{RT}{F}\ln\left(\frac{\alpha_{Ag}}{\alpha_{Hg}^{\frac{1}{2}}}\right) = \frac{RT}{F}\ln\left(\frac{1+\beta_1^{Ag}[L]+\beta_2^{Ag}[L]^2+\ldots+\beta_m^{Ag}[L]^m}{\{1+\beta_1^{Hg}[L]+\beta_2^{Hg}[L]^2+\ldots+\beta_k^{Hg}[L]^k\}^{\frac{1}{2}}}\right)$$

is obtained, where m and k are the coordination numbers of silver(I) and mercury(II), respectively, with ligand L.

When L is in high excess:

$$\frac{\alpha_{Ag}}{\alpha_{Hg}^{\frac{1}{2}}} \cong \frac{\beta_m^{Ag}}{(\beta_k^{Hg})^{\frac{1}{2}}}[L]^{(m-k/2)}$$

The coordination number of mercury(II) is often 4, and the relation $k/2 \leqslant m \leqslant k$ is generally valid. Hence, as [L] increases, $\alpha_{Ag}/\alpha_{Hg}^{\frac{1}{2}}$ also increases, or approaches a constant value. It follows that the concentration of the ligand as well as the ratios

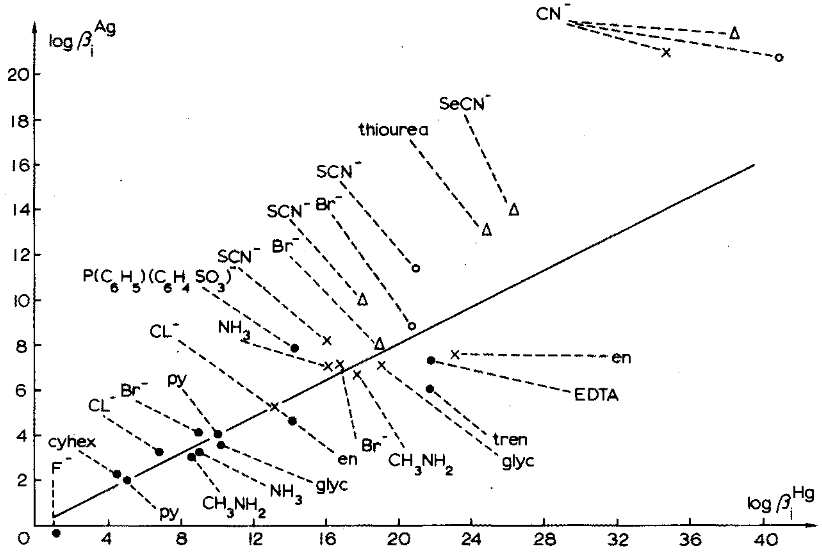

Fig. 2. Relationship between the ith overall constant of silver(I) and mercury(II) for different complexing agents (also see Table I). ● i=1, × i=2, △ i=3, ○ i=4.

$\beta_m^{Ag}/(\beta_k^{Hg})^{\frac{1}{2}}$ and m/k should be as high as possible to allow polarographic determination. Moreover, from eqn. (3), for $\Delta E_{\frac{1}{2}} \geqslant 100$ mV, and assuming $E_{\frac{1}{2}}^{Ag} \cong E_o^{Ag}$ and $\bar{D}_{Ag} \cong \bar{D}_{Hg}$, we get:

$$\frac{\alpha_{Ag}}{\alpha_{Hg}^{\frac{1}{2}}} \geqslant \frac{4.3}{[Ag]^{\frac{1}{2}}}$$

Figure 2 shows a plot of log β_i^{Ag} *versus* the log β_i^{Hg} for a large number of ligands, measured at the same temperature and if possible at the same ionic strength (Table I). It can be shown that, for any value of i and for monodentate saturated ligands, the points lie approximately on a straight line.

It can be seen from Fig. 2 that the ligands which have coordinating atoms that are not highly polarizable are located below the straight line (EDTA, ethylenediamine, diethylenetriamine, glycinate), and the ligands which either are π-acceptors or have polarizable coordinating atoms ($P(C_6H_5)_2(C_6H_4SO_3)$, SCN^-, $SeCN^-$, thiourea, CN^-) are clearly located above this line. Hence a complexing agent from the latter

TABLE I

OVERALL CONSTANTS OF SILVER(I) AND MERCURY(II) WITH DIFFERENT LIGANDS
(Values given in literature[a] for 25° unless otherwise stated, and for an ionic strength as close as possible to 0.5 M)

Ligand	*Ag(I)*					*Hg(II)*				
	Ionic strength (M)	*log β_1*	*log β_2*	*log β_3*	*log β_4*	*Ionic strength (M)*	*log β_1*	*log β_2*	*log β_3*	*log β_4*
F^-	0.5	−0.17	—	—	—	0.5	1.03	—	—	—
Cl^-	1.0	3.36	5.2	—	—	0.5	6.74	13.22	14.17	15.22
Br^-	0.1	4.15	7.11	7.95	8.89	0.5	8.94	16.88	19.15	20.90
NH_3	1.0	3.37	7.15	—	—	2.0	8.8	16.15	17.15	17.93
CH_3NH_2	0.5	3.15	6.68	—	—	0.5	8.6	17.9	18.3	—
Diethylenetriamine (tren)	0.1 (20°C)	6.1	—	—	—	0.5 (20°C)	21.8	—	—	—
Ethylenediamine (en)	0.1	4.7	7.7	—	—	0.1	14.3	23.3	23.06	—
Glycinate (glyc)	0.5 (20°C)	3.7	7.0	—	—	0.5 (20°C)	10.3	19.2	—	—
EDTA	0.1 (20°C)	7.32	—	—	—	0.1 (20°C)	21.80	—	—	—
Pyridine (py)	0.5	2.01	4.16	—	—	0.5	5.1	10.0	10.4	—
Cyclohexene (cyhex)	1.0 (0°C)	2.28	—	—	—	1.0	4.34	—	—	—
$P(C_6H_5)_2$-$(C_6H_4SO_3)$[b]	?	8.0	—	—	—	1.0	14.3	24.3	29.3	32.6
SCN^-	4.0	4.59	8.28	10.06	11.26	1.0	—	16.07	18.95	20.94
$SeCN^-$	0.3	—	10.7	13.9	—	0.3	—	—	26.4	28.87
Thiourea[c]	0	—	—	13.05	—	?	—	22.1	24.7	26.8
CN^-[c]	0.3	—	21.1	21.8	20.7	0.1	18.0	34.7	38.5	41.5

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[a] Values are taken from Sillen and Martell[15] unless otherwise mentioned.
[b] Values from Jørgensen[16].
[c] Values from Ringbom[17].

category must be chosen for the polarographic determination of silver at a mercury electrode.

Experimental results

Many complexing agents were selected by means of the following guidelines:
they should satisfy the criteria described above;
they should form chemically stable soluble complexes with silver(I);
they should be simple to use in order to be suitable for analytical purposes;
they should be electrochemically inert in the region of the oxidation potential of mercury and of the reduction potential of silver.

The potentiometric behaviour of the Ag(I)/Ag couple with a silver electrode dipping in a silver(I) solution, and of the Hg(II)/Hg couple with a mercury pool electrode dipping in mercury(II) solution, were studied in the presence of various ligands[18]. Under these conditions, the ligands which produced the maximum difference in potential between the electrodes were cyanide, thiocyanate and thiourea. These results seem to confirm the data of Fig. 2.

Polarographically, it was not possible to separate the silver(I) from the mercury(II) wave[18]. This is not very surprising, as the values of the ratio $\beta_m^{\mathrm{Ag}}/(\beta_k^{\mathrm{Hg}})^{\frac{1}{2}}$ are very small. Hence this determination does not seem possible in aqueous medium with the classical complexing agents.

POLAROGRAPHY OF SILVER IN NONAQUEOUS MEDIA (ACETONITRILE)

Choice of solvent

There are relatively few nonaqueous solvents that can be used in polarography, particularly for the study of inorganic compounds. These solvents should be able to dissolve and to dissociate an appreciable concentration of electrolyte to permit good electrical conductivity[19]. They should also be chemically and electrochemically inert to allow the study of the redox reaction over a large potential range. Furthermore, in our particular case the solvent should form stronger complexes with silver(I) than with mercury(II).

Ethylenediamine is a weak complexing agent (Fig. 2), which is confirmed by the results of Schaap and Messner[20] who could not obtain a reduction wave of silver(I) in this medium, but reported, for the normal potential of the Ag(I)/Ag couple, the value of $+1.53$ V *versus* a zinc amalgam covered by solid $ZnCl_2$, as reference electrode. However, an attempt was made to verify the report of Gutmann and Schöber[21] who claim to have obtained a polarographic wave of silver(I) in this solvent. They reported a $E_{\frac{1}{2}}$ value of -1.84 V *versus* a modified calomel electrode. The present polarographic measurements, under the same conditions as Gutmann and Schöber, showed no evidence of a reproducible reduction wave of silver(I). Moreover, a potentiometric study indicated that in the ethylenediamine–0.1 *M* $NaNO_3$ medium, the normal potential of the Ag(I)/Ag couple was higher than that of the Hg(II)/Hg couple[18].

From the solvation properties of ions[22], the nitriles would appear to be suitable solvents. Kolthoff and Coetzee[23] have studied the influence of some nitrile solvents (acetonitrile, benzonitrile, phenylacetonitrile, acrylonitrile, propionitrile) on the half-wave potential value of silver by DME polarography. However, these authors did not consider the possibilities of application to quantitative analysis, and they were not interested in the separation of the mercury and silver waves. Hence, the reduction of silver was studied again. It was ascertained that a silver wave well separated from the oxidation wave of mercury even for low concentrations of silver could only be obtained in acetonitrile. In all the other solvents the reduction wave of silver disappeared completely with very small amounts of water.

Experimental conditions and apparatus

Sargent type XVI, Metrohm Polarecord E 261, and Beckman Electroscan 30 polarographs were used. A dropping mercury electrode (DME) was used for the classical polarography and a Metrohm HMDE E 410 for stripping methods (anodic stripping polarography and anodic stripping chronopotentiometry).

The reference electrode (Ag|AgCl|aq. KCl) was separated from the solvent by a bridge filled with acetonitrile and containing the same electrolyte (0.1 *M* $LiClO_4$) as the solvent. The reactants were puriss. Merck products, except for $LiClO_4$ (Kodak).

Polarographic study of the system Ag(I)/Ag(Hg) in acetonitrile

The resistance of the system was measured with an a.c. ohmmeter. The minimum value, obtained at the fall of the drop was 16700 Ω for a drop time of 1.28 s. This value was checked by measuring the displacement of the half-wave potential with respect to the increase of the corresponding current[14]. The polarograms obtained under these conditions were corrected for the ohmic drop produced by this resistance. From the corrected values of E, the curves E *vs.* log $(i/(i_d - i))$ were plotted (Fig. 3). The slope of the straight lines was 60 ± 2 mV and the value of the intercept on the ordinate (equal to the half-wave potential) was 350 ± 3 mV with respect to the reference electrode used. The relatively high errors in these values arise mainly from the error incurred in the determination of the resistance. The value obtained for the slope of the straight line confirms that the Ag(I)/Ag system can be considered as reversible by this method, as has already been mentioned by Kolthoff and Coetzee[23].

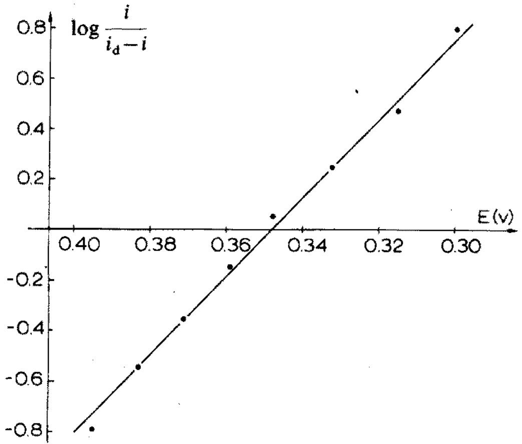


Fig. 3. Relation log $(i/i_d - i) = f(E)$ for the reduction polarogram of silver(I) in acetonitrile. The potentials were corrected for the ohmic drop and were taken *versus* the reference electrode: Ag|AgCl| saturated aqueous KCl solution ||0.1 *M* $LiClO_4$ in acetonitrile|| solution. Electrolyte, 0.1 *M* $LiClO_4$ in acetonitrile; concentration of Ag(I), 10^{-3} *M*; drop time, 1.28 s; cell resistance, 16700 Ω; temperature, 25° ±0.1°.

The diffusion coefficient D of silver(I) was calculated from the maximum current of the polarographic curves, and from the Ilkovič equation[14,24].

$$i_d = 607\ n\ D^{\frac{1}{2}}\ c\ m^{2/3}\ t^{1/6} = kc$$

where i_d = mean limiting current during a drop life (μA),
n = total number of electrons exchanged ($n=1$ for the Ag(I)/Ag(Hg) system),
c = concentration of Ag(I) in solution (mmoles l^{-1}),
m = mercury flow rate (mg s^{-1}),
t = drop time (s).

k was determined for different values of c (Table II). The value obtained for D was $(5.8 \pm 0.6) \cdot 10^{-6}$ cm^2 s^{-1}. This value is lower than that obtained in water ($15.5 \cdot 10^{-6}$ cm^2 s^{-1}) with potassium nitrate as supporting electrolyte[14]. Thus, since the viscosity of acetonitrile is lower than that of water it appears that silver(I) is probably more solvated in acetonitrile than in water.

TABLE II

VALUES OF THE MEAN DIFFUSION CURRENT OF THE POLAROGRAPHIC REDUCTION WAVE OF SILVER(I) IN ACETONITRILE, FOR DIFFERENT CONCENTRATIONS OF SILVER(I)
(Experimental conditions: 0.1 M LiClO$_4$, drop time 5 s, flow rate of Hg 2.19 mg s^{-1}, temperature 25° ±0.1°. Reference electrode, graphite rod)

c(mM)	i_d(μA)	$i_d/c=k$
0.02325	0.075	3.23
0.0465	0.151	3.25
0.0930	0.302	3.25
0.1163	0.372	3.20
0.2303	0.739	3.21
1.1076	3.544	3.20

A calibration curve ($\bar{i}_d = f(c)$) was found to be linear in the range 5–250 μg Ag$^+$ ml^{-1}. The slope of this straight line was constant only when the acetonitrile contained less than 2% water; in this case the water content had no influence on the polarographic curve. For higher water contents, i_d increased slightly, probably owing to the increase of the diffusion coefficient. The water content must therefore be controlled in order to obtain reproducible results. However, the water content must not exceed 10% by volume, because the waves of silver and mercury cannot then be separated; in fact, for more than 4–5% water content, the separation of the two waves becomes difficult.

Study of the Ag(I)/Ag(Hg) system by anodic stripping and cyclic voltammetry

In this case, in addition to the reference electrode and HMDE, a platinum wire auxiliary electrode was included in order to eliminate as far as possible the ohmic drop caused by the resistance of the solution.

Matsuda[25] has theoretically calculated the relationship $i = f(E)$, which is obtained in cyclic voltammetry, for the case of a reversible redox system, when the number of cycles is sufficiently large so that a steady state cyclic curve is attained. In particular, by applying the diffusion equations for linear and semi-infinite conditions to *ox* and *red* particles, he obtained the equations:

$$E_p^a - E_p^c = 2.22\,\frac{RT}{nF} + [Z^a(E_i, E_f) - Z^c(E_i, E_f)] \tag{4}$$

$$\frac{|i_p^a|}{|i_p^c|} = \frac{F^a(E_i, E_f)}{F^c(E_i, E_f)} \tag{5}$$

where E_p^a, E_p^c, i_p^a, i_p^c are defined in Fig. 4 and the functions Z and F depend only on E_i, E_f and the half-wave potential $E_{\frac{1}{2}}$ of the system. When $E_f \ll E_p^c$ (for reduction):

$$Z^a(E_i, E_f) \simeq Z^c(E_i, E_f)$$

and

$$F^a(E_i, E_f) \simeq F^c(E_i, E_f)$$

Hence:

$$E_p^a - E_p^c \simeq 2.22\,\frac{RT}{nF} \tag{6}$$

$$\simeq 57/n \text{ mV} \qquad (\text{for } T = 298°\text{K})$$

and

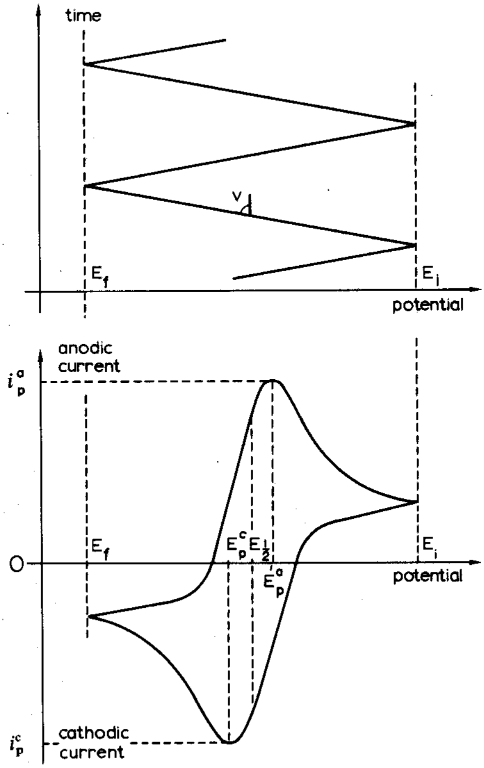
$$\frac{|i_d^a|}{|i_p|} \simeq 1$$

Nicholson and Shain[26] have also shown that in the case of a single cycle the dependence of the functions $E_p^a - E_p^c$ and $|i_p^a|/|i_p^c|$ with respect to the scan rate are very good criteria for determining the degree of reversibility of a redox system; if the system is completely reversible, these functions are close to $57/n$ and 1, respectively, irrespective of the scan rate.

One set of experiments was carried out by varying the scan rate, maintaining $E_p^c - E_f = 250$ mV and $E_i = +0.570$ V with respect to our modified Ag/AgCl reference electrode. Under these conditions, eqns. (6) and (7) are valid for reversible system. In the present case; although $E_p^a - E_p^c$ was constant and close to 60 mV, it was not possible to obtain a constant value for $|i_p^a|/|i_p^c|$ (Fig. 5, curve 1). This behaviour can be explained if one supposes that the system under investigation is reversible, but that linear diffusion and especially the semi-infinite condition are not applicable in the case of the reduced particle. Indeed, the reduced silver forms an amalgam and the larger the difference $E_p^c - E_f$ and the slower the scan rate, the larger is its concentration in the mercury drop.

This assumption is confirmed in curve 2 of Fig. 5, which was obtained by using $E_p^c - E_f = 50$ mV. For this case, with the values $E_i = 0.570$ V, $E_f = 0.270$ V and $E_{\frac{1}{2}} = 0.350$ V, eqns. (4) and (5) become: $(E_p^a - E_p^c) = 62$ mV and $|i_p^a|/|i_p^c| = 0.67$ respectively (Fig. 5, curves 3 and 4).

It can be seen that the relations are obeyed well if one considers the fact that the increase of the silver concentration caused by electrolysis is not completely eliminated, that the method adopted to measure i_p^a and i_p^c does not take into account the capacitance current, and finally that the resistance of the medium gives rise to relatively important errors in the potential measurements of the anodic and cathodic peaks. Moreover, for eqns. (4) and (5), it is assumed that there is no convection in the solution. But, in practice, the time required to attain steady-state cyclic curves is generally long enough for convection to occur in solution.



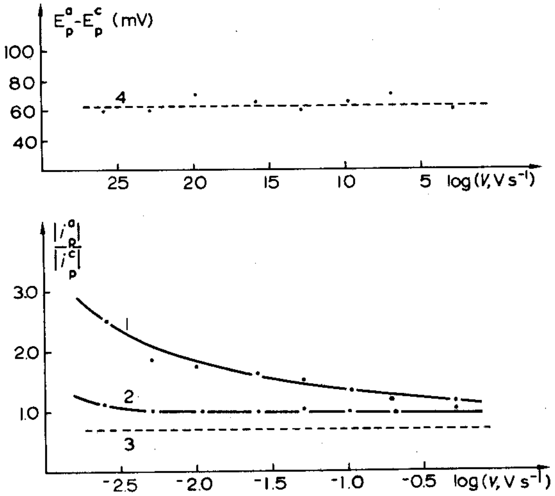


Fig. 4. Schematic representation of the imposed function $E = f(t)$ and the measured function $i = f(E)$ in cyclic voltammetry.

Fig. 5. Influence of the scan rate, V, on the relations $|i_p^a|/|i_p^c|$ and $E_p^a - E_p^c$ in cyclic voltammetry for the case of Ag(I)/Ag(Hg) in acetonitrile. Electrolyte, 0.1 M $LiClO_4$; concentration of Ag(I), 10^{-4} M; indicator electrode, HMDE; auxiliary electrode: platinum wire; reference electrode: Ag|AgCl| saturated aqueous KCl solution ||0.1 M $LiClO_4$ in CH_3CN|| solution; temperature 25° ± 0.1°. (1) Experimental curve corresponding to $E_i = +0.570$ V and $E_f = +0.070$ V. (2) Experimental curve for $E_i = 0.570$ V and $E_f = 0.27$ V. (3) Theoretical curve for $E_i = 0.570$ V and $E = 0.270$ V. (4) Experimental points and theoretical curves corresponding to $E_i = 0.570$ V and $E_f = 0.270$ V.

Hence the Ag(I)/Ag(Hg) couple can be considered as reversible within the range of the scan rate used in anodic stripping polarography, and generally the reoxidation peak of silver can easily be measured in this medium.

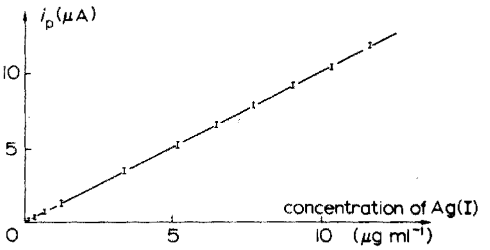
The possibility of determining silver(I) by stripping polarography under these conditions was studied. The calibration curve obtained (Fig. 6) shows that the relationship between the height of the anodic peak and the concentration of silver(I) in solution is linear from 0.2 to 120 μg ml^{-1}. The sensitivity could be extended by increasing the pre-electrolysis time and the scan rate.

Study of the Ag(I)/Ag(Hg) system by chronopotentiometry with preamalgamation

An attempt was also made to apply the method developed by Kemula and Strojek[27] to this system. This method consists of pre-electrolysing the metal under investigation with stirring at constant potential for a given period of time. At the end of this first step the stirring is stopped and a constant anodic current of 10^{-8} A is applied while the amalgam potential is recorded as a function of time. A sudden rise in potential[27,28] indicates the end of the reoxidation and the corresponding time τ is proportional to the concentration in solution.

This method requires an electrometer with a very high impedance to record the potential. A Vibron electrometer (Electronic Instrument Ltd.) was used; its impedance was 10^{15} Ω. The other conditions used were the same as for the preceding methods.

Plotting the oxidation time τ against the concentration of silver(I) in solution gave a straight line (Fig. 7); which shows that the method can be applied to the determination of very small concentrations of silver(I) (1 – 100 ng ml^{-1}).



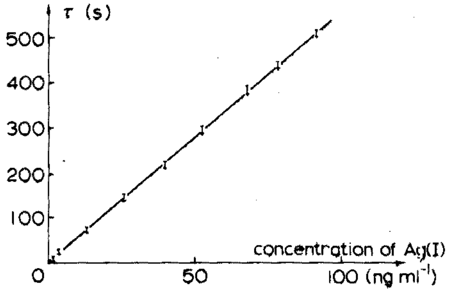


Fig. 6. Calibration curve for silver(I) in acetonitrile by anodic stripping voltammetry. Each value is the average of 4 measurements. Electrolyte, 0.1 *M* $LiClO_4$; indicator electrode, HMDE; reference electrode, Ag|AgCl| saturated aq. KCl solution ||0.1 *M* $LiClO_4$ in CH_3CN|| solution; pre-electrolysis time, 5 min at −0.2 V; temperature, 25°; scan rate, 16.7 mV s^{-1}.

Fig. 7. Calibration curve for the determination of silver(I) in acetonitrile by anodic stripping chronopotentiometry. 4 measurements of τ were made for each silver concentration. Electrolyte, 0.1 *M* $LiClO_4$; indicator electrode, HMDE; reference electrode, Ag|AgCl| saturated aqueous KCl solution ||0.1 *M* $LiClO_4$ in CH_3CN|| solution; pre-electrolysis time, 15 min at −0.2 V; current applied for the dissolution, 10^{-8} A; temperature, 25°.

CONCLUSION

It appears that, among all the media which can be used in polarography, acetonitrile is one of the very few which permits the determination of traces of silver at a mercury electrode.

Moreover, this solvent presents some advantages over the other organic solvents. The choice of the reference electrode causes no problems, as an aqueous reference electrode can be used, the junction potential of which is reproducible; a mercury pool electrode also gives satisfactory results. The addition of a few percent of water does not modify the results. Thus no special precautions to ensure dehydration are needed. This property, together with the sensitivity of chronopotentiometry with preamalgamation, allows the determination of 50 ng ml^{-1} of silver in aqueous medium, since it is possible to dissolve this aqueous sample in acetonitrile and to make the determination in this solvent. Finally, since acetonitrile is compatible with the use of the mercury electrode, a good reproducibility is obtained in the measurements.

SUMMARY

The determination of trace amounts of silver by voltammetry at a mercury electrode is described. The choice of conditions for obtaining separate reduction or oxidation signals for silver(I) and mercury is discussed. Theoretical and experimental studies showed that in aqueous medium none of the complexing agents tested provides separation of the silver(I) and mercury waves. When acetonitrile is used as solvent, silver can be determined at a mercury electrode without preconcentration, by d.c. polarography, anodic stripping voltammetry and anodic stripping chronopotentiometry with sensitivities as low as $5 \cdot 10^{-5}$ *M*, $5 \cdot 10^{-7}$ *M* and 10^{-8} *M*, respectively. It was confirmed that in acetonitrile medium, Ag(I)/Ag(Hg) behaves reversibly in the first two methods.

RÉSUMÉ

Une étude du dosage de traces d'argent par voltamétrie sur électrode de mercure a été effectuée. Le travail porte principalement sur le choix des conditions à utiliser pour obtenir un signal d'oxydation ou de réduction de l'argent nettement séparé de celui correspondant à l'oxydation du mercure. Une étude théorique et pratique montre qu'en milieu aqueux aucun des nombreux complexants étudiés ne permet de remplir les conditions ci-dessus. Par contre, l'utilisation de l'acétonitrile comme solvant permet de doser l'argent sur électrode de mercure sans préconcentration avec des sensibilités de $5 \cdot 10^{-5}$ *M*, $5 \cdot 10^{-7}$ *M* et 10^{-8} *M* par polarographie ordinaire, "anodic stripping voltammetry" et "anodic stripping chronopotentiometry" respectivement. On a vérifié que dans ce milieu le système Ag(I)/Ag(Hg) se comporte réversiblement dans le cas des deux premières méthodes.

ZUSAMMENFASSUNG

Es wird die Bestimmung von Spurenmengen Silber durch Voltammetrie an einer Quecksilberelektrode beschrieben. Die Wahl der Bedingungen, bei denen für Silber(I) und Quecksilber getrennte Reduktions- oder Oxidationssignale erhalten werden, wird diskutiert. Theoretische und experimentelle Untersuchungen zeigten, dass in wässrigem Medium keiner der untersuchten Komplexbildner eine Trennung der Silber(I)- und Quecksilberwellen ergibt. Wenn Acetonitril als Lösungsmittel verwendet wird, kann Silber an einer Quecksilberelektrode ohne Voranreicherung durch Gleichstrompolarographie, sowie durch Voltammetrie und Chronopotentiometrie nach dem Verfahren des anodischen Strippings bestimmt werden. Die zugehörigen Empfindlichkeiten sind $5 \cdot 10^{-5}$ *M*, $5 \cdot 10^{-7}$ *M* und 10^{-8} *M*. Es wurde festgestellt, dass sich Ag(I)/Ag(Hg) in Acetonitril-Medium bei den beiden ersten Methoden reversibel verhält.

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ELECTROREDUCTION AND POLAROGRAPHIC DETERMINATION OF 2-PHENYLINDAN-1,3-DIONE IN SERUM

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2-Phenylindan-1,3-dione (Phenindione, Fenhydren), designated in this paper as PID, is a widely used anticoagulant for blood. In recent years, coulometric and photometric procedures have been outlined for determination of the drug in tablets[1,2] and procedures have also been given for the determination of the drug in whole blood by phosphorescence[3] and in biological materials by spectrophotometry[4]. However, these methods are very tedious and they involve time-consuming separations of the drug from proteins.

Recently, Stradyn and Kadyš[5] observed that PID is polarographically active and that the drug is adsorbed on the mercury electrode. Hence, it might be possible to determine PID in biological fluids by polarography without any preceding protein separation, as has been done for nitrazepam[6]. The present work was carried out in order to study the electroreduction of PID in aqueous solutions and to investigate the application of polarography to rapid analysis of the drug in serum.

EXPERIMENTAL

The instruments and equipments used for polarographic, voltammetric and coulometric experiments have been described previously[6]. The capillary characteristics of the dropping mercury electrode, measured in 0.1 M potassium nitrate (open circuit) at a mercury height of 59 cm were $m = 2.097$ mg s^{-1} and $t = 3.43$ s.

PID is only slightly soluble in water and stock solutions were prepared by dissolving the appropriate amount of the commercial product (Merck AG, Germany) in ethanol. Solutions used for analysis were prepared by dilution of the stock solution with an aqueous buffer solution to give the desired concentration. The remaining chemicals were reagent grade and were used without further purification.

RESULTS

Preliminary experiments showed that the polarographic waves of PID are only poorly developed when sulphuric acid, acetate or phosphate buffers are used as supporting electrolyte. However, well-defined polarograms are obtained from citrate buffers. No maximum appears at any pH value and the two d.c. polarographic steps are followed by a.c. polarographic waves, indicating a relatively fast electron-transfer reaction. Hence, citrate buffer was chosen as supporting electrolyte.

PID is decomposed in alkaline solutions[7]. Hence, reproducible polarograms are hard to obtain at pH values above 6 and the following experiments were restricted to lower pH values. In the pH range 0.5–6 no shift in potentials or decrease in the limiting current was observed 5 h after preparing the solution. The effect of ethanol (from the stock solution) on the polarograms was investigated by recording polarograms of PID in citrate buffer with various amounts of ethanol present. The limiting current decreased with increasing amount of ethanol present, but it remained fairly constant at ethanol concentrations less than 10%.

The following experiments were performed with 5% ethanol in 0.15 *M* citrate buffer as supporting electrolyte. All solutions containing PID were discarded 5 h after preparation.

The effect of pH on the current–voltage curves was investigated by recording polarograms of 0.25 m*M* PID in citrate buffers. The pH of each solution was adjusted to the desired value by addition of sulphuric acid or sodium hydroxide. In the pH range 3–6, there are two well-defined waves (Fig. 1). At lower pH values the second wave is masked by the hydrogen wave and only the first wave appears on the polarogram. The half-wave potentials are shifted linearly to more negative values with increasing pH (Table I), which implies that hydrogen ions are consumed in the reduction. Below pH 6 the half-wave potentials may be expressed by the equations:

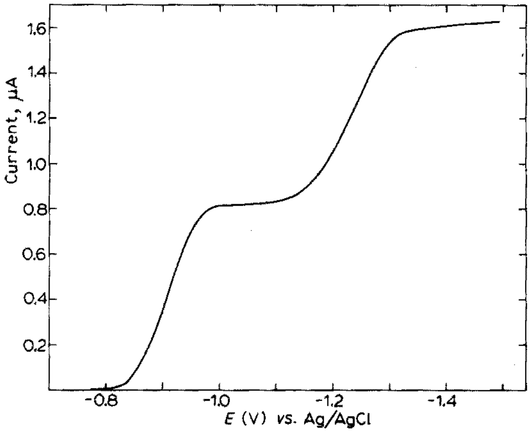


Fig. 1. Polarogram of 0.14 m*M* PID in 0.15 *M* citrate buffer pH 4.9 with 5% ethanol present.

$$E_{\frac{1}{2}} = -0.620 - 0.067 \cdot \mathrm{pH}$$

and

$$E_{\frac{1}{2}} = -1.120 - 0.030 \cdot \mathrm{pH}$$

As indicated in Table I, the height of the first wave is independent of pH of the electrolyte, whereas that of the second wave decreases with increasing pH values. The value $E_{\frac{3}{4}} - E_{\frac{1}{4}}$ decreases with increasing pH of the electrolyte, indicating a more reversible electrode reaction at higher pH values. Hence, citrate buffer pH 4.9 containing 5% ethanol was used as supporting electrolyte in the following experiments.

TABLE I

EFFECT OF pH ON POLAROGRAMS OF 0.25 m*M* 2-PHENYLINDAN-1,3-DIONE IN 0.15 *M* CITRATE BUFFERS WITH 5% ETHANOL PRESENT

pH	*First wave*			*Second wave*		
	$-E_{\frac{1}{2}}$ (V)	i_d (μA)	$-(E_{\frac{3}{4}}-E_{\frac{1}{4}})$ (mV)	$-E_{\frac{1}{2}}$ (V)	i_d (μA)	$-(E_{\frac{3}{4}}-E_{\frac{1}{4}})$ (mV)
1.2	0.700	1.42	70			
2.0	0.750	1.41	70			
3.0	0.820	1.40	70	1.22	1.4	
4.0	0.890	1.43	65	1.240	1.40	60
4.5	0.925	1.42	60	1.255	1.34	60
5.0	0.955	1.41	60	1.265	1.27	50
5.5	0.990	1.43	60	1.290	1.17	45

TABLE II

EFFECT OF PRESSURE OF MERCURY ON THE HEIGHTS OF THE POLAROGRAPHIC WAVES OF $5 \cdot 10^{-5}$ *M* 2-PHENYLINDAN-1,3-DIONE IN 0.15 *M* CITRATE BUFFER pH 4.9 AND 5% ETHANOL PRESENT

h	*First wave*			*Second wave*		
	$i(\mu A)$	$i \cdot h^{-\frac{1}{2}}$	$i \cdot h$	$i(\mu A)$	$i \cdot h^{-\frac{1}{2}}$	$i \cdot h$
46.9	0.250	0.0365	0.00535	0.214	0.0312	0.00459
51.9	0.260	0.0360	0.00501	0.232	0.0324	0.00450
56.9	0.274	0.0365	0.00481	0.254	0.0339	0.00449
61.9	0.284	0.0360	0.00460	0.264	0.0336	0.00428
66.9	0.294	0.0360	0.00439	0.280	0.0345	0.00419
71.9	0.306	0.0360	0.00426	0.300	0.0355	0.00420

The effect of drop time on the limiting current was investigated by recording polarograms of $5 \cdot 10^{-5}$ *M* PID at various heights of the mercury column. The value $i \cdot h^{-\frac{1}{2}}$, where *h* is the height of the column after correction for the "back pressure", for the first wave is constant (Table II), indicating that the current is diffusion-controlled. However, the height of the second wave increases more rapidly with increasing height of the column, which implies that this electrode reaction is partly controlled by an adsorption process. The adsorption of the drug on the electrode surface was verified by drop-time measurements. As shown in Fig. 2 the presence of PID causes a large decrease in the drop time over a considerable potential range. The temperature coefficient (determined in the range 25–45°) of the limiting current was 1.5 and 1.1% per degree for the first and the second wave, respectively.

Polarograms recorded from citrate buffer pH 4.9 with various amounts of PID present, showed that the height of the first wave increases linearly with the concentration. As indicated in Table III, the height of the first wave is greater and

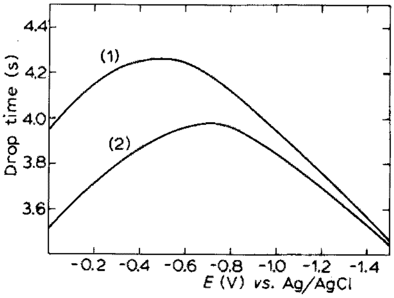


Fig. 2. Electrocapillary curves of 0.15 *M* citrate buffer pH 4.9 containing 5% ethanol in the absence (1) and in the presence of 0.5 m*M* PID (2).

TABLE III

POLAROGRAPHIC DATA FOR THE REDUCTION OF VARIOUS AMOUNTS OF 2-PHENYLINDAN-1,3-DIONE IN 0.15 *M* CITRATE BUFFER pH 4.9 CONTAINING 5% ETHANOL

Conc. (*mM*)	*First wave*				*Second wave*	
	i_d (μA)	i_d/c ($\mu A\ mM^{-1}$)	$-E_{\frac{1}{2}}$ (V)	$-(E_{\frac{3}{4}}-E_{\frac{1}{4}})$ (mV)	i_d (μA)	i_d/c ($\mu A\ mM^{-1}$)
0.25	1.410	5.65	0.94	60	1.100	4.40
0.10	0.565	5.65	0.94	58	0.495	4.75
0.050	0.286	5.72	0.93	53	0.240	4.80
0.025	0.138	5.52	0.92	50	0.126	5.05
0.010	0.0575	5.75	0.92	40	0.051	5.10
0.0050	0.0282	5.65	0.92	35		
0.0025	0.0140	5.60	0.92	35	Not reproducible	
0.0010	0.0056	5.60	0.92	30		

more reproducible than that of the second wave. Hence, the first polarographic wave is most useful for the determination of small amounts of the drug. The height of this wave is proportional to the concentration in the entire range 0.2–50 μg PID per ml.

Coulometric reductions at controlled potential of PID in citrate buffer pH 4.9 were performed to determine the number of electrons involved in the overall electron-transfer reaction. The experiments were carried out in the absence of air with a small electrolysis cell and a mercury pool as working electrode.

The potential of the mercury pool was first controlled at −1.10 V. After electrolysis for 30 min 0.97 C was consumed in the reduction of $5.3 \cdot 10^{-6}$ mol of PID, which yields the value $n = 1.9$ for the first polarographic step. The experiment was repeated with a new solution containing the same amount of PID and with the potential of the working electrode controlled at −1.40 V; 1.90 C was consumed in the complete reduction of PID, corresponding to a value of $n = 3.7$. These experiments imply that two electrons are involved in each of the two polarographic steps.

Cyclic voltammetry experiments were performed at a hanging mercury drop electrode. Reproducible results were obtained provided that the mercury drop was changed between each experiment and just before the next potential sweep. No anodic peak resulting from reoxidation of the reduction product was observed at any scan rate or any switching potential, indicating irreversible electrode reaction.

ABLE IV

OLTAMMETRIC DATA FOR THE REDUCTION OF 0.25 mM PID IN CITRATE BUFFER pH 4.9 CONTAINING % ETHANOL

can rate	First wave				Second wave			Third wave		
$_1(V\ s^{-1})$	$-E_p(V)$	$i_p(\mu A)$	$i_p/cv^{\frac{1}{2}}$	i_p/cv	$-E_p(V)$	$i_p(\mu A)$	$i_p/cv^{\frac{1}{2}}$	$-E_p(V)$	$i_p(\mu A)$	$i_p/cv^{\frac{1}{2}}$
.005	0.865	0.23	12.7	180	1.010	0.57	32.1	1.265	1.00	56.3
.010	0.870	0.40	16.0	160	1.005	0.62	24.8	1.260	1.40	56.0
.020	0.880	0.80	22.5	160	1.010	0.62	17.6	1.265	1.97	56.0
.050	0.900	1.80	32.1	145	1.000	0.56	10.0	1.265	3.45	52.0
.100	0.915	2.80	35.8	112	0.985	0.60	7.6	1.265	4.10	52.2
.200	0.920	6.00	53.7	120	0.975	0.50	4.5	1.265	5.87	52.5
.500	0.94	15.63	88.4	125	0.96	0.45	2.5	1.270	9.20	52.1

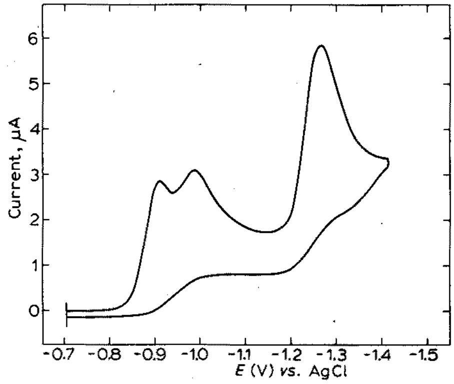


Fig. 3. Cyclic voltammogram of $2.5 \cdot 10^{-4}$ M PID in citrate buffer pH 4.9. Scan rate 0.1 V s^{-1}.

Voltammograms recorded from solutions with PID concentrations above 10^{-4} M exhibit three cathodic peaks (Fig. 3). As indicated in Table IV, the peak potential of the third wave is independent of the scan rate and pretty close to the half-wave potential of the second polarographic step ($E_{\frac{1}{2}} = -1.267$). However, the potential of the first voltammetric peak is shifted to more negative values and that of the second peak is shifted to less negative values with increasing scan rate. At fast scan rates the peak potential of both waves approaches the half-wave potential of the first polarographic step ($E_{\frac{1}{2}} = -0.948$ V).

Voltammograms recorded at PID concentrations below 10^{-4} M exhibit only the first and the third peak. As shown in Fig. 4 the first voltammetric wave has the characteristic symmetrical shape of an adsorption wave. Moreover, the current

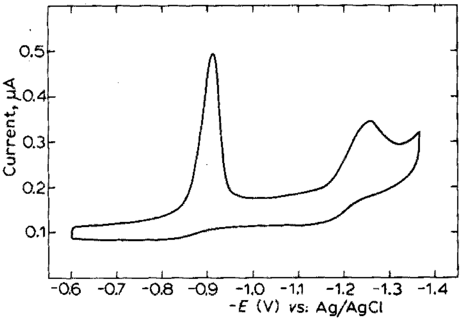
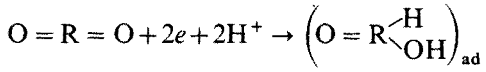


Fig. 4. Cyclic voltammogram of $2.5 \cdot 10^{-6}$ *M* PID in citrate buffer pH 4.9. Scan rate 0.1 V s^{-1}.

function, $i_p/cv^{\frac{1}{2}}$, of the first wave increases with increasing scan rate, while i_p/cv remains nearly constant (Table IV). Consequently, the first voltammetric peak is a "prewave" resulting from strong adsorption of the reduction product[8]. At high concentrations and low scan rates the voltammetric behaviour of PID approaches that of an uncomplicated reduction. However, as the scan rate is increased, the adsorption peak (first wave) increases rapidly with only a small decrease in the second "diffusion peak" (Table IV). The current function of the second electrode reaction (third wave) is almost independent of the scan rate, indicating a simple electron-transfer reaction.

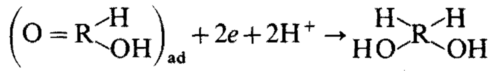
DISCUSSION

It is evident from the experimental results that PID is reduced in two 2-electron steps. In acidic medium the following electrode reactions may be postulated. First wave:



$$O = R = O + 2e + 2H^+ \rightarrow \left(O = R\begin{smallmatrix}H\\OH\end{smallmatrix}\right)_{ad}$$

Second wave:



$$\left(O = R\begin{smallmatrix}H\\OH\end{smallmatrix}\right)_{ad} + 2e + 2H^+ \rightarrow \begin{smallmatrix}H\\HO\end{smallmatrix}R\begin{smallmatrix}H\\OH\end{smallmatrix}$$

The reduction product from the first electrode reaction is strongly adsorbed on the electrode surface and gives rise to a prewave in cyclic voltammograms. Polarograms of the drug exhibit only one drawn-out wave corresponding to the first electrode reaction. Obviously, the prewave is completely overlapped by the "diffusion wave". However, at very low concentration of the depolarizer the surface of the electrode becomes unsaturated, and only the prewave is observed. Hence the value $E_{\frac{3}{4}} - E_{\frac{1}{4}}$ decreases with decreasing concentration of the depolarizer and approaches the theoretical value for a fast 2-electron reduction (Table III).

ANALYTICAL APPLICATIONS

Polarographic determinations of drugs in biological fluids are usually not possible because the waves are greatly distorted by the adsorbed film of the proteins present in such materials. However, the strong adsorption of PID indicated that this drug might be determined in biological fluids without any time-consuming separation from the proteins.

Various amounts of PID were added to 5.0 ml of horse serum and diluted to 50 ml with citrate buffer pH 4.9. After removal of dissolved air with pure nitrogen, the polarogram was recorded. In order to avoid foaming during the deaeration, a minute amount of n-octanol was added to the solution.

The half-wave potential of the first PID wave was not affected by the presence of serum and the height of the wave increased linearly with the concentration. The second wave was seriously distorted in the presence of serum and was unsuitable for determinations. The experiments were repeated by mixing equal volumes of serum and citrate buffer. The first polarographic wave was still well-defined, even in the presence of 50% serum. However, the diffusion current decreased in the presence of serum. The value i_d/c, which was 5.65 μA mmole^{-1} in citrate buffer, decreased to 4.25 in the presence of 10% serum and to 2.62 in the presence of 50% serum. This effect is probably due to increased viscosity of the electrolyte and implies that the determination of PID must be performed at a constant percentage of serum in the supporting electrolyte.

TABLE V

POLAROGRAPHIC DETERMINATION OF 2-PHENYLINDAN-1,3-DIONE IN 5.00 ml OF HORSE SERUM

(The samples were diluted to 50 and 10 ml, respectively, with citrate buffer pH 4.9)

μg PID per ml serum	*% serum in electrolyte*	*Conc. (mmol l^{-1})*	*i_d (μA)*	*i_d/c (μA mmol^{-1})*
555	10	0.250	1.060	4.24
444	10	0.200	0.850	4.25
222	10	0.100	0.425	4.25
167	10	0.075	0.318	4.24
111	10	0.050	0.212	4.24
88.9	10	0.040	0.168	4.20
44.4	10	0.020	0.085	4.25
22.2	10	0.010	0.042	4.20
16.7	10	0.0075	0.033	4.40
111	50	0.250	0.655	2.62
88.9	50	0.200	0.530	2.65
44.4	50	0.100	0.258	2.58
22.2	50	0.050	0.130	2.60
11.1	50	0.025	0.066	2.64
4.4	50	0.010	0.026	2.60

The results of a few experiments (Table V) indicate that the drug can be determined in the concentration range 4–500 μg per ml of serum by simply diluting the sample with citrate buffer pH 4.9 and recording the polarogram. In order to avoid foaming during the deaeration, a minute amount of n-octanol may be added to the electrolyte.

SUMMARY

The electroreduction of 2-phenylindan-1,3-dione has been investigated by polarography, cyclic voltammetry and coulometry at controlled potential. In citrate buffer pH 4.9, the drug is reduced in two well-defined 2-electron steps. The height of the first polarographic wave is independent of pH and proportional to the concentration in the range 10^{-6}–$2.5 \cdot 10^{-4}$ M. The drug is strongly adsorbed at the electrode surface, and can therefore be determined in the presence of surface-active substances like proteins. A procedure has been developed for the direct polarographic determination of microgram quantities of the drug in serum. The proposed method is very rapid and accurate and permits determination of 4–500 μg per ml of the drug in serum.

RÉSUMÉ

On examine l'électroréduction de la 2-phénylindan-1,3-dione, par polarographie, voltammétrie cyclique et coulométrie à potentiel contrôlé. En milieu tampon citrate de pH 4.9, le produit est réduit en deux paliers de 2 électrons, bien définis. La hauteur de la première vague polarographique est indépendante du pH et proportionnelle à la concentration (de 10^{-6} à $2.5 \cdot 10^{-4}$ M). La drogue est fortement adsorbée à la surface de l'électrode et peut par conséquent être dosée en présence de substances tensio-actives, telles que les protéines. Une méthode rapide et précise est proposée pour son dosage dans le sérum (4 à 500 mg ml^{-1}).

ZUSAMMENFASSUNG

Die elektrochemische Reduktion von 2-Phenylindan-1,3-dion wurde durch Polarographie, cyclische Voltammetrie und Coulometrie bei kontrolliertem Potential untersucht. In Citratpuffer pH 4.9 wird das Arzneimittel in zwei gutdefinierten 2-Elektronenstufen reduziert. Die Höhe der ersten polarographischen Welle ist unabhängig vom pH-Wert und proportional der Konzentration im Bereich 10^{-6}–$2.5 \cdot 10^{-4}$ M. Das Arzneimittel wird an der Elektrodenoberfläche stark adsorbiert und kann daher in Gegenwart von grenzflächenaktiven Stoffen wie Proteinen bestimmt werden. Es wurde ein Verfahren für die direkte polarographische Bestimmung von Mikrogramm-Mengen des Mittels in Serum entwickelt. Die vorgeschlagene Methode ist sehr schnell und genau und ermöglicht die Bestimmung von 4–500 μg des Arzneimittels pro ml Serum.

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CURRENT-SAMPLED POLAROGRAPHIC TECHNIQUES FOR THE MEASUREMENT OF SPECIES REDUCED AT MORE NEGATIVE POTENTIALS THAN THE MAJOR COMPONENT

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One potentially great advantage of polarography, compared with some other analytical methods, is the possibility of simultaneously determining two or more depolarizers, when their half-wave potentials ($E_{\frac{1}{2}}$) are sufficiently separated under the conditions of measurement.

The resolvability of polarographic waves, however, depends not only on the separation in $E_{\frac{1}{2}}$, but also on the concentration ratio of both depolarizers. If two depolarizers, A and B are present, the latter being in a considerable excess and reduced at more negative potentials, then B may be easily determined. This is achieved by using the diffusion current for A as the reference current for B and recording B at a lower sensitivity setting. If A is present in large excess, it should in principle be possible to determine B by compensating for the diffusion current of A, and increasing the sensitivity. However, in practice, with conventional d.c. polarography, this is impossible; the second wave cannot be separated from A, because of the increased sensitivity, which produces greatly magnified serrations in the curve corresponding to the fall of each drop[1].

Schmidt and von Stackelberg[1] have reported that at a concentration ratio of 10:1, the wave separation is inadequate; at 50:1 and over, the second substance can hardly be detected even qualitatively. Figure 1 shows a series of d.c.

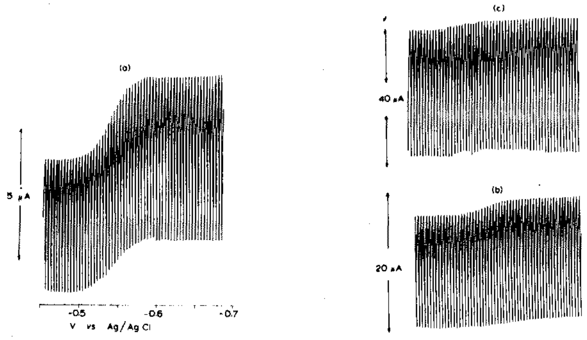

Fig. 1. Measurement of the cadmium(II) electrode process in 0.5 M $NaClO_4$ in the presence of increasing concentrations of copper. $c_{Cd} = 1.3 \cdot 10^{-3}$ M. Natural drop time used. $c_{Cu} = 1.65 \cdot 10^{-3}$ M (a); $7.46 \cdot 10^{-3}$ M (b); $4.00 \cdot 10^{-2}$ M (c).

polarograms of a cadmium(II) solution in 0.5 M sodium perchlorate with increasing concentration of copper. The $E_{\frac{1}{2}}$ values of the 2-electron cadmium(II) and copper(II) reduction waves are *ca.* -0.55 and $+0.05$ V *vs.* Ag/AgCl (5 M sodium chloride), respectively, and the observations of Schmidt and von Stackelberg were confirmed. Statistically, one would encounter the situation where A is in a considerably larger amount than B, compared with the reverse case, in half the situations in routine polarographic analysis. Despite this, very little has been done to improve the rather poor measurements obtainable in such cases by conventional d.c. polarographic techniques.

Recently, Bond and Canterford[2] have examined the possibility of using a.c. polarography to determine a trace of one species in the presence of a large concentration of another species reduced at more positive potentials. A.c. polarographic techniques theoretically have great advantages in this situation[1,2], although experimentally some instrumentation difficulties are caused by the considerable *iR* drop introduced by the high d.c. currents from the more positive electrode process[2]. There is also the limitation that only reversible, or nearly so, electrode processes can be used.

In addition to the obvious analytical advantage in being able to determine B in the presence of large concentrations of A, there is the possibility that observing and measuring the electrode process of B under such conditions, could lead to a means of studying some interesting coupled chemical reactions[2]. In the presence of A, the electrode process for B must occur at a region near the surface of the dropping mercury electrode, where a high concentration of the product from the preceding electrode process for A, is present. If any of the products from this electrode process can interfere with the electrode process for B, then chemical reaction, coupled with the normal charge-transfer process, could occur and be studied.

In an attempt to improve practical knowledge concerning analytical applications of polarography in an important area, and to examine a potential means of studying the influence of preceding electrode processes, the present work was undertaken. Instead of using conventional d.c. polarography, the possibility of using the current-sampled techniques of Tast d.c. polarography, derivative Tast d.c. polarography and pulse polarography was considered.

In the past, Tast polarography has been used to improve the sensitivity of d.c. polarography by its ability to discriminate against the charging current[1,3–5]. This is achieved by measuring the current for a short duration near the end of the life of each drop of mercury, where the ratio of faradaic to charging current is most favourable. Similar considerations also apply in pulse polarography[1]. However, the important feature from the point of view of this work, is not the ability of these techniques to discriminate against the charging current, but the form of the read-out obtained. The read-out of these current-sampled techniques is virtually void of any serrations from the action of the dropping mercury electrode, provided that measurements are taken over a very short time; this provides a means of overcoming some of the problems found in d.c. polarography in determining a small concentration of one depolarizer in the presence of a large concentration of another species which is reduced at more positive potentials[6]. The application of such measurements has been suggested previously. However, until the advent of three-electrode potentiostats, as used in this work, ohmic *iR* drop effects resulting from the large currents provided by the more positive electrode process, severely restricted satisfactory experimentation[7].

EXPERIMENTAL

Reagents

All chemicals used were of reagent-grade purity. Zinc(II), cadmium(II), copper(II), thallium(I) and lead(II) were added as their nitrates. Uranium(VI) was added as uranyl nitrate and iron(III) as its chloride.

All solutions were de-aerated with oxygen-free nitrogen unless otherwise stated and thermostated at $(25.0 \pm 0.1)^\circ$.

Apparatus

All polarograms were recorded with the PAR Electrochemistry System Model 170 (Princeton Applied Research Corporation, Princeton, N.J., U.S.A.). A three-electrode system was employed with Ag/AgCl (5 *M* NaCl) as the reference electrode, and tungsten as the third or auxiliary electrode.

A controlled drop time of about 2 s was used unless otherwise specified. The controlled drop time was obtained with a PAR Model 172 Mechanical Drop Timer. "On Line Sync." was used with all measurements unless otherwise stated and a mercury-drop-synced, current-sampling time of 15 ms was used in all cases. No recorder damping was used in any measurement.

RESULTS AND DISCUSSION

Tast polarography

Recording of Tast polarography. In the absence of any preceding electrode process, the current sensitivity of the instrument can be set so that the polarogram of the electrode process to be measured occupies at least half the full scale of the current axis.

In the presence of a more positively reduced species, the total d.c. current consists not only of d.c. current from the electrode process being examined but also a contribution from the d.c. current of the preceding electrode process (Fig. 2). With most polarographic recorders it is possible to compensate only about five full-scale-deflection-equivalents of current. Hence, if the current from the preceding electrode process exceeds that of the electrode process being measured by 4–5 times, it would be impossible (with most instruments) to compensate the current at sensitivity settings near full-scale deflection, and a lower sensitivity would be needed to record the polarogram. Thus, even though the Tast technique might allow measurements to be made little advantage would be obtained without a different recording procedure from that conventionally supplied with polarographic instrumentation.

Fortunately, recorders such as are commonly used in potential and pH measurements frequently have facilities to enable this recording problem to be overcome; the feature required is a particular form of scale expansion, which enables any given section of the scale to be expanded. Thus, if, for example, the

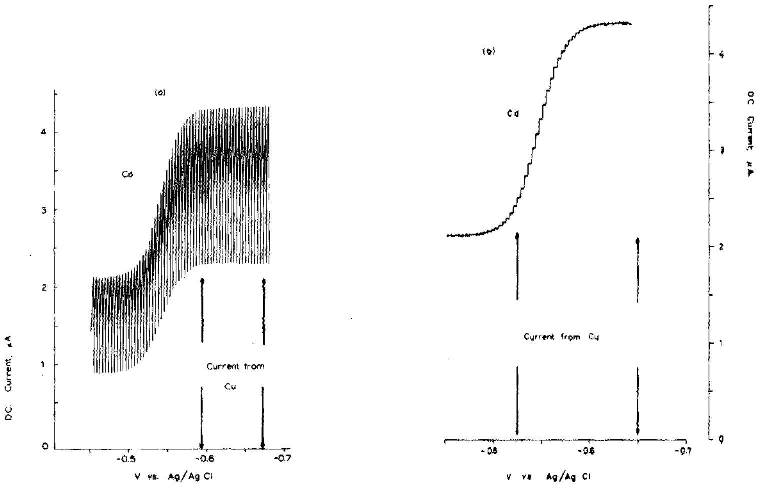

Fig. 2. Measurement of the cadmium(II) electrode process in the presence of the more positively reduced copper(II) depolarizer. (a) Conventional d.c. polarography. Natural drop time used. (b) Tast d.c. polarography. Medium = 0.5 M $NaClO_4$. Controlled drop time used. $c_{Cd} = 1.3 \cdot 10^{-3}$ M. $c_{Cu} = 1.65 \cdot 10^{-3}$ M.

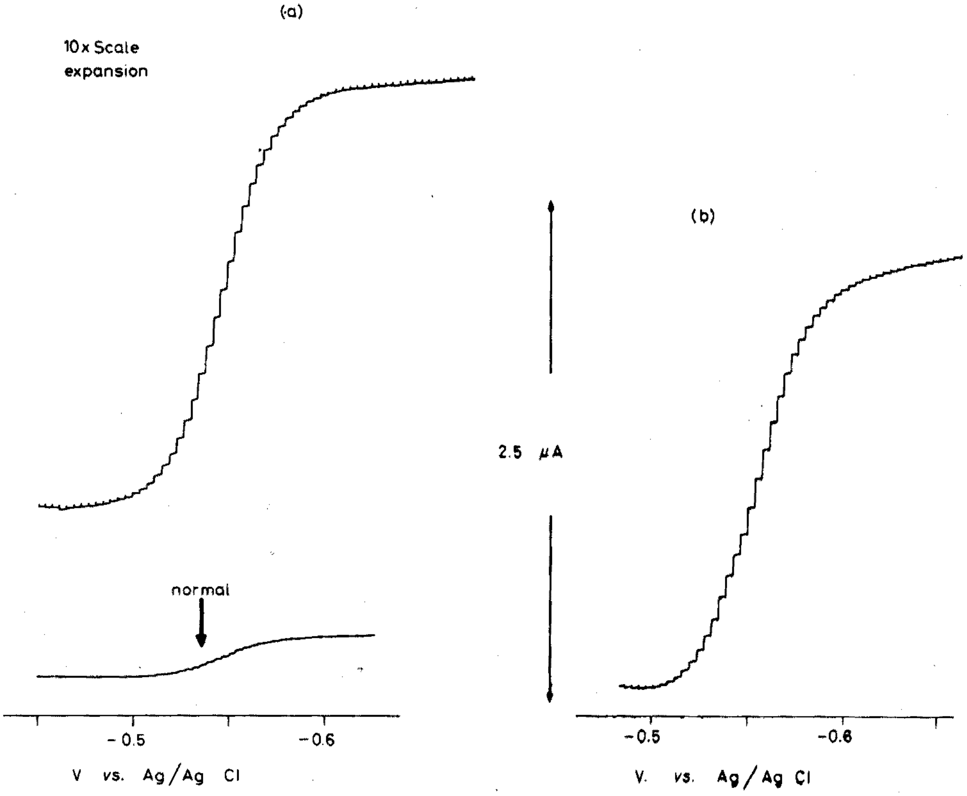

Fig. 3. Use of scale expansion to facilitate measurement of an electrode process in the presence of a more positively reduced depolarizer. $c_{Cd} = 1.3 \cdot 10^{-3}$ M; c_{Cu} = (a) $6.35 \cdot 10^{-3}$ M; (b) $4.00 \cdot 10^{-2}$ M. Medium, 0.5 M $NaClO_4$.

current from the preceding electrode process is twenty times larger than the current to be measured, an initial 10-fold decrease in sensitivity can be used so that the required current appears on scale. A subsequent 10-fold scale expansion where the required wave appears, reinstates the initial conditions, and there is no loss in the accuracy of measurement. Figure 3 shows this procedure.

With derivative Tast polarography, the recording procedure is conventional, provided that the diffusion current or plateau region from the preceding electrode process is parallel to the X-axis. In this case, the derivative of the diffusion current remains close to zero, no matter what the concentration of the species involved in the first wave, and the reference point is independent of the concentration.

General principles. To study the concentrations for the preceding electrode process which can be tolerated in the Tast technique, the systems listed in Table I were studied. The species to be determined were fixed in turn at *ca.* 10^{-5}, 10^{-4} and 10^{-3} M and increasing concentrations of the more positively reduced depolarizer were then added. For all systems, both the maximal concentration tolerable and the highest tolerable ratio of the concentrations, for which meaningful measurements could be made, were limited not by chemical reactions, but by measurement "noise". Figure 4 shows the noise problem in the d.c. Tast method. With derivative Tast polarography, the noise problem became even more severe (Fig. 5).

TABLE I

POLAROGRAPHIC SYSTEMS CONSIDERED

Species determined		*More positively reduced species*		*Medium*
Depolarizer	$E_{\frac{1}{2}}$ (*V vs. Ag/AgCl*)	*Depolarizer*	$E_{\frac{1}{2}}$ (*V vs. Ag/AgCl*)	
Zinc(II)	−0.966	Copper(II)	0.054	0.5 M $NaClO_4$
Zinc(II)	−0.966	Cadmium(II)	−0.558	0.5 M $NaClO_4$
Cadmium(II)	−0.558	Copper(II)	0.054	0.5 M $NaClO_4$
Cadmium(II)	−0.558	Uranium(VI)	−0.162	0.5 M $NaClO_4$
Cadmium(II)	−0.686	Iron(III)	at open circuit[a]	5 M HCl
Tin(II)	−0.580	Iron(III)	at open circuit[a]	5 M HCl
Zinc(II)	−0.966	Lead(II)	−0.322	0.5 M $NaClO_4$

[a] Iron(III) is reduced by mercury at open circuit.

The instrumentation limitations arise from measurements being made in the presence of the large current from the other depolarizer. First, in the presence of extremely high concentrations, the d.c. current can exceed the capacity

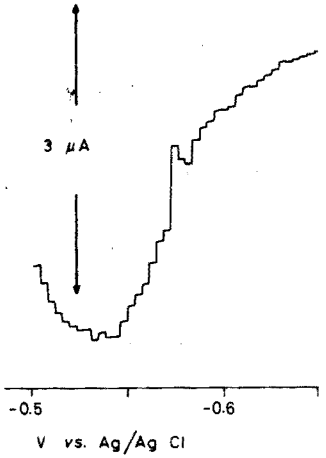

Fig. 4. Noise encountered with a high concentration of the more positively reduced depolarizer with Tast d.c. polarography. $c_{Cd} = 1.3 \cdot 10^{-3}$ M; $c_{Cu} = 0.1$ M. Medium, 0.5 M $NaClO_4$.

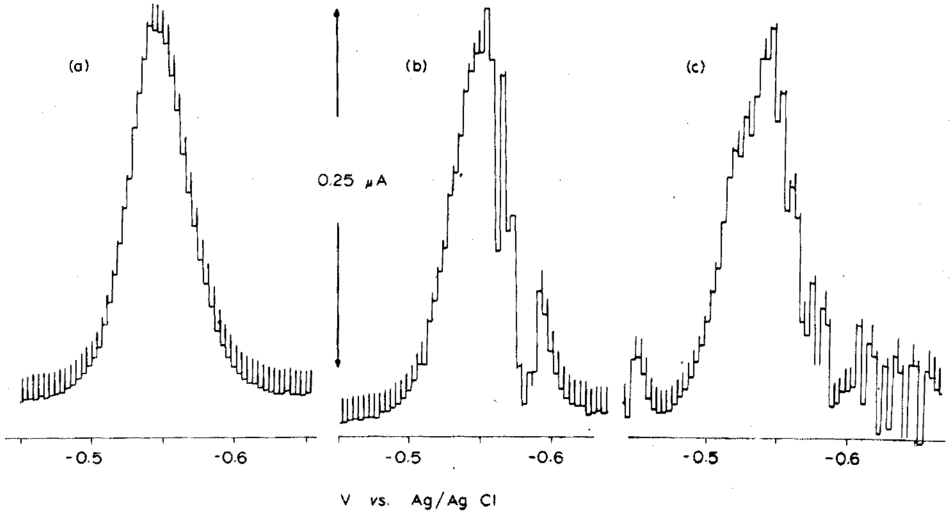

Fig. 5. Noise encountered with derivative Tast d.c. polarography in the presence of a more positively reduced depolarizer. $c_{Cd} = 1.3 \cdot 10^{-3}$ M; $c_{Cu} = 1.65 \cdot 10^{-3}$ M (a); $7.46 \cdot 10^{-3}$ M (b); $4.00 \cdot 10^{-2}$ M (c).

of the instrument and cause overloading. Secondly, in measuring the current from the species being determined, the current from each drop of mercury is considerably larger than if the depolarizer alone were being determined. The read-out of the Tast method requires the measurement of only the current associated with the last few milliseconds of each drop. Thus, for noise-free read-out, current–drop time curves must be highly reproducible. With increasing current associated with each drop, the percentage reproducibility of the current–drop time curves does not alter. However, the variation of the absolute magnitude of the current flow during the last few milliseconds of each drop can become significant under these conditions. Under extreme conditions, when the variation approaches that of the relatively small current actually being measured, the "noise" prohibits accurate measurements. With the experimental arrangement used here, and with conventional Tast d.c. polarography, this condition was reached when the current measured from the more negative electrode process was *ca.* 1/100–1/200 of the total current flowing through the cell.

For all systems listed in Table I, it was found that with the 10^{-4}–10^{-5} *M* concentrations of the species being determined and with a 100-fold amount of the other depolarizer, no interference arose from the preceding electrode process. Thus, the $E_{\frac{1}{2}}$ and the limiting current in Tast polarography, and E_p and the peak current in derivative Tast polarography, as well as the nature of the electrode process, were all independent of concentration of the more positively reduced species to the 2% level.

However, when the concentration of the required species was 10^{-3} *M*, and an extremely high concentration of copper, in particular was present, some significant changes were observed.

TABLE II

VARIATION OF SOME POLAROGRAPHIC PARAMETERS FOR THE REDUCTION OF CADMIUM ON ADDITION OF THE MORE POSITIVELY REDUCED COPPER(II)

($c_{Cd} = 1.3 \cdot 10^{--3}$ *M*; medium, 0.5 *M* $NaClO_4$)

Copper(II) (M)	*Tast d.c. polarography*		*Deriv. Tast d.c. polarography*	
	$-E_{\frac{1}{2}}$ *(V vs. Ag/AgCl)*	i_d *(μA)*	$-E_p$ *(V vs. Ag/AgCl)*	i_d *(μA/V)*
0	0.558	2.15	0.560	2.60
$1.65 \cdot 10^{-3}$	0.558	2.15	0.561	2.60
$6.35 \cdot 10^{-3}$	0.558	2.15	0.561	2.60
$7.46 \cdot 10^{-3}$	0.567	2.20	0.570	2.60
$4.00 \cdot 10^{-2}$	0.575	2.35	0.580	2.75
$1.00 \cdot 10^{-1}$	0.590	2.40	0.595	2.90

Table II gives some data for the addition of copper to a 10^{-3} *M* cadmium solution in 0.5 *M* sodium perchlorate. For this sytem, with copper concentrations above about 10^{-2} *M*, the $E_{\frac{1}{2}}$ and E_p value of cadmium became more negative and the d.c. limiting and derivative d.c. peak currents increased in magnitude. Changes in d.c. ($E_{\frac{1}{4}}$–$E_{\frac{3}{4}}$) values and derivative half-widths also suggested that the nature of the electrode processes changed.

With copper(II) concentrations greater than 10^{-2} *M*, the copper(II) electrode process is probably no longer diffusion-controlled. This concentration of copper is such that migration currents, as well as diffusion currents are probably present. Furthermore, extremely severe maxima are often present at these high concentrations. With copper(II), the maximum extends to more negative potentials, the higher the concentration, and at very high concentrations almost overlaps the cadmium potential region. At very high concentrations copper also makes a significant contribution to the ionic strength and even the viscosity of the solution; some of the changes in the cadmium reduction process may result from these phenomena. Furthermore, instrumental artefacts could become important with the very high currents passing through the cell, *i.e.* despite the use of a three-electrode polarograph, uncompensated resistance terms and overloading of electronic components could become important.

In view of the above, further comment on the origin of the influence of high copper concentrations on the cadmium process, would be purely speculative.

The important feature arising from this work is that the use of Tast d.c. polarography provides a convenient and simple approach to the problem of determining species more negatively reduced than the major electroactive species and that the concentration limits tolerable are in fact set mainly by instrumentation problems. It must be stressed that many of the measurements of the type described in this paper are only possible with a three-electrode potentiostat to eliminate most of the *iR* drop effects arising from the exceedingly high currents produced by the preceding electrode process. Moreover, the performance of the instrument is probably governed by drop reproducibility and by the synchronization of the electronic circuitry with the drop. With extremely high concentrations of the more positively reduced species, the electronic capacity of the instrument can be overloaded and the point at which this is reached must vary substantially from instrument to instrument.

Pulse polarography

Essentially the same findings were obtained with pulse polarography. With normal pulse polarography, which has the same current-sampled read-out form as in Tast polarography, offset of the current axis had to be used. In derivative or differential pulse polarography which display a read-out form analogous to derivative Tast polarography, the same recorder setting on the current axis could be used, no matter what the concentration of the more positive depolarizer.

In all cases the tolerable concentration limit of the more positive electrode process was principally determined by "noise" contained in the read-out. "Noise" was accentuated by the presence of a very high concentration and by a large concentration ratio of the more positively reduced depolarizer. With the instrument used in this work, the concentration of the more positively reduced species had to be kept below about 10^{-2} M to avoid overloading of the electronic circuitry. Barker[8, 9] has reported similar findings; it would appear that with most instruments extremely high concentrations of more positively reduced species must be avoided.

One electrochemical phenomenon which could lead to difficulties of measurement is the presence of maxima; these are especially pronounced at extremely high depolarizer concentrations, and occur in both Tast methods and pulse polarography. Copper is an example of such a system. Hawkridge *et al.*[10] have recently described some aspects of the maxima observed for the copper system. In Fig. 2 of their paper they show a polarogram of $8 \cdot 10^{-3}$ M copper(II) in 1 M Na_2SO_4. Similar results were obtained in this work for both Tast and pulse techniques; the influence of the maximum extends several hundred millivolt beyond the half-wave potential and prohibits the measurement of more negatively reduced depolarizers.

Barker has reported that with pulse polarography, concentration ratios of major/minor constituents in the ratio 5000:1 can be tolerated when a minor constituent is determined in the presence of a more readily reduced major constituent[8]. He has also found that in such experiments the concentration of the major constituent must not exceed 10^{-2} M; otherwise, irregularities caused by the large cell current severely affect the determination. Consequently, high intrinsic sensitivity is essential to achieve the above sort of performance. In this work, with differential pulse polarography, a "typical" system and "normal care" in setting up the DME and associated circuitry, it was found that a 200–500-fold amount could be tolerated but that the performance was strongly governed by the variables described above.

SUMMARY

With conventional d.c. polarography, a particular depolarizer cannot be determined accurately in the presence of a considerable concentration of another species which is reduced at more positive potentials. Current-sampled read-out has been suggested previously to improve the situation; this idea has now been tested experimentally. The read-out of Tast (current-sampled), derivative Tast and pulse polarographic techniques permits determinations of this type to be achieved accurately and conveniently over quite a wide concentration range, provided that a three-electrode potentiostat is used to minimize ohmic *iR* drop effects. The maximal concentration and the limiting concentration ratio of the two depolarizers were generally fixed more by instrumental than chemical limitations, although at very high concentrations of the major species some evidence of electrochemical interference was found.

RÉSUMÉ

Par polarographie conventionnelle à courant continu, il n'est pas possible de doser avec précision un dépolarisant déterminé, en présence d'une quantité importante d'autres particules se réduisant à des potentiels plus positifs. D'autres techniques polarographiques sont alors proposées permettant d'effectuer des dosages de ce type, avec précision.

ZUSAMMENFASSUNG

Mit der konventionellen Gleichstrompolarographie kann ein einzelner Depolarisator nicht genau bestimmt werden, wenn eine beträchtliche Menge einer anderen Spezies zugegen ist, die bei positiveren Potentialen reduziert wird. Zur Verbesserung der Verhältnisse ist die Strom-Abtastung vorgeschlagen worden; dieser Vorschlag wurde jetzt experimentell geprüft. Verfahren der Tast- (Stromabtastung), Derivativ-Tast- und Pulse-Polarographie erlauben Bestimmungen dieser Art auf genaue und bequeme Weise innerhalb eines weiten Konzentrationsbereiches, vorausgesetzt, dass ein Drei-Elektroden-Potentiostat zur Verringerung der

Ohmschen iR-Tropfeneffekte verwendet wird. Die maximale Konzentration und die Grenze des Konzentrationsverhältnisses der beiden Depolarisatoren war im allgemeinen mehr durch instrumentelle als durch chemische Beschränkungen festgelegt, obwohl bei sehr hohen Konzentrationen des Hauptbestandteils Hinweise auf elektrochemische Störungen gefunden wurden.

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A NEW ASSAY FOR CHOLINESTERASE POTENTIOMETRIC DETERMINATIONS IN FLOW STREAMS

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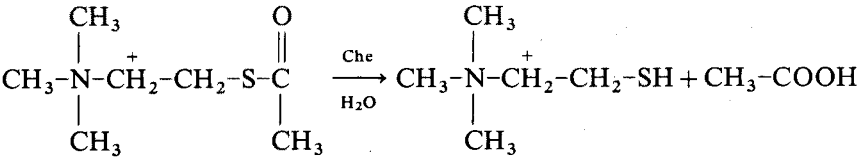
Cholinesterase catalyses the hydrolysis of acetylcholine which acts at nerve endings as a transmitter of impulses from nerve to muscle fiber[1].

Among several analytical procedures which have been developed for the assay of cholinesterase, fluorimetric and spectrophotometric methods are very frequently used[2,3].

As an electrochemical method[4] recently an acetylcholine-selective electrode has been introduced[5] and its analytical application for reaction-rate determination of the system cholinesterase–acetylcholine has been evaluated[5,6]. This electrode uses a liquid ion-exchange membrane which has a selectivity ratio for acetylcholine over choline of 15:1. As choline is the product of the acetylcholine hydrolysis, the decrease in acetylcholine concentration is monitored in reaction-rate determinations. Because of the logarithmic nature of the electrode response, however, a more sensitive potentiometric method would involve the detection of the increasing amount of product rather than the decreasing substrate concentration. Thus in an alternative method the acetic acid produced could be measured potentiometrically. This procedure, however, is limited by the pH-dependent activity of cholinesterase.

Cholinesterase also hydrolyzes acetylthiocholine yielding the hydrolysate thiocholine, *i.e.*,



$$CH_3-\overset{CH_3}{\underset{CH_3}{\overset{+}{N}}}-CH_2-CH_2-S-\underset{CH_3}{\overset{O}{\overset{\|}{C}}} \xrightarrow[H_2O]{Che} CH_3-\overset{CH_3}{\underset{CH_3}{\overset{+}{N}}}-CH_2-CH_2-SH+CH_3-COOH$$

It has been shown that thiols give a potentiometric response at sulfide electrodes[7,8]. Therefore, in another approach for the determination of cholinesterase, the thiocholine produced can be monitored at a silver sulfide membrane electrode.

In order to eliminate errors in the electrode response which are due to the non-enzymic hydrolysis of acetylthiocholine two sulfide electrodes were used as indicating and reference electrodes and were placed into a flow stream.

This type of approach proves to be a sensitive and accurate method for the determination of cholinesterase.

EXPERIMENTAL

Potentiometric measurements were made with two high impedance differential amplifiers[9], the output of which was connected to an Orion digital pH meter (Model 801). The signal obtained was displayed on a potentiometric recorder (Sargent Model SRLG).

Thiocholine-sensitive membranes were prepared from pressed mixtures of silver sulfide–silver iodide salts in the ratio of 10:1. Plexiglas tubes were used as the electrode body onto which pressed pellets and flow-through caps were fitted[10]. A silver wire immersed in a 10^{-2} M silver nitrate solution was employed as internal reference.

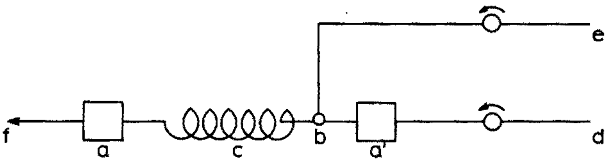


Fig. 1. Flow diagram for continuous assay of cholinesterase activity. (a, a') Indicating sulfide electrode and reference sulfide electrode respectively. (b) Mixing chamber. (c) Delay coil. (d) 1.5 ml min^{-1} substrate solution. (e) 0.5 ml min^{-1} enzyme solution. (f) Waste.

The flow system is shown in Fig. 1. The enzyme solution was introduced into the substrate via a mixing chamber after the first electrode (reference electrode) and passed through a delay coil which was immersed in a controlled temperature bath and permitted a reaction time of 1 min before the increase in thiocholine concentration was monitored at the indicating electrode. The outflow from this system was gravity-fed to waste.

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

All chemicals were reagent grade. Acetylthiocholine chloride (ATCCl), acetylthiocholine iodide (ATCI), thiocholine iodide (TCI), and cholinesterase (Che) horse serum were obtained from Sigma Chemical Company, St. Louis.

The enzyme was assayed spectrophotometrically[11] with acetylcholine (AC) as substrate and the activity was found to be 3.6 units per mg of solid. One unit is defined as 1 μM of choline produced per mg of enzyme in 1 min at pH 8.0.

All solutions were prepared on the day of measurement and refrigerated until used.

RESULTS AND DISCUSSION

The potentiometric response of silver sulfide and mixed silver sulfide–silver iodide membranes was tested in stationary 0.5 M phosphate-buffered sulfide, ATCCl and TCCl solutions. A saturated calomel electrode was used as reference. The investigation showed that the calibration graphs in buffered ATCCl and TCCl solutions yielded different slopes (Fig. 2). This might be a different structure of the double-layer capacity at the membrane surface when zwitterions are being measured.

The electrodes proved to be more selective towards TC^+ than ATC^+ ions at lower concentrations. This effect was not observed at higher ATC^+ or TC^+ concentrations. The electrode selectivity towards HS^- over TC^+ was *ca.* 10^5-fold.

Electrode response times were found to be relatively long (3–4 min) and no

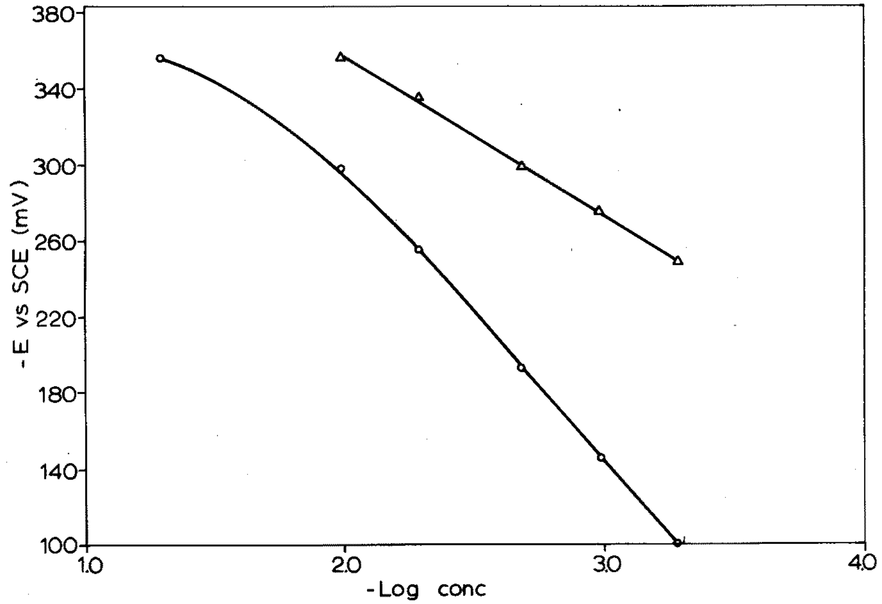


Fig. 2. Electrode calibration in buffered (0.5 *M* phosphate) (△) acetylthiocholine chloride (ATCCl) and (○) thiocholine chloride (TCCl).

improvement was observed when different anions like iodide ions were used. Chloride anions were less of an interference and gave the lowest detection limits for the determination of cholinesterase. Pure silver sulfide membranes gave similar response times, and the theory that iodide ion present in the form of silver iodide incorporated in the membrane would decrease the electrode response time was not confirmed.

Effect of temperature, buffer and pH

For the determination of the optimal temperature, measurements were carried out using $2 \cdot 10^{-3}$ *M* ATCCl in 0.5 *M* phosphate buffer solutions at pH 7.5. The temperature for the enzyme-catalyzed hydrolysis was varied from 14° to 50° and the temperature dependence of this reaction was taken as the potential difference between two enzyme concentrations of 0.05 units and 0.005 units respectively (Fig. 3). The optimal temperature was found to be 36°. Enzyme and substrate solutions should be stored in a refrigerator when not in use and are stable up to 10 h. At room temperature, however, considerable hydrolysis of the thioester takes place and for best results solutions should be prepared fresh daily and kept refrigerated until used.

The enzyme activity is dependent on the pH and nature of the buffer used. Measurements were carried out with phosphate and TRIS buffer at various pH, substrate and enxyme concentrations (Fig. 4). In all cases the optimal pH was found to be between pH 7 and pH 7.5 which agrees well with values reported previously[12].. Phosphate buffer was more favorable than TRIS buffer and was used in all experiments at a concentration of 0.5 *M*. The ionic strength had to be maintained at such a high level, in order to suppress potential oscillations at the electrodes which were caused by (and in sequence with) the surges of the perisaltic pump[13].

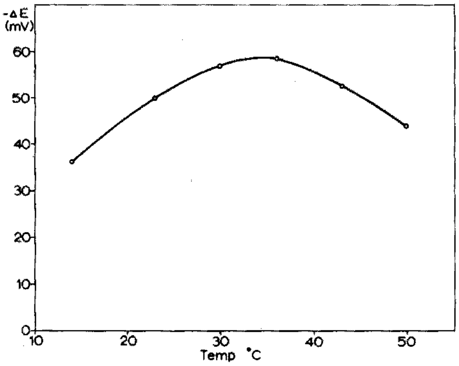


Fig. 3. Effect of temperature on the enzymic activity.

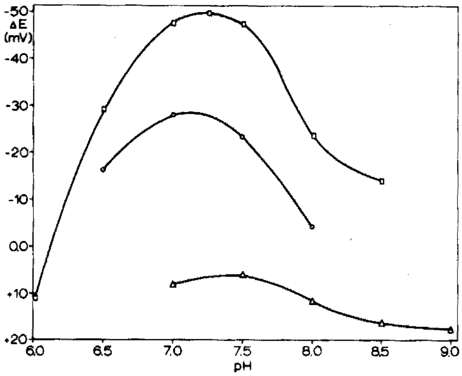


Fig. 4. Dependence of enzymic activity on nature of buffer and pH. (□) 0.5 *M* phosphate buffer, 10^{-3} *M* ATCCl; (○) 0.5 *M* phosphate buffer, $2\cdot10^{-3}$ *M* ATCCl; (△) 0.5 *M* TRIS buffer, 10^{-3} *M* ATCCl. The pH-dependent response is taken as the electrode potential difference ΔE between two enzyme activities of 0.05 and 0.005 units, respectively.

Substrate dependence and cholinesterase assay

Theoretical considerations on the correlation between the enzyme activity and substrate concentration expressed in the Michaelis–Menten equation have been adequately delt with[10]. The increase in TC concentration which was monitored after a constant time (60 s) can be expressed as (S_0-S) in the equation:

$$E\cdot t=\text{const}\cdot\ln(S_0/S)+(S_0-S)$$

where E is the enzyme concentration, S_0 the initial ATCCl substrate concentration and S the ATC substrate concentration at the indicating electrode.

The determination of the optimal substrate concentration was carried out over the concentration range of $5\cdot10^{-4}$ *M*–$5\cdot10^{-2}$ *M* ATC solutions, buffered with 0.5 *M* phosphate at pH 7.5. The electrode response was measured with two enzyme concentrations of 0.05 units and 0.005 units.

The optimal substrate concentration was observed to be within the range of $5\cdot10^{-4}$ *M*—10^{-3} *M* ATC^+Cl. A decrease in the electrode potential at substrate concentrations higher than 10^{-3} *M* can be attributed to enzyme inhibition or the decreasing electrode selectivity towards TCCl at high ATCCl concentrations.

The electrode response towards cholinesterase was calibrated under optimal conditions (Fig. 5) *i.e.*, substrate concentration $2\cdot10^{-3}$ *M* and 10^{-3} *M* ATC, 0.5 *M* phosphate buffer. At low enzyme activity the potential difference, ΔE, was directly proportional to the enzyme activity (Fig. 5), while at higher enzyme contents an exponential electrode potential was obtained. The temperature was maintained at 36°. The enzyme concentration range varied from 0.001 to 0.250 units. The detection limit was found to be 0.002 units which corresponds to 4.0 mV in potential difference from the baseline. The standard deviation of the potential measurement was ±1.0 mV. The response time for each determination was of the order of 3–4 min. The sensitivity of this technique can be improved by increasing the reaction time of the ATCCl hydrolysis.

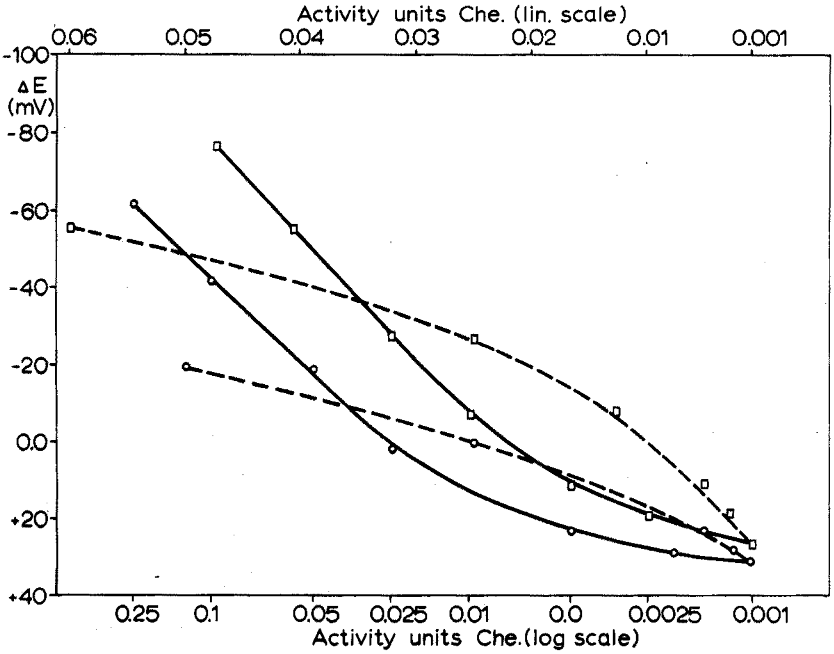


Fig. 5. Calibration of electrode response *vs.* enzyme activity. (□) 10^{-3} *M* ATCCl, 0.5 *M* phosphate buffer; (○) $2 \cdot 10^{-3}$ *M* ATCCl, 0.5 *M* phosphate buffer; (---) linear scale, (——) log scale.

Conclusions

The potentiometric procedure described which uses acetylthiocholine chloride as substrate and silver sulfide membrane electrodes in a flow stream as monitoring system provides an accurate and sensitive method for the determination of cholinesterase. Apart from a rather long response time this method compares favorably with other spectrophotometric and fluorimetric methods and can be easily adapted to automated systems.

The authors gratefully acknowledge the financial support of the National Science Foundation (Grant No. GP-31518). The authors would like to thank Miss M. Stamm who helped in some of the experiments described.

SUMMARY

A potentiometric assay procedure for cholinesterase is described which uses acetylthiocholine chloride as substrate and monitors with two silver sulfide electrodes placed in a flow stream the amount of thiocholine produced in the enzyme-catalyzed reaction. This procedure provides an accurate and sensitive determination of cholinesterase.

RÉSUMÉ

Une méthode potentiométrique est décrite pour le dosage de cholinestérase, utilisant le chlorure d'acétylthiocholine comme substrat et des électrodes de sulfure d'argent. Ce procédé permet un dosage précis et sensible de cholinestérase.

ZUSAMMENFASSUNG

Es wird ein potentiometrisches Bestimmungsverfahren für Cholinesterase beschrieben, bei dem Acetylthiocholinchlorid als Substrat verwendet wird. Mit zwei Silbersulfidelektroden wird im Durchfluss die bei der enzymkatalysierten Reaktion erzeugte Menge Thiocholin gemessen. Mit diesem Verfahren ist eine genaue und empfindliche Bestimmung von Cholinesterase möglich.

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SHORT COMMUNICATION

A polarographic method for the direct determination of uranium(VI) in trialkylamine sulphate extracts

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(Received 10th July 1972)

Tri-alkylamines, immiscible with aqueous phases, are currently of considerable interest in the large-scale recovery of uranium from sulphate leach liquors[1,2]. The amines employed are usually mixtures with each of the hydrocarbon chains having 8 to 12 carbon atoms. Conditions for achieving maximum extraction with minimum interference (coextraction or displacement) from indigenous substances have been extensively explored[3–8]. Physicochemical aspects of the process remain obscure, however, and in the course of some work in this field a need arose to determine the uranium in the amine phase.

A polarographic method developed for the determination is presented here. The method has been examined with a view to assessing its potential for the determination of uranium(VI) in commercially derived amine extracts.

Experimental

The sulphate salts of cationic and the sodium salts of anionic inorganic substances were used in preparing the aqueous solutions from which uranium(VI) was extracted. The quality of each was at least that of a Laboratory Grade Reagent. Tri-*n*-octylamine (TOA; Koch-Light Ltd., Colnbrook, England or Aldrich Chemical Co., Milwaukee, U.S.A.) was used as received. Mono- and di-alkylamines with hydrocarbon chains in the C_8 to C_{12} range were used (Koch-Light Ltd.). The authors are indebted to General Mills Inc., Kankakee, U.S.A. for the provision of a sample of Alamine 336.

Octan-2-ol (capryl alcohol) and *n*-decanol (B.D.H.) and *n*-tridecanol (R.N. Emanuel Ltd., London) were used.

A d.c.-scanning polarographic analyser (Chemtrix Inc., Beaverton, U.S.A., Model SSP-2) having IR compensation for high solution resistance was used in a single sweep mode. The reference electrode was Hg/Hg_2SO_4 in aqueous 0.5 *M* sodium sulphate which made contact with the cell solution at a ceramic plug.

The uranium extract was obtained by equilibration of the amine and aqueous uranium bearing phases. Either a 5% (v/v) or a 15% (v/v) solution of TOA in high boiling (120–160°) ligroin was used. Each solution was made 2% (v/v) in octanol. The aqueous phase uranium(VI) was made up in 0.5 *M* sodium sulphate which had the pH adjusted to 0.85 or 1.5 with sulphuric acid; the amine phase was pre-equilibrated with a portion of 0.5 *M* sodium sulphate at one or other of these pH ratings. In the extraction of uranium the volume ratios of amine to aqueous phase were 3:10 and 1:10 for the 5% and 15% amine solutions respectively. One ml of the uranium bearing 15% amine extract or 3 ml if 5% in amine were diluted to 20 ml with methanol and the resulting solution was polarographed directly.

The instrumental operating conditions were as follows: scan range, 1 V; start potential, 0.2–0.3 V; sweep mode, saw-tooth; sweep velocity, 1 V s^{-1}; Hg drop-time, 4.8 s; scan delay time, 3.8 s; Hg drop weight, 6.2 mg. The first derivative of the current/voltage curve as traced on the oscilloscope (Tektronic Guernsey Ltd., Type 564 Storage Oscilloscope) screen was used throughout in the measurements.

Results and discussion

Figure 1a provides a typical scan of a uranium bearing solution and Fig. 1b that of a "blank" taken through all the stages of the extraction and sample preparation. In Fig. 2 the first derivative peak height is plotted against uranium concentration in the amine and also in the original aqueous phase from which extraction was carried out. Tests on the raffinates following extraction showed that they contained negligible uranium. When 5% TOA + 2% octanol solutions in ligroin were used as extractant, a curve of the same form and for most practical purposes coincident with that in Fig. 2 was obtained. The departure of the curve from linearity may be associated with the cathodic reaction(s) which do not appear to be reversible or with the measurement of the peak height. (The latter was assumed to be represented by the distance from the oscilloscope base-line to the peak maximum.)

The chemical content of an aqueous leach liquor will of course vary with the mineral. The compositions of two synthetic liquors on which much development work has been carried out are listed in Table I. Thorium, iron(II), aluminium, sodium, magnesium, calcium, zinc, nickel, copper(II), cobalt(II), manganese(II), chromium(III) and vanadium(IV) are not extracted significantly[4,5]. Iron(III) is extracted to a limited extent, but uranium(VI) displaces it from tertiary amines like TOA[4]. Molybdenum(VI) is extracted at least as readily as uranium(VI)[4]. Vanadium(V) is also extracted but only appreciably at high pH (> 1.8)[4]. Nitrate, chloride, phosphate and fluoride inhibit extraction[4], the first two severely,

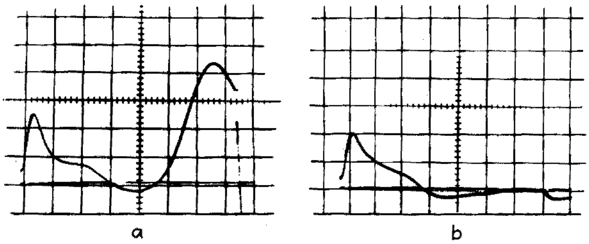

Fig. 1a. A 1st derivative polarographic scan and the relevant base-line from a 15% trioctylamine sulphate solution containing 5 g U l^{-1} treated as described in the experimental section.
Fig. 1b. A scan of a similar amine solution taken through all the stages of the extraction in the absence of uranium.

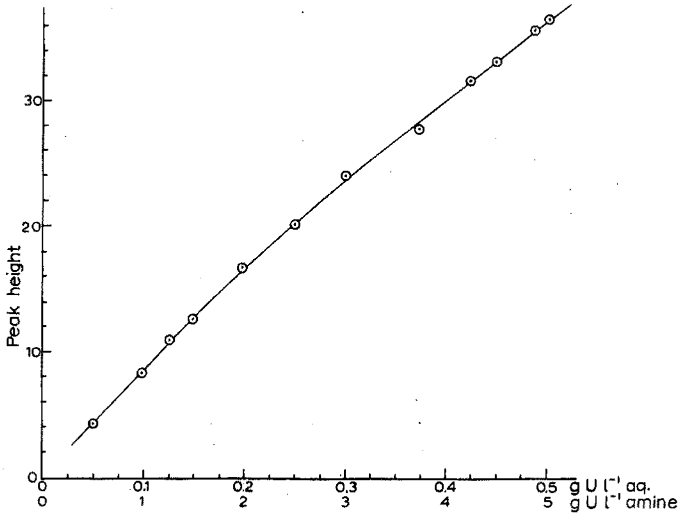

Fig. 2. A plot of peak height from 1st derivative scans against uranium concentration in the aqueous phase and in the TOA extract. A 15% amine solution was used in the essentially complete extractions under conditions described in the experimental section.

TABLE I

LEACH LIQUORS AND THEIR CONTENTS

	A[a] *(g l^{-1})*	*B*[b] *(g l^{-1})*
U	1.25	0.25
Fe(II)	—	1.8
Fe(III)	5.8	0.5
Al	3.3	—
SO_4^{2-}	50	16–20
PO_4^{3-}	2.0	—
F^-	1.7	—
SiO_2	—	1.5
SCN^-	—	0.02
pH	0.85	1.5

[a] "Synthetic Marysvale" liquor used to test[4] the Amex process[3] in the U.S.A. [b] Used in the development of the Purlex Process in South Africa[7,8]. (This is a modification of the Amex process.)

the last two only slightly or not at all if sufficient iron(III) or aluminium is present.

The polarographic method described has been tested with extracts from aqueous solutions at pH 0.85 or 1.5 and having concentrations of the components other than sulphate up to 1.5 times those listed in the Table without observing any interference in the determination of the uranium content. It should be pointed out that 0.5 *M* sodium sulphate was inadvertently used in our experiments involving components in the synthetic leach liquor employed in South African work. Such a change might be expected to affect the sulphate content of the extract as will the pH of the aqueous phase. However, amine extract from an aqueous solution at pH 0.85 gives the same polarographic response as that from an aqueous solution at pH 1.5 having the same uranium concentration. It is therefore unlikely that the use of 0.5 M instead of 0.2 M sodium sulphate solutions at pH 1.5 will affect the polarographic measurement, although it could marginally affect the extraction of the uranium[5]. Vanadium(V) is only partially extracted; it does not interfere up to at least 0.05 g l^{-1} in an aqueous phase at pH 1.5 equilibrated with 15% TOA. On the other hand, molybdenum(VI), which is frequently present in ore bodies[2], interferes at aqueous phase concentrations greater than about 0.025 g l^{-1}, *i.e.* at 0.25 g l^{-1} in the 15% TOA into which it is extracted.

The polarographic determination described does not appear to be sensitive to the composition of the amine or the alcohol used although selectivity in the extraction process can be affected[6] if due attention is not accorded to the former. Thus use of tri-alkylamines from different sources (*e.g.* Alamine 336) and other long-chain alcohols in the extraction or addition of small amounts of mono- or di-alkylamines to extracts did not influence the polarographic response. A measurement takes 5–8 min from receipt of the amine extract and the reproducibility is 2–3% at the middle of the concentration range covered in Fig. 2.

Polarographic methods have been automated[9,10]; provided that the molybdenum(VI) content of the leach liquor is sufficiently low, a method based on that described above could probably be adapted for on-line monitoring of uranium(VI) in the amine phase. In addition, if conditions permit satisfactory recovery in the extraction step, the method, within the limitations set out here, could be used to determine uranium in ore samples.

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SHORT COMMUNICATION

Polarographic determination of traces of arsenic in selenium

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(Received 10th June 1972)

There are few methods available for the determination of arsenic in selenium[1–3]. In the Russian Standard method[2], arsenic is extracted with carbon tetrachloride and back-extracted from the organic phase with water; the solution is evaporated to dryness and arsenic is determined as arsenomolybdate. In the British Standard method[3], arsenic is reduced with zinc in acidic solution to arsine, which is absorbed in a silver diethyldithiocarbamate solution in pyridine and the pink coloration is measured spectrophotometrically. These methods proved to be too time-consuming, or insufficiently selective or sensitive for the present purpose.

In this communication, a new rapid and accurate method based on the reducing power and complex-forming capacity of ascorbic acid[4,5] is proposed. The interference of the selenium(IV) is easily eliminated by reduction to selenium with ascorbic acid, which simultaneously yields a well formed wave of an arsenic(III)–ascorbic acid complex[6].

Reagents and apparatus

Standard arsenic solution. Dissolve 0.2473 g of arsenic trioxide in a 250-ml volumetric flask by boiling with 100–150 ml of re-distilled water and dilute to the mark.

A Heyrovsky Polarograph Model LP-60 was used to record all polarograms. The dropping mercury electrode had the following characteristics: $m = 1.23$ mg s^{-1}, $t = 4.76$ s, measured in 0.1 M potassium chloride in short circuit. The reference electrode was the S.C.E. Purified nitrogen was used to remove oxygen.

Procedure

Weigh 0.35–1.00 g of powdered sample and transfer to a beaker. Add 1 ml of nitric acid (d = 1.40) and 2 ml of sulphuric acid (d = 1.84) and heat on a sand-bath until dissolution is complete. Add 2 ml of (1 + 1) sulphuric acid, heat to fumes of sulphur trioxide, remove the cover and evaporate to dryness. If sulphuric acid remains, it interferes with the complete reduction of selenium(IV). Add 0.35–1.00 g (the same quantity as the sample) of solid ascorbic acid, stirring with a glass rod, dilute with hot water, stir again and place on a steam bath for 30 min. Filter through a coarse filter paper into a 50-ml volumetric flask, and wash the filter and beaker with hot water. Cool, add a drop of methyl orange indicator and neutralize by dropwise addition of sodium hydroxide solution. Cool, add 0.1 ml of aqueous 0.05% gelatin solution, and dilute to the mark. Transfer a suitable volume of this solution to the polarographic cell and record the polarogram between −0.4 and −1.6 V *versus* S.C.E. Measure the height of the wave and determine the arsenic concentration by reference to a calibration graph.

Results and discussion

The most suitable conditions for dissolving the sample and recording the polarograms were first considered. The classical treatment of the sample with nitric and sulphuric acids permits complete and rapid decomposition, but sulphuric acid must be removed because it prevents quantitative reduction of selenium(IV) by ascorbic acid. Arsenic(III) showed a well defined wave with $E_{\frac{1}{2}} = -1.10$ V[5,6] in the ascorbic acid solution as supporting electrolyte. It was shown that few elements interfere with the determination of arsenic; some (Hg, Te, Cu, Ag) are reduced by the ascorbic acid, and others (Fe, Pb, Sb, Ni, Co, Mo, Bi) do not give waves in the same potential region as arsenic(III) in the supporting electrolyte used. Consequently, the method is very selective and much more rapid than the conventional ones.

In the medium used, the calibration graph was linear over the range $4 \cdot 10^{-3}$–$1 \cdot 10^{-1}$ mmole of arsenic(III) concentrations; the equation calculated by the method of least squares[7] was:

$$i = (11.8 \pm 1.4)\, C_{\mathrm{As}}$$

where i is the limiting current (μA) and C_{As} is the arsenic(III) concentration (mM).

Different amounts of arsenic(III) (0.75–0.0375 mg) were added to samples of arsenic-free selenium and arsenic was determined by the proposed method. A statistical analysis of the results[8] was made and a 95% confidence ellipse for these data was constructed. By the method of least squares, a slope of $b = 0.9592$ and an intercept of 0.0175 were found. The lines $a = 0$ and $b = 1{,}000$ are included in the joint confidence region, hence systematic errors are absent. From a chemical viewpoint, this means that the removal of the major constituent has no influence on the arsenic determination, and that arsenic(V) is quantitatively reduced to arsenic(III) by the ascorbic acid. Some of these results are shown in Table I.

TABLE I

RESULTS FOR ARSENIC IN SELENIUM

Sample	*i* (*μA*)	*As taken (mg)*	*As found (mg)*
1	2.60	0.75	0.82
2	2.05	0.60	0.64
3	1.30	0.45	0.41
4	1.00	0.30	0.32
5	1.10	0.38	0.35

It can be concluded that the given procedure is suitable for the rapid and accurate determination of arsenic in selenium.

Finally, a set of repeat analyses of an industrial selenium product (St-1 and St-2) was carried out. The mean values found were $(0.0151 \pm 0.0046)\%$ As, and $(0.0065 \pm 0.0017)\%$ As ($s = 0.0037$ and 0.0011, respectively). Triplicate analyses of sample St-2 by the Russian standard method[2] gave $(0.0055 \pm 0.0004)\%$ As. A direct comparison of the mean values showed no significant difference between them ($t = 1.9 < t(95.8) = 2.38$)[7]. The results show that the accuracy and the precision of the method are satisfactory[9,10]. The determination limit of the method proposed is 0.001% of arsenic.

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SHORT COMMUNICATION

Determination of copper, lead, cadmium and zinc in estuarine water by anodic-stripping alternating-current voltammetry on the hanging mercury drop electrode

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The increasing interest in trace analysis has made it necessary to find analytical techniques which are sufficiently sensitive and at the same time rapid and precise. Anodic-stripping a.c. voltammetry on the hanging mercury drop electrode (HMDE), for those metals to which the technique is applicable, has proved to be a very sensitive technique, and the detection limit is lower than with the corresponding d.c. technique[1,2]. Analysis can be done in more dilute solutions than by the d.c. technique, or time can be saved by employing shorter pre-electrolysis time at the same concentration level. In trace analysis of sea water, anodic-stripping voltammetry has the advantage over other techniques that the high sodium concentrations present do not interfere.

The present work was carried out in order to investigate the use of anodic-stripping a.c. voltammetry, with phase-sensitive detection, on the HMDE, for the determination of copper, lead, cadmium and zinc in sea water.

Experimental

The three-electrode a.c. polarograph Tacussel, type PRG 3, was used for pre-electrolysis and recording of current–voltage curves. A saturated calomel electrode (S.C.E.) served as reference electrode and a platinum coil was employed as auxiliary electrode. A Metrohm E 410 hanging mercury drop electrode with a surface area of 2.22 mm^2 was used as working electrode. The solutions were stirred with the aid of a Beckman Rotating Electrode consisting of the 188501 variable Speed Drive Unit and the 188551 Rotating Electrode Body. A three-edged teflon tip was used as stirring bar.

Dissolved air was removed from the solutions by bubbling oxygen-free nitrogen through the cell for 15 min and passing it over the solutions during the experiments. All experiments were performed at $25 \pm 0.1°$.

Water was purified by ion exchange, distilled and stored in polythene bottles. Chemicals for standard solutions and acetate buffer were of reagent grade.

To limit contamination, the electrodes, the cell and the volumetric equipment were frequently washed with 1 *M* hydrochloric acid and distilled water before each experiment.

Samples of sea water were collected from the Oslofjord at a depth of 40 m, filtered through a 0.45 μm. Sartorius membrane filter (GMBH, 50 mm) and stored in acid-cleaned 1-l polythene bottles, containing 1 ml of "Suprapure" 15 *M* nitric acid.

For determination of copper, lead and cadmium, 25 ml of filtered acidified sea water was pipetted into the voltammetric cell. In this acidified solution zinc could not be determined because of hydrogen evolution. To determine zinc, 25 ml of filtered acidified sea water plus 2.5 ml of 1 *M* acetate buffer pH 4.6 were pipetted into the cell; in this medium zinc exhibited a well shaped wave.

To determine the concentration of the trace elements from the peak heights, a standard technique was used; the peak heights were directly proportional to concentration.

The results were compared with results obtained on the same sea water sample by atomic absorption after extraction[3] at the Institute of Marine Biology, sect. C, University of Oslo.

Results and discussion

An electrodeposition time of 2 min, at a deposition potential of −0.8 V for the determination of copper, lead and cadmium, and −1.2 V for the determination of zinc, was chosen because this was long enough to allow sufficient enrichment. The stirring rate during the deposition was regulated between 5 and 50 r.p.s.; the peak heights increased with increasing stirring rate. The optimal rate was found to be at 40 r.p.s.; at higher stirring rates the mercury drop tended to fall off.

Under these conditions, the recordings were optimal when the other parameters were: a frequency of 15 Hz, an amplitude of the a.c. voltage of 20 mV a scan-rate of 150 mV min^{-1}, and a zero demodulation phase-angle.

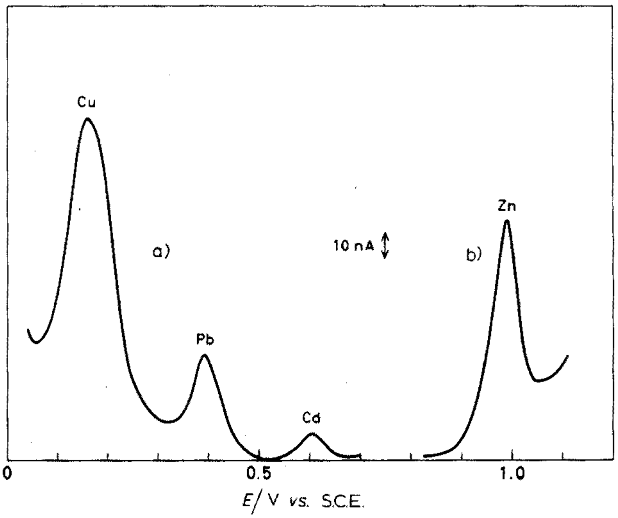

Fig. 1. Anodic-stripping a.c. voltammograms recorded in (a) acidified sea water and (b) acidified sea water containing acetate buffer pH 4.6.

The peak potentials of the respective metals were copper (−0.16 V), lead (−0.39 V), cadmium (−0.61 V) and zinc (−0.99 V). Some typical stripping voltammograms are shown in Fig. 1. The reproducibility of the method was established by ten successive recordings in the same sea water solution; the relative standard deviation was found to be 2% for copper, lead and zinc, and 3% for cadmium.

Table I shows the concentrations of the metals found in the sea water.

TABLE I

ANALYSIS OF SEA WATER FROM THE OSLOFJORD

Analysis no.	*Cu* ($\mu g\ l^{-1}$)	*Pb* ($\mu g\ l^{-1}$)	*Cd* ($\mu g\ l^{-1}$)	*Zn*[b] ($\mu g\ l^{-1}$)
1	3.74	1.35	0.23	3.3
2	3.63	1.17	0.12	3.9
3	3.16	1.40	0.17	3.3
4	3.94	1.25	0.21	3.0
5	3.80	1.29	0.29	4.4
Average	3.70	1.29	0.19	3.6
s_r (%)	8	7	21	16
Atomic adsorption[a]	3.0	1.1	0.12	2.0

[a] The mean of two analyses.
[b] Results obtained after subtracting a blank on 2.5 ml of 1 *M* acetate buffer in 25 ml of distilled water.

Determination of copper, lead, cadmium and zinc in sea water by atomic absorption after preconcentration on chelating resins[4] or by solvent extraction is very time-consuming. Anodic-stripping a.c. voltammetry is more convenient. The technique is rapid, the reproducibility is satisfactory and the detection limit is low. Except for the determination of zinc, the analysis can be performed without adding any reagents, which reduces the possibility of contamination. The results in Table I show a relative high standard deviation in the determination of zinc; this may be due to interference from copper in the acetate buffer. As reported by Florence[5] this can be improved by simple dilution of the sample to keep the copper concentration low.

The results obtained by the stripping technique are in good agreement with the results obtained by atomic absorption.

The author acknowledges valuable discussions with Drs. Einar Jacobsen and Walter Lund. He also would like to express his gratitude to the Institute of Marine Biology, sect. C, University of Oslo, for the sea water samples and Mr. T. Andersen and Mr. L. Kirkerud, at the same Institute, for the data from atomic absorption.

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SHORT COMMUNICATION

The loss of copper and nickel during pre-atomization heating periods in flameless atomic absorption determinations

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(Received 5th July 1972)

The use of flameless atomic absorption spectrometry as an analytical technique is increasing in popularity. However, the information available on the application of this technique is very limited compared to the wealth of information on the applications of flame atomic absorption spectrometry. Because of this a great deal of care is required in new applications of the flameless technique to avoid unnecessary experimental problems. One problem encountered in the development of a method for the determination of copper and nickel is discussed here.

Several papers have already been published describing the determination of copper[1–6] and nickel [4–9] by flameless atomic absorption spectrometry but none of these mention losses during pre-atomization heating cycles. It will be shown that quite considerable errors of analysis can be encountered if the experimental conditions are not completely understood or strictly controlled.

Experimental

All results were obtained with a Perkin-Elmer Model 306 atomic absorption spectrophotometer, equipped with an HGA-70 Graphite Furnace, a deuterium background corrector and a Model 165 recorder.

Oxford "Sampler" micropipettes fitted with disposable plastic sampling tips were used for introducing all solutions into the graphite tube.

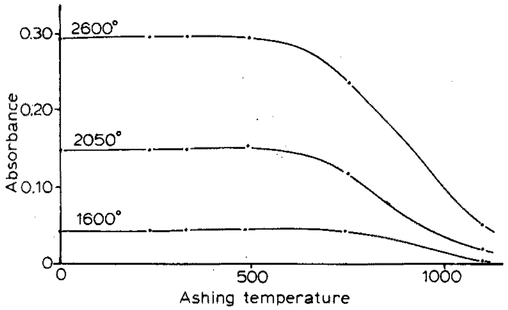
Copper and nickel standard solutions were prepared by dissolving the pure metals in the minimum quantity of nitric acid and then diluting appropriately with distilled water.

The operation of the Perkin-Elmer HGA-70 Graphite Furnace has been described previously[4]. Argon was used to provide the inert atmosphere in the graphite furnace. A 20-μl aliquot, of a 0.1 μg ml^{-1} solution of copper, and a 20-μl aliquot of a 3.0 μg ml^{-1} solution of nickel were used in all the measurements described. A drying time of 40 s was used in all cases; the other times and programme settings are described in the appropriate place in the text. A 10-V atomization stage was used in the copper determinations and a 9-V atomization stage in the nickel determinations, unless otherwise stated.

Results and discussion

During the development of a method for the determination of copper and nickel by flameless atomic absorption spectrometry low recoveries were obtained for both elements when high pre-atomization heating temperatures were used. These recoveries were also found to be dependent on the time of this heating period. Since these observations were at variance with published information, a more detailed investigation was undertaken.

The variations of the atomic absorption signals for copper and nickel in aqueous solution with changes in the ashing and atomization temperatures are shown in Figs. 1 and 2. For both elements losses occur during the pre-atomization heating period when the temperature of this stage exceeds about 600°. These losses are independent of the final atomization temperature.



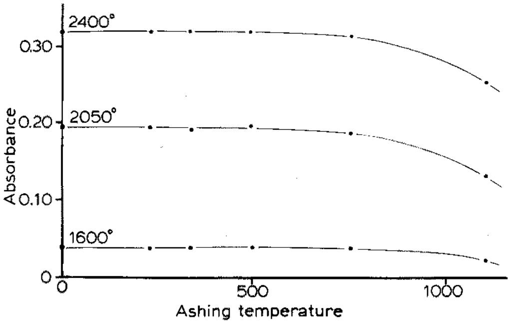


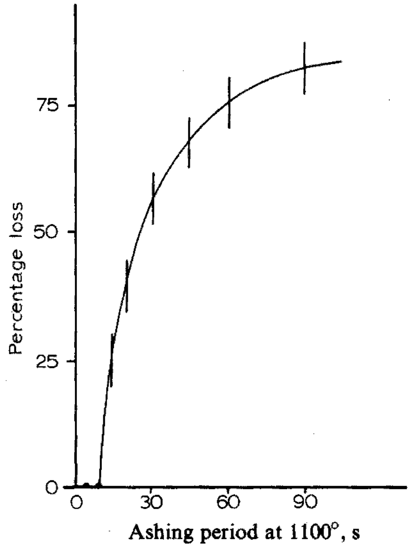
Fig. 1. The variation in the atomic absorption signal for copper with variations in the ashing and atomization temperatures. A 20-μl aliquot of a 0.1 μg Cu ml^{-1} solution is used. The drying time, at 100°, is 40 s and the ashing time is 60 s.

Fig. 2. The variation in the atomic absorption signal for nickel with variations in the ashing and atomization temperatures. A 20-μl aliquot of a 3.0 μg Ni ml^{-1} solution is used. The drying time, at 100°, is 40 s and the ashing time is 60 s.

The percentage losses of copper and nickel as functions of the heating time at 1100° before atomization were studied (Figs. 3 and 4). A rapid loss of copper is seen with a 50% reduction in concentration within 30 s. In the case of nickel the loss was less rapid, but a 50% reduction in concentration still occurred after 2–3 min. The rates of loss of the two elements were also observed in various media, other than the purely aqueous solution; these included 1% solutions of hydrochloric, orthophosphoric, nitric and sulphuric acids. For copper the rate of loss during the pre-atomization heating period was independent, within certain limits, of the solution composition. For nickel, the aqueous, nitric and hydrochloric acid solutions showed approximately twice the rate of loss of the sulphuric and orthophosphoric acid solutions.

An initial induction period was observed of 5–10 s, where no losses of copper or nickel occurred. These periods merely represent the time required for the graphite tube to heat from 100° to the temperatures at which copper and nickel are lost.

It can be assumed that, on drying, the metals form the salts of the acid anions present in solution. With regard to copper, four quite different copper salts appear to behave in an almost identical manner under the conditions described above. The three copper(II) salts containing oxyanions probably decompose to the oxide, as will be the case for the aqueous solution, before the atomization stage but copper(II) chloride should decompose to copper(I) chloride[10]. Since copper(I) chloride boils at



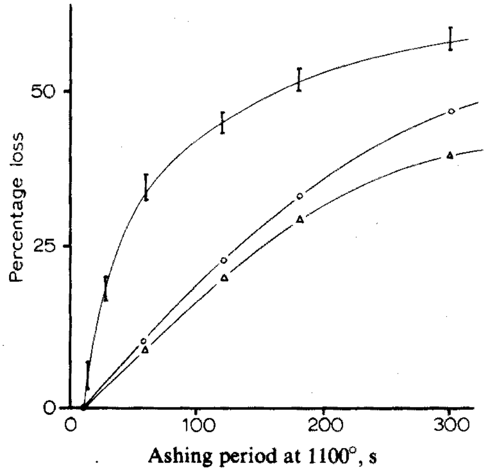


Fig. 3. The percentage loss of copper as a function of the heating time at 1100°. A 20-μl aliquot of a 0.1 μg Cu ml^{-1} solution is used. The drying time at 100° is 40 s and the atomization temperature *ca.* 2600°. Each position on the graph represents the spread of results obtained for an aqueous solution and 1% solutions of HCl, HNO_3, H_2SO_4 and H_3PO_4.

Fig. 4. The percentage loss of nickel as a function of the heating time at 1100°. A 20-μl aliquot of a 3.0 μg Ni ml^{-1} solution is used. The drying time at 100° is 40 s and the atomization temperature *ca.* 2400°. (Δ) 1% H_3PO_4; (○) 1% H_2SO_4; (I) the spread of results for an aqueous solution, 1% HCl and 1% HNO_3.

ca. 1000° while copper(II) oxide only melts at around 1300°, it is difficult to envisage the same rate of evaporation of these two compounds in the graphite tube.

For nickel the situation is more complex[11]. Nickel chloride sublimes at 973° and nickel orthophosphate is stable up to red heat, while nickel sulphate and nitrate probably decompose to the oxide. A much greater loss of nickel would therefore have been expected in the case of the chloride than for the others. It appears reasonable to assume therefore that this approach is incorrect.

It is more likely from the observed results that for copper the oxide is formed in all cases on heating the solutions to dryness in the graphite tube. Then as the temperature is raised over 600°, carbon from the graphite tube reduces the oxide to the metal[10] and there exists a sufficient partial vapour pressure of copper to cause evaporation and subsequent loss of the metal as argon flows through the tube. Carbon reduction of the four copper salts again would not be expected to give results identical with each other.

A similar situation can be predicted in the case of nickel[11] with reduction of the oxide to the metal or the subsequent evaporation of the metal occurring at a slower rate than for copper. A possible variation which occurs is that some sulphate and phosphate are indeed formed on drying the appropriate solutions; these are more difficult to reduce than the oxide, so that the loss of nickel during the heating stages is decreased.

This scheme is more plausible, for it explains the presence of a very small but positive atomic absorption signal which occurred during the pre-atomization heating period for copper. No absorption signal was observed during this stage for nickel, but this is in agreement with the fact that the loss of nickel is much slower and any signal would therefore probably be too small to see. If the losses of copper and nickel were due to the volatility of metal compounds, then there would be no accompanying atomic absorption signals.

From the foregoing discussion it is clear that serious errors could be encountered in the determination of copper and nickel if pre-atomization heating temperatures above 600° were used. A maximum programme setting of 5 is therefore recommended for the determination of copper or nickel with the Perkin-Elmer HGA-70 Graphite Furnace. When it is necessary to use higher temperatures, for example in the analysis of impurities in fuel oils[8] or similar materials and sea waters[12] or other solutions with a high sodium chloride content, then the heating periods should be strictly controlled to minimize errors. This would entail the necessity of using identical ashing temperatures and times for standards and samples, so that losses would tend to be the same in both cases. This approach will unfortunately only be an idealized situation since a complex sample matrix will undoubtedly affect any losses of the elements.

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SHORT COMMUNICATION

The internal standard addition method in X-ray fluorescence analysis of biological materials

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(Received 21st March 1972)

The advantages of the internal standard method in X-ray fluorescence analyses have previously been discussed[1,2]. A major advantage of the method is that some of the errors caused by day-to-day instrumental fluctuations and variations in sample preparation and handling are eliminated. In addition, errors caused by variations in the matrix composition from sample to sample are reduced. The method therefore especially lends itself to the analysis of biological materials.

A major problem in applying the internal standard method to the analysis of biological materials for the light elements is the fact that virtually all the light elements which may serve as internal standards are present in the sample in significant but varying concentrations. It may be expected that the internal standard addition method which has previously been described[3] and successfully used in the X-ray fluorescence analysis of geological materials[4] may overcome this problem. With the method, the advantages of the internal standard method are retained while the criteria of a good internal standard may still be met.

The internal standard method improves with decreasing concentration of the elements analyzed[2]. For samples in which the elements analyzed are present in very low concentrations in a non-interfering matrix, interelemental absorption and enhancement effects are small. Therefore any of the elements may be employed as an additive internal standard if the X-ray fluorescence intensity increases linearly with the concentration of each element over the range of interest. The additive internal standard method was employed in this laboratory in the X-ray fluorescence analysis of human blood serum for Cl, S, P, Ca, and K. The results were compared with those obtained by the conventional method with standardization curves.

Experimental methods

The instrument used was a Philips PW 1220 vacuum-path X-ray spectrometer. The chromium target was operated at 50 kV and 40 mA. The detector was a flow counter with P-10 gas operated at 1740 V. The analyzing crystal was EDDT for P, S, and Cl and LiF for Ca and K.

Oven-dried analytical reagent grade K_2CO_3, $CaCO_3$, $(NH_4)H_2PO_4$, NaCl, and methionine were used to prepare the standard solutions.

The blood serum analyzed was a pooled sample obtained from twenty M. D. Anderson Hospital patients. Potassium was used as the additive internal standard. To prepare the standard-containing serum, equal volumes of the pooled serum and a solution containing 8.295 mg of potassium per 100 ml were mixed.

Serum samples to be analyzed were pipetted onto aluminum foil planchets as previously described[4,5]. Sample volumes of 10 μl of the unknown serum and 20 μl of the standard containing serum were used. The planchets were dried on a hot plate at 50° for 2–3 min before analysis. Samples of standard solutions containing known amounts of Cl, K, P, S, and Ca were prepared in the same manner except that 20 μl of 1% methylcellulose solution was planchetted with the samples to increase adherence.

Samples were counted with the X-ray spectrograph for 40 s for each element, except for phosphorus which was counted for 100 s. Background values were obtained by counting blank aluminum planchets (for blood serum) or aluminum planchets onto which 20 μl of 1% methylcellulose was dried (for standards). Concentration values were calculated as previously described[3].

Results and discussion

Table I lists the concentrations of Cl, S, P, Ca, and K found for the pooled blood serum by the internal standard addition method. The concentrations listed are the means of five analyses; standard deviations are also given. Since the blood serum was obtained from cancer patients, the concentrations of K, Cl, and Ca are not necessarily expected to lie within the normal ranges, although, as can be seen, each value lies either in or close to its respective normal range[7].

TABLE I

CONCENTRATIONS OF Cl, S, P, Ca AND K IN HUMAN BLOOD SERUM FOUND BY X-RAY FLUORESCENCE ANALYSES

Standardization method	*Concentration[a] (mg/100 ml)*				
	Cl	*S*	*P*	*Ca*	*K*
Internal standard addition method	337 ± 7	101 ± 2	12.4 ± 0.4	10.7 ± 0.2	17.9 ± 0.9
Standardization curve method	321 ± 28	94 ± 4	11.0 ± 0.4	9.3 ± 0.3	16.8 ± 1.2

[a] Uncertainties are standard deviations.

Also given in Table I for comparison are the mean concentrations (of five analyses) and the standard deviations found by the conventional standardization curve method. The values agree reasonably well, but two important differences are noticeable. First, the concentrations obtained by the additive internal standard method are larger for all elements. This suggests that perhaps the X-ray absorption effects of the protein matrix may be compensated for when the internal standard method is used. Secondly, the standard deviations are generally lower for the internal standard method.

A disadvantage of the internal standard method is that it relies on measurements of two samples. Hence, random measurement errors are greater than for methods in which only a single measurement is made. However, this disadvantage is compensated for by the reduction of errors in sample handling and instrumental fluctuations. The greatest advantage of the method over the conventional standardization curve is that the need of preparing all samples uniformly is eliminated.

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SHORT COMMUNICATION

Matrix effects of iron and nickel in aqueous solutions and powdered samples in X-ray fluorescence spectrometry

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Tertian[1] has shown that, for certain solid solutions, the fluorescent intensity Y for a given element and the concentration X of the sample in the flux or the solvent are connected by a simple relationship:

$$Y = \frac{X}{1+\phi X}$$

where Φ is a matrix factor characteristic of the sample to be analyzed dissolved in a given flux for the required element. It follows that two Y measurements at two different concentrations of X, make it possible to calculate the matrix effect.

Tertian[1] assumed that a series of unknown samples can be prepared so that the matrix factor for element A in the unknown is the same as for the standard. For the unknown intensity measurements, the following equations were then valid:

$$K_A = \left[\frac{1}{\alpha}\,\frac{(C_n - C_1)}{(C_n \cdot C_1)}\right]\left[\frac{(Y_n \cdot Y_1)}{(Y_n - Y_1)}\right] \tag{1}$$

$$\%A = \frac{100}{H}\left[\frac{(C_n - C_1)}{(C_n \cdot C_1)}\right]\left[\frac{(Y_n \cdot Y_1)}{(Y_n - Y_1)}\right] \tag{2}$$

Thus, theoretically, for the determination of element A in a sample, only two measurements are required on a standard sample for the calculation of K_A from eqn. (1), and two measurements are needed on the unknown for the calculation of A% from eqn. (2). However, in practice, series of standards and unknown samples are prepared and in this case eqns. (1) and (2) can readily be programmed for computer use. A typical computer program for such calculations written in Fortran IV for an IBM 1401 computer, can be obtained from the authors on request.

A report of the application of the Tertian method to aqueous solutions and simple powdered samples is given in this communication.

Sample preparation

Solutions. All stock solutions were made up as *ca.* 8% salt solutions where possible. Standard solutions were made from primary standards or from samples carefully analyzed here or in commercial laboratories. Solutions for analysis were made by successive dilution of the stock solutions to 0.02% with calibrated pipettes. All solutions were analyzed in liquid cells 1 cm deep and 3 cm in diameter, covered with thin mylar film.

Solids. All solid samples were ground to a powder with a mortar and pestle or in a Spex-800 Mixer-Mill. Samples and borax were ground to pass through a 200-mesh sieve, weighed accurately and mixed thoroughly in the Spex Mixer-Mill. The powders were then pressed into $1\frac{1}{4} \times \frac{1}{8}$ in tablets at 30,000 p.s.i. Powdered samples were made at a concentration of 5% by weight of sample to borax and successively diluted with borax to 0.02%.

Fluorescence analysis

Equipment. All measurements were made on a General Electric XRD-5 X-ray fluorescence spectrometer equipped with a G.E. SPG-3 detector system. For the heavy metal analyses, a scintillation detector, LiF crystal and air path were used. The spectrometer was equipped with a helium tunnel assembly, a PET crystal was available and a flow proportional counter could readily be added for analysis of lighter elements.

Procedure. All analyses were carried out with a tungsten target tube operated at 50 kV and 25 mA. Complete fluorescence spectra of the standard and unknown were initially recorded in order to determine if interfering elements were present, to choose the analytical peak, and to decide how the background was to be measured. For the elemental analysis reported, the analytical peaks were: for iron, FeK α at 57.59° 2θ, and for nickel, NiK α at 48.73° 2θ. The background measurements were made at $+2°$ 2θ (59.59°) for iron and at $-2°$ 2θ (46.73°) for nickel. Peak and background intensities were measured by the stationary crystal–stationary counter method (peak heights). All measurements were for 100-s intervals in order to accumulate a minimum of *ca.* 10,000 counts. The standard counting error was therefore 1% or less. Some typical counting results are shown in Table I.

TABLE I

COUNTING RESULTS OF IRON PRIMARY STANDARD

($Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$; 99.63% pure)

Sample	*Sample concentration (% by weight)*	*Peak intensity (counts/100 s)*	*Background intensity (counts/100 s)*	*Net intensity*
1	0.022	12690	9010	3680
2	0.031	13660	8590	5070
3	0.062	18310	9350	8960
4	0.124	24620	9750	14870
5	0.248	37390	9060	28330
6	0.496	60490	8740	51750
7	0.992	108840	8760	100080
8	1.984	194750	8960	185790
9	3.968	334790	8460	326330
10	7.935	521920	8350	513570

Choice of sample type

It was decided to attempt to apply the method of Tertian first to aqueous solutions, because such applications have not been reported previously, and because dilute aqueous solutions of many of the substances under consideration can be readily made. Secondly, attempts were made to apply the method to powdered samples, because, again, such applications have not been reported previously; moreover a diluent of low atomic weight, borax, is readily available, sample preparation is rapid and simple, and found in most analytical laboratories. Most samples that cannot be treated as aqueous solutions, can be readily powdered.

Determination of the optimal concentration range

Table II shows the computation of the matrix and proportionality factor (K from eqn. 1) for an iron standard. The stock solution was made by dissolving 10.5153 g of iron(II) ammonium sulfate hexahydrate (99.63% pure) in 100.0 ml of water and 20.0 ml of 6.0 M hydrochloric acid. The larger values of K for the more dilute solutions can be attributed to the failure of such dilute solutions to provide an "infinitely thick" sample under the conditions of the measurements. Because the last five values of K were nearly constant, the computation was repeated for only those samples; the results are shown in Table III. The optimal concentration for iron in this case is thus seen to be above 0.07%.

TABLE II

COMPUTATION OF MATRIX AND PROPORTIONALITY FACTOR K BY MEANS OF $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$

Sample no.	*Sample concentration (% by weight)*	*%Fe*	*K ($\cdot 10^{-7}$)*
1	0.022	0.002	—
2	0.031	0.004	3.21
3	0.062	0.009	2.20
4	0.124	0.018	2.00
5	0.248	0.035	1.85
6	0.496	0.070	1.79
7	0.992	0.141	1.76
8	1.984	0.281	1.74
9	3.968	0.563	1.73
10	7.935	1.126	1.73

The optimal concentration range for the unknown can be established similarly. Since the percentage of the element is calculated with an average K value, the variation in values is independent of the correctness of the K value although the magnitude is not. Table IV shows the calculation of the percent iron in an iron(III) nitrate solution where the K value used was too high.

When the correct percentage of the required element is not known, the optimal concentration range can still be established as the range in which the variation does not exceed the tolerances desired. In this case the error will be less than 3% if the

TABLE III

CALCULATION OF FACTOR K WITH $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$

Sample	*Sample concentration (% by weight)*	*%Fe*	*K ($\cdot 10^{-6}$)*
6	0.496	0.070	—
7	0.992	0.141	7.62
8	1.984	0.281	7.65
9	3.968	0.563	7.65
10	7.935	1.126	7.67
		Average $K = 7.65 \cdot 10^6$	

TABLE IV

CALCULATION OF PERCENT IRON IN ORIGINAL SAMPLE FROM A CALCULATED K VALUE

Sample no.	*Sample concentration (% by weight)*	*%Fe in original sample (calculated from eqn. 2)*
1	0.02	—
2	0.03	21.10
3	0.07	14.86
4	0.14	12.95
5	0.28	12.20
6	0.55	11.82
7	1.11	11.62
8	2.22	11.52
9	4.44	11.47
10	8.88	11.44
	Measured % Fe = 13.82	

sample concentration is greater than about 0.5% by weight (an iron concentration of not less than 0.08%).

The optimal concentration range was determined as described above for all standards and unknowns. This procedure required about 35 min for each sample. However, once the range had been established, it was only necessary to run 2–5 samples in all subsequent analyses of the same or similar samples; this reduced the time to 5–15 min per sample. In many cases, instrumental adjustments can be made, so as to reduce the counting time significantly, and the total analysis time is then further reduced.

Analysis of iron solutions

The results obtained for several iron-containing salt solutions are shown in Table V. The salt solutions were prepared by dissolving *ca.* 10 g of the salt in 100.00 ml of water and 20.0 ml of 6 M hydrochloric acid. The iron standard used was that shown in Table III ($K_{av} = 7.65 \cdot 10^6$).

TABLE V. CALCULATION OF PERCENT IRON IN VARIOUS IRON SAMPLES

Sample no.	*Sample concentration (% by weight)*	*% Iron found*	*True % iron*	*Average error (%)*
$Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$				
1	0.49	—		
2	0.98	13.87		
3	1.96	14.22		
4	3.93	14.26		
5	7.86	14.34		
	Average % iron	14.17	14.19	0.14
$Fe(NO_3)_3 \cdot 9H_2O$				
1	0.55	—		
2	1.11	13.75		
3	2.22	13.79		
4	4.44	13.57		
5	8.88	13.56		
	Average % iron	13.67	13.82	0.109
$Na_2Fe(CN)_5NO \cdot 2H_2O$				
1	0.49	—		
2	0.99	18.62		
3	1.98	18.72		
4	3.96	18.65		
5	7.91	18.71		
	Average % iron	18.67	18.74	0.37
Iron ore (Thorn Smith sample #165) in solution				
1	0.06	—		
2	0.13	47.64		
3	0.26	42.00		
4	0.52	41.70	40.56	—
Iron ore (Thorn Smith sample #165) as solid				
5	0.26	—		
6	0.95	40.03		
7	2.41	40.50		
8	4.82	40.94		
	Average % iron	40.49	40.56	—
Iron ore (Thorn Smith sample #173) in solution				
1	0.06	—		
2	0.13	24.94		
3	0.25	23.07		
4	0.50	22.20	18.53	—
Iron ore (Thorn Smith sample #173) as solid				
5	0.27	—		
6	0.83	18.28		
7	2.39	18.53		
8	4.45	18.70		
	Average % iron	18.50	18.53	—

Table V also shows the results for two solutions of iron ores. Because of the low solubilities of these ores, the concentrations were limited to the equivalent of 0.5 g of sample in 100.0 ml of water and 20.0 ml of 6 *M* hydrochloric acid. The results are obviously poor, undoubtedly because of the low concentration of the solutions. It was not practicable in this particular case to prepare more concentrated solutions, and the possibility of using deeper sample holders was not examined. Since the samples were available as powdered solids that could readily be ground into finer powders, they were therefore analyzed in this manner.

Analysis of iron ores as solids

Unknown samples and standards were prepared as previously described. The standard had a K_{av} value of $5.34 \cdot 10^6$. The results of the analysis of two samples are also shown in Table V. It is probably somewhat fortuitous that the average values are so close to the true values, but the analysis is probably accurate to within 1%.

Analysis of solutions containing both iron and nickel

Solutions containing both iron and nickel were analyzed to determine if the enhancement effect by the nickel K_α line on the iron *K* line would be effectively compensated for by the Tertian procedure. The samples were also analyzed for nickel content. The standard used for the iron analysis was the same as that used above, *i.e.* $K_{av} = 7.65 \cdot 10^6$. The nickel standard solutions were analyzed solutions of nickel nitrate ($K_{av} = 2.42 \cdot 10^7$). The solutions for analysis were made from a mixture of iron(III) nitrate and nickel(II) nitrate salts. The results of these analyses (Table VI) were less satisfactory than the previous ones, but there was no evidence of enhancement effects.

TABLE VI

CALCULATION OF PERCENT NICKEL AND IRON IN STANDARD UNKNOWN SAMPLES

Sample	*Sample concentration (% by weight)*	*% Iron*	*% Nickel*
1	1.22	—	—
2	1.52	7.65	9.17
3	2.03	7.47	8.91
4	3.05	7.63	8.88
	Average %	7.58	8.99
	True %	7.89	8.68

Conclusion

In the analyses discussed, the Tertian method is applicable to simple aqueous solutions and powdered samples; it is also shown to be simple from the computational point of view. In general, the method seems to be significant enough to justify further study. There are two main areas in which further study might be concentrated: first, a wide range of substances, both in solution and solid states, should be studied in order to establish the general applicability of the method, and, secondly very dilute solutions should be examined. In this respect, attempts are being made to apply this method to the analysis of biologically important solutions, in particular, the determination of iron in blood.

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SHORT COMMUNICATIOS

Complex formation of nickel(II) and cobalt(II) with 4-(2-pyridylazo)-resorcinol

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4-(2-Pyridylazo)-resorcinol (PAR) was reported in earlier papers[1,2] as an excellent reagent for spectrophotometric determination of nickel(II) and cobalt(II) in alkaline media. In connexion with the use of PAR as a colorimetric reagent for these cations, it is of interest to know the composition and stability of the complexes formed. There is uncertainty concerning the composition of the complexes at pH·8, hence a detailed examination seemed desirable. Previous work[1] indicated that a 1:3 metal–ligand was formed, but more recent work with a pure sample of PAR has proved that in fact the molar ratio of nickel(II) or cobalt(II) ions to ligand is 1:2 in both slightly acidic and alkaline media. With increasing pH, the absorption maximum shifts toward shorter wavelengths and the molar absorptivity of the complexes increases ($\varepsilon = 37200$, λ_{max} 520 nm[3] at pH 3.3 and $\varepsilon = 79400$, λ_{max} 496 nm at pH 8.0 for the nickel complex). The colour of the nickel(II)–PAR complex turns from red to orange, while the colour of the cobalt(II)–PAR complex does not change visibly ($\varepsilon = 65500$, λ_{max} 510 nm). As will be shown later, this property of nickel(II)–PAR complex and its higher absorptivity is due to splitting off of protons, a fully deprotonated species being formed. The free reagent in alkaline media has its wavelength of maximal absorbance at 485 nm.

Reagents and apparatus

4-(2-Pyridylazo)-resorcinol (Koch-Light). A 10^{-4} *M* solution was standardized by spectrophotometric titration with $1.260 \cdot 10^{-4}$ *M* copper(II) at pH 5 and a wavelength of 520 nm. The copper(II) was preferred for titration because of the 1:1 molar ratio of its PAR complex[4].

Nickel(II) nitrate and cobalt(II) nitrate. The titres of stock solutions were controlled by compleximetric titration in the usual way. Solutions of lower concentration were obtained by dilution.

The pH was adjusted by adding dilute sodium hydroxide or nitric acid solutions. The ionic strength was maintained at 0.1 with sodium nitrate[1,2].

Absorbances were measured on a VSU-1 Universal Spectrophotometer, and visible spectra were recorded on a Specord u.v.–vis. Spectrophotometer. An L. Seibold pH meter (type GLD) was also used.

Investigation of the reactions and determination of the stability constants

To explain the reactions and to establish the stability constants spectrophotometrically, methods based on the relationship $A = \mathrm{f(pH)}$ were employed, on account of the high stability of the complexes studied. The straight-line portions of the absorbance–pH plots for equimolar solutions, and for solutions containing a slight excess of metal ion or of ligand, lay in the pH range 4–6 for cobalt(II)–PAR complexes and in the pH range 6–8 for nickel(II)–PAR complexes.

To represent the corresponding reactions, the fraction of PAR in its ionic forms was calculated in relation to the pH by means of the values $\mathrm{p}K_1 = 2.66$, $\mathrm{p}K_2 = 5.48$ and $\mathrm{p}K_3 = 12.31$[5]; the results are shown in Fig. 1. It is evident that cobalt(II)–PAR complexes can be formed with H_2R or HR^- species, while the HR^- anion predominates in the range for nickel(II) complex formation. Thus, in a solution containing metal ions and PAR in a 1:2 molar ratio, the reactions can be written:

$$M^{2+} + 2\,H_2R = MH_{4-n}R_2^{(4-n)-2} + n\,H^+ \tag{1}$$

$$M^{2+} + 2\,HR^- = MH_{2-n}R_2^{(2-n)-2} + n\,H^+ \tag{2}$$

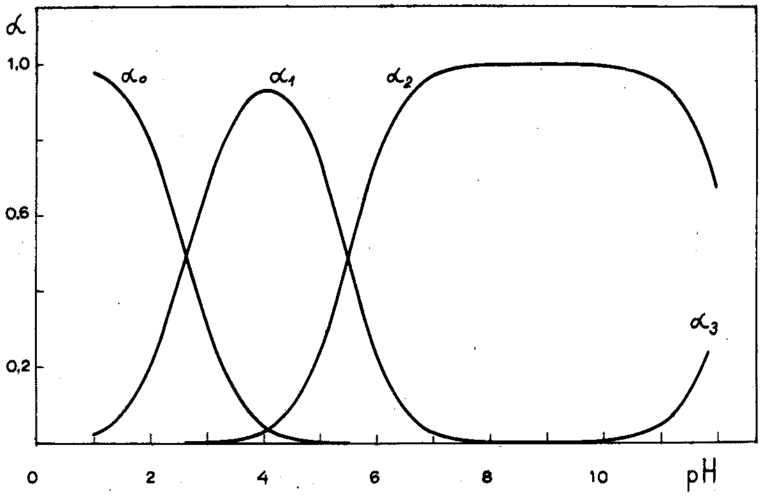


Fig. 1. Fraction of PAR present in various ionic forms depending on pH. α_0, as H_3R^+; α_1, as H_2R; α_2, as HR^-; α_3, as R^{2-}.

The number of protons released during complex formation was examined by applying the equation:

$$K_{\mathrm{eq}} = \frac{A \cdot A_0^2 [H^+]^n}{4C_M^2 (A_0 - A)^3} \tag{3}$$

in its logarithmic transformation:

$$\log \frac{A}{(A_0 - A)^3} = \log K_{\mathrm{eq}} - \log \frac{A_0^2}{4C_M^2} + n\,\mathrm{pH} \tag{4}$$

where A is the absorbance at a given pH value, A_0 is the maximal absorbance (at higher pH value), and C_M is the total metal concentration. The straight lines with slopes $n = 1.9$ (Ni) and $n = 2.2$ (Co) confirmed the splitting off of the two protons

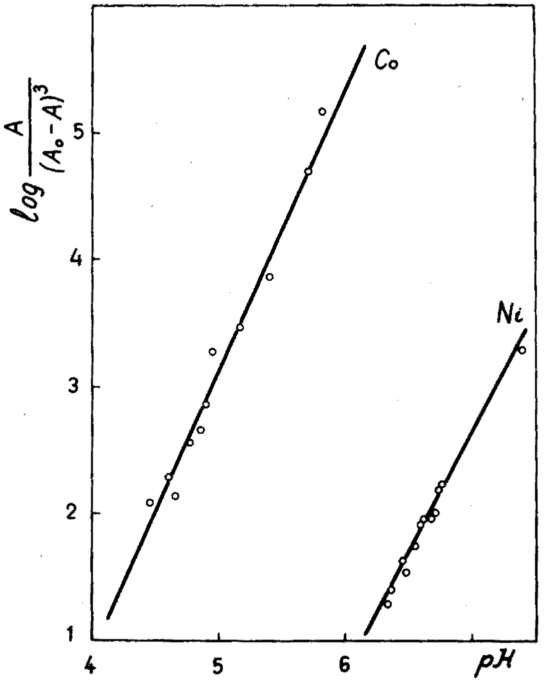


Fig. 2. Logarithmic plots according to eqn. (4). $C_{Ni}=1.012\cdot10^{-5}$ M; $C_{Co}=0.973\cdot10^{-5}$ M; $C_{PAR}=2.012\cdot10^{-5}$ M.

(Fig. 2). Therefore the following equilibria should be valid in pH range studied:

$$M^{2+}+H_2R+HR^- = M(HR)R^- + 2\,H^+ \tag{5}$$

$$M^{2+}+2\,HR^- = MR_2^{2-} + 2\,H^+ \tag{6}$$

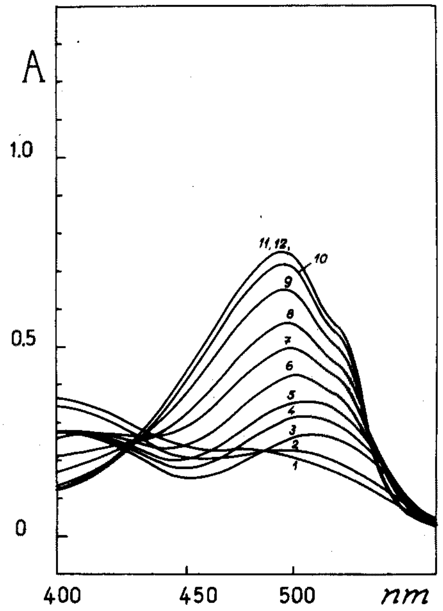
The red colour of the cobalt(II)–PAR complex is considered to be due to a monoprotonated form, such as $Co(HR)R^-$, in contrast to the orange NiR_2^{2-}. The complexes formed at lower pH value have the composition $M(HR)_2$.

The formation of two different species in each of these complexing reactions depending on pH is evident from the absorbance spectra (Figs. 3 and 4). The complex formed at lower pH gradually turns into the corresponding monoprotonated or deprotonated species, as the pH is increased. The presence of two different protonated species agrees with the reactions proposed. Accordingly, three kinds of stability constants are needed to characterize the metal complexes: β_2^{2H}, β_2^{1H} and β_2.

From the intercepts of the plots (Fig. 2) the equilibrium and stability constants were calculated (Table I). If the dissociation constant of only the hydroxy group *ortho* to the azo group, pK_2[6–8], had been used, a higher stability constant would have been obtained for the Co(HR)R complex ($\log \beta_2^{1H}=25.6$).

In order to verify the results established in equimolar solutions, the following equations were applied[9]:

$$\beta_2^{1H} = \frac{[M(HR)R]}{4(C_M-[M(HR)R])^3}\left\{\frac{[H^+]}{K_2}+1+\frac{K_3}{[H^+]}\right\}\left\{\frac{[H^+]^2}{K_2K_3}+\frac{[H^+]}{K_3}+1\right\} \tag{7}$$



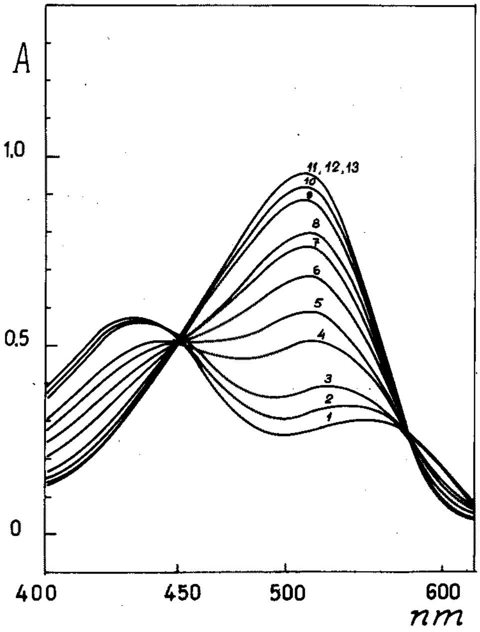


Fig. 3. Dependence of absorbance spectra on pH for nickel(II). $C_{Ni} = 1.012 \cdot 10^{-5}$ *M*; $C_{PAR} = 2.012 \cdot 10^{-5}$ *M*; pH: (1) 2.82; (2) 3.03; (3) 4.90; (4) 5.29; (5) 5.56; (6) 5.85; (7) 6.30; (8) 6.60; (9) 7.15; (10) 7.80; (11) 8.70; (12) 8.95.

Fig. 4. Dependence of absorbance spectra on pH for cobalt(II). $C_{Co} = 7.78 \cdot 10^{-6}$ *M*; $C_{PAR} = 1.610 \cdot 10^{-5}$ *M*; pH: (1) 2.67; (2) 2.98; (3) 3.30; (4) 3.72; (5) 3.95; (6) 4.30; (7) 4.50; (8) 4.87; (9) 5.10; (10) 5.65; (11) 5.85; (12) 6.40; (13) 7.20.

$$\beta_2 = \frac{[\mathrm{MR_2}]}{4(C_\mathrm{M} - [\mathrm{MR_2}])^3} \left\{ \frac{[\mathrm{H^+}]^2}{K_2 K_3} + \frac{[\mathrm{H^+}]}{K_3} + 1 \right\}^2 \qquad (8)$$

The slopes $n = 1.7$ (Ni) and $n = 2.0$ (Co) were obtained graphically, which again proved the splitting off of two protons during the reactions.

By means of the equation:

$$\log \frac{A}{(2A_0 - mA)(A_0 - A)^2} = \log K_\mathrm{eq} - \log \frac{A_0^2}{m C_\mathrm{M}^2} + n\,\mathrm{pH} \qquad (9)$$

where $m = C_\mathrm{R}/C_\mathrm{M} < 1$[10], the stability constants determined for a slight excess of metal ions were found to be of the same order of magnitude as those obtained in equimolar solutions. For solutions with a small excess of reagent (with correction for the absorbance of the free ligand), according to the equation:

$$\log \frac{\Delta A}{\Delta A_0 - \Delta A} = \log K_\mathrm{eq} + 2 \log C_\mathrm{R} + n\,\mathrm{pH} \qquad (10)$$

slopes of about unity were obtained for complex formation with either metal, *i.e.*

one proton split off. Hence, the complex formation can be written as:

$$M^{2+} + 2\,HR^{-} = M(HR)R^{-} + H^{+} \tag{11}$$

The release of one proton on complex formation can be explained by addition of the second PAR molecule through a coordinate bond[11].

The values of the molar absorptivity and the wavelength of maximal absorbance of nickel(II)–PAR are constant and do not depend on the M:L ratio employed. The species NiR_2^{2+} and $Ni(HR)R^-$ are optically identical at higher pH, the latter being formed only in the presence of excess of ligand.

The data obtained are summarized in Table I.

TABLE I

THE STABILITY CONSTANTS OF THE PAR COMPLEXES OF NICKEL(II) AND COBALT(II)

Metal ion	*Defined constant*	*Equimolar solution*	*Metal excess*	*Ligand excess*
Ni^{2+}	$\log \beta_2$	22.9 (eqn. 4)	22.3	
		21.9 (eqn. 8)	22.0	
			22.2	
			22.1	
			22.1	
Co^{2+}	$\log \beta_2^{1H}$	18.8 (eqn. 4)	18.6	17.4
		20.3 (eqn. 7)	18.6	

The value of the stability constant of the cobalt(II)–PAR complex for solutions containing excess of ligand agrees very well with the value $\log \beta_2 = 17.1$ determined potentiometrically by Geary *et al.*[12] in aqueous solution. The stability constant found for the nickel(II)–PAR complex is lower than that determined by Corsini *et al.*[13] potentiometrically in (1+1) water–dioxane (26.0).

The assumption that PAR forms three kinds of metal complex depending on the pH, agrees well with acid–base properties of both the reagent and its metal complexes[14,15].

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SHORT COMMUNICATION

Photometrische Bestimmung von Blei in unlegiertem und niedrig legiertem Automatenstahl

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(Eingegangen den 26 Juli 1972)

Die Produktion von Automatenstählen erfordert die laufende Bestimmung des Bleigehaltes in einer grossen Zahl von Stahlproben. Von grosser Bedeutung ist deshalb die Anwendung einer einfachen Bestimmungsmethode mit geringem Zeitaufwand. Vom Autor wurde bereits früher eine hierzu geeignete Methode mitgeteilt[1–3], die sich auf unlegierten Automatenstahl anwenden lässt und bei der das Blei als Bleijodid photometrisch bestimmt wird.

In der Zwischenzeit wurde die Methode verbessert und modifiziert, so dass sie auch auf niedrig legierte und tellurhaltige Stähle angewandt werden kann. Die Störung durch Kupfer und Tellur wird beseitigt, indem man das Kupfer mit Ferrum reductum und das Tellur mit $SnCl_2$ zum Metall reduziert und anschliessend abfiltriert. Die Methode ist nachfolgend angeführt.

Reagentien

Perchlorsäure (3+4). 3 Teile Perchlorsäure (70%) werden mit 4 Teilen Wasser gemischt.

Gelatinelösung. 10 g Gelatine werden in warmem Wasser (nicht über 40°) gelöst und auf 1 l aufgefüllt. Die Lösung muss täglich frisch zubereitet werden.

Natriumjodidlösung. 25 g Natriumjodid werden in Wasser gelöst und auf 1 l aufgefüllt.

Zinn(II)-chloridlösung. 100 g $SnCl_2 \cdot 2\,H_2O$ werden in 100 ml Salzsäure (1.19) gelöst und mit Wasser auf 1 l verdünnt.

Arbeitsvorschrift

(a) Te-freier Stahl. Bei Gehalten von 0.025 bis 0.250% Pb werden 2.0 g, bei höheren Gehalten (bis 0.500% Pb) 1.0 g Probe in 20 ml Perchlorsäure (3+4) gelöst und anschliessend in einen 50-ml Messkolben übergeführt. Zum Abscheiden des Kupfers setzt man etwa 0.5 g Ferrum reductum zu, kühlt 3–5 min im fliessenden Wasser auf 20° ab, füllt mit Wasser bis zur Marke auf und mischt. Nach dem Filtrieren durch ein weitporiges Rundfilter (Schleicher u. Schüll Schwarzband) wird ein aliquoter Teil des Filtrates von 5.0 ml (eine schwache Trübung ist ohne Bedeutung) in einen 50-ml Messkolben übergeführt, in dem 25 ml Phosphorsäure (d = 1.70) und 1 ml Gelatinelösung vorgelegt sind, und 10 ml Wasser

hinzugefügt. Man kühlt im fliessenden Wasser auf etwa 15° ab, fügt 5 ml Natriumjodidlösung hinzu, mischt und versetzt sofort mit 0.5 ml Zinn(II)-chloridlösung. Danach wird sofort mit Wasser bis zur Marke aufgefüllt und gut gemischt. Die Vergleichslösung wird mit einem aliquoten Teil der Probelösung (5.0 ml) nach derselben Vorschrift unter Fortlassen des Natriumjodid-Zusatzes hergestellt. 10 bis 15 min nach dem Auffüllen des Messkolbens photometriert man die Probelösung in einer 2-cm Küvette bei 400–420 nm gegen die Vergleichslösung. Der Gehalt der Probe wird an Hand der Eichkurve ermittelt und im Falle einer Einwaage von 1 g noch mit 2 multipliziert.

Die Eichkurve wird mit bleifreien Proben, denen bekannte Mengen Blei (Blei(II)-acetatlösung) zugesetzt werden, nach der Arbeitsvorschrift aufgestellt.

(b) Te-haltiger Stahl. Die Probe wird wie unter (*a*) gelöst, mit 2 ml $SnCl_2$-Lösung versetzt, 3 min gekocht und mit dem Überführen in den 50-ml Messkolben nach (*a*) fortgefahren.

Ergebnisse und Diskussion

Die beschriebene Methode eignet sich zur Bestimmung von 0.020–0.50% Pb in unlegierten und niedrig legierten Automatenstählen mit $\leqq 3\%$ Cr, $\leqq 3\%$ Mo, $\leqq 3\%$ Ni und $\leqq 1\%$ V. 0.02–0.07% Te stören nicht, wenn nach Variante (*b*) gearbeitet wird. Für den angeführten Gehaltsbereich beträgt die mittlere Standardabweichung $s = \pm 0.003\%$ Pb. Voraussetzung hierfür ist die genaue Einhaltung der Arbeitsbedingungen, vor allem der Temperatur und der Standzeit bei der Farbentwicklung. Die Temperatur soll im Bereich von 20–22° auf ±1°, die Standzeit innerhalb ±10 min reproduzierbar eingehalten werden. Der Zeitbedarf für eine Bestimmung beträgt 45 min. Die Bestimmungsgrenze[2] liegt bei 0.02% Pb.

Die Methode wird in unserem Laboratorium seit 15 Jahren mit Erfolg eingesetzt, wobei täglich etwa 100–200 Proben analysiert werden.

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SHORT COMMUNICATION

A combined ion-exchange–spectrophotometric determination of vanadium in sea and natural waters

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Because of its low concentration, vanadium has been generally determined in sea and natural waters after appropriate concentration. Techniques involving coprecipitation and solvent extraction have almost exclusively been used for this purpose. Recent advances have been noted in the papers of Chan and Riley[1] and Riley and Taylor[2]. In addition, methods involving solvent extraction of vanadium from sea and natural waters, followed by X-ray fluorescence[3], atomic absorption[4,5] and neutron activation[6] have been reported.

Riley and Taylor[2] described the use of a chelating ion-exchange resin for the concentration of vanadium and molybdenum from sea water. Generally, ordinary anion and cation exchangers are of limited use for concentrating traces of metals from a large quantity of sea water[7,8]. However, increased adsorption of molybdenum and tungsten on Dowex 1 was found from an acidified sea water containing thiocyanate, which allowed a photometric method to be developed for the determination of the two metals in sea water[9]. In this communication the utility of the Dowex 1–thiocyanate system was extended to concentrate vanadium from sea water, the subsequent determination being done colorimetrically with 4-(2-pyridylazo)resorcinol as reagent.

Experimental

Apparatus. A Hitachi 101 spectrophotometer was used for all photometric measurements.

Reagents. Vanadium(V, IV) stock solutions. Dissolve appropriate amounts of ammonium metavanadate and vanadyl dichloride in 0.1 *M* hydrochloric acid, respectively, to yield *ca.* 500 μg V(V) per ml and 1.5 mg V(IV) per ml. Standardize with EDTA to Cu–PAN indicator.

PAR solution. Dissolve 0.25 g of 4-(2-pyridylazo)resorcinol in 8.5 ml of 1% sodium hydroxide solution and dilute to 250 ml with deionized water.

Hypobromite solution. Mix 6 ml of saturated bromine water and 100 ml of 1 *M* sodium hydroxide solution.

Ion-exchange column. Slurry 5.0 g of Dowex 1-X8, SCN-form, 100–200 mesh, with deionized water and pour into a column, i.d. 2.5 cm, pulled to a tip and plugged with glass wool at the outlet. The resulting bed height is usually 2.5 cm long.

Determination of vanadium. If the sample contains thiocyanate, add nitric acid and heat carefully to destroy the thiocyanate. Evaporate the sample solution to a few ml, add 0.5 ml of sulfuric acid and 5 ml of nitric acid and evaporate again to white fumes of sulfur trioxide. Cool. Add 5 ml of deionized water, neutralize with ammonia (1+1) and evaporate to near dryness. Take up the residue with 5 ml of deionized water, add 2 ml of the hypobromite solution and stand for 30 min with occasional stirring. Add 0.5 ml of 1.2% phenol solution and 2.5 ml of phosphate buffer pH 6.5 (0.5 *M* disodium hydrogenphosphate and 0.5 *M* sodium dihydrogenphosphate). If necessary, readjust the pH with 1 *M* hydrochloric acid. Add 2 ml of 0.01 *M* CyDTA and 1.0 ml of the PAR solution. Dilute to 25 ml with deionized water and stand for 5 min. Measure at 545 nm against a blank solution which has been taken through the same procedure.

Determination of distribution coefficient. Weigh out 1-g portions of the resin, SCN-form, dried over a saturated potassium bromide solution, and place in conical flasks with glass stoppers, containing 41-ml portions of 0.5 *M* sodium chloride solution previously adjusted to 0.1 *M* in hydrochloric acid and containing varying amounts of thiocyanate and 0.491 mg of vanadium(V) or 1.49 mg of vanadium(IV). Shake the mixtures mechanically for 20 h at room temperature and separate the two phases by filtration. Analyze the filtrates for vanadium. Compute the distribution coefficient according to:

K_d = (amount of vanadium per g of resin)/(amount of vanadium per ml of solution)

Procedure. Acidify the sea water sample to 0.1 *M* with respect to hydrochloric acid and percolate through a 0.45 μ Millipore filter. Take a 2-l sample from the filtrate and add 15.2 g of ammonium thiocyanate to give 0.1 *M* in thiocyanate. Pass the thiocyanate solution down the column at a flow rate of about 10 ml min^{-1}. Wash the column with 250 ml of 0.1 *M* ammonium thiocyanate–0.1 *M* hydrochloric acid solution. Discard the effluent. Strip the vanadium by elution with 40 ml of concentrated hydrochloric acid. Proceed as described for the determination of vanadium.

Results and discussion

In order to study the adsorbability of vanadium(V, IV) on Dowex 1 from thiocyanate media, K_d values were measured for vanadium(V, IV) as a function of thiocyanate concentration in 0.5 *M* sodium chloride–0.1 *M* hydrochloric acid solution. Results are listed in Table I. Vanadium(V) and vanadium(IV) behaved similarly, and their adsorption increased rapidly with increasing thiocyanate concentration. Above 0.1 *M* thiocyanate concentration, the K_d values were sufficiently high to adsorb vanadium of any valence state from sea water on the resin.

The adsorbed vanadium was easily stripped from the column by elution with concentrated hydrochloric acid. An alkaline eluent, 1 *M* sodium hydroxide–1 *M* sodium chloride, proved less effective; a recovery of 96% was obtained for a 2-g resin column with 70 ml of this eluent. In contrast, merely 20 ml of hydrochloric

TABLE I

DISTRIBUTION COEFFICIENTS FOR VANADIUM AS A FUNCTION OF THE THIOCYANATE CONCENTRATION

NH_4SCN (M)	0.01	0.03	0.10	0.30	1.0
K_d V(V)	780	2100	$>10^4$	$>10^4$	$>10^4$
V(IV)	680	1900	9600	$>10^4$	$>10^4$

TABLE II

DETERMINATION OF VANADIUM IN ARTIFICIAL SEA, SEA AND FRESH WATERS

Run	*Added (μg)*	*Found (μg)*	*Original V content (μg l^{-1})*	*Run*	*Added (μg)*	*Found (μg)*	*Original V content (μg l^{-1})*
0.5 M sodium chloride solution (A)				*Sea water (C)*[b]			
1	–	0.29	0.15	10	–	3.34	1.67
2	3.93	4.12	0.10	11	–	3.20	1.60
3	3.93	4.08	0.08	12	–	3.43	1.72
4	3.93	3.93	0.00	13	3.93	7.18	1.63
			av. 0.08±0.06	14	7.86	11.1_6	1.65
							av. 1.65±0.05
Sea water (B)[a]				*Lake water (D)*[c]			
5	–	3.47	1.74	15	–	1.78	0.89
6	–	3.38	1.69	16	–	1.73	0.87
7	–	3.18	1.59	17	–	1.53	0.77
8	3.93	7.41	1.74	18	1.97	3.66	0.85
9	7.86	11.0_2	1.58	19	3.93	5.48	0.78
			av. 1.67±0.08				av. 0.83±0.05

[a] Collected on the shore of Iso, Kagoshima Bay, on October 13th, 1971. [b] Collected 2 km off the coast of Koshiki Jima, East China Sea, on November 12th, 1971. [c] Collected at Ikeda Lake, Kagoshima, on December 5th, 1971.

acid was necessary to recover vanadium quantitatively from the same column.

Uptake of vanadium from thiocyanate media on Dowex 1 and elution with hydrochloric acid provide a selective separation of vanadium from many other metals[10]. In addition, although PAR is an unselective reagent for vanadium(V)[11,12], CyDTA can mask the PAR reaction of metals such as Mg, Mn, Mo(VI), W(VI), Sn(II), Al, Co, Cr, Cu(II), Fe(III), Zn, Cd, Hg(II), Pb, Ni, Ga, Ag, etc., so that the PAR method can become very selective[13].

Results of repeated determination of vanadium in 0.5 *M* sodium chloride solution, two sea waters and one fresh water are given in Table II. To each sample known amounts of vanadium(V) were added and the overall recoveries were also estimated. Generally, the overall precision is satisfactory. The vanadium contents of sea water obtained here are within the values previously reported, which vary between 0.2 and 7 μg V l^{-1} of sea water[7]. Recently, values of 1.82±0.05[1], 3.12±0.04[2] and 0.86±0.14[3] μg V l^{-1} have been reported.

In order to establish the concentration of organically bound vanadium, 1-l samples of B, C, and D (Table II) were refluxed with 10 ml of sulfuric acid and 0.2 g of potassium permanganate for 2 h at 100°, and then the vanadium was determined. Results (μg V per l) were: 2.43 and 2.54 for B, 2.14 and 2.06 for C, and 1.36, 1.39 and 1.33 for D. These values are 30–60% higher than the corresponding values obtained without oxidation.

Effect of storage of samples

Twenty l of the sea water (sample B), acidified to 0.1 M in hydrochloric acid and filtered through a 0.45-μ Millipore filter, was stored for 3 months (October 31st, 1971 to January 23rd, 1972) in a polyethylene bottle and then reanalyzed for vanadium. A consistent value of 1.72 μg V l^{-1} was obtained; thus there was no evidence that vanadium had become precipitated or adsorbed on the wall of the container during storage. A sea water sample was also stored without acidification and filtration, and portions were analyzed periodically over 50 days. A 2-l portion of the sample was taken each time, filtered through the 0.45-μ Millipore filter, and then analyzed. Results (μg V l^{-1}) obtained were: 1.59 at date collected (January 26th, 1971), 1.61 after 22 days, 1.61 after 43 days and 1.70 after 50 days. Therefore, as far as vanadium is concerned, the addition of acid to sea-water samples seems not to be of primary importance.

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SHORT COMMUNICATION

Froth flotation separation of small amounts of uranium*

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Separation of uranium by means of flotation is not widely used. Methods have been described for separation of mg amounts of uranium by flotation[1,2]. Adsorbing colloid flotation techniques based on an iron(III) hydroxide–sodium dodecyl sulfate–air system[3] or a thorium hydroxide–sodium dodecanoate–air system[4] have been developed for the separation of uranium from sea water. The recoveries of uranium were 82% and 90%, respectively.

Uranium(VI) forms a 1:1 complex with arsenazo III (2,2′-[1,8-dihydroxy-3,6-disulfo-2,7-naphthylenebis(azo)]-dibenzenearsonic acid) at pH 1.1–3.4[5]. The complex is probably anionic because of the presence of the sulfonate groups in the reagent. If a cationic surfactant were present, the uranium(VI)–arsenazo III complex would form an ion-association compound that should be separable by means of foam. A study has been made in order to demonstrate this possibility, and the results are described in this paper. As the cationic surfactant, a quaternary ammonium compound, zephiramine, was used.

Experimental

Reagents and apparatus. Arsenazo III and zephiramine (Dojindo Co., Ltd., Kumamoto-shi, Japan) were used.

To prepare the uranium solution (1.00 mg ml^{-1}) dissolve 0.500 g of pure uranium metal in 10 ml of concentrated nitric acid and 12 ml of 30% hydrogen peroxide by heating. Evaporate to near dryness, dissolve the residue in 0.2 *M* nitric acid, and dilute the solution to exactly 500 ml with 0.2 *M* nitric acid. From this stock solution prepare a working standard solution containing 10 μg U ml^{-1}, by diluting with water.

Absorbance measurements were made with a Hitachi Model 139 spectrophotometer in 1-cm cells. A Hitachi-Horiba Model M-5 glass electrode pH meter was used for pH measurements.

The apparatus for flotation is shown in Fig. 1. The flotation cell was a glass cylinder (20 × 1.5 cm o.d.) which was fitted with a sintered-glass filter to generate small bubbles.

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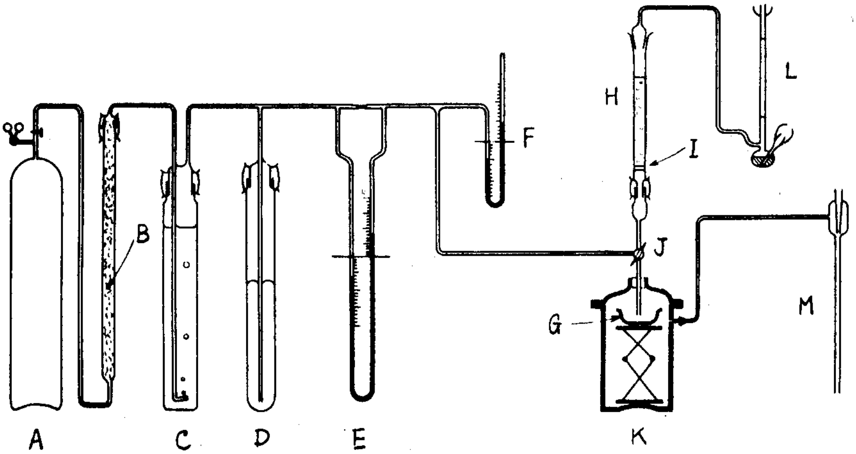

Fig. 1. Apparatus for flotation. (A) Nitrogen tank; (B) glass wool; (C) gas washing bottle; (D) regulator; (E) flowmeter; (F) manometer; (G) silica dish; (H) flotation cell; (I) sintered-glass filter; (J) T-bore stopcock; (K) bell jar; (L) soap film meter; (M) aspirator.

Procedure

Transfer the sample containing 0–150 μg of uranium(VI) to a 50-ml volumetric flask, add 5.0 ml of aqueous 0.1% arsenazo III solution and 5 ml of 1 *M* acetate buffer pH 3.5 solution, and dilute to volume with water. Transfer 0.15 ml of aqueous 1% zephiramine (tetradecyldimethylbenzylammonium chloride) solution to the flotation cell. Pipet 20 ml of the sample solution into the flotation cell. Pass nitrogen at a flow rate of about 1 ml min^{-1} into the solution for several min. After the solution has become colorless or pale pink, transfer the residual solution to a silica dish through the glass filter. If the residual solution is not to be analyzed, it may be discarded.

Dissolve the scum with three 3-ml portions of hot concentrated nitric acid and transfer the solution to another silica dish through the glass filter. Wash the cell with two 2-ml portions of water, and add the washings to the dish. Evaporate the solution in each dish to dryness. To the residue add 1 ml of 60% perchloric acid and 1 ml of concentrated nitric acid, and evaporate to dryness. Repeat the treatment with perchloric and nitric acids again.

Dissolve the residue in 10 ml of 0.3 *M* hydrochloric acid, and transfer the solution to a 25-ml volumetric flask. Add 1 ml of aqueous 1% ascorbic acid solution, 1 drop of aqueous 0.04% cresol red solution, 1.5 *M* ammonia solution until the color turns to red from yellow (pH of the solution must be 1.5–2.0), and 1.0 ml of the arsenazo III solution, and dilute to the mark with water. Measure the absorbance of the solution at 650 nm, using the reagent blank as the reference.

Construct the calibration curve for uranium (0–60 μg) by omitting the separation step.

Results and discussion

Uranium(VI) was determined spectrophotometrically with arsenazo III[6]. The use of the same reagent for separation and determination was convenient.

Effect of arsenazo III and surfactant concentration. For 20-ml solutions (pH 3.5) containing 40 μg of uranium and 1.5 mg of the surfactant, the amount of arsenazo III added was varied in the range 0.1–4 mg. Quantitative recoveries of uranium were obtained when 0.4–3 mg amounts of arsenazo III were used; the low recovery obtained with 4 mg of arsenazo III and 1.5 mg of zephiramine was improved by using 3 mg of zephiramine. A suitable arsenazo III concentration was 2 mg per 20 ml of solution.

When the flotation separation method was applied to solutions at pH 1.5–2.0 containing 40 μg of uranium and 2 mg of arsenazo III per 20 ml, essentially quantitative recoveries were obtained when the zephiramine added was in the range 1–2 mg per 20 ml; 1.5 mg was therefore generally used.

TABLE I

EFFECT OF FOREIGN IONS

Addition		*U found (μg)*			
		U absent		*40 μg U taken*	
		Residual solution	*Scum*	*Residual solution*	*Scum*
Al	1 mg	1	1	2	38
Ca	10 mg	15	1	15	40
	100 mg	—	1	—	36, 38
	100 mg	—	1[a]	—	40[a], 40[a]
Dy	100 μg	0	16	2	42
	100 μg	0[b]	0[b]	0[b,c]	26[b,c] 27[b,c].
Fe(III)	1 mg	48	40	48	44
	1 mg	1[d]	1[d]	1[d]	39[d]
Mg	40 mg	0	0	3, 2	40, 39
	500 mg	—	1	—	40, 40
Na	100 mg	0, 0	0, 1	1, 2	40, 38
	1 g	—	1	—	40, 40
Th	30 μg	0	20	1[e]	47[e]
	200 μg	1	130	3	165
V(V)	100 μg	0	1	1, 1	40, 39
	1 mg	2	3	35, 37	8, 5
Zr	200 μg	1, 2	13, 23	5, 12	38, 36
	0 μg	0[f]	1[f]	6[f]	35[f]
	40 μg	5[f]	1[f]	8[f]	35[f]
	100 μg	27[f]	3[f]	19[f]	35[f]
	200 μg	31[f], 45[f]	4[f], 2[f]	32[f], 49[f]	33[f], 32[f]
	0 μg	1[g]	1[g]	2[g]	39[g]
	40 μg	1[g]	1[g]	4[g]	39[g]
F^-	0.5 mmole	0	0	3	38
	5 mmole	1	1	20, 3	21, 39
PO_4^{3-}	0.1 mmole	0	1	0	39, 39

[a] 2 mg zephiramine. [b] U determined as the U(IV)–arsenazo III complex[7]. [c] 30 μg U taken. [d] 10 mg of ascorbic acid added before separation. [e] 30 μg U taken. [f] 40 mg of oxalic acid added before separation. [g] 40 mg of oxalic acid, 4 mg of arsenazo III, and 2.5 mg of zephiramine.

Effect of pH before addition of zephiramine. The effect of the pH of the 20-ml solution containing 40 μg of uranium and 2 mg of arsenazo III on the recovery of uranium was studied; the amount of zephiramine used was 1.5 mg. Acetate buffer solutions were used in the pH range 3.5–5.0, and hydrochloric acid and ammonia were used to adjust the pH to 0–3 and 7, respectively. Satisfactory recoveries were obtained in the pH range 1.5–6. When an acetate buffer was used, a pH range of 3–5 was suitable. It is of interest to note that this pH range is much wider than that for the spectrophotometric determination of uranium(VI) with arsenazo III[6].

Effect of gas flow rate. This effect was not especially studied because the solution had an intense color before separation and became colorless when the separation was completed.

Recovery of uranium. Solutions (20 ml) containing 2 mg of arsenazo III, 1.5 mg of the surfactant, and 20, 40, and 60 μg of uranium were analyzed by the Procedure. The absorbances obtained were the same as those obtained without foam separation. The relative standard deviation for 6 analyses of solutions containing 40 μg of uranium was 0.7%.

Effect of foreign ions. The effect of some ions on the separation and determination of uranium is shown in Table I. Aluminum (1 mg), 100 mg of calcium, 1 mg of iron(II), 500 mg of magnesium, 1 g of sodium, 100 μg of vanadium, 0.5 mmole of fluoride, and 0.1 mmole of phosphate did not interfere with the separation and determination of 40 μg of uranium; 43 mmole of chloride, 2.5 mmole of nitrate, and 21 mmole of sulfate also did not interfere. Thorium accompanied uranium. Zirconium (40 μg) could be separated by adding oxalic acid and increasing the amount of arsenazo III.

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SHORT COMMUNICATION

The vacuum-fusion determination of gases in silicon carbide

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(Received 18th July 1972)

In the nuclear field, silicon carbide is used as coating material in the fabrication of coated particle fuels, and determination of its impurities, of which gases represent the largest part, is often required. To our knowledge, the only work on the subject means of the Balzers Exhalograph E A1. As it was part of a general work on the vacuumfusion analysis of various oxides, precise details such as working temperature, fusion analysis of various oxides, precise details such as working temperature, weight and relative amount of samples with respect to the bath or flux employed, etc., were not given; nevertheless their paper clearly indicated that, in comparison with the classical bath (Ni 80%–Fe 20%) or flux (Pt) techniques, the recovery of oxygen was almost doubled when the samples were thrown into the hot graphite crucible of the instrument in sealed graphite capsules. Their explanation of the results was that with the classical techniques, losses of oxygen occur mainly because of the formation of the very volatile silicon monoxide, which escapes from the crucible without being reduced by the carbon to carbon monoxide, on which is based the vacuum-fusion extraction of the oxygen; the containment of the samples in closed graphite capsules forces the silicon monoxide to react with the carbon and permits a full recovery of oxygen.

In addition, as Paesold *et al.* also say, incomplete gas extraction can occur through the incorrect choice of some of the experimental factors. Their nitrogen results show good agreement between the capsule and flux techniques, whilst the result for the bath technique is very low.

In view of these results, and of the interest in silicon carbide, a further investigation was decided upon.

Experimental

Specimens. The determinations were carried out on five specimens, as received, of silicon carbide in powder form, with particle dimensions smaller than 177 μm. The weight of the samples used was in the range 30–60 mg.

Instruments. Two commercial vacuum-fusion instruments were employed: the Feichtinger StRe 0583 (H. Feichtinger, Schaffhausen, Switzerland)[2] and the Heraeus VH6 (W. C. Heraeus GmbH, Hanau/Main, Germany)[3]. Both the instruments accumulate the analysed samples in the crucible and both use, for the determination of the extracted gases, gas chromatographs, which are calibrated by the injection of known amounts of hydrogen, nitrogen and carbon monoxide.

Whilst the Feichtinger is currently used in the laboratory as purchased, the Heraeus was modified: its gas chromatograph and the related ionization detector were replaced by a home-made chromatograph and thermistor detector, giving a greatly increased linearity of response over the former. The calibration gases were delivered by means of a system of magnetic valves, which deliver fixed and known amounts; the modifications result in an overall increase in precision and accuracy.

Techniques. After preliminary experiments the techniques used finally were the following.

(a) Nickel flux. This was used with the standard Feichtinger instrument. Each sample, in a light platinum container (120–140 mg) made from thin platinum foil, was dropped into the crucible at 1650° and was immediately followed by 1 g of nickel, added in small pieces. The crucible was then degassed for 15 min. The gas contents of the samples were then evaluated, allowance being made for the gases coming from platinum, nickel and the blank of the instrument.

(b) Platinum flux. This was also used with the standard Feichtinger instrument. Each sample was held in the light platinum container (120–140 mg) as before, and was then dropped into the crucible at 1800°, and degassed for 15 min. The gas contents of the samples were evaluated, allowance being made for the gases coming from platinum and the blank of the instrument.

(c) Graphite capsule. This technique was used with the Heraeus instrument, the small standard crucible of which had been replaced with another of 26 mm internal diameter, 32 mm internal height and a capacity of 4 capsules. Some details of the capsules (Fig. 1) which, together with their screwed covers, weighed about 2 g, deserve description.

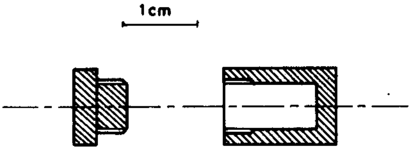

Fig. 1. Graphite capsule.

As graphite contains large amounts of gases, the capsules were predegassed at 1800° in the instrument itself after manufacture. Despite the cover they were not vacuumtight and thus, when placed in the sample holder of the instrument, which was at the same high vacuum as the furnace, any air enclosed in them was evacuated; after predegassing, although they were exposed to air for some days, they did not readsorb large quantities of gases. Typical values obtained with the technique which follows were about 1 p.p.m. hydrogen, 0.5 p.p.m. nitrogen, and 2 p.p.m. oxygen.

Each sample in the usual light platinum container was enclosed in the capsule and thereafter dropped into the crucible at 1700° and degassed for 15 min. During this time, some surges to 1900°, lasting a total of 2 min, were made in order to complete the gas extraction. The gas contents of he samples were evaluated, allowance being made for the gases coming from platinum, capsule and the blank of the instrument.

Results and discussion

Table I shows the results obtained together with results obtained for comparison purposes by neutron activation analysis[4].

TABLE I

ANALYTICAL RESULTS

Specimen	*Pt flux*		*Ni flux*		*Graphite capsule*		*Activation analysis*
	N (p.p.m.)	*O (p.p.m.)*	*N (p.p.m.)*	*O (p.p.m.)*	*N (p.p.m.)*	*O (p.p.m.)*	*O (p.p.m.)*
SiC 1	3200	4160	2700	4030	2960	3820	
	3060	3970	3340	4130	3000	3830	
Average	3130	4065	3020	4080	2980	3825	4670
SiC 2	2980	4440	3000	4660	3210	4560	
	3030	4720	3300	4540	3260	4660	
Average	3005	4580	3150	4600	3235	4610	5035
SiC 3	1370	5280	1370	5340	1360	5320	
	1390	5200	1470	5680	1310	5250	
			1230	5500			
			1450	5340			
Average	1380	5240	1380	5465	1335	5285	5255
SiC 4	380	4470	690	4260	415	4770	
	450	4490	600	4420	475	4460	
Average	415	4480	645	4340	445	4615	4930
SiC 5	235	2540	505	2620	485	2640	
	335	2610	465	2440	465	2830	
Average	285	2575	485	2530	475	2735	2400

Despite the very different environmental conditions, the agreement among the oxygen vacuum-fusion results is excellent, and no indication is given that the platinum and nickel flux techniques cause severe oxygen losses. It is probable that such losses, if they occur, are mainly a function of the inner surface area and of the ratio of the inner surface area to the inner volume of the crucible used: the higher the surface area and the ratio, the lower the losses.

The Feichtinger instrument was operated according to our usual practice, with the standard graphite crucible and funnel KA 41 and KA 62/621 (Fig. 2), of which the latter is at a temperature well below that of the crucible; the inner surface area and the surface area-to-volume ratio of such a crucible can be estimated to be about 37 cm^2 and 2 cm^{-1}, respectively. Some experiments carried out on specimens 1 and 3 by the nickel flux technique, with the same funnel but a smaller crucible (type C: inner surface area of about 23 cm^2 and ratio of about 3 cm^{-1}) gave oxygen recoveries lower by a factor of about 0.85, which seems to support the hypothesis made.

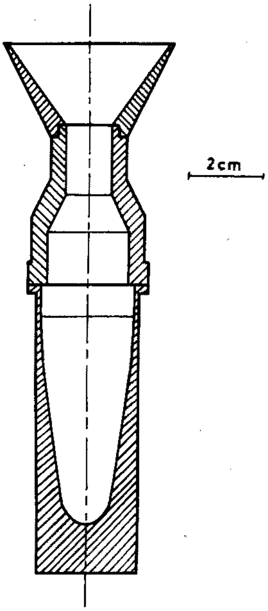

Fig. 2. Crucible and funnel.

The agreement between the vacuum fusion and the activation results is satisfactory.

As far as the nitrogen is concerned, excellent agreement was observed at relatively high nitrogen contents, whilst the nickel flux technique appeared to give a more complete extraction at low contents.

The hydrogen determination gave no difficulties as the hydrogen was already completely released at temperatures lower than those used in the present work.

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SHORT COMMUNICATION

A new method for column packing in reversed-phase chromatography

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(Received 10th June 1972)

Reversed-phase (extraction) column chromatography is an extremely versatile technique and has been applied successfully to the separation of various metals and organic compounds. Several hundred papers describing various extraction systems and a wide variety of inert supports are listed in the excellent bibliography of Eschrich and Drent[1].

Column preparation is of prime importance in reversed-phase chromatographic processes[2]. Cerrai and Ghersini[2] state: "Column preparation is a very critical step; it is the only one where "reversed-phase art" plays an important role", and further: "An ideal column should allow for elution without any applied overpressure". The commonest method of preparing the chromatographic column is to treat the support with the extractant before column packing. The treated support is then slurried with an aqueous solution and added to the column in small portions applying gentle pressure with a glass rod[3–5]. Filling with slurries of untreated support has also been used[2,6]; after the column has been prepared, the extractant is percolated through the column and the excess is removed by elution with an aqueous solution. Packing with dry treated or untreated support has also been reported[2,7].

A review of the literature shows that columns prepared by the previously mentioned techniques usually require the application of pressure to force the eluent through the column at practical flow-rates[8–10]. Hornbeck[11] recognized this shortcoming, particularly insofar as it requires increased operator attention.

In reversed-phase extraction chromatography, column beds are made of a material of suitable particle size, which supports the extractant. In general, the smaller the particle size, the larger the surface area (*i.e.* higher column efficiency); but small particle size means a high pressure drop through the column. For a definite amount of support of a given particle size, this pressure drop was found to depend also on the technique used for column preparation which regulates the degree of bed homogeneity.

In previous work on "foam chromatography"[12,13], *i.e.* the application of foamed supports in reversed-phase extraction chromatography, a vacuum technique was developed for column packing. This method is simple and rapid, and produces quite homogeneous foam beds. The present work is a further extension of this vacuum technique in order to apply it to ordinary granular supports. This is of course desirable for economy both in time and effort of the operator; moreover, the column can be packed very easily, in a reproducible manner, by anyone. In this communication, columns prepared by the ordinary[14] and vacuum techniques of packing are compared for efficiency, capacity and other properties of practical analytical interest. An example of analytical application is also presented.

Experimental

Reagents and materials. All reagents were of analytical grade. Tri-*n*-butyl phosphate(TBP) used as stationary phase was purified as described by Hamlin *et al.*[14]. Voltalef (polytetrafluoroethylene) powder grade 300 LD CHR (Plastimer, 5 Rue du Général Foy, Paris) was sieved to 0.25-mm particle diameter by means of a series of standard sieves, before use.

Palladium and bismuth solutions were prepared and standardized as described previously[13].

Columns. The chromatographic columns were made of 10-mm i.d. Pyrex tubing, fitted with a fritted glass disc at the bottom (*cf.* Fig. 1).

Spectrophotometer. A Hungarian spectrophotometer type MOM-203 was employed with 1-cm silica cells.

Column preparation. Voltalef powder (0.25 mm diameter) was treated with purified TBP (1 ml g^{-1}), which had been previously equilibrated with nitric acid by shaking for 5 min with twice its volume of 1 *M* nitric acid. The treated Voltalef powder was pressed between two sheets of filter paper to remove excess of TBP. The treated support was then introduced into the column by means of spatula, and a close packing was achieved by knocking the wall of the column with a rubber rod. In this way, any adsorbed or suspended particles settled down in an ordered manner under their own gravity. The bed was held by two cotton wool plugs. To avoid air bubbles during packing, tap (1) (Fig. 1) was connected to a water-suction pump

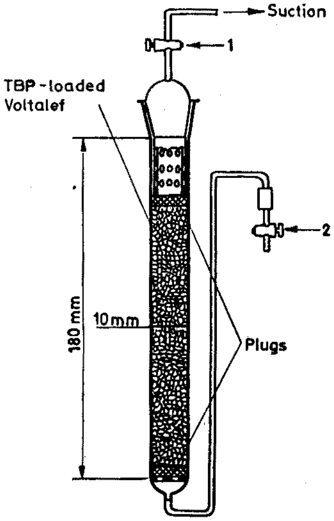


Fig. 1. Column in packing step.

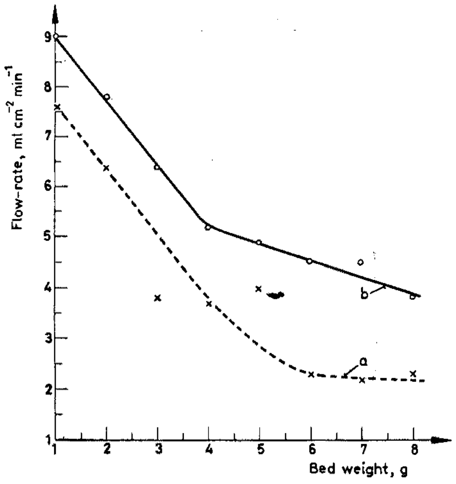


Fig. 2. Flow-rate *vs.* weight of loaded Voltalef powder. (a) Normal packing; (b) vacuum packing.

while tap (2) was closed. The flat-bottomed connection of tap (1) prevented the support from moving upward during suction. After about 5 min of evacuation, water was allowed to fill the column gradually through tap (2). Then the stopper of tap (1) was replaced with a separatory funnel.

Procedure. A mixture of 1 ml of palladium chloride solution (0.618 mg Pd^{2+} ml^{-1}), 1 ml of bismuthyl perchlorate solution (1 mg Bi^{3+} ml^{-1}) and 2 ml of 0.2 *M* perchloric acid containing 6% thiourea and 2% sodium perchlorate was used as the feed solution. Sorption of this mixture took place at a flow-rate of 1 ml min^{-1}; 20 ml of 0.1 *M* perchloric acid solution (containing 3% thiourea and 1% sodium perchlorate), was then used to wash the column. The bismuth–thiourea complex was eluted with 0.5 *M* perchloric acid and the palladium complex was then washed out with water[13].

Determination of the break-through capacity. The column was washed with 20 ml of distilled water and then a solution containing 0.267 mg Pd^{2+} ml^{-1}, 0.1 *M* perchloric acid, 3% thiourea and 1% sodium perchlorate, was percolated through the column at 1 ml min^{-1}. The palladium–thiourea complex was well retained by the bed, and its retention within the column could be followed by the downward movement of the yellow band. The break-through capacity was determined from the actual volume collected just before the appearance of the palladium–thiourea complex in the effluent solution minus the free-column volume. The resultant value was multiplied by the concentration of the original solution.

Determination of the interstitial volume. To estimate the interstitial volume, TBP solution was poured on the TBP-treated Voltalef column and the volume of the aqueous effluent before the appearance of the TBP layer was taken as a measure of the interstitial volume.

Analytical methods. Palladium and bismuth were determined spectrophotometrically as their thiourea complexes at 360 and 470 nm respectively[13].

Results and discussion

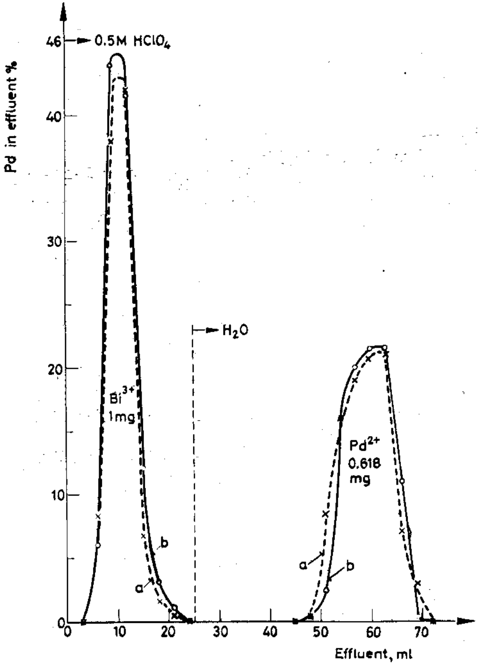
The aim of this work was to achieve a standard, easily reproducible packing technique which would readily produce homogeneous beds with good flow characteristics without affecting the column performance. Attention was directed towards the vacuum technique of packing which had proved to be very suitable for filling columns with foam material[12,13]. This technique of packing is simply based on the application of suction to one side of a closed column, which has been previously filled with the dry treated support. After evacuation of the column, water is allowed to fill it gradually from the other side.

Application of this vacuum-packing technique for column fillings of TBP-treated Voltalef powder gave a good homogeneous bed with improved flow characteristics. The flow-rate was found to depend on the amount of the support used. In general, the bed height was increased by increasing the amount of the support (at constant column cross-section) and consequently the flow resistance increased. Figure 2 shows a plot of the flow-rate (attained by gravity) as a function of the weight of treated support for columns packed by the ordinary[14] and by the proposed vacuum technique. It is clear that the decrease in flow-rate with increase in column height is more pronounced in the case of ordinary columns, and that vacuum-packed columns generally allow higher flow-rates. The relative difference in flow-rates increased when the bed height was increased. This may be attributed to the increased inhomogeneity of the bed obtained by the ordinary technique.

In order to determine the feasibility of using the new packing technique, column performance was tested by means of elution and break-through capacity curves. The model was the separation of palladium and bismuth. The elution curves were found to be approximately the same in the case of both packing methods (*cf.* Fig. 3).

Columns packed by the normal and vacuum techniques were also used for the determination of the break-through capacity and the overall capacity. The results calculated from the curves of Fig. 4 showed equal break-through capacities (7.2 mg Pd^{2+} g^{-1} of treated powder). The sharpness of the break-through capacity curves was also found to be the same (Fig. 4). The relationship between the bed height and the weight of dry treated support was found to be linear and identical for columns packed by the two techniques *i.e.* the density of the column fillings was about the same. In all cases, the interstitial volume was also found to be equal (1.3 ml).

In conclusion, the vacuum technique of packing is recommended for column filling in reversed-phase chromatography. It eliminates the tedious handling that would otherwise be necessary to obtain homogeneous beds. This technique is rapid, reproducible and simple and requires little technical skill. Relatively higher flow-rates can be attained simply by gravity flow.



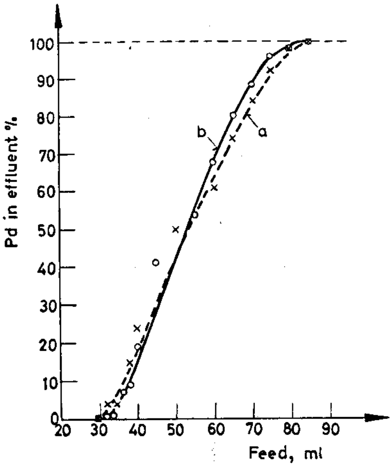


Fig. 3. Separation of palladium and bismuth on TBP-loaded Voltalef (0.25 mm) at room temperature. Flow-rate: 1.0 ml min^{-1}. (a) Voltalef packed by the normal technique; (b) Voltalef packed by the vacuum technique.

Fig. 4. Break-through curve for palladium–thiourea complex on TBP-loaded Voltalef (0.25 mm). Weight of loaded support: 1.0 g. Feed Pd–thiourea complex: 0.267 mg Pd^{2+} ml^{-1}. Flow-rate: 1 ml min^{-1}. (a) Voltalef packed by the normal technique; (b) Voltalef packed by the vacuum technique.

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SHORT COMMUNICATION

5,7-Dibromo-8-hydroxyquinoline N-oxide as a reagent for the separation and gravimetric determination of cerium(IV) and thorium(IV)

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5,7-Dibromo-8-hydroxyquinoline N-oxide (5,7-dibromo-oxine N-oxide; DBONO) has been used for the spectrophotometric determination of iron(III)[1], uranium(VI)[2] and ruthenium(III)[3]. Recently, the stability constants of its complexes with bivalent and tervalent metal ions in 75% (v/v) aqueous dioxane medium have been determined[4]. During the investigations, it was observed that a red brown precipitate was obtained on addition of ethanolic DBONO solution to aqueous cerium(IV) solution; precipitation was found to be quantitative over the pH range 3.5–10.0. With thorium(IV), the reagent formed a yellow precipitate, the precipitation being quantitative over the pH range 8.6–10.3. Both these complexes had to be ignited to the dioxides since there was no suitable wash liquid for the removal of excess of reagent. Since the precipitation of cerium(IV) and thorium(IV) with DBONO occurred at different pH ranges, the separation and determination of the two metals was successful.

Reagents and instruments

5,7-Dibromo-8-hydroxyquinoline N-oxide (DBONO) was prepared by bromination of 8-hydroxyquinoline N-oxide and was used as a fresh ethanolic 0.2% solution. Solutions of cerium(IV) and thorium(IV) were prepared from B.D.H. AnalaR samples of ammonium cerium(IV) nitrate and thorium nitrate respectively and were standardised with 8-hydroxyquinoline[5]. All other salts used were either of B.D.H. AnalaR or Merck p.a. grade. The pH of the solutions, adjusted with hydrochloric acid and sodium hydroxide, was measured with a Beckman pH-meter model H2 and a glass electrode.

Gravimetric determination of cerium(IV)

To about 60–80 ml of a solution containing cerium (4–30 mg of CeO_2) add an ethanolic solution of DBONO (about 6 mg per mg of CeO_2), adjust the pH to 3.5–10.0, and filter through Whatman paper No. 40. Transfer all the precipitate with hot water as the wash liquid and continue washing the precipitate with hot water until free from nitrate. Slowly ignite the precipitate to the oxide and weigh as CeO_2 after igniting at 900° for 1 h.

TABLE I

DETERMINATION OF CERIUM AND THORIUM IN THE PRESENCE OF FOREIGN IONS

(Cerium at pH 3.5–4.0 and thorium at pH 9.0–9.5. Cerium oxide taken, 7.5 mg. Thorium oxide taken, 6.9 mg)

Interfering ion	*Taken as*	*Determination of cerium(IV)*			*Determination of thorium(IV)*		
		Foreign ion (mg)	*CeO_2 found (mg)*	*Error (mg)*	*Foreign ion (mg)*	*ThO_2 found (mg)*	*Error (mg)*
Acetate	$NaOAc \cdot 3H_2O$	32.50	7.5	0.00	11.32	6.85	0.05
		75.25	7.45	0.05	72.70	6.85	0.05
Oxalate	$(NH_4)_2C_2O_4$	15.27	7.45	0.05			
		83.32	7.55	0.05			
Tartrate	Tartaric acid	32.33	7.55	0.05	27.20	6.92	0.02
		121.37	7.55	0.05	72.60	6.90	0.00
Fluoride	NaF	11.32	7.40	0.10			
		82.37	7.45	0.05			
Citrate	Citric acid	11.25	7.45	0.05	11.50	6.92	0.02
		80.03	7.45	0.05	72.70	6.95	0.05
Uranyl	$UO_2(NO_3)_2$	13.52	7.42	0.08			
		79.27	7.48	0.02			
Pb^{2+}	$Pb(NO_3)_2$	15.27	7.42	0.08			
		65.23	7.47	0.03			
Ag^+	$AgNO_3$	11.18	7.54	0.04	5.26	6.88[a]	0.02
		69.27	7.52	0.02	59.62	6.85[a]	0.05
Hg^{2+}	$HgCl_2$	9.21	7.48	0.02			
		59.27	7.50	0.00			
Cd^{2+}	$CdCl_2 \cdot 2\frac{1}{2}H_2O$	27.27	7.52	0.02	11.25	6.95	0.05
		82.20	7.54	0.04	80.25	6.95	0.05
Be^{2+}	$BeCO_3$	21.21	7.50	0.00	5.27	6.92	0.02
		92.97	7.46	0.04	70.00	6.88	0.02
Zn^{2+}	$ZnSO_4 \cdot 7H_2O$	9.27	7.55	0.05	11.29	6.88	0.02
		69.87	7.60	0.10	76.27	6.85	0.05
Mn^{2+}	$MnSO_4 \cdot 7H_2O$	10.07	7.58	0.02			
		83.34	7.52	0.02			
Co^{2+}	$CoSO_4 \cdot 7H_2O$	11.13	7.48	0.02	19.92	6.85[b]	0.05
		76.72	7.46	0.04	65.62	6.85[b]	0.05
Ba^{2+}	$BaCl_2$	18.18	7.45	0.05	6.27	6.95	0.05
		121.37	7.50	0.00	59.25	6.87	0.03
Ca^{2+}	$CaCl_2$	11.37	7.47	0.03	11.27	6.87	0.03
		78.72	7.45	0.05	7.90	6.92	0.02
Fe^{3+}	$(NH_4)_2SO_4 \cdot FeSO_4 \cdot 6H_2O$	5.27	7.50	0.00	41.27	6.90[b]	0.00
		37.50	7.50	0.00	69.35	6.92[b]	0.00
Al^{3+}	potash alum	6.27	7.50	0.00			
		39.50	7.55	0.05			
Cr^{3+}	chrome alum	11.27	7.48	0.02			
		36.27	7.45	0.05			
		50.70	7.90	0.40			

[a] In the presence of 1 g of NH_4NO_3.
[b] In the presence of 1 g of tartaric acid.

Gravimetric determination of thorium(IV)

To about 60–80 ml of a solution containing 5–30 mg of ThO_2, add the ethanolic solution of DBONO (about 4 mg per mg of ThO_2), adjust the pH to 8.6–10.3, and filter through Whatman paper No. 40; then proceed as described above for cerium(IV), and weigh as ThO_2.

Effect of pH on the precipitation of cerium(IV) and thorium(IV)

Solutions containing cerium (7.5 mg CeO_2) or thorium (20 mg ThO_2) were used; it was observed that the precipitation of cerium(IV) as the DBONO complex was quantitative over the pH range 3.5–10.0 whereas thorium(IV) was quantitatively precipitated over the pH range 8.6–10.3. Various methods of adjusting the pH were tested; adjustment with hydrochloric acid or sodium hydroxide was preferable. Digestion of the precipitates is not recommended.

Interference of foreign ions

For cerium(IV). When cerium(IV) was determined with DBONO at pH 3.5–4.0, 10-fold amounts of acetate, oxalate, tartrate, fluoride, lead(II), silver(I), mercury(II), cadmium(II), uranyl(II), thorium(IV), zirconium(IV), beryllium(II), zinc(II), manganese(II), cobalt(II), barium(II), calcium(II), and 5-fold amounts of iron(II), aluminium(III), chromium(III) did not interfere (Table I). Bismuth(III), antimony(III) and tin(II) salts were hydrolysed at the pH used and so interfered. Phosphate, arsenate, borate and vanadate precipitated with cerium(IV) and interfered. Iron(III), nickel(II) and copper(II) formed soluble complexes which were adsorbed on the cerium(IV)–DBONO complex when present in quantities larger than that of cerium(IV).

For thorium(IV). In the determination of thorium(IV) with DBONO at pH 9.0–9.5, 10-fold amounts of tartrate, citrate, acetate, cadmium(II), beryllium(II), zinc(II), barium(II), and calcium(II) did not interfere. The interference of silver(I) could be overcome by adding ammonia solution, and that of cobalt(II) and iron(II) by adding tartrate. Phosphate, oxalate, copper(II), lead(II), bismuth(III), tin(II), antimony(III), iron(III), uranyl(II), zirconium(IV), aluminium(III) and chromium-

TABLE II

SEPARATION AND DETERMINATION OF CERIUM AND THORIUM IN PRESENCE OF EACH OTHER

Weight taken (mg)		*pH of the determination*		*Weight found (mg)*	
CeO_2	*ThO_2*	*CeO_2*	*ThO_2*	*CeO_2*	*ThO_2*
27.20	27.60	6.0	10.0	29.70	25.60
		3.5	9.8	27.20	27.60
		3.7	9.6	27.00	27.60
13.6	27.60	3.7	10.0	13.55	27.65
9.10	27.60	3.7	9.4	9.05	27.45
13.60	13.80	3.6	9.7	13.70	13.75
13.60	41.40	3.4	9.5	13.45	41.50
13.60	55.20	3.5	9.8	13.65	55.25

(III) interfered in this determination as their salts were hydrolysed and precipitated at the pH required.

Separation and simultaneous determination of cerium(IV) and thorium(IV)

Cerium(IV) could be precipitated with DBONO at pH 4.0 without interference from thorium. After the separation of cerium(IV), thorium(IV) could be precipitated with DBONO in the filtrate at pH 8.6–10.3. The results of such separations are given in Table II.

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ERRATA

M. Cremer, H. N. Elsheimer and E. E. Escher, Microcoulometric measurement of water in minerals, *Anal. Chim. Acta*, 60 (1972) 183–192.

page 189, 6th line up should read: "sample is exposed to the atmosphere. A Sartorius semimicro balance has been used";
4th line up, "serpentine–bruce mixture" should read: "serpentine–brucite mixture".

G. G. Guilbault and G. J. Lubrano, Enzyme electrode for glucose, *Anal. Chim. Acta*, 60 (1972) 254–256.

page 255, the last paragraph should read: "The authors thank S. S. Kuan for preparing the chemically bound glucose oxidase. The financial assistance of the National Institutes of Health (Grant No. GM-17268) in the research covered in this paper is gratefully acknowledged."

(Continued from page 4 of cover)

Short Communications

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