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PHYSICAL INORGANIC CHEMISTRY MONOGRAPH 2

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MASS SPECTROMETRY OF INORGANIC AND ORGANOMETALLIC COMPOUNDS

by M. R. LITZOW, *Union Carbide Corporation, Cincinnati, Ohio, U.S.A.*
and T. R. SPALDING, *Chemistry Department, The City University, London, England*

1973. 636 pages. Dfl. 150.00 (about US$52.60) ISBN 0-444-41047-3

Over the past 10 years mass spectroscopic methods have developed rapidly and their significance for chemists interested in inorganic and organometallic compounds is fully realized. Compounds of almost all the Main Group and Transition Metal elements have now been studied and some correlations between the effects of structure, electronic configuration and mass spectra are emerging. Thermochemical data is also being obtained on a wide variety of compounds by mass spectrometric techniques.

The present book is the first to cover this expanding field in detail. It is written in two parts, the first dealing in a general way with the basic instrumentation, techniques and the information obtainable from mass spectrometry. This section will be particularly helpful for readers who are not entirely familiar with the possibilities of mass spectrometry.

The second part deals with each Main Group and the compounds of Transition Metals and some Noble gas compounds. The spectra and fragmentation of a large number of different types of compounds are discussed in full. The general level of this second part is for the chemist who uses mass spectrometry as a diagnostic tool and is interested in the fragmentation behaviour of the compounds he studies. No other book has covered the ground in such detail.

CONTENTS:

PART I. Introduction. Basic instrumentation (M. R. Litzow). Mass spectra and types of ions observed (M. R. Litzow). Information obtainable using mass spectrometry (M. R. Litzow).
PART II: Introduction (T. R. Spalding). The Group I elements (M. R. Litzow). The Group II elements (M. R. Litzow). The main Group III elements (M. R. Litzow). The main Group IV elements (T. R. Spalding). The main Group V elements (T. R. Spalding). The main Group VI elements (M. R. Litzow). The main Group VII elements (M. R. Litzow). Compounds of the transition metals (M. R. Litzow). The rare gases (M. R. Litzow). Index.

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Analytica Chimica Acta, 65 (1973) 253–259

SIMULTANEOUS DETERMINATION OF MANGANESE, COPPER, ARSENIC, CADMIUM, ANTIMONY AND MERCURY IN GLACIAL ICE BY RADIOACTIVATION

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(Received 20th November 1972)

Information was desired on the concentration in glacial ice of the elements manganese, arsenic, copper, cadmium, antimony, and mercury. In previous work, concentrations of selenium and mercury[1,2] in the parts-per-trillion range had been measured by the sensitive and specific neutron-activation technique. Since the elements under consideration were expected to occur in similarly small concentrations, the neutron-activation technique was again chosen. This paper describes a method developed to enable samples to be analyzed for all six elements with a single irradiation.

EXPERIMENTAL

Samples, nitric-acid blank, and comparators

The samples were collected from the Greenland ice-sheet in the summer of 1971 by C. Langway, U. S. Army Cold Regions Research and Engineering Laboratory, Hanover, New Hampshire. At the site of collection the ice was put into polyethylene containers leached with nitric acid and rinsed with double-distilled water. The ice was kept frozen until 12 h before it was prepared for irradiation and was then thawed at room temperature. Immediately after complete melting aliquots of each sample were transferred in a laminar-flow hood to 9–12 irradiation vials of 60 ml capacity; each vial contained 3.5 ml of high-purity nitric acid (Ultrex, J. T. Baker, Phillipsburg, N. J.). Nitric-acid blanks, consisting of vials filled with the same high-purity nitric acid, were also prepared.

Comparators were prepared by putting 1 μg of manganese and 10 μg each of arsenic, copper, cadmium, antimony, and mercury into individual vials containing 57 ml each of 1 *M* nitric acid. The comparators were irradiated at the same time as the samples.

Irradiation and postirradiative processing

The samples, nitric-acid blank, and comparators were irradiated for 60 min at 250 kW (full power) in a thermal flux of $1.8 \cdot 10^{12}$ n cm^{-2} s^{-1}. The Mark I TRIGA nuclear reactor of Gulf Energy and Environmental Systems, La Jolla, Calif., was used. The specimens were rotated about the core of the reactor at 1 rev min^{-1}.

After irradiation the sample aliquots were recombined, and sample weight, corrected for nitric-acid contribution, was determined. The nitric-acid blank was diluted with distilled water to a final volume of 500 ml. The carriers of the radioelements (20 mg for cadmium and 10 mg of each of the others) were added to the sample and the nitric-acid blank; only the respective carrier was added to the comparator.

The comparators were prepared for measurement as follows. The mercury and copper solutions, after addition of 2 ml of concentrated ammonia liquor, were diluted to 75 ml with water and the sulfides precipitated. The arsenic and antimony solutions were treated with 2 ml of concentrated sulfuric acid and evaporated to dense fumes of sulfur trioxide; after cooling, the solutions were diluted to 40 ml with water, and the sulfides were precipitated and separated. The manganese solution was made ammoniacal and heated; bromine was then added to precipitate the oxide. Iron carrier (5 mg) was added to the cadmium comparator and the solution was made ammoniacal. After the precipitated iron(III) hydroxide had been discarded, the solution was evaporated until essentially all ammonia had evolved. The volume was raised to 40 ml with water and cadmium hydroxide precipitated by adding sodium hydroxide pellets. The precipitate was dissolved in 0.5 ml of concentrated hydrochloric acid; the volume was then raised to 40 ml with water and the sulfide precipitated.

Unless otherwise noted the sulfide precipitations here and below were effected by passing hydrogen sulfide through the solutions for 30 s. Precipitates were separated from the solutions by filtration through 0.45 μm Gelman Millipore membranes.

Sequential separation of elements

The samples and nitric-acid blank were treated as shown in the following scheme; notes on the scheme are given in the subsequent paragraphs.

Mercury. Ascorbic acid (1 g) was added 5 min before the introduction of 2.5 ml of freshly prepared tin(II) chloride (15–20 ml of concentrated hydrochloric acid in contact with about 5 g of granular tin for 5–10 min). When the solution had stood for 10 min, the mercury was collected.

Copper, arsenic, antimony group. After the separation of mercury, 10 ml of concentrated sulfuric acid were added to the filtrate. The solution was reduced in volume to about 5 ml on a hot plate; completely to remove the ascorbic acid, 10 ml of concentrated nitric acid were added and the volume was again reduced to 5 ml. After addition of 15 ml of 9 *M* sulfuric acid and 10 ml of water, the solution was cooled in an ice bath. Hydrogen sulfide was then bubbled through the cool solution for 30 min, and the mixed sulfides of copper, arsenic, and antimony were collected. The filtrate contained cadmium and manganese.

Arsenic. The sulfides were treated with 10 ml of concentrated nitric acid and 2–3 ml of concentrated sulfuric acid, and the mixture was heated to dryness. The residue was dissolved in about 35 ml of concentrated hydrochloric acid and the solution allowed to stand until it cleared. Arsenic sulfide was precipitated by treating the solution for 5 min with hydrogen sulfide gas. The sulfide was collected by centrifugation; it was then washed with 10 ml of concentrated hydrochloric acid, and the wash was added to the filtrate containing the antimony and copper fractions.

Copper. The copper–antimony filtrate was treated with 50 ml of concentrated nitric acid and 3 ml of concentrated sulfuric acid and then evaporated until dry. The residue was dissolved in 35 ml of concentrated hydrochloric acid and passed through a column of 200–400 mesh Dowex 50-W cation-exchange resin in the chloride form. The resin column was 1.4 cm in diameter and 8–9 cm long, and the flow rate was adjusted to about 1 ml min^{-1} by slight positive pressure. After passage of the filtrate the resin was washed with 20 ml of concentrated hydrochloric acid. The wash and effluent were diluted four-fold with water and copper sulfide was precipitated and collected.

Antimony. The antimony retained on the resin column was eluted with 35 ml of distilled water. Several milliliters of concentrated hydrochloric acid were added to the eluate and antimony sulfide was precipitated and collected.

Cadmium. The filtrate containing cadmium and manganese was adjusted to pH 1–2 with concentrated ammonia liquor and cadmium sulfide was precipitated and collected.

Manganese. After cadmium separation, the filtrate was adjusted to pH 9 with ammonia solution and the solution was treated in the manner described for the manganese comparator.

Radiochemical purifications

As shown in Fig. 1, mercury, arsenic, and cadmium received further radiochemical purification before measurement.

The mercury was dissolved in 5 ml of aqua regia. The solution was partially neutralized with 4 ml of concentrated ammonia liquor and diluted to 100 ml; 5 mg

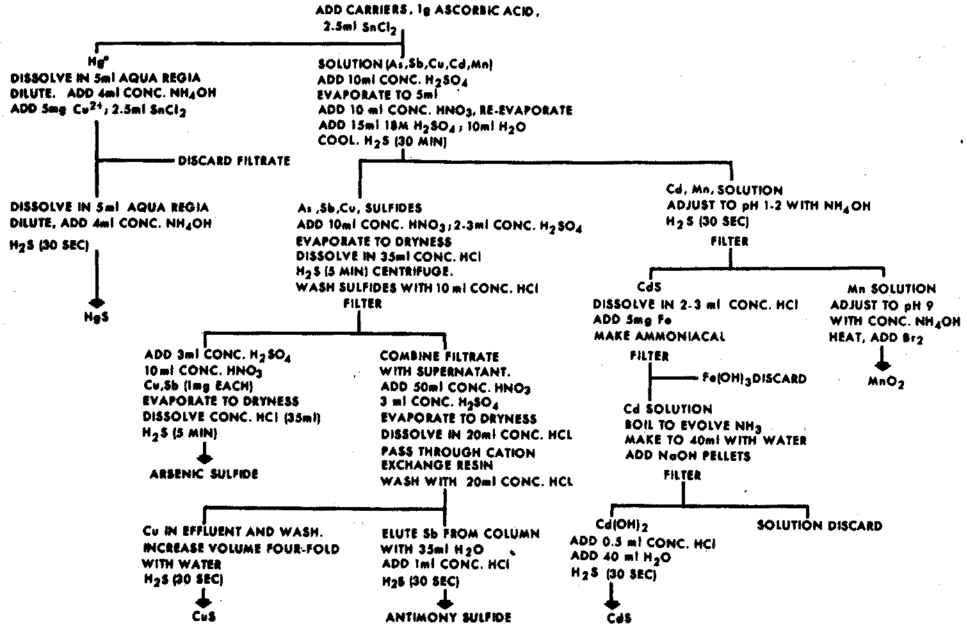

Fig. 1.

of copper holdback carrier were added and the metal was again precipitated with tin(II) chloride. Dissolution of the metal was repeated; the solution was made alkaline with 5 ml of concentrated ammonia liquor and diluted to 75 ml with water, and the sulfide was precipitated and collected.

The arsenic sulfide was treated with 10 ml of concentrated nitric acid, 2–3 ml of sulfuric acid, and 1 mg each of copper and antimony holdback carrier. The mixture was evaporated till dry and dissolved in 35 ml of concentrated hydrochloric acid, and the sulfide was reprecipitated and collected.

The cadmium sulfide was dissolved in 0.5 ml of concentrated hydrochloric acid and diluted to 40 ml with water. Iron carrier was added and purification carried out as described for the comparator.

Radioactivity measurements

Except for cadmium, the precipitates were prepared for measurement by transferring the deposits on the filter discs to 1-ml counting vials. The cadmium precipitate was deposited on a filter paper disc of 0.75 in diameter; the disc was then mounted on a brass planchet.

The γ-rays of 2.5-h ^{56}Mn (0.85 MeV), 12.8-h ^{64}Cu (0.51 MeV), 26.4-h ^{76}As (0.56 MeV), 2.74-d ^{122}Sb (0.56 MeV), and 65-h ^{197}Hg (0.077 MeV) were measured with a sodium-iodide (T1) detector coupled to a pulse-height analyzer. The β-rays of 53-h ^{115}Cd were counted in a wide-β-ray Beckman system. The count for arsenic and cadmium was deliberately started 24 h after radiochemical purification. For a number of samples the radioactive decay of all the isotopes was followed for as long as practical and at least for the period of a half-life.

Carrier yields

Carrier yields were determined by re-irradiating the counted samples and comparing the induced γ-ray activity with that of carrier standards similarly irradiated. These irradiations lasted *ca.* 15 s; the precise time was determined by a timing device actuated and stopped by the pneumatic insertion and removal of the sample from the reactor core. Reactor power relative to full power was 40% for cadmium, 10% for arsenic, antimony, copper, and mercury, and 1% for manganese.

RESULTS AND DISCUSSION

Of the six elements measured, arsenic and antimony pose an isotopic exchange problem. Preliminary experiments with arsenic and antimony tracers in the +3 and +5 oxidation states and respective +3 carriers indicated that complete isotopic exchange occurred in hot sulfuric acid. Therefore, this treatment was incorporated as one of the initial steps in separating the elements.

In the bombardment of nitric acid with neutrons, radiation products are formed that inhibit the reduction of mercury by tin(II) chloride. This effect was overcome by treatment of the solution with ascorbic acid.

In the precipitation of arsenic with hydrogen sulfide from the hydrochloric acid solution, the antimony in the solution underwent partial reduction. Since only antimony(V) is adsorbed by the cation-exchange resin, an oxidative step was

TABLE I

COUNTING DATA AND DETECTION LIMITS

Element	*Background radiation*			*Counting rate at end of irradiation (counts min^{-1} ng^{-1})*	*Average carrier yield (%)*	*Time from irradiation to first count (h)*	*Detection limit*[a] *(ng)*
	Total counts	*Duration of count (min)*	*Twice standard deviation (counts min^{-1})*				
Mercury	330	30	1.2	6.5	78	31	0.3
Antimony	153	30	0.8	5.0	64	30	0.3
Arsenic	256	30	1.0	11.5	44	27	0.4
Cadmium	80	200	0.08	1.0	40	24	0.3
Copper	34	30	0.4	9.0	81	7	0.1
Manganese	33	30	0.4	420	74	6	0.01

[a] The detection limit takes into account the average carrier yield and the time from irradiation to the first count.

introduced before the separation of the antimony from the copper on the column.

Measurements of the decay of the isolated fractions indicated that the method of separation yielded radiochemically pure substances. The one possible exception was arsenic, whose spectrum 7 h after irradiation suggested the presence of a trace of ^{64}Cu; no such trace was evident after 24 h, however, and this delay was therefore introduced before the count. A delay before measurement was also required for cadmium, though not for reasons of impurity; 24 h were allowed for attainment of equilibrium with the β-emitting 4.5-h ^{115}In daughter product. Mercury and antimony were usually counted one day after irradiation to allow early counting of the more rapidly decaying manganese and copper isotopes. The minimum duration for all counts was 30 min (200 min for ^{115}Cd).

Counting data and detection limits for each element are shown in Table I. The detection limit is defined as the point where the counting rate exceeds two standard deviations of the instrument background count. The values given take into consideration the average carrier yield and the radioactive decay occurring between the end of irradiation and the usual time of the first count. All the elements were detectable at the subnanogram level.

TABLE II

CONCENTRATION OF ELEMENTS IN SAMPLES AND NITRIC-ACID BLANK

Element	*Concentration in samples ($ng\ kg^{-1}$)*		*Concentration in nitric-acid blank ($ng\ kg^{-1}$)*	*Quantity introduced into samples (ng)*
	Average	*Range*		
Mercury	49	29–78	54	1.7–2.3
Antimony	32	8–91	60	1.9–2.5
Arsenic	20	2–38	100	3.2–4.2
Cadmium	630	144–1380	< 5[a]	< 0.2
Copper	1669	165–15,700	600	19–25
Manganese	249	91–784	3500	110–147

[a] None detected in 57 ml with a detection limit of 0.3 ng.

The concentration of the elements in the nitric-acid blank and the average values and ranges in the 22 samples, corrected for nitric-acid contribution, are given in Table II. At the low end of the range for arsenic and manganese, the nitric-acid contribution was significant; nonetheless the amount was known with enough certainty to allow reliable correction.

This work was supported in part by the Office of Naval Research under grant NR 083-290; the U.S. Atomic Energy Commission under grant AT (11-1)-34, project 84, Division of Biology and Medicine; and the National Science Foundation under grant GA 27306.

SUMMARY

A method was developed to measure simultaneously the concentration of the elements manganese, copper, arsenic, cadmium, antimony, and mercury in glacial ice. Samples and comparators were irradiated for 60 min in a thermal flux of $1.8 \cdot 10^{12}$ n cm^{-2} s^{-1}. The six elements were separated from the irradiated samples sequentially; mercury, arsenic, and cadmium received additional radiochemical purification. The γ-rays of the ^{56}Mn, ^{64}Cu, ^{76}As, ^{122}Sb, and ^{197}Hg and the β-rays of the ^{115}Cd–^{115}In were measured. All the elements were detectable at the subnanogram level. Comparison of the detection limits with the concentration of elements in the samples indicated that, even with the moderate neutron flux available and for ice from a relatively uncontaminated environment, the methods used were sensitive enough for adequate characterization.

RÉSUMÉ

Une méthode est décrite pour mesurer simultanément les concentrations en manganèse, cuivre, arsenic, cadmium, antimoine, et mercure dans la glace de glacier. Les échantillons et les étalons sont irradiés pendant 60 min dans un flux thermique de $1.8 \cdot 10^{12}$ n cm^{-2} s^{-1}. Les six éléments sont séparés; mercure, arsenic et cadmium sont soumis à une purification radiochimique additionelle. On mesure les rayons-γ de ^{56}Mn, ^{64}Cu, ^{76}As, ^{122}Sb et ^{197}Hg et les rayons-β de ^{115}Cd et ^{115}In. Tous les éléments peuvent être décelés en quantité de l'ordre du subnanogramme. Une comparaison des limites de détection avec la concentration des éléments dans les échantillons, même peu contaminés, montre que les méthodes utilisées sont suffisamment sensibles pour une caractérisation valable.

ZUSAMMENFASSUNG

Es wurde eine Methode entwickelt für die gleichzeitige Bestimmung der Konzentration der Elemente Mangan, Kupfer, Arsen, Cadmium, Antimon und Quecksilber in glacialem Eis. Proben und Vergleichsproben wurden 60 min lang in einem thermischen Fluss von $1.8 \cdot 10^{12}$ n cm^{-2} s^{-1} bestrahlt. Die 6 Elemente wurden von den bestrahlten Proben nacheinander abgetrennt; Quecksilber, Arsen und Cadmium wurden zusätzlich radiochemisch gereinigt. Die γ-Strahlen von ^{56}Mn, ^{64}Cu, ^{76}As, ^{122}Sb und ^{197}Hg sowie die β-Strahlen von ^{115}Cd–^{115}In wurden gemessen. Alle Elemente waren im Subnanogrammbereich nachweisbar. Der Vergleich der Nachweisgrenzen mit der Konzentration der Elemente in den Proben ergab, dass sogar bei dem zur Verfügung stehenden mässigen Neutronenfluss und bei Eis aus einer verhältnismässig wenig verunreinigten Umgebung die angewendeten Methoden für eine hinreichende Charakterisierung empfindlich genug waren.

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THE DETERMINATION OF CHLORINATED ALIPHATIC HYDROCARBONS IN AIR, NATURAL WATERS, MARINE ORGANISMS, AND SEDIMENTS

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(Received 17th January 1973)

The total annual world production of chlorinated short-chain aliphatic hydrocarbons probably exceeds $3 \cdot 10^6$ tons[1]. Although some of the compounds concerned are used as intermediates in the chemical industry, at least half of the total production is probably employed as industrial solvents and as dry cleaning and degreasing fluids. The great majority of the solvents used in the latter roles will be lost to the environment, either to the air by evaporation, or to the hydrosphere by discharge in effluents. These compounds are comparatively stable, and appear to have life times of several years in the environment. It would be expected therefore that appreciable concentrations of them would have built up in the air and in surface waters. At present, nothing appears to be known about the levels which these compounds have reached in the environment, although they will obviously be very low. A research project has been initiated here recently with the aims of obtaining some information on this important matter, and of examining the mechanisms by which these compounds finally disappear. In addition, it is intended to examine the occurrence of these substances in marine organisms since we have obtained some evidence that they are quite strongly concentrated by molluscs.

This paper describes analytical methods for the determination of a range of chlorinated aliphatic hydrocarbons at their present baseline concentrations in air, waters, sediments and marine organisms. In each of these methods, the compounds are stripped from the samples and collected on a column packed with a silicone-coated stationary phase and cooled to −78°. When stripping has been completed, the column is allowed to warm up, and the chlorinated hydrocarbons are swept by a current of argon into a gas chromatograph fitted with an electron-capture detector. Collection of the test compounds from air is carried out by adsorption on activated charcoal traps, from which they are subsequently removed by heating in a current of nitrogen. Water samples are stripped by bubbling with nitrogen[2]. Samples of sediments and tissues of marine organisms are stripped by heating in a current of nitrogen.

EXPERIMENTAL

Gas chromatography was carried out with a Pye Type R gas chromatograph equipped with an electron-capture detector. Argon was used as carrier gas and a

10% methane–90% argon mixture was employed as quench gas in the detector. Separation of the chlorinated hydrocarbons was usually performed at 35° in 4 m × 0.4 cm diameter glass columns filled with 3% silicone oil SE 52 on 80–100 mesh Chromosorb W (AW DMCS). Transfer of the compounds from the trap to the column was achieved with a Pye pneumatic chromatography valve. A Kent Chromalog integrator was used for the determination of the chloro compounds.

Sample trap

The sample trap which is used for removal of the chlorinated hydrocarbons from the nitrogen stripping gas is shown diagrammatically in Fig. 1. It consists of a 30-cm length of 6-mm bore copper tubing, coiled at its centre, and packed with 3% silicone oil SE 52 on 80–100 mesh Chromosorb W (AW DMCS). At each end there is a 2-way stopcock with brass barrel and spring-loaded PTFE plug; one arm of each stopcock is connected together with a by-pass tube. When in use, the sample trap is placed inside a covered expanded-polystyrene block filled with solid carbon dioxide. Connection of the arms of the stopcock to the rest of the apparatus is made with standard 1/16″ stainless-steel unions. Before use the sample trap is purged with purified nitrogen.

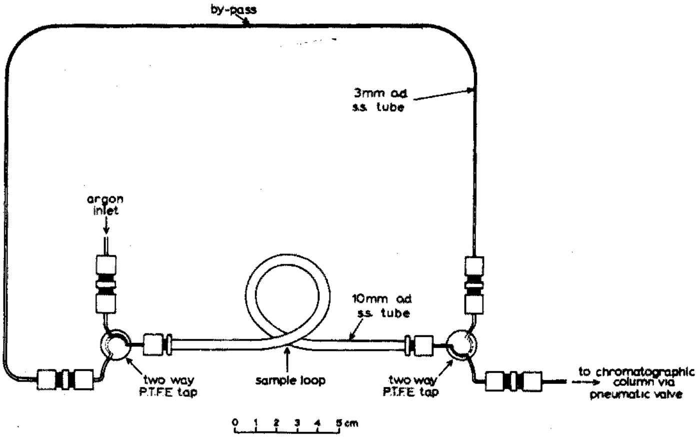


Fig. 1. Sampling trap and associated pipework.

Gas purification

Commercial grades of nitrogen contain significant amounts of chlorinated hydrocarbons. Gas to be used for stripping samples has therefore to be purified by passage through traps packed with activated charcoal and cooled to −78°.

The use of silicone or hydrocarbon greases as lubricants must be avoided throughout the apparatus as they absorb chlorinated hydrocarbons strongly.

Sampling and stripping of water samples

Because of the permeability of polythene and many other plastics to chlorinated hydrocarbons, collection of water samples must be carried out with metal sampling bottles. Glass bottles which have been heated to 150° overnight are

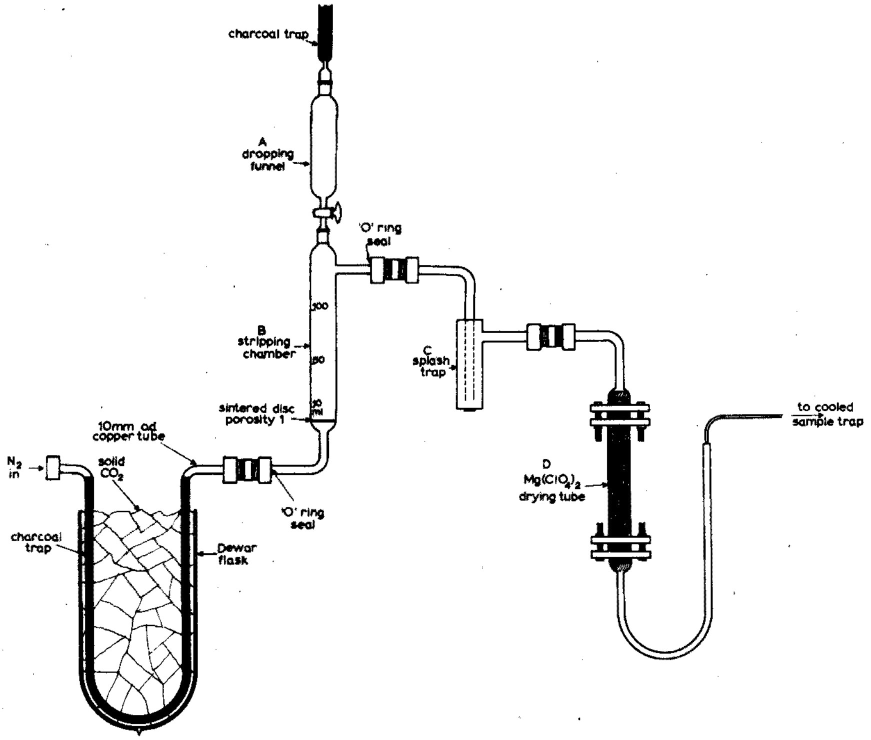


Fig. 2. Apparatus for stripping of water samples.

used for storage; closure is effected by aluminium-lined screw caps. Bottles should be practically filled with the sample. Separation of the chloro compounds from water samples is carried out with the apparatus shown diagrammatically in Fig. 2. Before use, it is swept clean for 20 min with a current of purified nitrogen (100 ml min^{-1}) with the stopcocks of the sample trap (Fig. 2) in the by-pass position. For the last few minutes the gas is allowed to escape via the charcoal trap at the top of the dropping funnel (A). The flow of nitrogen is then interrupted, and the stopcocks are turned to allow gas to pass through the sample trap. The sample is transferred rapidly to the dropping funnel and the charcoal trap is replaced. Tests with purged waters showed that negligible amounts of chlorinated hydrocarbons are taken up during the transference. The sample (100 ml for unpolluted waters, or correspondingly less for contaminated ones) is run into the calibrated stripping chamber (B) and the stopcock of the funnel is closed. The flow of nitrogen is restarted immediately, and the gas is bubbled through the sample at a rate of 30 ml min^{-1}. It is then passed consecutively through a splash trap (C), a 24 cm × 5 cm^2 column of anhydrous magnesium perchlorate (D) and finally through the sample trap, cooled to $-78°$. After 1.5 h, the stopcocks are turned to seal the tube, which is then removed.

Blank determinations are carried out in the same manner with a water sample which has been previously purged of gas in the stripping chamber. Usually the blanks are very small.

Examination of air samples

The traps used for adsorption of chlorinated hydrocarbons from air are shown diagrammatically in Fig. 3. They are constructed of brass and are filled with B.D.H. granular charcoal for gas absorption which is retained in position with brass gauze mesh. Before the traps are used, they are heated to 300° overnight while a current of purified nitrogen is passed through them. The passage of nitrogen is continued until the traps are cold. They are then closed with brass caps until required. In operation, the tube attached to the cap of the trap is connected to the intake end of a suction pump which has both its rotor and housing constructed of graphite (Edwards Model ECB1). The outlet side of the pump is connected to a Rotameter flow meter which has a range of 0–10 l min^{-1}. The air to be sampled is drawn through the trap at a rate of 10.0 ± 0.3 l min^{-1}, the rate of flow being controlled by the needle valve on the Rotameter. The sample volume is adjusted according to the type of sampling area. At sea, away from land, 100 l will generally be found to be adequate. Inshore, and on land, away from industrialized areas, 50 l will probably be satisfactory. In cities, where the level of contamination is relatively high, 5- or 10-l samples will suffice; these should be collected at an air flow rate of 2.5 l min^{-1}. If minor components (*e.g.* methyl chloride or freons) are sought, sample volumes of up to 1 m^3 should be used; but with such large volumes it will not be possible to determine the major components as their amounts will probably be above the working range of the detector. After sampling is complete the caps on the ends of the trap are replaced.

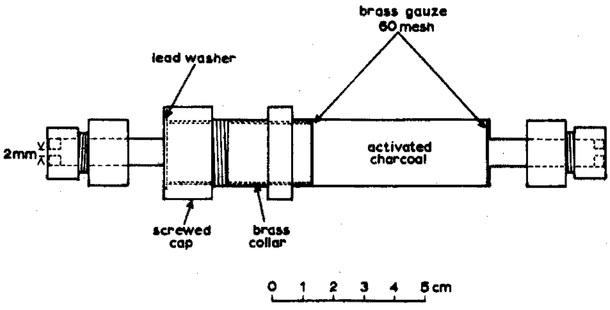


Fig. 3. Activated charcoal trap for air sampling.

On returning to the laboratory, the tube attached to the cap of the charcoal trap is connected quickly to a supply of purified nitrogen. The trap is then inserted in a tube furnace and its other end is connected rapidly to a drying train and sample trap assembly similar to that used in the analysis of the water samples (Fig. 2). With the stopcocks of the sample trap set to the by-pass position the apparatus is flushed out with nitrogen (60 ml min^{-1}) for 10 s. It has been found that negligible contamination occurs during the insertion of the charcoal trap into the system and flushing is only required to clear the stopcocks. The stopcocks are then turned to allow the gas to pass through the trap, which has previously been cooled to −78°. Over a period of 15 min the temperature of the tube furnace is raised to 250°, and it is then maintained at this temperature. After 80 min the stopcocks are turned so as to seal off the sample trap which is then disconnected. Blank determinations are performed by submitting an unused charcoal trap to the desorption stage of the process. Blanks are normally insignificant.

Examination of marine organisms and sediments

The apparatus used for stripping the chlorinated hydrocarbons from marine organisms and sediments is shown diagrammatically in Fig. 4. It consists of a glass combustion tube A contained within a tube furnace. One end of this tube is connected via a B19 joint to a supply of purified nitrogen. The other leads to a drying tube containing anhydrous magnesium perchlorate. This is followed by another tube containing a layer of pulverized marble chips to absorb any hydrogen chloride generated from salts in the sample and a layer of anhydrous magnesium perchlorate. This is connected by means of stainless-steel capillary tubing to a sample trap cooled to −78°. Before use, the apparatus is flushed for 10 min with purified nitrogen at a flow rate of 100 ml min^{-1}. Meanwhile the wet sample (250 mg) is weighed into a previously ignited platinum boat contained inside a small weighing bottle. The platinum boat is rapidly transferred to the combustion tube, and flushing with nitrogen is continued for a further 3 min. The stopcocks on the sample trap are then turned so that nitrogen passes through the trap itself. The tube furnace is switched on and the temperature of the combustion tube is raised over a period of 10 min to 200° and then maintained at this for a further 30 min. After this, the stopcocks of the sample trap are closed and the trap is disconnected from the rest of the apparatus. Blank runs are carried out in the same manner but with the omission of the sample. Normally the blank is very small.

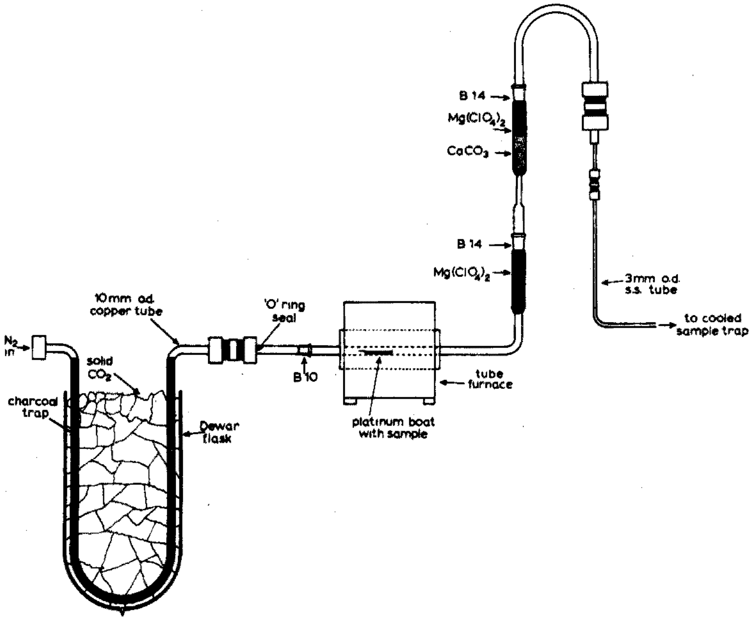


Fig. 4. Apparatus for analysis of solid samples

Gas chromatography of chlorinated aliphatic hydrocarbons

The chlorinated compounds collected on the sample trap are injected into the gas chromatograph column via a pneumatic sampling valve which is contained within the main column oven. The mode of employment of this valve is best explained by reference to Figs. 5a and 5b. The sample trap is connected externally to the oven when the ports in the glass-loaded PTFE pad of the valve are in the position indicated in Fig. 5a. In this position, argon carrier gas passes directly to the column while another stream of argon flushes out the arms and by-pass of the sample trap. After flushing for 15 s, tap A is turned to the off position as shown in Fig. 5b, and the stopcocks at the ends of the sample trap are turned so as to unseal the trap tube. The pneumatic valve is activated so as to bring the pad into the position depicted in Fig. 5b. Argon carrier gas now passes through the sample trap and directly to the chromatographic column carrying with it the chlorinated hydrocarbons. Gas chromatography is carried out isothermally at 35° with an argon carrier-gas flow rate of 30 ml min^{-1}.

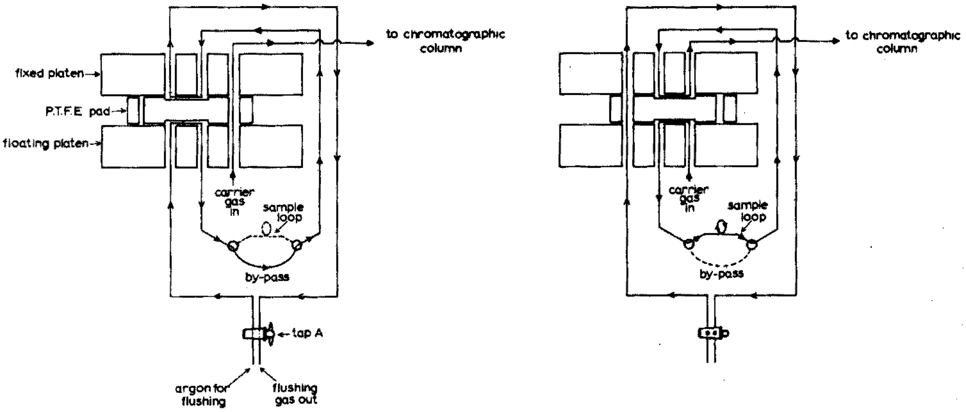
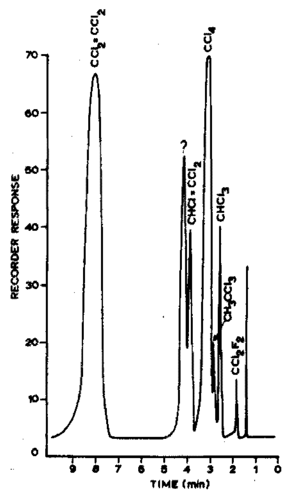


Fig. 5. Schematic diagram showing connections to pneumatic chromatographic sampling valve.

Standardization is carried out by injection of a standard solution, containing suitable concentrations of chloro compounds, directly into the gas chromatograph. In calculating the results of analyses allowance must be made for the incompleteness of the recovery process. Alternatively, calibration can be performed by injecting known amounts of the compounds into samples which have been previously stripped (as described below) and then analyzing by the proposed method.

RESULTS

At the outset of this work no data were available about either the types of chlorinated aliphatic hydrocarbons present in the environment or their concentrations. Preliminary tests were therefore carried out during the early stages of the development of the analytical methods to obtain information on these points. These showed the presence of readily detectable concentrations of the principal commercial chlorinated solvents, such as carbon tetrachloride, chloroform, trichloroethylene and



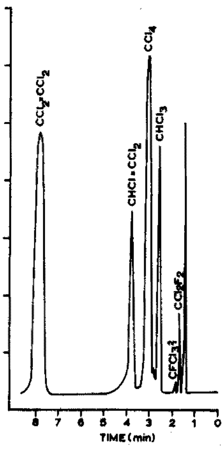


Fig. 6. Chromatogram from 100 l of air from the eastern Atlantic (lat. 38°58′N, long. 12°49′W).

Fig. 7. Chromatogram obtained from 100 ml of sea water collected from the surface in the eastern Atlantic (lat. 26°20′N, long. 14°49′W).

perchloroethylene, in air and natural water samples (Figs. 6 and 7) both from industrial areas and from regions far from land. Concentrations of these compounds in air and water samples, well away from obvious sources of pollution, lay in the range 2.5–6.5 ng m^{-3} and 18.5–0.5 ng l^{-1} respectively. In addition to these relatively major components, a number of other short-chain halogen compounds have been found to be present at very low concentrations, particularly in air. These include methyl chloride, and dichlorodifluoromethane, and several other compounds which have not yet been identified. As would be expected, the concentrations of the chlorinated hydrocarbons were found to be one or two orders of magnitude higher in samples collected in, or near, urban areas.

Examination of samples of marine mollusc tissues and estuarine sediments, showed the presence of significant amounts of chlorinated hydrocarbons. These included not only the major chlorine compounds found in air and water samples, but also several other halogen-containing compounds, the compositions of which have not yet been determined (Fig. 8). Some of the latter appear to be present in relatively large amounts.

The proposed methods were tested with amounts of chloro compounds similar to those which would be present in samples.

Water

In testing the method for water analysis, 100-ml aliquots of sea water were placed in the stripping chamber B in Fig. 2. The dropping funnel of the apparatus was replaced by a PTFE B19 cone fitted with chromatographic injection serum cap, and the chlorinated hydrocarbons were purged from the sample with a current of purified nitrogen. Microlitre volumes of a standard solution of the chlorinated hydrocarbon in pentane were then injected into the water in the stripping chamber. The cooled sample trap was then connected to the apparatus and the analysis was

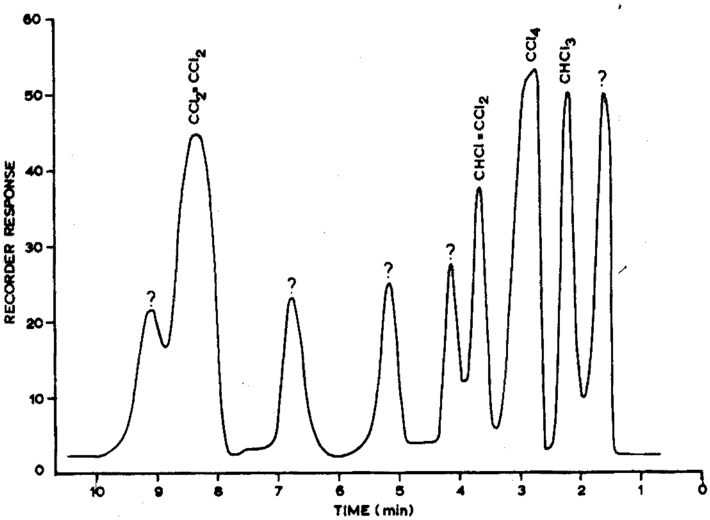


Fig. 8. Chromatogram from 0.2 g of mud from the River Mersey showing a number of unknown peaks.

TABLE I

RECOVERY OF CHLORINATED HYDROCARBONS SPIKED INTO STRIPPED SEA WATER

Compound	*Concentration added to water ($ng\ l^{-1}$)*	*Average recovery (%)*	*Coefficient of variation (%)*
Chloroform	1.5–8	96	12 (at 1.7 ng l^{-1})
Carbon tetrachloride	0.04–0.18	60	11 (at 0.04 ng l^{-1})
Trichloroethylene	18–82	103	6 (at 19 ng l^{-1})
Tetrachloroethylene	2–8	97	2 (at 6 ng l^{-1})

carried out as described in the experimental section. Average recoveries and coefficients of variation on replicate determinations for the commonest chlorinated hydrocarbons in natural waters are given in Table I. From this data it will be seen that nearly quantitative recoveries were obtained for chloroform, trichloroethylene and tetrachloroethylene. However, for carbon tetrachloride the recovery was considerably poorer, averaging a reasonably consistent 60%.

Air

Because of the danger of losses of the chlorinated hydrocarbons through adsorption onto the walls of containers, it was not possible to check the method for the analysis of air samples with purified air enriched with known concentrations of these compounds. Instead, the efficiency with which the compounds are trapped by the charcoal traps was checked by drawing 0.2 m^3 of air through two traps *in series* at a rate of 10 l min^{-1}. The trap nearer the pump was then heated to 250° as described in the experimental section. No significant amounts of chlorinated hydrocarbons were found to be present in this trap, which suggests that the compounds have been taken up completely by the first trap.

TABLE II

RECOVERY OF CHLORINATED HYDROCARBONS FROM AIR

Compound	*Amount (ng)*	*Average recovery (%)*
Chloroform	0.1–0.9	95
Carbon tetrachloride	0.09–0.23	89
Trichloroethylene	0.6–10	80
Tetrachloroethylene	0.12–1.5	103

The recovery of chlorinated hydrocarbons from the charcoal trap was next examined. Known microlitre volumes of a standard solution, containing the four main compounds known to be present in the air, were injected into a stream of purified nitrogen passing through a trap. After a further 100 l of nitrogen had passed through the trap the adsorbed chloro derivatives were recovered and determined as described on p. 264. The results of these experiments (Table II) indicated that the compounds could be recovered almost quantitatively from the adsorption traps, and thus from the air. Replicate tests carried out on air from outside the laboratory, with four traps in parallel, showed coefficients of variation of 8, 15, 14 and 13% for chloroform, carbon tetrachloride, trichloroethylene and tetrachloroethylene at the measured atmospheric levels of 1, 8.0, 360 and 28 ng m^{-3}.

Solid samples

The recovery of chlorinated hydrocarbons from solid samples by the proposed procedure was next determined. Samples of mollusc tissues and sediments were stripped of their content of these compounds by heating in the apparatus. After the combustion tube had been allowed to cool, known microlitre volumes of the standard solution of the chloro compounds were injected into the boat while the apparatus was still sealed. The determination was then carried out as described in the experimental section. Data on the recovery of some chlorinated hydrocarbons which are presented in Table III indicate that the procedure gives a reasonably satisfactory recovery for most of them.

TABLE III

RECOVERY OF CHLORINATED HYDROCARBONS FROM SOLID SAMPLES

Compound	*Wt. range (pg)*	*Recovery (%)*
Chloroform	115–1300	57
Carbon tetrachloride	4.6–18	83
Trichloroethylene	500–5500	94
Tetrachloroethylene	52–525	83

The authors wish to thank Mr. R. H. Tennant for assisting in the construction of the apparatus. They are grateful to Mr. J. Murphy for providing Figs. 1–5.

SUMMARY

A gas chromatographic procedure is described for the determination of chlorinated aliphatic hydrocarbons in the atmosphere, natural waters, aquatic organisms and sediments. Air samples are passed through activated carbon traps and the chloro compounds are later desorbed by heating in a current of nitrogen. Chloro compounds are stripped from water samples by bubbling with nitrogen and from bio-materials and sediments by heating in a current of nitrogen. In each instance, the chlorinated compounds are trapped in copper columns packed with Chromosorb coated with silicone oil, and cooled to −78°. The chloro compounds are subsequently swept off these columns into a gas chromatographic column with a current of argon. Detection of the chromatographic peaks is performed with an electron-capture detector. The procedure gives near quantitative recoveries of a range of chlorinated hydrocarbons from natural samples.

RÉSUMÉ

Une méthode de chromatographie gazeuse est décrite pour le dosage d'hydrocarbures aliphatiques chlorés dans l'atmosphère, les eaux naturelles, les organismes aquatiques et sédiments. Les échantillons d'air sont envoyés sur charbon actif; les composés chlorés sont ensuite entraînés par un courant d'azote. Les composés chlorés des échantillons d'eau sont également libérés par l'azote qu'on fait barboter. Dans le cas des bio-substances et des sédiments, on procède par chauffage dans un courant d'azote. On les absorbe ensuite sur colonnes de cuivre avec "Chromosorb" revêtu d'huile de silicone et refroidies à −78°. Les chloro-composés sont entraînés ensuite dans une colonne de chromatographie gazeuse par un courant d'argon. La détection des pics chromatographiques s'effectue à l'aide d'un détecteur à capture électronique. Les résultats sont quantitatifs pour de nombreux produits naturels.

ZUSAMMENFASSUNG

Es wird ein gaschromatographisches Verfahren beschrieben für die Bestimmung von chlorierten aliphatischen Kohlenwasserstoffen in der Atmosphäre, natürlichen Wasserproben, Wasserorganismen und -sedimenten. Luftproben werden durch Fallen mit aktiviertem Kohlenstoff geleitet und die Chlorverbindungen später durch Erhitzen in einem Stickstoffstrom desorbiert. Die Chlorverbindungen werden aus den Wasserproben gewonnen, indem Stickstoff durchgeleitet wird, und aus Biomaterialien und Sedimenten, indem in einem Stickstoffstrom erhitzt wird. In jedem Fall werden die chlorierten Verbindungen in Kupfersäulen festgehalten, die mit Siliconöl beschichtetem Chromosorb gefüllt sind und auf −78° gekühlt werden. Die Chlorverbindungen werden aufeinanderfolgend mit einem Argonstrom aus diesen Säulen in eine gaschromatographische Säule überführt. Der Nachweis der chromatographischen Peaks erfolgt mit einem Elektroneneinfangdetektor. Bei dem Verfahren wird eine Reihe von chlorierten Kohlenwasserstoffen aus natürlichen Proben nahezu quantitativ gewonnen.

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A NEUTRON ACTIVATION PROCEDURE FOR THE DETERMINATION OF DISSOLVED SILVER IN SEA WATER

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Despite the current upsurge of interest in trace metals in the sea, little is known about the distribution of silver in the oceans. Data are also sparse for the concentration of the element in coastal and estuarine waters in which pollution by silver may cause serious ecological problems because of the extreme toxicity of this element to many forms of marine life. Developments in this field have been hampered largely by the lack of analytical methods having sufficient sensitivity to permit the determination of the element at its natural level of *ca.* 0.03 μg l^{-1} in unpolluted waters. Because the concentration is so low it is necessary to concentrate silver from a large volume of water before determining it. Methods used for this purpose include freeze-drying[1], coprecipitation[2–4], cocrystallization[5], and solvent extraction[6]. Silver has been estimated in the concentrates by the following spectroscopic procedures: spectrophotometry[4,5], atomic absorption spectrometry[6,7], and emission spectroscopy[3]. However, these techniques are insufficiently sensitive for the analysis of unpolluted samples, unless inconveniently large samples are employed. Silver can be determined with much greater absolute sensitivity by neutron activation analysis. Although much greater sensitivity could be achieved by using the ^{107}Ag(n, γ) ^{108}Ag reaction, because of the very short half-life (2.3 min) of the ^{108}Ag nuclide, most workers have preferred to make use of the induced activity of ^{110m}Ag ($t_{\frac{1}{2}}$ 253 days) arising from the reaction ^{109}Ag(n, γ)^{110m}Ag. This reaction has been used by Schutz and Turekian[1,7] to determine silver, in freeze-dried samples of ocean water. The very high activities of ^{24}Na and ^{42}K which are induced during the irradiation are a disadvantage of this method, and it was decided to investigate the possibility of preconcentrating silver before irradiation.

Concentration of silver from sea water

A survey of the literature suggested that anion exchange might provide a satisfactory means for the selective concentration of silver from sea water. Chao *et al.*[8] claim to have concentrated silver at the level of 0.1–1 μg l^{-1} from fresh waters by acidifying the sample to 0.1 *M* with respect to hydrochloric acid, and passing it through a 2.5 cm × 1.8 cm^2 column of anion exchanger. Elution was performed by means of 350 ml of acetone–nitric acid–water mixture (100+5+5). In order to assess the applicability of this technique to sea water, batchwise measurements were

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made of the distribution coefficient (K_d) of silver between acidified sea water and the anion exchanger Deacidite FF-IP. These showed that over a hydrochloric acid concentration range of 0.0–0.5 *M*, the K_d values were too small to ensure quantitative uptake of silver by the resin. Attempts were therefore made to find more suitable adsorption conditions. Measurements were made of the distribution coefficient of silver between this resin and sea water which was 0.1 *M* with respect to hydrochloric acid and which contained various concentrations of ammonium thiocyanate. The results of these experiments are presented below:

Thiocyanate concentration (*M*)	0.0	0.01	0.05	0.25
K_d	$9.1 \cdot 10^2$	$2.7 \cdot 10^3$	$> 10^4$	$3.3 \cdot 10^3$

These data suggested that satisfactory uptake of silver by the anion exchanger should be achieved if the sea water was first rendered 0.1 *M* and 0.05 *M* in hydrochloric acid and ammonium thiocyanate, respectively. Tests carried out with silver-110m as tracer showed that under these conditions, silver could be removed quantitatively from 4 l of sea water by using a 6 cm × 0.8 cm diameter column of Deacidite FF-IP (chloride form, 52–100 mesh) ion exchanger, at a flow rate of 2–3 ml min^{-1} These operating conditions were used in all subsequent work.

TABLE I

ADSORPTION OF METAL IONS FROM 2 l OF ACIDIFIED SEA WATER IN THE PRESENCE OF 0.05 *M* THIOCYANATE BY DEACIDITE FF-IP AND THEIR SUBSEQUENT ELUTION WITH 20 ml OF 0.4 *M* THIOUREA

Element	*Concentration* ($\mu g\ l^{-1}$)	*Method used*[a]	*Percentage adsorption*	*Percentage found in thiourea eluate*
Silver	0.02–0.35	R	100	99.8 ± 1.2
Antimony(III)	5000	C		2.1
Bismuth(III)	<0.02	R	100	0.0
Cadmium(II)	<200	R	*ca.* 30	0.0
Cobalt(II)	<0.5	R	*ca.* 40	5.3
Copper(II)	50	R	*ca.* 80	81.7
Gallium(III)	<100	R	0	0.0
Gold	<0.05–20	R	100	81.5 ± 2.1
Indium(III)	<100	R	*ca.* 90	0.0
Iridium(III)	<10	R	*ca.* 5	0.3
Mercury(II)	<0.5	R	100	26.8
Molybdenum(VI)	50	C		0.0
Palladium(II)	<100	R	100	49.2
Platinum(VI)	<150	R	100	55.0
Ruthenium(III)	<200	R	*ca.* 40	1.1
Tellurium(IV)	<250	R	*ca.* 65	0.0
Tin(IV)	<100	R	100	0.0
Tungsten(VI)	100	R	*ca.* 90	0.0
Uranium(VI)	2500	C		0.0
Vanadium(V)	500	C		0.0
Zinc(II)	<0.5	R	100	8.2

[a] C = colorimetric; R = radionuclide used as tracer.

It proved surprisingly difficult to elute silver quantitatively from the anion-exchanger column. Recovery was far from complete when elution was carried out with aqueous solutions of mineral acids. Very severe tailing occurred when elution was carried out with non-aqueous solutions of the latter[8]. It was therefore decided to use a complexing agent for the elution. Thiourea was selected for study as it forms a strong cationic complex with silver[9]. Although pronounced tailing occurred when the column was eluted with 0.25 *M* thiourea solution, a quantitative recovery could be obtained with as little as 20 ml of 0.4 *M* thiourea if the elution was carried out at 100°. Subsequent elutions were carried out under these conditions.

Anion-exchange resins are known to take up several elements from acidified sea water[10]. An investigation was made of the behaviour of the more important of these metals in the ion-exchange separation of silver described above. It was found (Table I) that of the other elements which were adsorbed by the ion-exchange column only gold, copper, platinum(IV), palladium(II), mercury(II), zinc(II), cobalt(II), ruthenium(III), iridium(III) and antimony(III) were eluted to any appreciable extent by the 0.4 *M* thiourea.

Neutron activation of the silver concentrate

It is necessary to remove the thiourea before carrying out neutron irradiation of the silver concentrate. It was found that a silver recovery of *ca.* 97% could be obtained if the following process was used. The eluate was evaporated to dryness in a silica basin and the dried residue was transferred to a silica irradiation tube. This was heated at 200° until a solid sticky residue was obtained, and the ashing was then completed at 500°. After the tube had been sealed, it was irradiated for 24 h with a thermal neutron flux of $3.5 \cdot 10^{12}$ n cm^{-2} sec^{-1} in the Joint Universities Research Reactor at Risley, Lancs.

Radiochemical separation scheme

In addition to the desired silver-110m activity, the irradiated concentrate contains many other induced radionuclides. These arise from the irradiation of other elements also concentrated by the ion-exchange process (see Table I), or introduced as impurities in the reagents, etc. It is necessary therefore to remove these unwanted activities before counting the silver-110m activity. An attempt was made to separate silver by using cation exchange from a non-aqueous medium[11] combined with precipitation. However, the method, although it was effective, proved too time-consuming and a conventional radiochemical technique, including deposition with zinc[12] was adopted.

EXPERIMENTAL

Counting of the silver chloride precipitate was carried out with an end-window Geiger tube coupled to an Ekco preamplifier (Type N 558) and scaler (Type N530F). The radiochemical purity of the precipitate was checked with a Laben "Spectrascope" 400-channel γ-spectrometer with a lithium-drifted germanium detector.

Ion-exchange column

Wash Deacidite FF-IP resin (52–100 mesh) with a current of water to remove "fines", and then digest it twice by stirring with 2 *M* hydrochloric acid. Wash the resin with water, drain it and allow to dry at room temperature. Prepare a slurry of 2.0 g of the resin and transfer to a 0.8-cm diam. ion-exchange column. The length of the resulting bed is *ca.* 6 cm. Before use, pass 50 ml of 0.1 *M* hydrochloric acid through the column.

Reagents

Hydrochloric acid 6.5 M. Redistil 6.5 *M* hydrochloric acid using a silica distillation apparatus.

Ammonium thiocyanate solution 5 M. Dissolve 190 g of analytical-reagent grade ammonium thiocyanate in redistilled water and dilute to 500 ml. This quality of ammonium thiocyanate contains several p.p.b. of silver; this must be removed by allowing the solution to stand for 2½–3 days with a few pieces of aluminium foil.

Thiourea solution 0.4 M. Prepare a solution containing 30.4 g of thiourea per litre using redistilled water.

Determination of silver in sea water

Centrifuge the sea water immediately after collection, to remove suspended matter, and make it 0.1 *M* with respect to hydrochloric acid. To a 4-l aliquot of the acidified water, add 40 ml of 5 *M* ammonium thiocyanate solution and mix well. Pass the resultant solution through the anion-exchange column at a flow rate of 2–3 ml min^{-1}. When all the sample has run through the column heat it to 100° in a water bath and wash the resin with 30 ml of recently boiled distilled water. With the column still at 100°, elute silver with 20 ml of 0.4 *M* thiourea solution. Collect the eluate in a silica basin and evaporate it to dryness on a water bath. Transfer the residue to a silica activation capsule and then heat it in a muffle furnace at 200° until its contents become solid, taking care to avoid losses from spattering. Raise the temperature to 500° and maintain at this temperature until only a small amount of black residue remains. Seal the capsule and decontaminate the outside by washing with hot 50% (v/v) nitric acid and then with water. Prepare blanks and standards by submitting to the whole process 1-l aliquots of redistilled water both alone and spiked with 200 ng and 500 ng of silver. Pack the cleaned capsules containing the sample concentrates, blanks and standards into aluminium irradiation cans and irradiate them for at least 24 h at a neutron flux of $>3\cdot10^{12}$ n cm^{-2} sec^{-1}.

Allow the irradiated capsule to cool for 2–3 days. After opening, transfer its contents to a 200-ml beaker and then rinse it out with 2–3 ml of concentrated nitric acid; add the washings to the beaker. Add 6 ml of concentrated hydrochloric acid and evaporate to dryness. To the residue add solutions containing 10 mg each of silver(I), gold(III), copper(II), mercury(II) and platinum(VI) (the four latter elements are intended to serve as hold-back carriers). Add 0.4 *M* thiourea solution gradually until a clear solution is obtained, and then evaporate to dryness. Decompose the thiourea by the cautious drop-wise addition of nitric acid and then evaporate to dryness again. Moisten the residue with concentrated hydrochloric acid and dilute to *ca.* 30 ml with water. Separate the silver chloride by centrifugation and reject the supernatant liquid. Wash the precipitate with 0.01 *M* hydrochloric acid, centrifuge and reject the washings.

Dissolve the silver chloride in diluted (1+1) ammonia liquor. Centrifuge, reject the residue, and acidify the supernatant liquid with nitric acid to reprecipitate silver chloride. Separate the precipitate by filtration and then dissolve it in 20 ml of concentrated hydrochloric acid. Treat the solution with *ca.* 3 g of zinc foil. Collect the precipitated metallic silver by filtration and wash it with hot water until free from chloride. Dissolve it in a few drops of 5 *M* nitric acid, dilute to *ca.* 30 ml and add *ca.* 5 mg of copper (as nitrate) as a hold-back carrier and 0.5 ml of 10% sodium chloride solution. Separate the precipitate by centrifugation, dissolve the precipitate in a minimum volume of 9 *M* ammonia solution, and add 5 mg of iron (as ferric alum) as a scavenging agent. Centrifuge off the precipitated iron(III) hydroxide and wash it with a small volume of dilute ammonia solution. Combine the centrifugate and washings and make faintly acidic with hydrochloric acid. Filter off the precipitated silver chloride using a tared glass fibre filter which has been previously washed and dried at 110°. Wash the precipitate with water and finally with ethanol. Dry the precipitate and filter at 110° for 20 min. Allow them to cool in a desiccator and weigh to determine the chemical yield of the separation process. Count the silver-110m activity of the precipitate using an end-window Geiger counter. Confirm the radiochemical purity of the recovered silver-110m by γ-spectrometry.

RESULTS

The precision of the procedure was tested by carrying out replicate analyses on two composite samples of sea water from the Irish Sea. These gave average silver concentrations of 40 and 26 ng l^{-1} with coefficients of variation of ± 10 and $\pm 27\%$ respectively. These waters were analyzed after spiking with 200 and 400 ng Ag l^{-1} respectively; silver recoveries of 100% and 102% were achieved. The chemical yields of the radiochemical separations were in the range 60–70%. The identity and radiochemical purity of the silver-110m from the samples was confirmed by examination of their γ-spectra. Figure 1 shows the spectrum from a typical silver chloride precipitate together with that of silver-110m. The energy levels of the peaks

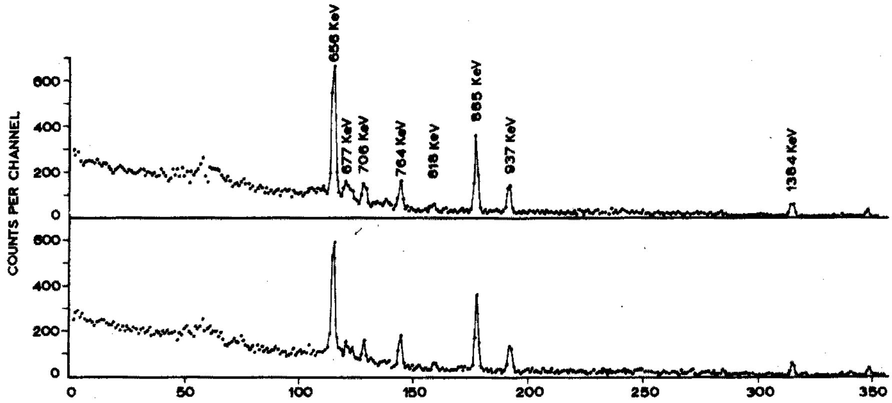

Fig. 1. γ-Ray spectra of silver-110m (upper curve) and of typical separated activity from irradiated concentrate of Irish Sea water (lower curve).

agreed well with the literature values[13,14]. No extraneous γ-peaks were found in the spectra of any of the samples.

FILTRATION AND STORAGE OF SEA WATER SAMPLES

The risk of adsorption poses serious problems in the filtration and storage of sea water samples to be analyzed for silver. Because of the ease with which silver is adsorbed by both inorganic and organic marine particulates, it is essential that these should be removed immediately after the samples have been collected. Significant losses of dissolved silver (up to 25%) occur when samples are filtered through membrane filters. However, particulate matter can be removed with no appreciable loss by centrifugation in either a bucket centrifuge, or in a Shârpless continuous centrifuge fitted with a plastic-lined rotor.

The adsorption of silver by the walls of containers composed of various materials has been studied by both West *et al.*[15] and Robertson[16]. The latter worker recommended that sea water should be acidified to pH 1.5 and stored in polyethylene. When this storage technique was tested radiochemically with centrifuged sea water which had been acidified to pH 1.8 with hydrochloric acid, it was found that no significant adsorption of silver occurred within 6 weeks. Under the same conditions unacidified sea water lost 20% of its dissolved silver in the first 10 days of storage.

The authors wish to thank the staff at the Joint Universities Research Reactor for carrying out the irradiation of the samples. They are also grateful to Dr. F. D. S. Butement for providing facilities for γ-spectrometry.

SUMMARY

A neutron activation procedure has been developed for the determination of silver in sea water. The element is preconcentrated by an anion-exchange procedure. The concentrate is submitted to irradiation with thermal neutrons. Silver-110m is separated from other radionuclides by means of a conventional radiochemical separation scheme. The method gave a coefficient of variation of ±10% at a silver level of 40 ng l^{-1}.

RÉSUMÉ

Une méthode par activation neutronique a été mise au point pour le dosage de l'argent dans l'eau de mer. On procède à une préconcentration à l'aide d'un échangeur anionique. Le concentré est soumis à une irradiation aux neutrons thermiques. L'argent-110*m* est séparé d'avec les autres radionucléides au moyen de la séparation radiochimique conventionnelle. Cette méthode donne un coefficient de variation de ±10% pour une teneur en argent de 40 ng l^{-1}.

ZUSAMMENFASSUNG

Es wurde ein Neutronenaktivierungsverfahren entwickelt für die Bestimmung von Silber in Meerwasser. Das Element wird nach einer Anionenaustausch-Methode

angereichert. Das Konzentrat wird mit thermischen Neutronen bestrahlt. Silber-110m wird von anderen Radionukliden mit Hilfe eines konventionellen radiochemischen Trennungsganges abgetrennt. Mit der Methode wurde ein Variationskoeffizient von ± 10% bei einem Silbergehalt von 40 ng l^{-1} erhalten.

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THE RATE OF LOSS OF MERCURY FROM AQUEOUS SOLUTION WHEN STORED IN VARIOUS CONTAINERS*

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Accurate detection of heavy metal pollutants in trace quantities has become increasingly important, as many of them have been shown to be highly toxic, even in the p.p.b. range. However, storage of liquid samples has always been a problem because of losses of metal from solution to container walls over extended periods of time. This fact is well known among workers involved in determination of heavy metals but quantitative data are lacking. Several reports have shown through radioactive isotope studies that losses of metal ions occur by adsorption to container walls. Robertson[1] tested polyethylene and pyrex for the adsorption of eleven different trace metals in sea water and found severe losses of indium, scandium, iron, silver, uranium and cobalt. Benes and Rajman[2] studied the adsorption of mercury(II) on polyethylene and found that a 5-day old solution at pH 7 lost *ca.* 85% of the initial 6 p.p.b. mercury(II); they also showed that mercury loss was an exponential function of time. Benes[3], in a separate study, looked at the same problem on a Sial glass surface and found considerable adsorption. A recent study by Coyne and Collins[4] tested the loss of mercury from natural water stored in polyethylene jugs and analyzed by the flameless atomic-absorption technique. Their data on mercury loss with respect to time seem to be the fastest yet reported; *ca.* 80% of the initial 50 p.p.b. of mercury in unpreserved creek water was lost in 15 min. All the previous studies indicate that a serious loss of mercury from dilute aqueous solution can take place during storage.

The present study was undertaken to determine the loss of mercury in environmental water samples and in distilled water samples stored in various containers. Losses of mercury in solution of different concentration and pH were monitored with respect to time. The rates of loss of mercury ions in various containers were compared and kinetic analyses of the experimental data were conducted. Possible ways of reducing the loss of mercury from environmental water samples are discussed.

EXPERIMENTAL

Containers tested were 1-l (or 32-oz.) Nalgene conventional polyethylene,

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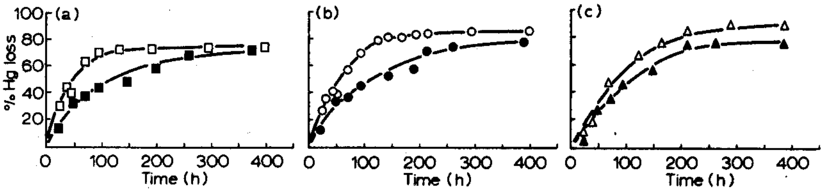
Nalgene polyvinyl chloride, and soft glass narrow-mouth bottles. Pre-use cleaning involved thorough soap and water scrubbing, overnight storage in sulphuric acid–dichromate cleaning solution, followed by thorough rinsing with distilled water, a rinse for 5 min with fresh aqua regia and a final rinse again with distilled water. Each bottle was then filled with 900 ml of sample solution. Sample solutions were spiked with 25 p.p.b. of mercury prepared from mercury(II) nitrate monohydrate. Experiments were performed with both distilled water and natural water. The natural water was collected from a nearby creek and its composition is given as follows[5]: conductivity 836.3 μmho cm^{-1}; Cl 88.5 p.p.m.; NO$_3$ 1.36 p.p.m.; NH$_4$ 0.09 p.p.m.; poly-PO$_4$ 0.01 p.p.m.; ortho-PO$_4$ 0.98 p.p.m.; Na 22.0 p.p.m.; Ca 12.7 p.p.m.; Mg 4.6 p.p.m.; K 5.6 p.p.m.; Fe 1.2 p.p.m. The pH values of the solutions were adjusted with sulfuric acid and sodium hydroxide.

Each experiment was monitored for mercury loss at convenient intervals for a total of 17 days. Experiments were repeated three times to insure reproducibility. Analysis was done by flameless atomic absorption with a Perkin-Elmer 303 spectrophotometer attached to a 10-mV recorder. For each measurement, 10 ml of water solution was pipetted from the container for mercury determination. The sample analysis procedure included oxidation with sulfuric acid–potassium permanganate (dissolution of excess permanganate with hydroxyammonium chloride) and reduction with tin(II) chloride in a circulating system. All glassware used in the analysis system was stored overnight in sulfuric acid–dichromate cleaning solution, rinsed thoroughly and oven-dried before use. Reagent blanks averaged one-third the peak height of the smallest standard peak (0.05 μg in 75 ml of solution). The detection limit for mercury was about 0.2 p.p.b. Standards for atomic-absorption analysis were prepared fresh daily immediately before the measurement from a 1000-p.p.m. stock solution of mercury(II) nitrate monohydrate which was prepared fresh weekly. All standards were prepared in 1-l volumetric flasks with distilled water and acidified with 10 ml of concentrated sulfuric acid.

RESULTS AND DISCUSSION

Figure 1 shows the results of experiments with 25 p.p.b. of mercury in distilled water and in the creek water at pH 7 stored in various containers. In polyethylene, loss



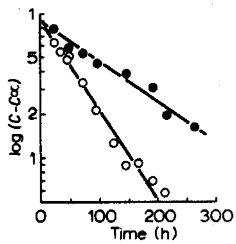


Fig. 1. Percentage mercury(II) loss from aqueous solution as a function of time when stored in polyethylene (a), polyvinyl chloride (b) and soft glass containers (c). Initial concentration 25 p.p.b. Hg at pH 7. (□, ○, △) Distilled water; (■, ●, ▲) creek water.

Fig. 2. Plot of log$(C-C_\alpha)$ *versus* time for mercury(II) in aqueous solution stored in polyvinyl chloride container. Initial concentration 25 p.p.b. Hg at pH 7. (○) Distilled water; (●) creek water.

of mercury(II) in distilled water at pH 7 reached a value of about 75% of the initial concentration in 150 h; this observation is consistent with the previous report by Benes and Rajman[2]. In the case of polyvinyl chloride, mercury loss in distilled water reached 90% after 150 h of storage. The glass container showed a slower rate for the adsorption of mercury in distilled water; after 350 h of storage, mercury loss was about 85% of the initial 25-p.p.b. concentration. Mercury loss in the creek water (at pH 7) was found in general to be slow compared with the distilled water experiments (Fig. 1). Nevertheless, severe loss of mercury from the creek water was observed in every experiment. The composition of the creek water used for this experiment is not atypical of a moderately polluted stream.

During this study, it was noticed that subsequent experiments with the same glass bottles resulted in smaller loss of mercury. This was presumably due to the poisoning of the container surface walls. The results given in Fig. 1 represent experiments with new glass bottles. This phenomenon was only observed in glass containers regardless of thorough cleaning after each experiment. It may be related to the stronger bonding between mercury(II) and silicates.

Figure 2 shows a plot of $\log(C-C_\alpha)$ *versus* time for mercury loss from aqueous solution at pH 7 in a polyvinyl chloride container; C_α is the equilibrium concentration of mercury(II) in solution when t becomes very large, and C is the concentration of mercury(II) in solution at any time. A linear relationship is observed between $\log(C-C_\alpha)$ and time, suggesting first-order kinetics for the loss of mercury in solution under this experimental condition. Similar linear relationship between $\log(C-C_\alpha)$ and time, was also observed for the polyethylene and glass containers studied. The rate constants for the loss of mercury(II) in different containers were determined from the slope of the line by the least-squares method and are give in Table I. The corresponding half-lives of mercury loss in solution calculated from the equation $t_{\frac{1}{2}}=0.693/k$ are also given.

TABLE I

RATE CONSTANTS AND HALF-LIVES OF MERCURY LOSS IN AQUEOUS SOLUTION AT pH 7 AND 25 p.p.b. Hg^{2+}

Container	*Distilled water*		*Creek water*	
	$k\ (h^{-1})$	$t_{\frac{1}{2}}\ (h)$	$k\ (h^{-1})$	$t_{\frac{1}{2}}\ (h)$
Polyethylene	$1.82 \cdot 10^{-2}$	38.0	$0.731 \cdot 10^{-2}$	94.9
Polyvinyl chloride	$1.46 \cdot 10^{-2}$	47.4	$0.674 \cdot 10^{-2}$	102.8
Soft glass	$0.970 \cdot 10^{-2}$	71.4	$0.650 \cdot 10^{-2}$	106.6

The half-life of mercury loss in distilled water depends on the nature of container and increases in the order of polyethylene (1.58 days), polyvinyl chloride (1.98 days), and soft glass (2.98 days). The two types of polymer containers showed a faster rate for the adsorption of mercury than the glass container. The same order of half-life was observed for the creek water although corresponding values of half-life were considerably longer (polyethylene 3.95 days, polyvinyl chloride 4.38 days, and soft glass 4.44 days). Competition for active sites for adsorption in the presence of various cations in the creek water might be a possible cause of rate differences observed between two systems. Chemical combinations between mercury(II) and various ions and particles in the solution of creek water might also affect the rate of loss of mercury. The detailed mechanism of mercury loss is however not known. Volatilization of mercury from solution is also a possibility if the container is left uncapped and open to the atmosphere. However, volatilization is difficult to reduce or compensate for without affecting the original design of the experiment, and no precautions were taken to eliminate the possibility of volatilization, except for using tightly stoppered bottles in all experiments.

The results of experiments with 25 p.p.b. of mercury in the creek water at pH 2 (acidified with sulfuric acid) when stored in various containers are shown in Fig. 3. After about 380 h of storage, the loss of mercury reached a saturation value of 88% in polyvinyl chloride, 81% in glass, and 80% in polyethylene. The corresponding values of half-life for the loss of mercury in these containers are 1.7 days for polyvinyl chloride, 3.5 days for glass, and 4.0 days for polyethylene. Acidification of the creek water to pH 2 did not show any reduction of the loss of mercury. There was also no observable difference, with respect to mercury loss, when either nitric acid or sulfuric acid was used for the acidification. However, acidification to pH 0.5 with nitric acid was found to curtail mercury loss substantially whereas sulfuric acid did not. The loss of mercury at pH 0.5 with nitric acid was not detectable after 110 h of storage and was less than 2% after 380 h of storage in the various containers. Coyne and Collins[4] also found that nitric acid was the only effective acid preservative for mercury.

Losses of mercury from the creek water with an initial mercury concentration of 250 p.p.b. at pH 7 stored in various containers were as follows:

	t=194 h	*t=412 h*
Polyethylene	16.0%	16.3%
Polyvinyl chloride	43.0%	55.1%
Glass	10.1%	11.8%

In each type of container, the percentage loss of mercury from the creek water with 250 p.p.b. of mercury(II) was much lower than the loss found with 25 p.p.b. of mercury at the same pH. However, such high mercury levels in the natural water are probably of little practical value, because the significant level of mercury for many environmental monitoring programs is in the range 1–100 p.p.b.

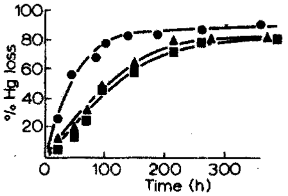


Fig. 3. Percentage mercury(II) loss from the creek water as a function of time when stored in the various containers. 25 p.p.b. Hg and pH 2. (■) Polyethylene, (●) polyvinyl chloride, (▲) soft glass.

It appears that accurate data for mercury can only be relied on after correction for mercury loss in storage. Such a correction is by no means trivial because the surface adsorption and other manners of mercury loss during storage seem to be highly individual. The data presented here agree well with previous investigations[2,3]. Coyne and Collins[4] reported extremely rapid mercury loss from unpreserved natural water when stored in one-gallon polyethylene jug. The composition of the creek water employed in Coyne and Collins' work was not given. Their data for the loss of mercury also do not seem to follow first-order kinetics. In their experiment virtually all added mercury would be lost from the solution within a few days of storage. The differences between the present data and those of Coyne and Collins are probably due to the differences in the containers employed and in other parameters involved. Nevertheless, of the three types of containers tested, polyvinyl chloride is probably the worst with respect to storage, but neither of the others can be judged better than the other. A preliminary test with teflon containers showed that they also adsorbed a considerable amount of mercury from solution. No recommendation can be made about the best container. The only condition which can reduce mercury loss from aqueous solution to a significant degree during storage seems to be acidification to pH 0.5 with nitric acid. It is possible that other chemical treatment may also reduce mercury loss during storage. Coyne and Collins[4] have shown that the acetic acid–formaldehyde (10:1) preservative routinely used by many laboratories is ineffective in preventing mercury loss. The use of acid and potassium permanganate as a preservative to prevent the loss of mercury from solution by volatilization has been suggested recently[6–8]. This preservation technique has not been commonly used or recommended by environmental testing laboratories. The present experimental data on acidification to pH 0.5 suggest that volatilization was probably not significant. The use of complex-forming agents such as iodide or cyanide to prevent the loss of mercury from solution has also been reported[9]. Until clear facts are available on other possibilities, it is recommended that sampling for mercury be done in containers other than polyvinyl chloride, that they be immediately acidified with nitric acid to a pH of less than 0.5, and that they be analyzed as soon as possible.

We express gratitude to the U.S. Office of Education for the fellowship that permitted Mr. R. M. Rosain to conduct this work, to Mr. Thomas Smith who helped in the analysis of samples during an NSF undergraduate participation program, and to the Bunker Hill Mining Co., Kellogg, Idaho, for their consultation and encouragement.

SUMMARY

Solutions of natural water and distilled water were spiked with mercury(II) (25 p.p.b.) and stored in polyethylene, polyvinyl chloride, and soft glass containers. Losses of mercury at different pH values were monitored by flameless atomic absorption for a total of 17 days. Severe losses of mercury were observed at pH 2 and 7. Mercury loss from solution followed first-order kinetics; the half-lives of mercury loss under various conditions were calculated. Acidification of the solutions to pH 0.5 with nitric acid curtailed mercury loss substantially. Possible ways of reducing the loss of mercury from environmental water samples are discussed.

RÉSUMÉ

Des échantillons d'eau naturelle et d'eau distillé ont été contaminés par le mercure(II) (25 p.p.b.) et conservés dans des récipients en polyéthylène, chlorure de polyvinyle et verre. Les pertes de mercure, à différentes valeurs de pH ont été déterminées par absorption atomique sans flamme, en fonction du temps, au total 17 jours. Des pertes de mercure importantes sont observées au pH 2 et au pH 7, suivant une cinétique de premier ordre. Les pertes en mercure peuvent être considérablement diminuées en amenant le pH des solutions à 0.5, au moyen d'acide nitrique. On examine les possibilités de diminuer les pertes en mercure des échantillons d'eau de l'environnement.

ZUSAMMENFASSUNG

Proben von in der Natur vorkommendem Wasser und destilliertem Wasser wurden mit Quecksilber(II) (25 p.p.b.) versetzt und in Polyäthylen-, Polyvinylchlorid- und Weichglasbehältern aufbewahrt. Die Verluste an Quecksilber bei verschiedenen pH-Werten wurden durch flammenlose Atomabsorption in einem Gesamtzeitraum von 17 Tagen kontrolliert. Wesentliche Quecksilberverluste wurden bei pH 2 und 7 beobachtet. Der Quecksilberverlust aus der Lösung folgte einer Kinetik erster Ordnung; die Halbwertszeiten des Quecksilberverlustes unter verschiedenen Bedingungen wurden berechnet. Ansäuerung der Lösungen auf pH 0.5 mit Salpetersäure setzte den Quecksilberverlust wesentlich herab. Möglichkeiten zur Verminderung des Quecksilberverlustes in wässrigen Proben werden diskutiert.

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DETERMINATION OF LEAD IN GASOLINE BY HEATED VAPORIZATION ATOMIC-ABSORPTION SPECTROMETRY

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Atomic-absorption analysis for lead in gasoline has been widely used throughout industry since the pioneering work of Robinson[1]. However, a serious problem in this analysis is that different tetraalkyl lead additives may require different calibration curves[2–4]. This problem has been minimized by careful control of dilution ratios and aspiration rates[2]. More recently, it has been shown that this defect can be avoided by the addition of iodine to the gasoline samples diluted in ethyl isobutyl ketone (MIBK); under these conditions, a single calibration curve could be used for alkyl lead compounds[5].

The recent development of heated vaporization atomic absorption[6–8] with devices such as the carbon rod[9–11] or graphite furnace[12,13] have been quite extensively applied to the determination of lead[14–17]. Brodie and Matousek[16] determined lead naphthenate directly in lube oils with a carbon rod. Bratzel and Chakrabarti[17] have thoroughly examined the same device for the determination of lead cyclohexane butyrate and tetraethyl lead in a variety of petroleum samples.

In this laboratory, different signal responses were observed for the various tetraalkyl lead compounds in gasoline when analyzed by atomic absorption with a carbon rod. Investigation of this problem led to the development of an iodine addition procedure which provides results that show good repeatability and compare favorably with those obtained by X-ray fluorescence. When used with an alkyl lead standard, the procedure allows the simple rapid determination of lead in gasoline which is independent of the lead alkyl substitution.

EXPERIMENTAL

Apparatus

All measurements were made at 283.3 nm with a modified Jarrell-Ash 82-500 atomic absorption spectrophotometer equipped with a R-213 photomultiplier. Vaporization of the samples was carried out with a Varian-Techtron carbon rod atomizer complete with power supply and gas control unit, details of which have been given elsewhere[11,18]. "MiniMassman"-type carbon rods, made of Ringsdorff RW1 high-purity graphite were used in this study. A brass mask was placed over the 0.100-mm entrance slit of the monochromator to protect the photomultiplier from the continuum radiation emitted by the carbon rod. A 10-mV recorder (Leeds & Northrup, Speedomax W) with a 0.5-s time constant was used to record the absorbance signals. Samples were introduced onto the rod with a Teflon-tipped microliter pipet (Pfizer 644E).

Reagents

Reagent-grade methyl isobutyl ketone (Matheson, Coleman, and Bell) and iodine (Baker and Adamson) were employed. The gasoline samples were prepared by the addition of concentrates of tetraethyl lead (TEL), tetramethyl lead (TML) or mixed alkyl lead (MLA-250 or MLA-500) (all available from Ethyl Corp.) to a gasoline which had been found by X-ray fluorescence to contain less than 0.01 g Pb/gal. The isooctane (Burdick & Jackson) used to prepare calibration standards had been percolated through silica gel before use.

Operating conditions

The 283.3-nm resonance line was used rather than the more sensitive 217.0-nm line because its greater intensity permits better detection limits[17]. Furthermore, under the conditions used, no background corrections were necessary. The optimal voltage and time settings for the dry, ash, and atomize cycles are summarized in Table I. Although greater sensitivity could readily be obtained by using a higher atomizing voltage with a shorter duration, the settings given resulted in a linear calibration curve for the working range. When shorter durations were used, some lead remained on the rod and "memory" effects were observed. At gas flow rates of 1 l min^{-1}, no difference was observed between nitrogen and argon as the sheathing gas. A hydrogen diffusion flame had no effect on the alkyl lead standard. For simplicity, the analyses were carried out with 1 l min^{-1} nitrogen as a sheath-gas.

TABLE I

OPERATING PARAMETERS FOR THE DETERMINATION OF LEAD IN GASOLINE WITH THE TECHTRON MODEL 61 CARBON ROD

(Inert gas flow: N_2 1 l min^{-1})

	Voltage	*Time (s)*
Dry	6	10
Ash	7.5	10
Atomize	3.5	5

Procedure

TEL in isooctane was prepared to be *ca.* 0.25 g TEL/gal, and its value was determined by X-ray fluorescence. Calibration solutions (0.132–1.32 μg ml^{-1}) were prepared by dilution of this standard with a freshly prepared iodine solvent (2 mg iodine per ml in methyl isobutyl ketone). The absorbance signals (peak height) for three 1-μl injections onto the carbon rod were recorded initially. If the three were within $\pm 10\%$ of their average, the average was used; if not, two more readings were obtained before the average was calculated. The average value for each calibration solution was used to construct a calibration curve; a straight line passing through the origin was obtained.

Each sample was initially diluted 1/500 in the iodine solvent, and the average absorbance was obtained in the same manner. For samples which gave signals less than the lowest calibration solution, a second dilution at a 1/50 ratio was prepared and analyzed. The concentration of lead in the samples was calculated from the value obtained from the calibration curve and its dilution factor.

In this study it was found convenient to prepare small working solutions since only microliter quantities are used. This was done by employing the Unopette micro-dilution technique which has been described in detail elsewhere[19,20]. The iodine solvent was dispensed into the polyethylene Unopette reservoir, an aliquot of sample was drawn into the Unopette micro-capillary, and the sample was mixed with the solvent in the reservoir. This preparation technique has been shown to have ±2% accuracy in a variety of analyses[21].

RESULTS

The procedure was applied to a series of 18 gasoline samples containing TEL, TML or mixed alkyls in triplicate (Table II). The results obtained compare favorably with those obtained by X-ray fluorescence which are also included in Table II.

The triplicate results demonstrate a repeatability of ±10% for the proposed method. Other workers[11,18] have reported that repetitive sampling from the same solution onto the carbon rod had a repeatability of ±2–8%. These workers introduced the sample aliquots through the inlet hole in the carbon rod with platinum or gold-plated syringes. The diameter of the Teflon tip on the microliter pipet syringe required that the sample be introduced directly onto the transverse

TABLE II

DETERMINATION OF LEAD IN GASOLINE

Sample	*Lead compounds*	*Atomic absorption*			*XRF value*
		1	*2*	*3*	
1	TML	1.01	0.94	1.01	1.04
2	MLA-500	0.61	0.66	0.58	0.76
3	TEL	0.044	0.040	0.036	—
4	TML	0.66	0.56		0.65
5	MLA-250	1.17	1.03	0.90	1.18
6	TEL	0.42	0.36	0.33	0.39
7	TML	0.028	0.027	0.027	0.05
8	MLA-250	0.36	0.36	0.29	0.44
9	TEL	2.02	1.92	1.92	2.05
10	MLA-250	0.093	0.093	0.092	0.09
11	TML	0.23	0.27	0.27	0.32
12	TEL	0.009	0.009	0.009	—
13	MLA-500	1.75	1.76	1.67	1.83
14	MLA-250	0.036	0.036	0.029	0.04
15	TEL	0.77	0.83	0.79	0.80
16	TML	1.49	1.43	1.61	1.54
17	TML	0.060	0.041	0.060	0.05
18	TEL	0.093	0.092	0.087	0.07
19	Pb Naphthenate[a]	1.15	1.26	1.06	1.00

[a] Standard for X-ray fluorescence.

bore of the rod. The averaging procedure given in the method is designed to compensate for the ±10% relative repeatability found with this injection technique.

The agreement between the results obtained by the carbon-rod atomic absorption and X-ray fluorescence (Table II) is consistent over the range of lead alkyl compounds used (TML, TEL, MLA-250 and MLA-500). This demonstrates that the iodine addition satisfactorily levels the response differences between the alkyl compounds.

DISCUSSION

The leveling effect of iodine on lead alkyl signals

Many procedures for the determination of lead in gasolines have been based on the reaction of lead alkyls with halogens followed by extraction into an aqueous phase for analysis[22,23]. Kashiki *et al.*[5] simplified this approach by aspirating solutions of gasoline in MIBK containing iodine into an atomic absorption flame. With this reagent-solvent, the response of the lead alkyls was leveled. Although the exact nature of this leveling effect has not been elucidated, it presumably involves the sequence of reactions

$$R_4Pb \rightarrow R_3Pb^{+} \rightarrow R_2Pb^{2+} \rightarrow Pb^{2+}$$

Griffing *et al.*[22] have reported that in organic solvents at room temperature the predominant species is dialkyl lead iodide. At elevated temperatures (*ca.* 100°) this may react further to give lead(II).

Solutions of TEL in isooctane without iodine gave a linear calibration curve when analyzed by the carbon rod technique. However, when TML samples were analyzed in this manner, only a small signal independent of TML concentration was observed. Apparently the TML (b.p. 110°) was being boiled off the rod with the isooctane. The TEL was not lost in this manner because it decomposed below its boiling point. When iodine was added to the TML solution a signal was observed, but on standing for 15–20 min the signal decreased significantly. Investigation demonstrated a similar effect in toluene, but in MIBK the signal remained stable for over 4 h.

However, unexpectedly poor repeatability was observed when samples were prepared in MIBK containing the iodine concentrations recommended by Kashiki *et al.* (0.2 mg ml^{-1})[5] and analyzed by the carbon-rod technique. When a solvent containing 1 mg of iodine per ml was used, the repeatability became satisfactory. The larger amount of iodine required for the carbon-rod method reflects the differences in the atomization process of the two atomic-absorption techniques. In the aspiration system used in flame atomic absorption, iodine remains in intimate contact with the lead until neutral atoms are produced[24]. In the carbon-rod system, iodine is lost in the drying and ashing cycles before atomization. The larger amount of iodine used in the latter procedure insures the conversion of all the alkyl lead compounds in a sample to lead-iodide before its atomization by the carbon-rod. Since MIBK is a methyl ketone which slowly consumes iodine by the iodoform reaction, and it is the free iodine which is required to react with the lead, 2 mg of iodine per ml was used to insure that sufficient iodine remained in solution.

Other effects

The high bias noted in the analysis of lead naphthenate (Table II) may reflect a difference in the mechanism of atomization of lead salts. Lead naphthenate would not be expected to react with iodine. Therefore, in the atomization there may be differences between the lead iodide and the lead carboxylate. This contrasts with the work of Kashiki *et al.*[25] who found that iodine leveled the response of nonreacting lead salts in the flame. These observations may again be explained by the differences in the atomization mechanisms in the two atomic-absorption techniques. The observation that different lead salts give different responses had been noted by other workers previously[10], and similar observations have been made in this laboratory when aqueous solutions were used.

These observations conflict with those of Bratzel and Chakrabarti[17] who concluded that the heated vaporization method was independent of the nature of the lead compound. Although both their study and the present study showed that the hydrogen diffusion flame had no effect on the signals obtained for standards, Bratzel and Chakrabarti used this flame, while we did not. The hydrogen diffusion flame has been reported to reduce the more severe anion interferences observed for lead signals obtained with the "West" type rods[16]; however, this has been generally attributed to the reduction of the temperature gradient above the rod[26]. The effect of the diffusion flame on the signal response for several lead salts is currently being studied.

Although the carbon rod procedure described here was scaled for the determination of lead in gasoline over the commercial levels, the technique may be readily extended to lower concentrations. Not only may the rod and inert gas conditions be optimized, but also the sample-to-iodine solvent ratio may be increased to increase the sensitivity of the technique. As long as the final sample solution contains *ca.* 50% methyl isobutyl ketone and not less than 1 mg of iodine, the alkyl lead compounds may be determined in this manner. By optimizing parameters and dilution conditions, the carbon-rod technique has been used successfully to determine 50 ng Pb ml^{-1} in isooctane (equivalent to 0.0002 g/gal).

Conclusion

On the basis of this study, a procedure which permits the determination of alkyl lead in gasoline over the range 0.025–2.5 g Pb/gallon is recommended; the sample is atomized by means of a carbon rod. The technique may be readily adapted to lower lead levels. The use of iodine in MIBK for sample preparation makes the procedure independent of lead alkyl type. However, the iodine does not compensate for differences between the lead alkyls and lead salts in the carbon rod determination. When used with TEL as a standard, the method described provides a simple rapid procedure for the determination of lead in gasoline which is independent of the alkyl type used.

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SUMMARY

Differences between lead alkyl compounds are observed when gasolines are analyzed directly by atomic absorption with a carbon rod atomizer. The addition of iodine in MIBK to sample solutions eliminates these differences. A procedure is described which provides a rapid simple determination of lead in gasoline (0.025–2.5 g/gal) independent of lead alkyl substitution.

RÉSUMÉ

Des différences entre composés plomb-alcoyle sont observées lorsque les essences sont analysées directement par absorption atomique, avec atomiseur à tige de carbone. Une addition d'iode dans la méthylisobutylcétone aux échantillons à analyser élimine ces différences. Une méthode est décrite pour le dosage simple et rapide du plomb dans l'essence (0.005 g à 0.5 g/litre), sans tenir compte de la substitution plomb-alcoyle.

ZUSAMMENFASSUNG

Zwischen Bleialkylverbindungen werden Unterschiede beobachtet, wenn Benzinproben direkt durch Atomabsorption mittels einer Graphitstabküvette analysiert werden. Durch Zugabe von Jod in MIBK zu den Probelösungen werden diese Unterschiede eliminiert. Nach der beschriebenen Methode kann Blei in Benzin (0.025–2.5 g/gal) schnell und einfach unabhängig von der Bleialkylsubstitution bestimmt werden.

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THE DETERMINATION OF LEAD AND NICKEL BY ATOMIC-ABSORPTION SPECTROMETRY WITH A FLAMELESS WIRE LOOP ATOMIZER*

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In an attempt to overcome the well-known limitations of flame atomization in atomic-absorption spectrometry, many studies have been undertaken in the development of flameless atomizers. The earliest investigator of furnaces as atomizers was L'Vov[1,2], who placed the sample on a carbon electrode and atomized it into a heated graphite furnace with an arc from a counter electrode. Lining the interior wall of the tube with tantalum or tungsten foil or pyrolytic graphite helped to eliminate diffusion through the porous graphite. Massmann[3] developed an electrically heated graphite furnace and cuvette for atomic absorption and atomic fluorescence studies. Modifications of the Massmann furnace have been described[4–6]. Woodriff *et al.*[7] developed a graphite furnace analogous to Massmann's but differing in the means of sample introduction; solutions were aspirated into the furnace through a side arm or placed in a graphite cup which was then moved into the furnace. West *et al.*[8–15] have extensively developed a graphite filament for atomic absorption and fluorescence analysis; early papers concentrated on varying cell design to optimize sensitivity. Interferences were extensively studied and the direct analysis of lubricating oils was reported. Serum[16] and used engine oils[17,18] have been successfully analyzed with graphite filaments. A tantalum ribbon has been utilized by Hwang *et al.*[19,20] and others[21]. Wire loop atomizers of platinum[22,23] or tungsten[23] have been investigated for atomic fluorescence. A tungsten wire loop atomizer has been used for flameless atomic absorption[24].

This investigation was directed to the development of a simple wire loop atomizer for flameless atomic-absorption spectroscopy that would possess all the advantages of other non-flame devices—small sample size requirements, increased atomization efficiency, and greater safety in operation—and yet offer several additional advantages of its own, eliminating the need for an elaborate power supply and water cooling of the electrical terminals, and decreasing the cost of analysis.

EXPERIMENTAL

Apparatus

A single beam Varian AA5 spectrophotometer was used. Varian hollow-cathode lamps were employed as light sources.

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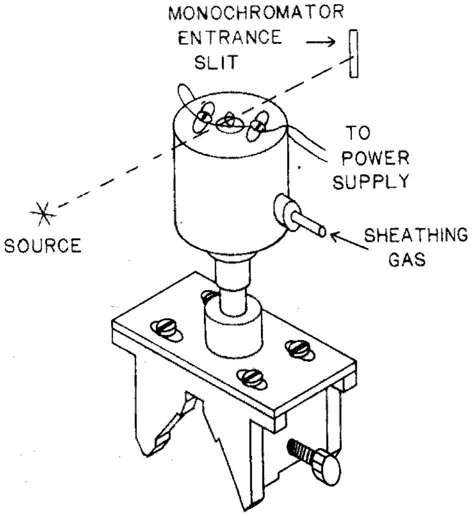
* This work is primarily taken from the M.S. thesis of J. V. Chauvin, L.S.U.N.O., 1972.



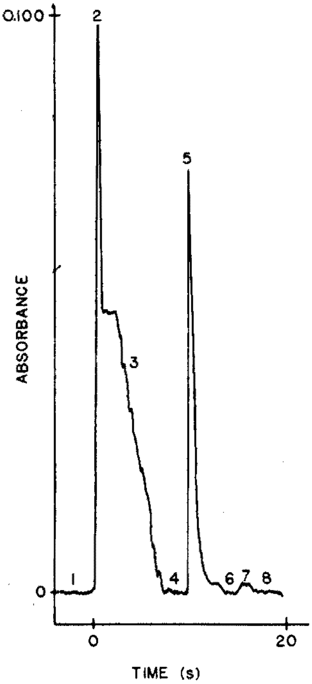


Fig. 1. Diagram of flameless atomizer and stand.

Fig. 2. Sampling cycle with unenclosed cell.

The entire burner assembly used for normal flame work, was removed and replaced with the flameless atomizer shown in Fig. 1. Loops were fabricated by twisting 80-mm lengths of a 97% tungsten–3% rhenium alloy wire around an artist's stylus or a syringe needle. The wire was obtained from General Electric (Tungsten 3D 218-Process CS) and was 10 mils in diameter. This particular alloy was chosen for several reasons: it has a high melting point (about 3200°) which makes the analysis of less volatile metals possible; it is more pliable and resistant to oxidation than 100% tungsten; and it is relatively inexpensive when compared to platinum.

The ends of the loop were connected directly to two terminals located on opposite sides of a sheathing gas outlet housed in a steel head which in turn was mounted on a stand. Proper alignment of the loop was achieved by adjusting the various Allen bolts and screws.

Improved sensitivity was achieved by placing the loop in an enclosure constructed of a piece of pyrex tubing that was 3–5 mm in inner diameter and about 30 mm in length with a 6-mm hole in the center of its length into which the loop extended. The glass enclosure was held in place by a movable support and side plates which insured correct alignment.

Power was furnished to the loop with a Variac and a 6-V stepdown transformer. Since at least two temperatures were required—a lower one for evaporating the solvent and a higher one for atomizing the sample—it was convenient to use two Variacs with a knife switch between them so that Variac settings did not have to be changed. A relay and clock permitted exact timing during the analytical cycle.

The loop was placed in a sheath of flowing inert gas (nitrogen or argon) which protected it from oxidation. A drying tube filled with calcium chloride was employed to desiccate the gas before it reached the cell. The optimal gas flow rate was found to be 2–3 l min^{-1}.

Scale expansion (maximum value of about 10 ×) was sometimes employed. A 10-mV variable voltage Sargent recorder was used as a readout device.

General method

Figure 2 shows a typical recording. The sequence recorded is as follows: (1) with no power supplied to the loop, a baseline was obtained at 0 absorbance units; (2) a 2-μl sample was placed on the loop, the sampling device temporarily blocked the light path; (3) the drying Variac (setting, about 14%) was switched on and as the solvent evaporated, absorption by the liquid decreased; (4) the drying Variac was disconnected and the baseline returned to zero; (5) the atomization Variac (setting, 22%–24%) was turned on and a peak appeared owing to the absorption of resonant radiant energy by neutral ground-state atoms produced by the high temperature of the loop; (6) the atomization Variac was disconnected and the baseline returned to its previous position; (7) with no sample present, the loop was heated to the atomization temperature with the atomization Variac and a higher baseline occurred; (8) the atomization Variac was turned off and the normal baseline was again obtained. When the enclosed cell was used, a much higher final baseline was obtained in step 7.

Peak heights were used for analysis. At least seven readings were taken for each data point obtained. A critical value table (based on Dixon's work[25] on processing data) was used as the criterion for rejecting outlying readings. The relative average deviation was 2–6%.

Solutions

All solutions were prepared from reagent-grade chemicals and doubly distilled water. Stock solutions of 831 p.p.m. lead as the acetate in 0.12 *M* hydrochloric acid, 1000 p.p.m. lead as the nitrate in water, and 1000 p.p.m. nickel as the chloride or nitrate in water, were made; dilutions of these stock standards were prepared as needed. Solutions of acids and salts (0.1 *M*) were used as interference sources.

Polyethylene bottles were employed for most of this investigation in order to avoid contamination and losses from adsorption.

Means of sampling

A 2-μl aliquot of the sample was placed on the loop with a micropipet (Drummond Scientific) or a Hamilton microliter syringe. Problems arising from the adsorption and desorption of ions at the surfaces of the sampling device were partially eliminated by treating the syringe and micripipet with a silicone coating (Beckman Desicote or Fisher Dricote). Unfortunately, it was extremely difficult to apply a uniformly thin and efficient coating to the capillary tubes. For this reason many rinses were required to establish equilibrium between the sampling device and the very dilute solutions. Micropipets offer several advantages over syringe: a separate micropipet can be used for each sample; caustic solutions can be analyzed without experiencing possible reactions with the steel plunger of the syringe; they are very inexpensive and result in speedier analysis.

Loop type and size

Early experiments without the glass enclosure indicated that an inner loop diameter of about 1.5 mm was satisfactory. A single twist-type loop was employed for these studies. In general, as the diameter of the loop decreased, the precision increased. The higher degree of reproducibility found with the smaller loops is ostensibly due to the fact that the probability of placing the sample at exactly the same place is higher with the smaller loops and a more even simple solution distribution could be achieved. It has been reported[26] that increased precision is obtained with a graphite furnace if extreme care is taken to apply samples to precisely the same position. When the glass enclosure was introduced into the experimental setup, double twist loops were used.

Different loops gave the same sensitivity within about 5%. One loop can be used for as many as 100–200 sampling cycles. This makes it possible to obtain a calibration curve and analyze knowns and unknowns with the same loop. Since there is no need for frequent loop changes, the speed of analysis is increased.

The most favorable loop position was found to be at the center and at the focal point of the light beam.

After each sample had been analyzed the loop was heated to about 2000°—about 1200° being used to analyze for lead. This kept the wire clean and prevented erratic readings caused by a residue buildup.

In order to prove that lead or nickel was in reality the absorbing species, experiments were run with a continuous hydrogen light source and no absorption was recorded. The use of "inactive" lines yielded similar results.

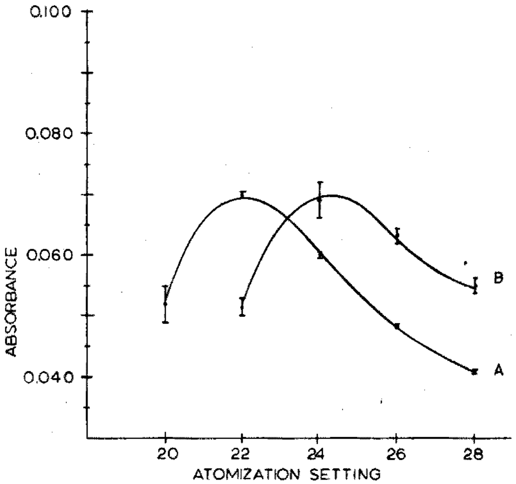


Fig. 3. Optimization of atomization setting. Experimental conditions: Sample: 5 p.p.m. Pb (as the nitrate); drying setting: 16; sheathing gas: N_2 at 3 l min^{-1}; slit width: 0.99 nm; scale expansion: maximum. (A) Unenclosed cell; (B) enclosed cell—4 mm i.d. glass enclosure, 30 mm long.

A series of experiments indicated that while the setting of the drying Variac was not too critical, a value of 14% gave the optimal results. Higher drying settings may cause premature loss of sample.

The atomization temperature is, however, important. At low temperatures, the sample is not completely vaporized while at increased temperatures the atoms leave the loop so rapidly that the detection system would be taxed to respond efficiently to their presence[9,11,15,20,23,24]. Other factors which may contribute to decreased sensitivity at high atomization temperatures include thermal expansion of the sheathing gas which would dilute the density of gaseous analyte atoms, increased turbulence, and possible line broadening[20]. All the atomization setting *versus* absorbance studies yielded similarly shaped curves with a maximum (Fig. 3). In some cases the curve was very sharp (the range between the most and least favorable settings was 0.03–0.04 absorbance units); in others it was more rounded (the range was 0.015–0.02 absorbance units).

Resonance lines at 217.0 nm and 283.3 nm are commonly used for the atomic absorption of lead. The most favorable in terms of sensitivity and precision was found to be the 217.0-nm line.

RESULTS AND DISCUSSION

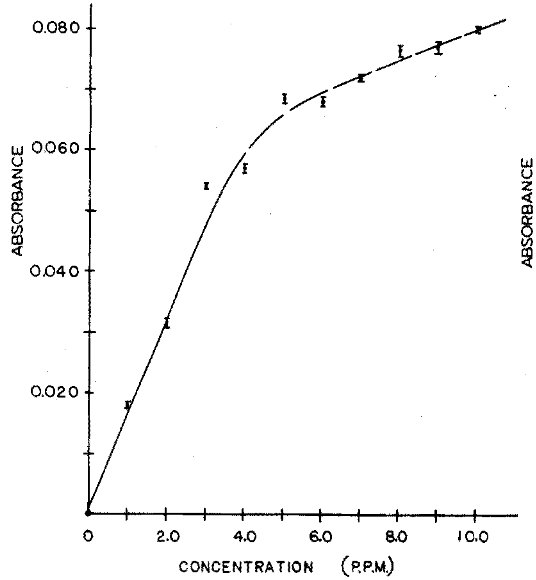
Numerous calibration curves were used to establish the detection limits and sensitivities for lead with the wire loop atomizer. One difficulty that persisted was that of non-zero intercepts. Blanks of the doubly distilled water with which the standards were prepared were analyzed for each calibration curve and always failed to show any discernible absorption signal. The major cause of the difficulty was probably related to the choice of baseline from which peak heights were measured (see Fig. 2). With the unenclosed cell, the increase in the baseline at the atomization temperature was relatively small (about 0.002 absorbance units). However, with the enclosed loop, the higher baseline increase (0.004–0.008 absorbance units) became a problem, because the baseline at the exact time of atomization was somewhere between the first and second baselines.

Two examples of typical calibration curves with unenclosed and enclosed cells are shown in Figs. 4 and 5. As can be seen the concentration range studied with the enclosure was an order of magnitude lower than that employed without it.

TABLE I

DETECTION LIMIT AND SENSITIVITY FOR LEAD WITH LOOP ATOMIZER

Cell	*Sheathing gas*	*Detection limit*		*Sensitivity*	
		Relative (p.p.m.)	*Absolute ($\cdot 10^{-10}$ g)*	*Relative (p.p.m.)*	*Absolute ($\cdot 10^{-10}$ g)*
Unenclosed	N_2	0.33	6.6	0.35	7.0
Unenclosed	N_2	0.42	8.4	0.40	8.0
Enclosed	N_2	0.16	3.2	0.14	2.7
Enclosed	N_2	0.13	2.6	0.08	1.5
Enclosed	Ar	0.06	1.2	0.04	0.8



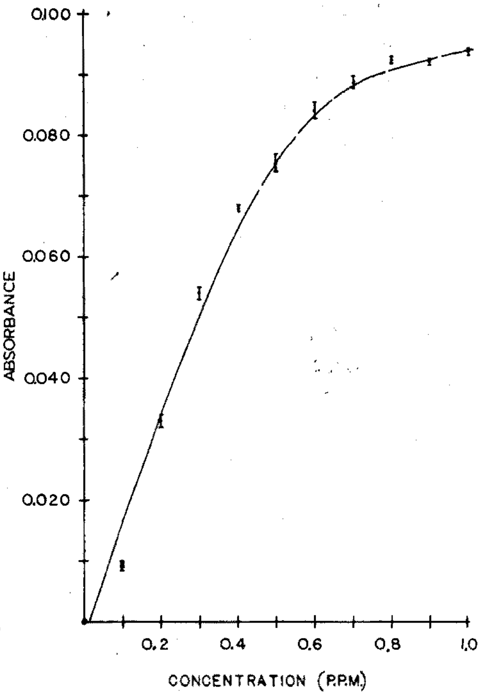


Fig. 4. Calibration curve for unenclosed atomizer. Samples: 0–1.0 p.p.m. Pb (as the nitrate). Atomization setting: 22. Other conditions as in Fig. 3.

Fig. 5. Calibration curve for enclosed atomizer. 5 mm i.d. chimney, 30 mm long. Samples: 0–1.0 p.p.m. Pb (as the nitrate). Drying setting: 18. Atomization setting: 24. Sheathing gas: Ar at 2 l min^{-1}. Scale expansion: maximum. Baseline used: higher baseline (loop at atomization temperature).

TABLE II

COMPARISON OF DETECTION LIMITS AND SENSITIVITIES FOR LEAD WITH VARIOUS ATOMIZERS

Atomizer	*Detection limit*			*Sensitivity (1% abs.)*	
	Relative (p.p.m.)	*Absolute (g)*	*Criterion*	*Relative (p.p.m.)*	*Absolute (g)*
Loop (this work)	0.06	$1.2\cdot10^{-10}$	S/N=2	0.04	$8.0\cdot10^{-11}$
Loop[23]	2.00	$4.0\cdot10^{-9}$	S/N=1	—	—
Carbon filament[13]		$4.0\cdot10^{-11}$	S/N=2		$7.0\cdot10^{-12}$
Tantalum ribbon[20]		$1.0\cdot10^{-11}$	—[a]		$3.0\cdot10^{-11}$
Flame[27]				0.11	$1.1\cdot10^{-7}$[b]
Flame[28]	0.01	$1.0\cdot10^{-8}$[b]	S/N=2	0.50	$5.0\cdot10^{-7}$[b]

[a] Two standard deviations of the noise levels based on ten consecutive readings.
[b] Calculated by this investigator, assuming a sample size of 1 ml.

Table I shows the absolute and relative detection limits (signal-to-noise ratio of 2) and sensitivities (1% absorption or 0.044 absorbance units) obtained for lead. These values were computed from the slope–intercept equation for a line—the slopes and intercepts were obtained from a least-squares fitting of the lower linear portion of the calibration curve. (The noise used for these calculations was the peak-to-peak noise at the baseline.) The detection limit and sensitivity obtained with the enclosed cell were better than those obtained with the unenclosed system. Argon yielded slightly better results than nitrogen probably because argon provided a more thermally favorable environment above the loop that would reduce vapor phase condensations.

Table II compares the lowest detection limit and sensitivity attained in this investigation with those reported by other workers in non-flame atomic spectrometry. The only lead work with loop atomizers available for comparison was that in atomic fluorescence reported by Bratzel *et al.*[23]. Improved results would undoubtedly be obtained with a faster detection system[12–14] and a means of integration.

Interferences

There are several well-known possible sources of interferences in atomic-absorption spectrometry, but physical and chemical interferences are generally the most serious in flameless work.

In order to study the effect of interfering materials on the sensitivity of the loop atomizer, twenty cations and sixteen anions were studied in molar amounts corresponding to 10, 100 and 1000 times a convenient lead concentration—one that yielded an absorbance reading of *ca.* 60% of the total scale used. This concentration was chosen because it lay in the linear portion of the calibration curve, with suitable scale expansion.

The procedure involved the analysis of a pure lead standard before and after the solutions containing the interference. All the samples were checked for background effects with a hydrogen hollow-cathode lamp and with suitable blanks. If the blanks absorbed, corrections were made by subtracting the average blank reading from the sample readings. Absorption signals obtained from the blanks were always due to molecular absorption or particulate light scattering.

Table III shows the results of the interference studies. Nitrate was employed as the counter anion for the cation studies. Tin(IV) was added as the chloride, and the arsenic(III) solution was prepared from arsenic trioxide dissolved in sodium hydroxide and acidified with nitric acid. The values reported in Table III were calculated from the ratio of the absorbance of the interference-containing sample and the average absorbance of the pure lead sample; since the unadulterated lead solution analyzed before and after the interference study yielded different readings, an average value was used. Enhancements or depressions of less than 10% (two times the relative average deviation of the method) were assigned values of zero and the others are rounded off to the nearest 5%.

It is apparent that the role played by the interfering materials is complex; no straightforward correlation could be found between these data and any one physical property, such as boiling points of the lead salts or the interfering salts, where these were available. Also as these compounds are heated, they often decompose and the characterization of the products is not available for all the

TABLE III

EFFECT OF CHEMICAL INTERFERENCES ON ABSORPTION OF LEAD

(The enclosed atomizer was used unless otherwise mentioned)

Interference	*Percentage error*		
	× *10*	× *100*	× *1000*
HCl	+40[a]	+30[a]	+30[a] (±0)
	+30	+30	+35
HNO_3	+40[a] (±2)	+30[a] (±5)	+60[a] (±10)
	+20	+25	+45 (±7)
H_3PO_4	+35[a]	−25[a]	−90[a] (±1)
	+35	−20	−80
H_2SO_4	+40[a] (±14)	+25[a]	+20[a] (±6)
	+20 (±4)	+15 (±5)	+10 (±6)
$K_2Cr_2O_7$	−15	−75	−90
$KMnO_4$	+20	0	+10
NaBr	0	−100	−100
NaCl	0 (±5)	−30 (±3)	−60 (±16)
$NaClO_4$	0	0	−90
NaCN	0 (±1)	0 (±3)	−95 (±1)
Na_2CO_3	−30 (±4)	−70	−95
NaF	+20	0	+10
$NaHCO_3$	−85	−100	−100
NaI	−70	−100	−100
$NaNO_3$	0 (±6)	+15 (±4)	+30 (±7)
NaOAc	−20	−30	−50
NaOH	−30	−90	−95
Na_2SO_4	0 (±6)	0 (±1)	−85 (±4)
$Na_2S_2O_3$	0	−60	−90
Na_3PO_4	0 (±3)	−15 (±1)	−65 (±6)
Ag(I)	0	−10	−75
Al(III)	0 (±4)	+10	−30
As(III)	−15	−15	−15
Ba(II)	+20	+30	+25
Ca(II)	+50 (±16)	+50 (±12)	0 (±13)
Cd(II)	+15 (±2)	+25 (±1)	−35 (±2)
Cr(III)	+30	+35	+30
Cu(II)	+25 (±14)	+50 (±22)	+35 (±22)
Fe(III)	+15 (±1)	0	0
Hg(II)	+25	+15	−10
K(I)	0 (±6)	+10 (±3)	+70 (±30)
La(III)	+70	+50	+50
Li(I)	+15	+70	+60
Mg(II)	0 (±4)	+15 (±8)	0 (±8)
Na(I)	0 (±6)	+15 (±4)	+30 (±7)
NH_4(I)	+15	+45	+50
Ni(II)	+20	+10	0
Sn(IV)	+50 (±17)	+40 (±11)	—
Zn(II)	+20 (±7)	+35 (±10)	+20 (±1)

[a] Unenclosed cell.

different salts used. Solubility problems had some effect on the anion studies especially with phosphate, sulfate, hydrogencarbonate, and acetate.

There does seem to be some relationship between the results and the volatility of the lead salt or the matrix from which it is atomized. This would imply that perhaps the interference occurred as the lead was being atomized from the loop, *i.e.*, the rate of production of free lead atoms is affected by the ease of vaporizing the lead compound at the temperature used, and by the thermal stability of the salt matrix surrounding the lead. With the relatively slow detection system used in these studies, any significant increase in the speed of vaporization would be reflected as a depression, as in the case of the volatile lead halides (chloride, iodide, and bromide) whose boiling points are about 950°, whereas decreasing the atomization rate would result in an enhancement, as in the case of most of the cation studies where the vaporization of lead oxide might have been retarded by the foreign salt. On the other hand, if the lead compound was not completely decomposed at the atomization temperature, *e.g.* with lead sulfate, phosphate, and sulfide (formed from the thermal decomposition of lead thiosulfate), a depression was obtained. Others[22,23,29,30] have suggested that such a mechanism is reasonable. An alternative mechanism, concerned with vapor phase condensation or co-precipitation of analyte atoms in an atmosphere saturated with a large excess of gaseous foreign metal atoms or molecules, has been proposed by West *et al.*[10–15], who have done extensive work in this area. This conclusion was partially based on the fact that there was a better, though not conclusive, correlation between the boiling point of the interfering metal and the results they obtained (almost exclusively depressions) than between any physical property of the interference that would influence the atomization efficiency[15].

Nickel

In order to confirm the potentiality of the loop atomizer for the determination of less volatile metals, nickel (b.p. 2730°) was studied. Either nickel nitrate or nickel chloride solutions were analyzed. Both salts produced similar absorbance readings for standards of the same concentration, therefore both were probably decomposed on heating to an intermediate nickel oxide (b.p. 1990°). Jackson and West[15] have reported that relatively high temperatures are necessary for the atomization of nickel. The temperatures (about 2000°) needed for atomizing nickel

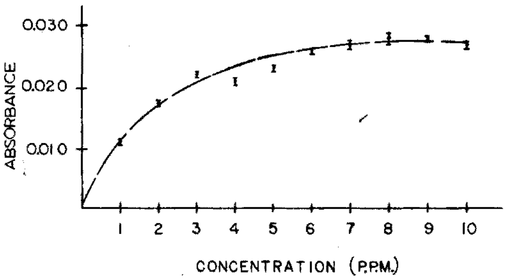


Fig. 6. Calibration curve for nickel. Samples: 0–100 p.p.m. Ni (as the chloride). Drying setting: 22. Atomization setting: 36. Sheathing gas: Ar at 1.5 l min^{-1}. Wavelength: 232.0 nm. Slit width: 0.08 nm. Scale expansion: × 10.

were much higher than those employed for lead; an optimal Variac setting of 36% was used. Enclosing the loop led to the formation of a deposit on the walls at these elevated temperatures, hence the unenclosed cell with single twist loops was utilized. Absorption was measured at 232.0 nm with background correction being made at 232.6 nm.

Figure 6 shows the calibration curve obtained for nickel at 232.0 nm. The severe curvature is a common feature at the atomic 232.0-nm line, because there is an unresolvable nickel ion line only 0.03 nm away[15]. In Table IV, the various reported detection limits and sensitivities for nickel are summarized. The use of a high-intensity source, faster response system, and integration device should better the detection limit and sensitivity for nickel with the loop atomizer.

TABLE IV

COMPARISON OF DETECTION LIMITS AND SENSITIVITIES FOR NICKEL WITH VARIOUS ATOMIZERS

Atomizer	*Detection limit*			*Sensitivity (1% abs.)*	
	Relative (p.p.m.)	*Absolute (g)*	*Criterion*	*Relative (p.p.m.)*	*Absolute (g)*
Loop (this work)	0.80	$1.6 \cdot 10^{-9}$	S/N=2	0.45	$9.0 \cdot 10^{-10}$
Carbon filament[15]	0.04[a]	$2.0 \cdot 10^{-10}$	S/N=2		$9.5 \cdot 10^{-11}$
Carbon filament[31]		$1 \cdot 10^{-10}$	—[b]		
Tantalum boat[30]					$3.0 \cdot 10^{-9}$[c]
Flame[27]				0.066	$6.6 \cdot 10^{-8}$[d]

[a] High-intensity nickel hollow-cathode lamp.
[b] Estimated from RSD of lowest weight of nickel analyzed.
[c] Not specified.
[d] Calculated by this investigator, assuming a sample size of 1 ml.

Conclusion

Although the loop atomizer appears to be an efficient and versatile means of producing an atomic vapor, it is still in a developmental stage. Variability in day-to-day usage implies that unestablished factors influence the observed sensitivity and precision. After further development, the loop atomizer should be applicable for trace metal analysis for clinical purposes and also for direct water analysis.

A single preconcentration technique with the wire loop atomizer has been described[32] which increases the sensitivity of this method up to 1000-fold.

SUMMARY

In an extension of studies of flameless atomizers for atomic-absorption spectrometry, an electrically heated tungsten–rhenium alloy wire loop was examined. Reduction of metallic salts to ground-state metal atoms was accomplished with the high temperature produced by the loop. Lead and nickel were investigated. Experimental parameters such as wavelength, slit width, atomization temperature and sheathing gas flow rate were optimized. Absolute detection limits of $6.6 \cdot 10^{-10}$ and $1.2 \cdot 10^{-10}$, and absolute sensitivities of $7 \cdot 10^{-10}$ and $8 \cdot 10^{-11}$ g of lead, were established for unenclosed and enclosed cells, respectively. The interferences of twenty cations and sixteen anions were studied; foreign cations generally enhanced the lead absorption by retarding its vaporization, allowing the slow detection system to respond more efficiently. Nickel was investigated as a representative less volatile metal; an absolute detection limit of $1.6 \cdot 10^{-9}$ and an absolute sensitivity of $9 \cdot 10^{-10}$ g of nickel were established.

RÉSUMÉ

On examine le comportement d'une boucle de fil en alliage tunstène–rhénium chauffé électriquement, dans le cadre d'une étude sur des atomiseurs sans flamme pour spectrométrie d'absorption atomique. La réduction des sels métalliques à l'état d'atomes métalliques se fait grâce à la température élevée produite. Plomb et nickel sont examinés en fonction de divers paramètres, longueur d'onde, largeur de fente, température d'atomisation, débit de gaz. Les interférences de vingt cations et seize anions sont décrites. Généralement, les cations étrangers renforcent l'absorption du plomb, en retardant sa vaporisation, et permettant au système lent de détection de répondre plus efficacement. Le nickel est examiné comme étant représentatif d'un métal moins volatil.

ZUSAMMENFASSUNG

Im Rahmen der Untersuchungen über flammenlose Atomisatoren für die Atomabsorptionsspektrometrie wurde eine elektrisch erhitzte Drahtschleife aus einer Wolfram–Rhenium-Legierung geprüft. Die hiermit erzielte hohe Temperatur führte zu einer Reduktion der Metallsalze zu den Metallatomen im Grundzustand. Blei und Nickel wurden untersucht. Die experimentellen Parameter wie Wellenlänge, Spaltbreite, Atomisierungstemperatur und Schutzgasströmungsgeschwindigkeit wurden optimiert. Es wurden absolute Nachweisgrenzen von $6.6 \cdot 10^{-10}$ und $1.2 \cdot 10^{-10}$ sowie absolute Empfindlichkeiten von $7 \cdot 10^{-10}$ und $8 \cdot 10^{-11}$ g Blei für unverschlossene bzw. verschlossene Zellen festgestellt. Die Störungen durch 20 Kationen und 16 Anionen wurden untersucht; Fremdkationen verbesserten im allgemeinen die Bleiabsorption, indem sie die Verdampfung verzögerten und dadurch das langsame Nachweissystem wirkungsvoller machten. Nickel wurde als ein repräsentatives, weniger flüchtiges Metall untersucht; eine absolute Nachweisgrenze von $1.6 \cdot 10^{-9}$ und eine absolute Empfindlichkeit von $9 \cdot 10^{-10}$ g Nickel wurden festgestellt.

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DETERMINATION OF SOME RARE-EARTH ELEMENTS BY PLASMA-JET EMISSION SPECTROMETRY

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Many methods have been reported for the determination of rare-earth elements by means of spectrophotometric methods[1] or flame emission spectrometric methods[2] based on solvent extraction procedures. However, spectrophotometric methods necessitate prior isolation of each of the rare-earth elements, and flame emission methods are not sufficiently sensitive. Emission spectrographic methods[3], X-ray fluorescence methods[4] and activation analyses with thermal neutrons[5] have been developed, but these various methods require cumbersome and expensive devices in order to obtain accurate results. Atomic absorption and emission methods with nitrous oxide–acetylene flames[6–8] and high-frequency plasma torch spectrometric methods[9,10] have been proposed in recent years for the determination of rare-earth elements.

Several studies of plasma-jet spectrometry based on an arc-jet plasma generator as a light source have recently been described[11–13]. In the work discussed here, the stabilizing effect of the magnetic field on the plasma jet by the Lorentz force was examined, and detection limits for some rare earth elements were established. Plasma-jet spectrometry was then applied to the determination of lanthanum, yttrium and gadolinium in a monazite sample from which thorium had been separated. When the calibration curves were prepared, the internal standard and background compensation method[13] was applied.

EXPERIMENTAL

Reagents

Standard stock solutions of rare-earth elements. Accurately weighed, spectroscopically pure, rare-earth oxides (Research Institute of Iron, Steel and Other Metals, Tohoku University) were dissolved in nitric acid; cerium oxide was dissolved in sulphuric acid. The solutions were evaporated in order to eliminate excess of acid, transferred to 100-ml volumetric flasks, and diluted with distilled water to the mark. These stock solutions contained 5.00 mg ml^{-1} of the rare-earth metal, and were diluted to the desired concentration at the time of use.

Standard magnesium solution. Magnesium metal (99.9%) was dissolved in hydrochloric acid, the solution was evaporated to dryness, and the residue was dissolved in water to make a solution containing 1 mg Mg ml^{-1}, which was diluted to the desired concentration as required. All acids were of analytical grade.

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Apparatus

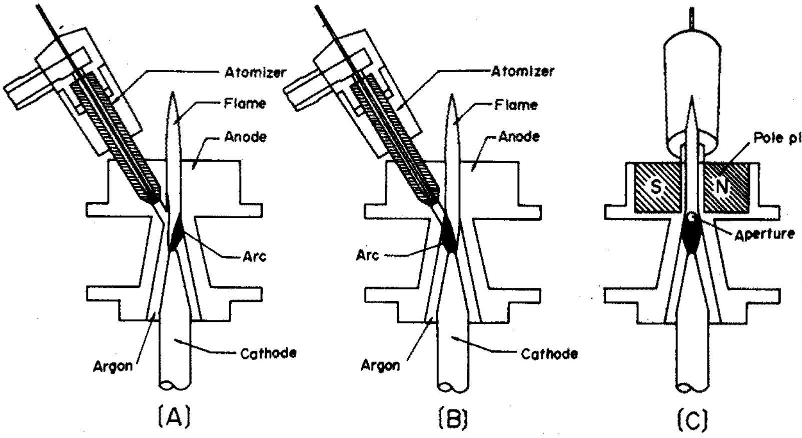
The plasma-jet generator and Hitachi 139 auto-recording spectrometer used were as described previously[11].

A magnet and gaussmeter (Denshi-Jiki Kogyo Model 420) were also used.

Effect of magnetic field on the spectral line intensity

The properties and physical characteristics of the plasma-jet source used in this work have been discussed in detail by Yamamoto[14], who pointed out that the plasma arc can be fixed by means of a magnetic field so that the plasma-jet flame can be stabilized when a sample solution is blown into the plasma arc. The stabilization of the plasma-jet flame by means of the magnetic field is shown schematically in Fig. 1. In the work described here, the improved nebulizer described in the earlier paper[12] was used, and the effect of the magnetic field on spectral line intensities and background intensities was investigated from the view-points of the stabilization of the plasma-jet flame, and of analytical sensitivity. Working conditions for the plasma generator and the spectrometer, except for the use of the magnet, were the same as described previously[13], *i.e.*, 400 A for the arc current, 10–15 l min^{-1} (Ar–He) for the tangential gas flow-rate and 5 l min^{-1} (Ar) for the carrier gas flow-rate.

As the magnetic force in the plasma-jet generator varied with the position of the nozzle of the copper anode, the magnetic force was measured. Results are presented in Fig. 2. The effects of the magnetic field on spectral line and background intensities were examined with settings on the basis of the position of point *c* in Fig. 2. As shown in Table I, the background intensities decreased with increasing magnetic force, and the ratio of the spectral intensity of the Y II 360.1-nm line to



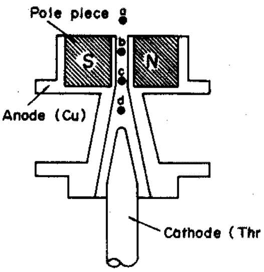


Fig. 1. Schematic diagram of the plasma-arc stabilization. (A) When the sample solution is blown into the plasma arc without the magnetic field, the plasma jet moves to the opposite side from the aperture of the sample injection. (B) The plasma arc is fixed to the aperture of the sample injection by means of the magnetic field. (C) When the sample solution is blown into the plasma arc, the plasma-jet flame becomes ideal owing to the magnetic field.

Fig. 2. Relationship between the magnetic force and the position of the copper anode nozzle (a) 310, (b) 420, (c) 440, (d) 360 gauss.

TABLE I

EFFECT OF MAGNETIC FIELD ON SPECTRAL LINE INTENSITY

Magnetic force at point C (Gauss)	*Background intensity (chart scale)*	$\frac{I_{YII3601}}{I_{BG3601}}$[a]
0	45	1.0
330	40	1.1
380	28	1.2
440	15	1.6
490	6	2.0

[a] $I_{YII3601}$ and I_{BG3601} are, respectively, the spectral intensities of the Y II 360.073-nm and Y II 360.192-nm lines, which were not separated by means of the spectrophotometer used, and the background intensity at 360.1 nm.

the background intensity increased. One reason for the decrease of background intensity is that the temperature of the plasma jet decreased, because larger amounts of the sample solution were mixed with the plasma than in the absence of the magnetic field, owing to the stabilization of the plasma arc by means of the magnetic field. Accordingly, analytical sensitivities were increased by this use of magnetic fields in plasma-jet spectrometry. Based on these examinations, all subsequent tests were carried out under the working conditions with 490 gauss at point *c*.

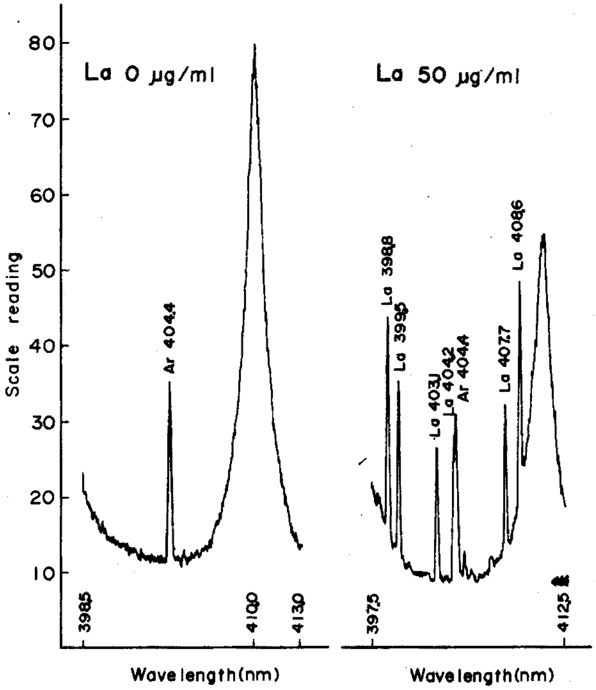


Fig. 3. Lanthanum spectrum from the plasma-jet flame.

Detection limits for some rare-earth elements

As the temperature of the plasma jet used was 7200–6200°K[11], high sensitivity for the determination of the rare-earth elements was expected. However, the background intensities from the plasma jet were strong and the background variation on scanning the wavelength was large (Fig. 3); it was also necessary to consider the spectral lines of argon which overlap with the spectral lines of the rare-earth elements in order to select appropriate analytical lines. The detection limits for some rare-earth elements were measured under optimal conditions (Table II); the detection limit is defined as the value where the signal intensity of the peak is three times the background fluctuation. As can be seen, the analytical sensitivities for the rare-earth elements were quite good.

TABLE II

DETECTION LIMITS FOR RARE-EARTH ELEMENTS

Element		*Wavelength (nm)*	*Detection limit* (*μg ml^{-1}*)		
			P.j.s.[a]	*A.a.s.*[b]	*F.e.s.*[c]
Sc[d]	II	424.6	0.4	0.8	0.07
Y	II	360.1	0.1	5.0	0.3
	II	361.1	0.3		
La	II	398.8	0.6	110	1
	II	399.5	0.5		
	II	403.1	0.5		
Pr	II	440.8	2.7	72	1
	II	446.8	5.3		
	II	449.6	4.0		
Nd	II	383.6	3.3	35	1
	II	445.1	3.3		
Sm	II	428.0	3.3	21	0.6
	II	442.4	2.7		
	II	443.3	2.0		
Gd	II	396.6	4.0	38	2
	II	371.2	3.0		
Ce		218.0	3.7	—	10
		222.2	7.3		
		222.5	3.7		

[a] Plasma-jet spectrometry.
[b] Atomic absorption spectrometry with pre-mixed flame[7].
[c] Flame emission spectrometry with pre-mixed flame[6].
[d] The detection limit for scandium was also measured because of the similarity of chemical properties.

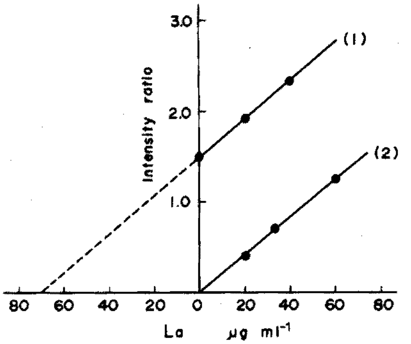
Application to the determination of La, Y and Gd in monazite

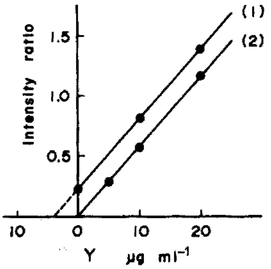
A monazite sample from which thorium had been separated was analysed. The standard addition method was used in order to establish the accuracy of the proposed method. For measurements of spectral line intensities, the internal standard and background compensation method[13] was again used. The Mg II 279.5-nm line was taken as the internal standard, because this line was not detected in the sample analysed by plasma-jet spectrometry.

Procedure. Three sub-samples of a monazite sample were weighed accurately and dissolved in nitric acid, and the solutions were evaporated to dryness. The residues were dissolved in hydrochloric acid and the solutions diluted with distilled water. The solutions were then evaporated, with occasional wáshing of the beaker walls with distilled water, in order to remove excess of hydrochloric acid. Each solution was transferred to a 100-ml volumetric flask, and 5.0 ml of magnesium solution containing 20.0 μg of magnesium was added as the internal standard. Then definite amounts of La, Y and Gd were also added to two solutions, but not to the third. All the solutions were then diluted with distilled water to the mark. The spectral line intensities were measured under the conditions mentioned above.

RESULTS AND DISCUSSION

As shown in Figs. 4–6, the gradients of the calibration curves for standard solutions which contained 1 μg Mg ml^{-1} and definite amounts of La, Y and Gd without sample were in agreement with the sample solutions prepared as above.





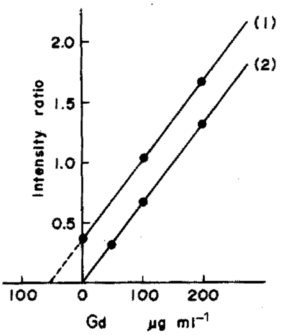


Fig. 4. Calibration curves by the standard addition method (1) and by standard solutions (2). Intensity ratio: $\dfrac{I_{\mathrm{LaII}\,4031}/I_{\mathrm{BG}\,4031}}{I_{\mathrm{MgII}\,2795}/I_{\mathrm{BG}\,2795}}$.

Fig. 5. Calibration curves by the standard addition method (1) and by standard solutions (2). Intensity ratio: $\dfrac{I_{\mathrm{YII}\,3601}/I_{\mathrm{BG}\,3601}}{I_{\mathrm{MgII}\,2795}/I_{\mathrm{BG}\,2795}}$.

Fig. 6. Calibration curves by the standard addition method (1) and by standard solutions (2). Intensity ratio: $\dfrac{I_{\mathrm{GdII}\,3712}/I_{\mathrm{BG}\,3712}}{I_{\mathrm{MgII}\,2795}/I_{\mathrm{BG}\,2795}}$.

The good linearity for both graphs indicated a reliable analytical accuracy of the proposed method. Therefore, the results obtained for the determination of La, Y and Gd in the monazite sample are listed in Table III. The precision of the determination of lanthanum in the monazite sample was also established: the coefficient of variation was 1.51% for 50 μg La ml^{-1} (11 measurements).

Plasma-jet spectrometry has made it possible to obtain good results for the determination of aluminium, boron[12] and rare-earth elements, which was rather difficult by flame emission and absorption spectrometry with the usual combustion

TABLE III

ANALYTICAL RESULTS

Sample taken (g)	La added (µg)	Intensity ratio	La found (µg)	La_2O_3 (%)
0.0378	—	0.500	—	32.9
	20	1.91	19.7	
	40	2.32	39.5	
	Y added (µg)	Intensity ratio	Y found (µg)	Y_2O_3 (%)
0.1075	—	0.215	—	0.59
	10	0.830	10.3	
	20	1.425	19.5	
	Gd added (µg)	Intensity ratio	Gd found (µg)	Gd_2O_3 (%)
0.1075	—	0.394	—	0.89
	100	1.012	95	
	200	1.654	193	

flames. For the determination of calcium and magnesium, high sensitivity was obtained[13]. On the other hand, it must be pointed out that problems remain, *e.g.* the use of acids and large amounts of diverse elements cause a flush of products which corrode the copper electrode. The stabilization of the plasma-jet flame by means of the Lorentz force of the magnetic field has not essentially settled these problems, but it is considered that the plasma-jet flame will become an excellent source for emission spectrometry, if the method of sample injection is improved.

SUMMARY

The effects of a magnetic field on spectral intensities in plasma-jet spectrometry were examined, and detection limits for rare-earth elements were calculated. Plasma-jet emission spectrometry was applied to the determination of lanthanum, yttrium and gadolinium in a monazite sample from which thorium had been separated. A standard addition method was used in order to improve accuracy, and the internal standard and background compensation method was applied to measurements of spectral line intensities to achieve good precision. The coefficient of variation was 1.51% for 50 µg La ml^{-1}.

RÉSUMÉ

On examine l'influence d'un champ magnétique sur les intensités spectrales de la spectrométrie à injection de plasma. Les limites de détection des éléments des terres rares sont calculées. Cette technique est appliquée au dosage du lanthane, de l'yttrium et du gadolinium dans une monazite, après séparation du thorium. On procède par addition d'étalon afin d'arriver à une exactitude plus grande. La méthode de l'étalon interne et la compensation du bruit de fond permettent d'arriver à une bonne précision. Le coefficient de variation est de 1.51% pour 50 μg La ml^{-1}.

ZUSAMMENFASSUNG

Der Einfluss eines magnetischen Feldes auf Spektralintensitäten bei der Plasmabrennerspektrometrie wurde untersucht; die Nachweisgrenzen für Seltenerd-Elemente wurden berechnet. Die Emissionsspektrometrie mit einem Plasmabrenner wurde auf die Bestimmung von Lanthan, Yttrium und Gadolinium in einer Monazitprobe angewendet, aus der Thorium abgetrennt worden war. Es wurde eine Standardzumischmethode angewendet, um die Genauigkeit zu verbessern, und die Methode des inneren Standards und der Untergrundkompensation wurde auf Messungen von Spektrallinienintensitäten angewendet, um eine gute Reproduzierbarkeit zu erreichen. Der Variationskoeffizient war 1.51% bei 50 µg La ml^{-1}.

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BIS-AROYLHYDRAZONES OF α-DIKETONES AS REAGENTS FOR COLORIMETRIC AND FLUORIMETRIC DETERMINATIONS OF CALCIUM, CADMIUM AND OTHER CATIONS

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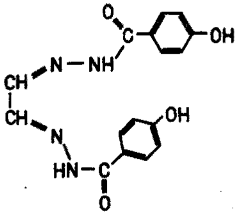
Aroylhydrazines (aromatic acid hydrazides) react with carbohydrates in alkaline solution to form colored products[1], and with various cations these products form complexes which have distinct absorption and fluorescence spectra[2]. Pinkus[3] showed that the reaction products are bis-aroylhydrazones of glyoxal and methylglyoxal. The present work evaluates the potential of the bis(4-hydroxybenzoylhydrazones) of glyoxal (A), methylglyoxal and dimethylglyoxal as reagents for the colorimetric and fluorimetric determination of cations. The greatest promise is for calcium(II), cadmium(II), lanthanum(III) and bismuth(III). Preliminary work with related aroylhydrazones leaves open the possibility that other cations could also be determined by reagents in this class.



A

EXPERIMENTAL

Instrumentation

Absorbances were measured with a Gilford 300 N microsample spectrophotometer. Spectra were scanned with a Unicam SP 800A double-beam spectrophotometer.

Fluorescence measurements were made with an Aminco-Bowman spectrophotofluorimeter fitted with a xenon arc lamp and an R136 photomultiplier. Mirrors and 1-mm slits were placed in the cell housing. Spectra were scanned with 0.1-mm slits in the scanning monochromator side of the cell housing. Fluorescence data are not corrected for instrument response.

Reagents

Aromatic acid hydrazides (aroylhydrazines) were obtained from Fluka AG. Other reagents were obtained from BDH Chemicals Ltd., except for methylglyoxal (pyruvic aldehyde), obtained as a 40% solution from L. Light & Co. Ltd.

The bis-aroylhydrazones were prepared by mixing excess of the acid hydrazide (in aqueous hydrochloric acid solution) with the α-diketone (in water). The precipitates were washed and purified by dissolving in cold dimethylformamide, filtering, and adding the filtrate to a large excess of water. Some samples were also recrystallized from a large excess of alcohol. A batch of glyoxal bis(4-hydroxybenzoylhydrazone) was kindly donated by Dr. B. Sturgeon of BDH Chemicals Ltd.

Methods

Bis-aroylhydrazone solutions (1 m*M*) in 10 m*M* aqueous sodium hydroxide solution were used to examine the effect of cations. The absorption spectra of these were scanned with water as the blank, and the spectra of these solutions with 20 μ*M* added cation were scanned with reagent as the blank. The spectra of the chelates were examined by scanning 20 μ*M* solutions of ligand in 10 m*M* sodium hydroxide with excess of cation against cation in 10 m*M* sodium hydroxide as blank.

The effects of using different bases, and of varying the concentration of base, were investigated. Reagents such as cyanide (20 m*M*) and citrate (0.2 *M*) were added to alter the selectivity of the color reactions. Fluorescence measurements were also made in ethanol and other solvents.

Trial analytical procedures

To a reagent consisting of 20 m*M* sodium cyanide, 10 m*M* sodium hydroxide and 1 m*M* glyoxal bis(4-hydroxybenzoylhydrazone) was added calcium chloride in various concentrations, and the absorbance at 460 nm was read. Similarly, cadmium acetate was added to a reagent containing 1 m*M* glyoxal bis(4-hydroxybenzoylhydrazone), 0.2 *M* trisodium citrate and 0.2 *M* ammonia, and the absorbance was read at 460 nm.

Trial continuous flow analytical systems for calcium are being studied in which the color reagent is prepared by heating 4-hydroxybenzoic acid hydrazide and glucose in alkali. The product is a mixture of hydrazones of glyoxal and methylglyoxal[3]. These are precipitated with excess of hydrochloric acid and washed, and this crude preparation is used as a *ca.* 2 m*M* solution of bis-hydrazones in 0.5 *M* sodium hydroxide. In a provisional continuous flow system designed for use with biological materials, the sample is diluted 4-fold with 0.1 *M* hydrochloric acid, and then dialysed against 0.1 *M* hydrochloric acid. The recipient stream is mixed with an approximately equal volume of color reagent. The resultant mixture passes through the colorimeter flow cell and the absorbance at 460 nm is recorded. Standard Technicon Basic AutoAnalyzer modules are used in all continuous flow analyses. Further details of these procedures will be published elsewhere.

RESULTS

Color reactions with 4-hydroxybenzoylhydrazones

The spectra of the bis(4-hydroxybenzoylhydrazones) of glyoxal, methylglyoxal and dimethylglyoxal in 10 m*M* alkali are shown in Fig. 1A. The absorbance maxima are at 374 nm, 361 nm and 348 nm, respectively, and the maximal absorbances also decrease in this order. The absorbance increases with increasing alkali concentration, as would be expected if these spectra are of the anionic form of the ligands.

Figures 1B and 1C show the effects of adding a 5-fold and 1000-fold excess of calcium (as chloride) to the ligand; the chelates formed with each ligand have maxima at 428 nm, 416 nm and 404 nm. A 5-fold excess of calcium does not give complete chelate formation (with 20 μ*M* ligand), and the formation constant of the calcium chelate increases from the glyoxal derivative to the dimethylglyoxal derivative, while the maximal absorbance of the chelate decreases. Figure 1D shows that chelate formation is complete with only a 5-fold excess of cadmium (as acetate), the maxima being at 439, 427 and 413 nm. With calcium, chelate formation is more complete at higher alkali concentrations, which is consistent with chelates being formed with the anions of the ligands.

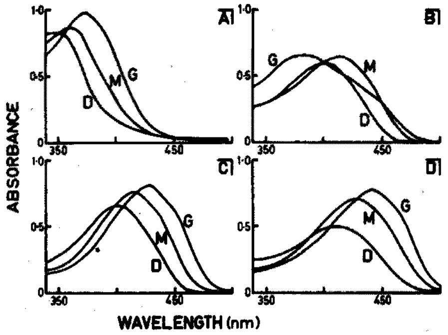


Fig. 1. (A) Absorption spectra of 20 μ*M* solutions of bis(4-hydroxybenzoylhydrazones) of glyoxal (G), methylglyoxal (M) and dimethylglyoxal (D) in 10 m*M* sodium hydroxide. (B) As for A with 100 μ*M* Ca^{2+} added. (C) With 20 m*M* Ca^{2+} added. (D) With 100 μ*M* Cd^{2+} added.

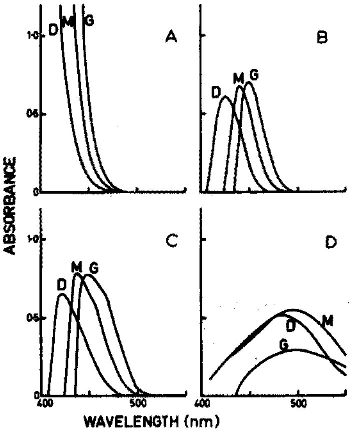


Fig. 2. (A) Absorption spectra of 1 m*M* solutions of bis(4-hydroxybenzoylhydrazones) of glyoxal (G), methylglyoxal (M) and dimethylglyoxal (D) in 10 m*M* sodium hydroxide, scanned against water. (B) As for A, with 20 μ*M* Ca^{2+} added and scanned against reagent. (C) As for A, with 20 μ*M* Cd^{2+} added, scanned against reagent. (D) As for A, with 20 μ*M* Bi(III) added, scanned against reagent.

The spectra in Fig. 2 were obtained with an excess of ligand (1 m*M*) in 10 m*M* alkali. In addition to calcium and cadmium, lanthanum (as the chloride) gave spectra closely similar to cadmium but with slightly higher maximal absorbances, and (with the glyoxal derivative) a slightly less pronounced shoulder at 470 nm. A species present in the bismuth solutions (made by diluting 1 *M* bismuth nitrate in 2 *M* nitric acid with water to 10 m*M* bismuth(III) and diluting this with reagent to 20 μ*M* bismuth) formed complexes absorbing at longer wavelengths, but no attempt was made to develop an assay system for bismuth. No responses were obtained from cerium(III) or (IV) sulfates.

Table I shows the responses of a number of other cations with these ligands. Glyoxal bis(4-hydroxybenzoylhydrazone) is the most selective of the three reagents. This selectivity can be increased: cyanide (also sulfide or thiols) eliminates the response by cadmium and copper(II) ions, and decreases the responses of lanthanum and other ions, giving an assay system which is highly selective for calcium.

TABLE I

SELECTIVITY OF COLOR REACTIONS BETWEEN CATIONS AND THE BIS(4-HYDROXY-BENZOYLHYDRAZONES) OF GLYOXAL AND METHYLGLYOXALS

(Cation (20 μM) added to 1 mM ligand in 10 mM sodium hydroxide. Glyoxal derivative absorbance read a 460 nm, methylglyoxal derivative at 450 nm, and dimethylglyoxal derivative at 440 nm. Reagent blanks subtracted)

Added cation	*Absorbance* $(\cdot 10^2)$				
	Methylglyoxal	*Dimethylglyoxal*	*Glyoxal*	*Glyoxal* + *NaCN*[a]	*Glyoxal* + Na_3*citrate*[b]
Mg^{2+}	1	15	1	2	0
Ca^{2+}	43	31	38	36	0
Sr^{2+}	8	8	4	3	0
Ba^{2+}	7	2	3	2	0
Zn^{2+}	18	36	4	0	5
Cd^{2+}	70	48	84	1	67
Sn^{2+}	0	0	0	0	0
Al^{3+}	0	0	0	0	0
La^{3+}	96	65	89	18	1
Bi^{3+}	45	43	24	23	0
Cu^{2+}	14	33	18	0	8
Mn^{2+}	6	39	2	2	0

[a] Ligand (1 mM) and NaCN (20 mM) in 10 mM NaOH.
[b] Ligand (1 mM) and trisodium citrate (0.2 M) in 0.2 M ammonia.

Citrate suppresses the responses of calcium, lanthanum and bismuth, leaving a reagent which is extremely selective for cadmium.

Trial analytical procedures

Reagents containing cyanide or citrate to improve selectivity can be used in colorimetric methods for calcium or cadmium. Under the conditions outlined in the Experimental and in Table I, calibration graphs are linear up to about 50 μM cation in the final solution. The apparent molar absorptivity of the calcium complex in the calcium assay system is about $1.5 \cdot 10^4$ l mole^{-1} cm^{-1}, and that of the cadmium complex in the cadmium assay system is about $2.8 \cdot 10^4$ l mole^{-1} cm^{-1}. These absorbances are only a little less than those of the chelates formed with excess of cation at 460 nm (Fig. 1).

The provisional continuous flow system using dialysis gives a stable base-line, and at a sampling rate of 60 h^{-1}, the peak absorbances are proportional to concentration up to at least 4 mM calcium in the sample. A number of biological samples were assayed for calcium by an atomic absorption procedure and by the provisional automated system with satisfactory agreement of results.

Fluorescence reactions with 4-hydroxybenzoylhydrazones

Table II shows the fluorescence responses of some cations (10 μM) in a solution of ligand (1 mM) and diethanolamine (2 M) in ethanol. The most intense fluorescences were obtained from lanthanum and cadmium, and the optimal excitation mode in these cases corresponds to the shoulder on the absorption spectra at

TABLE II

FLUORESCENCE REACTIONS BETWEEN CATIONS AND BIS(4-HYDROXYBENZOYLHYDRAZONES)

(Cation (10 μM) added to 1 mM ligand and 2 M diethanolamine in ethanol)

Cation	*Glyoxal*		*Methylglyoxal*		*Dimethylglyoxal*	
	Fl. (nm)[a]	*Intensity*[b]	*Fl. (nm)*[a]	*Intensity*[b]	*Fl. (nm)*[a]	*Intensity*[b]
Mg^{2+}	452/518	0.03	454/521	0.18	426/523	0.36
Ca^{2+}	453/523	0.24	439/526	0.20	426/533	0.24
Zn^{2+}	452/514	0.02	469/534	0.46	469/535	0.86
Cd^{2+}	468/533	0.73	469/535	0.54	441/531	0.33
$-^{r}\theta^{3+}$	467/534	2.13	469/536	2.04	454/536	1.11
Bi^{3+}	470/564	0.01	471/573	0.05	471/582	0.05

[a] Excitation and emission maxima.

[b] Maximum fluorescence intensity (arbitrary units; blanks subtracted).

about 470 nm. Fluorescence was not obtained with cerium(III) or (IV) sulfates.

In ethanol and other solvents, including water, relatively higher fluorescences can be obtained with calcium if a strong base is added, but the blank fluorescences are also higher than the 0.02–0.05 obtained in the work above, possibly because of contamination.

The bismuth derivatives gave a distinct fluorescence although it was only 1.5 to 3 times the blank. The maxima quoted (Table II) are uncertain because of the large contribution of the blank fluorescences. In the presence of sodium hydroxide, the weak fluorescence of this Bi(III) species and the glyoxal derivative appeared to be at longer wavelengths (about 515 nm/615 nm).

Figure 3 shows the fluorescence excitation and emission spectra of the lanthanum chelate with the glyoxal derivative, and the fluorescence response of different levels of lanthanum. This suggests that further work could lead to a sensitive fluorimetric determination of lanthanum, and it is probable that this could be adapted for

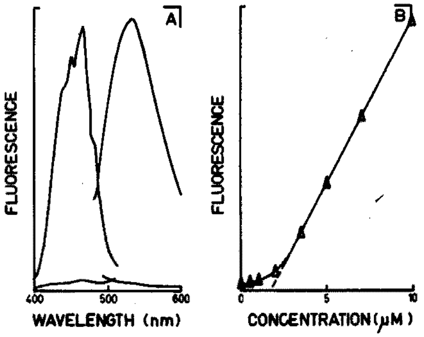


Fig. 3. (A) Fluorescence spectra of solution containing 10 μM lanthanum chloride, 1 mM glyoxal bis-(4-hydroxybenzoylhydrazone) and 2 M diethanolamine in ethanol. Lower curves are reagent blank fluorescence. (B) Fluorescence (excitation 467 nm, emission 534 nm) of same solutions with various La^{3+} concentrations.

other elements. The fluorescence response of lanthanum standards in the system suggests that, were the response linear at low cation concentration, less than 50 n*M* lanthanum could be determined.

Other bis-aroylhydrazones

The simplest member of this class of ligand is glyoxal bis(benzoylhydrazone). As expected, this is less readily soluble in alkali than the 4-hydroxyl derivatives. The anion form has a pale yellow color, with an absorbance maximum about 364 nm (Table III). The chelates with calcium and with the other cations included in Table III are not formed at such low concentrations as with the ligands described above, and the shift in absorption maxima is smaller (with a 1000-fold excess of calcium, the absorbance maximum was 392 nm). The chelates are only feebly fluorescent. Consequently, this is probably not such a useful reagent.

TABLE III

ABSORBANCE MAXIMA OF SOME GLYOXAL BIS-AROYLHYDRAZONES IN THE PRESENCE OF EXCESS CATION

Aroyl group[a]		*Added cation*				
		None	*20 mM Mg*	*20 mM Ca*	*100 μM Cd*	*100 μM La*
Benzoyl	λ_{max} (nm)	364	364	392	369	364
	$\varepsilon_{max} \cdot 10^4$	3.8	4.2	2.8	3.5	3.5
4-Chlorobenzoyl	λ_{max} (nm)	335	334	346	336	335
	$\varepsilon_{max} \cdot 10^4$	3.5	3.6	2.4	3.5	3.5
4-Aminobenzoyl	λ_{max} (nm)	373	375	412	374[b]	373[b]
	$\varepsilon_{max} \cdot 10^4$	4.8	4.9	3.7	4.2	4.3
4-Hydroxybenzoyl	λ_{max} (nm)	374	374	429	442	372[b]
	$\varepsilon_{max} \cdot 10^4$	4.9	4.8	4.1	4.0	4.4
3-Nicotinyl	λ_{max} (nm)	364	363	384	365	364
	$\varepsilon_{max} \cdot 10^4$	3.1	3.3	2.2	3.0	3.0
4-Nicotinyl	λ_{max} (nm)	355	354	380	366	366
	$\varepsilon_{max} \cdot 10^4$	2.4	2.4	1.7	2.2	2.2

[a] Aroylhydrazone concentrations 20 μ*M*, in 10 m*M* NaOH.

[b] Shoulders in spectra above 400 nm.

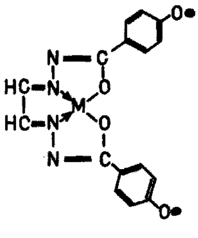
All aroylhydrazones of the glyoxal derivatives that were studied were found to give a visible color reaction with calcium and cadmium in alkali. Table III shows results obtained with partly purified preparations of a number of these reagents, in 10 m*M* sodium hydroxide with a 5–100-fold excess of cation. These preliminary results suggest that the 4-hydroxybenzoyl derivatives form especially useful chelates; some of the reagents, notably the nicotinyl ones, seemed to be unstable, especially to light.

Purified preparations were made for the 2-hydroxybenzoyl, 4-aminobenzoyl and 2-furoyl derivatives. The 2-hydroxybenzoyl derivatives were quite unlike the 4-hydroxy derivatives, and at the levels of cation used previously no effect was produced, although excess of calcium, cadmium or lanthanum did lead to a visible color. The glyoxal and dimethylglyoxal bis(4-aminobenzoylhydrazones) were less soluble in alkali than the 4-hydroxy derivatives. They gave intensely colored and fluorescent chelates, and the selectivity appeared similar to that of the 4-hydroxybenzoylhydrazones (Table III). The 2-furoyl derivatives were also similar reagents but rather less sensitive and with absorbance maxima at shorter wavelengths. With 1 m*M* dimethylglyoxal bis(2-furoylhydrazone) in 10 m*M* alkali, most cations gave apparent absorbance maxima in the 415–420 nm region (read against reagent). The molar absorptivity with calcium was $1.1 \cdot 10^4$, with magnesium about $0.7 \cdot 10^4$, and with cadmium and lanthanum $2.5\text{–}2.6 \cdot 10^4$. The bismuth(III) peak was at 444 nm, with a molar absorptivity of $1.3 \cdot 10^4$. These furoyl derivatives were also fluorescent.

Crude preparations of the derivatives made from thiophene-2-carboxylic acid hydrazide also gave visible color responses with calcium and cadmium. Visible color reactions were also obtained with benzil bis(4-hydroxybenzoylhydrazone) and with the red product formed between ninhydrin and 4-hydroxybenzoic acid hydrazide in acid solution. Attempts to prepare acylhydrazones which gave visible color reactions were not successful.

DISCUSSION

The reactions between cations and the bis-aroylhydrazones of α-diketones were observed because calcium in biological materials increased the sensitivity of methods of glucose determination which depend upon the formation of these hydrazones[1,2]. No attempt was made to isolate the chelates. In Fig. 1, differences between the maximal absorbances in the presence of 20 m*M* calcium (Fig. 1B) and the absorbances at the same wavelength in the presence of 100 μ*M* calcium (Fig. 1C) correspond to the differences at the maxima for ligands without calcium (Figs. 1A and 1B) in a manner consistent with the formation of a 1:1 chelate, although with excess of ligand other ratios may occur. The two carbonyl oxygens and the two nitrogens further from these seem to be suitably separated to give a quadridentate ligand B, and if the amide hydrogen atom is removed to form the anion, the intense absorbance of the chelates is readily understood.



B

A comprehensive study of potential analytical applications is not being undertaken because, of the cations which give favorable responses, only calcium is of major concern to this laboratory. This preliminary work establishes that ligands belonging to this class could be used in the colorimetric and fluorimetric analysis of calcium, cadmium, lanthanum and bismuth.

Only three α-diketones and a relatively few acid hydrazides were examined, and among the possible combinations it is probable that some valuable analytical reagents remain to be found. Furthermore, mixtures of the aroylhydrazones of glyoxal and methylglyoxal can be prepared by the reaction between aromatic acid hydrazides and carbohydrates in aqueous alkali[3], and these inexpensive mixtures could be satisfactory reagents for cation determination in automated continuous flow systems.

SUMMARY

The bis(4-hydroxybenzoylhydrazones) of glyoxal, methylglyoxal and dimethylglyoxal form colored chelates with Ca^{2+}, Cd^{2+}, La^{3+}, a Bi(III) species and other cations. The glyoxal derivative shows more selective reactions, and highly selective assays are possible for calcium and cadmium in the presence of cyanide and citrate, respectively; Beer's law was obeyed in the range 0–50 m*M* for both cations. The chelates were also fluorescent, the reaction for lanthanum being particularly sensitive. The formation of this type of chelate is a general property of the bis-aroylhydrazones of α-diketones.

RÉSUMÉ

Les bis(4-hydroxybenzoylhydrazones) de glyoxal, de méthylglyoxal et de diméthylglyoxal forment des chélates colorés avec les cations, en particulier Ca^{2+}, Cd^{2+}, La^{3+} et le bismuth(III). Le dérivé glyoxal donne une réaction très sélective avec le calcium et le cadmium, en présence de cyanure et de citrate, respectivement. La loi de Beer s'applique de 0 à 50 m*M* pour les deux cations. Les chélates sont aussi fluorescents; la réaction du lanthane est particulièrement sensible. La formation de ce type de chélate est une propriété générale des bis-aroylhydrazones des α-dicétones.

ZUSAMMENFASSUNG

Die Bis(4-hydroxybenzoylhydrazone) von Glyoxal, Methylglyoxal und Dimethylglyoxal bilden gefärbte Komplexe mit Ca^{2+}, Cd^{2+}, La^{3+}, einer Wismut(III)-Spezies und anderen Kationen. Die Glyoxal-Derivate ergeben Reaktionen grösserer Selektivität, und hochselektive Bestimmungen sind möglich bei Calcium und Cadmium in Gegenwart von Cyanid bzw. Citrat; das Beersche Gesetz ist bei beiden Kationen im Bereich 0–50 m*M* erfüllt. Die Chelate zeigten auch eine Fluoreszenz, wobei die Reaktion bei Lanthan besonders empfindlich ist. Die Bildung von Chelaten dieser Art ist eine allgemeine Eigenschaft der Bisaroylhydrazone von α-Diketonen.

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EXTRAKTION UND PHOTOMETRISCHE BESTIMMUNG VON ZINN UND BLEI MIT 2-(*o*-HYDROXYPHENYL)BENZTHIAZOLIN

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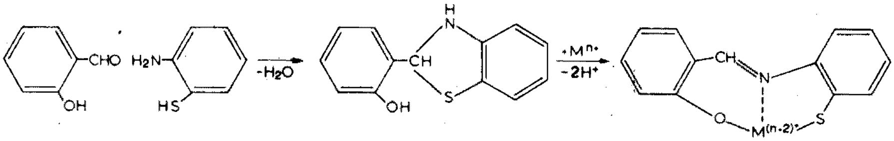
(Eingegangen den 12. Dezember 1972)

Bei der Kondensation von Salicylaldehyd mit *o*-Aminothiophenol wird an Stelle der erwarteten Schiffschen Base Salicylidenamino-2-thiophenol 2-(*o*-Hydroxyphenyl)benzthiazolin erhalten, welches aber mit thiophilen Metallionen leicht in die Metallchelate der Schiffschen Base übergeht[1–3].



Extrahierbarkeit und Farbigkeit der gebildeten Chelate ermöglichen den Einsatz des 2-(*o*-Hydroxyphenyl)benzthiazolins in der photometrischen Metallanalyse. So wird über die Verwendung der vermeintlichen Schiffschen Base aus Salicylaldehyd und *o*-Aminothiophenol zur extraktionsphotometrischen Zinnbestimmung in Gesteinen und Mineralien[4], sowie in Eisenlegierungen[5] berichtet. Über das komplexchemische Verhalten des Reagens und die daraus resultierenden Störeinflüsse für die Metallextraktion fehlen jedoch nähere Angaben, ausserdem ist die Anwendung der Methode nur für einen relativ kleinen Konzentrationsbereich[4] beschrieben. Deshalb wurde die Extraktion ausgewählter Metallionen mit Hilfe des potentiellen Komplexbildners 2-(*o*-Hydroxyphenyl)benzthiazolin und seine Anwendbarkeit zur extraktionsphotometrischen Bestimmung von Zinn und Blei ausführlich untersucht.

EXPERIMENTELLES

Reagenzien und Geräte

2-(*o*-Hydroxyphenyl)benzthiazolin vom Schmelzpunkt 132–133° wurde nach einer modifizierten Vorschrift[7] durch Kondensation von Salicylaldehyd mit 2-Aminothiophenol synthetisiert. Zur Darstellung von Bis(salicylidenamino-2-thiophenolato)-zinn(IV) wurden 1.04 g $SnCl_2 \cdot H_2O$ (0.005 mol) in 50 ml Eisessig gelöst und langsam zu einer mässig siedenden Lösung von 2.3 g 2-(*o*-Hydroxyphenyl)benzthiazolin (0.01 mol) in 100 ml Methanol gegeben. Die gelborange Lösung blieb bis zur Kristallisation des Komplexes am Sieden, danach wurde noch heiss abgesaugt und mit warmem Methanol gewaschen. Die Ausbeute betrug 1.8 bis 2 g.

Zur Durchführung der photometrischen Messungen dienten Spektralphotometer VSU 1 und Spektralkolorimeter "Spekol" mit Zusatzverstärker vom VEB Carl Zeiss, Jena.

Bestimmung der Extraktionskurven

2-(*o*-Hydroxyphenyl)benzthiazolin kam als $8.6 \cdot 10^{-3}$ *M* Lösung zum Einsatz. Die Reagenslösung wurde aus 0.2 g des Benzthiazolins, 1 g Ascorbinsäure und 100 ml Äthanol bereitet. Zur Untersuchung der pH-Abhängigkeit der Metallextraktion dienten im sauren bis neutralen Bereich Natriumacetat–Salzsäure-Puffer, im alkalischen Bereich Borax-Puffer. Die Metallionenkonzentration wurde mit wässrigen 10^{-3} *M* Lösungen der entsprechenden Metallnitrate oder -halogenide eingestellt. Als Extraktionsmittel kam ausschliesslich Toluol zum Einsatz.

Zusammensetzung des Zinn- und Bleikomplexes in Lösung

Als Zinn-Stammlösung diente eine 10^{-3} *M* Zinn(II)-chlorid-Lösung in 80 %igem Methanol, die 0.15 *M* an Salzsäure war. Das Reagens kam als 10^{-3} *M* Lösung ebenfalls in 80 %igem Methanol zur Anwendung. Für die Messung wurde eine entsprechende Menge (x) der Zinnlösung in einem 50 ml Masskolben mit 30 ml 80 %igem Methanol verdünnt, ($5x$) ml Reagenslösung zugegeben und mit 0.1 *M* methanolischer Kalilauge (80% Methanol) neutralisiert. Zur Neutralisation wurden pro ml Zinnlösung 1.5 ml Kalilauge benötigt. Die Extinktion der Lösung wurde 10 Min nach dem Auffüllen bis zur Eichmarke gegen das Lösungsmittel gemessen ($d = 1$ cm).

Zur Aufnahme der Molar-Verhältnis Kurven wurde je 1 ml der Metallsalzlösung in verschiedenen Proben mit 0.2 bis 5 ml der Ligandenlösung gemischt und nach Zusatz von Pufferlösung auf 8 ml aufgefüllt. Die verwendete Zinnlösung musste vor der Messung mit 1.5 ml 0.1 *M* methanolischer Kalilauge neutralisiert werden. Die Messung der Extinktion erfolgte bei $d = 1$ cm, im Falle des Zinns bei $d = 0.5$ cm.

Bei der Neigungsverhältnismethode wurden zu 1 ml konstanter Komponente (Metallsalzlösung oder Reagenslösung) steigende Mengen (0.2 bis 5 ml) der variablen Komponente (Reagenslösung bzw. Metallsalzlösung) gegeben, nach Zusatz von Pufferlösung im Masskolben mit Lösungsmittel auf Marke aufgefüllt, und schliesslich die Extinktion in gewohnter Weise bestimmt.

Reagenslösungen zur Zinnbestimmung

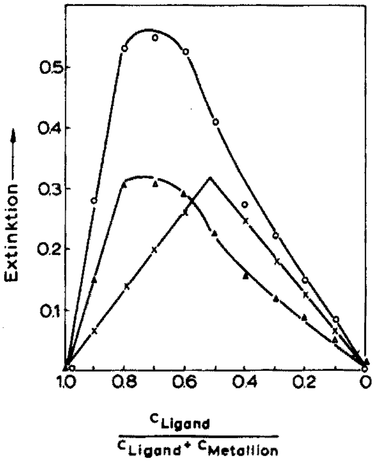
Zur Zinnbestimmung diente, wie bereits beschrieben, eine $8.6 \cdot 10^{-3}$ *M* Lösung von 2-(*o*-Hydroxyphenyl)benzthiazolin in Äthanol, die durch Zusatz von Ascorbinsäure stabilisiert war. Die Testung des Analyseverfahrens wurde mit einer $0.17 \cdot 10^{-3}$ *M* Zinn(II)-chlorid-Stammlösung durchgeführt, die 2 %ig an Salzsäure war.

Milchsäure wurde in Form einer 20 %igen Lösung verwendet. Als Pufferlösung kam der Natriumacetat–Salzsäure-Puffer nach Walpole vom pH = 2.25 zum Einsatz.

ZUSAMMENSETZUNG DES ZINN-, BLEI- UND ZINKKOMPLEXES

Als potentiell dreizähliger Ligand bildet 2-(*o*-Hydroxyphenyl)benzthiazolin mit Nickel 1:1 Komplexe[6, 7] und mit Kobalt 2:1 Komplexe[7]. Beim Zinn könnten in Lösung 1:1 Komplexe des Zinn(II) oder 2:1 Komplexe von Zinn(IV) vorliegen. Bei der Extraktion wird jedoch unabhängig von der Oxydationsstufe des Zinns in der Stammlösung immer der gleiche Komplex beobachtet. Die Zusammensetzung dieses Komplexes wurde nach der Jobschen Methode untersucht. Aus der graphischen Darstellung der Messergebnisse (Fig. 1) kann keine eindeutige Aussage über die Zusammensetzung des Chelats gemacht werden. Qualitativ ist aus der Form des Jobschen Diagramms zu entnehmen, dass der Zinnkomplex wahrscheinlich relativ instabil ist und die Methode deshalb versagt. In Übereinstimmung damit steht die Feststellung, dass bei der extraktionsphotometrischen Zinnbestimmung mit einem grösseren Reagensüberschuss gearbeitet werden muss[4]. Für den Zinkkomplex (vgl. Fig. 1), bei Extraktion mit Toluol, liefert die Methode in Übereinstimmung mit der kristallinen Substanz[3] eindeutig die Zusammensetzung 1:1. Die Jobsche Kurve wurde unter Zusatz eines konstanten Überschusses (10 fach) an Amin aufgenommen, da das Zinckchelat bei Abwesenheit von Amin nur sehr wenig löslich ist. Über die Nutzung dieses Effektes für eine photometrische Zinkbestimmung wurde kürzlich berichtet[8], jedoch wird dieses Bestimmungsverfahren durch wichtige Begleitelemente des Zinks wie Cadmium, Eisen, Kupfer, Kobalt und Nickel gestört.

Zur Ermittlung des Metall–Ligand-Verhältnisses im Zinn- und Bleichelat kamen weiterhin die Molar-Verhältnis- und die Neigungsverhältnis-Methode zur Anwendung. Bei der Molar-Verhältnis-Methode bleibt in üblicher Weise die Metallionenkonzentration konstant, während die des Liganden stufenweise erhöht wird. Aus der graphischen Darstellung der gemessenen Extinktionen gegen das Metall–Ligand-Verhältnis kann am Knickpunkt die Zusammensetzung des in der Lösung vorliegenden Komplexes abgelesen werden. Die erhaltenen Ergebnisse sind in Fig. 2 wiedergegeben. Danach liegen in den Lösungen Salicylidenamino-2-thiophenolato–blei und Bis(salicylidenamino-2-thiophenolato)–zinn vor. Durch die Neigungsver-



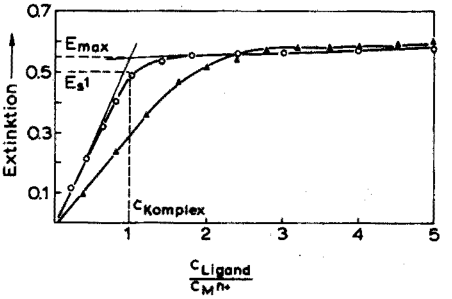


Fig. 1. Zusammensetzung des Zinn- und Zinkkomplexes mit Salicylidenamino-2-thiophenol nach Job. (×) Zn, 420 nm; (○) Sn, 410 nm; (△) Sn, 450 nm.

Fig. 2. Molar-Verhältniskurven für den Zinn- (△) und Bleikomplex (○) von Salicylidenamino-2-thiophenol. pH = 6.86; Metallionenkonzentration $1.25 \cdot 10^{-4}$ M; $\lambda = 410$ nm; $d = 1$ cm (Pb); $d = 0.5$ cm (Sn).

hältnis-Methode[9] fanden diese Ergebnisse eine weitere Bestätigung. Für die Komplexbildungsreaktion

$$m\mathrm{A} + n\mathrm{B} \rightleftharpoons \mathrm{A}_m\mathrm{B}_n$$

kann nach diesem Verfahren bei grossem Überschuss einer komplexbildenden Komponente die Dissoziation des Komplexes vernachlässigt und für die Gesamtkonzentration C_A und C_B

$$C_\mathrm{A} = [\mathrm{A}] + m[\mathrm{A}_m\mathrm{B}_n] \quad \text{oder} \quad C_\mathrm{A} = m[\mathrm{A}_m\mathrm{B}_n] \text{ für } C_\mathrm{B} \gg C_\mathrm{A}$$
$$C_\mathrm{B} = [\mathrm{B}] + n\,[\mathrm{A}_m\mathrm{B}_n] \quad \text{oder} \quad C_\mathrm{B} = n\,[\mathrm{A}_m\mathrm{B}_n] \text{ für } C_\mathrm{A} \gg C_\mathrm{B}$$

gesetzt werden. Die Gleichgewichtskonzentration $[\mathrm{A}_m\mathrm{B}_n]$ ist unter diesen Bedingungen nur noch eine Funktion der jeweiligen variablen Konzentration C_A bzw. C_B

$$[\mathrm{A}_m\mathrm{B}_n] = C_\mathrm{A}/m \qquad [\mathrm{A}_m\mathrm{B}_n] = C_\mathrm{B}/n$$

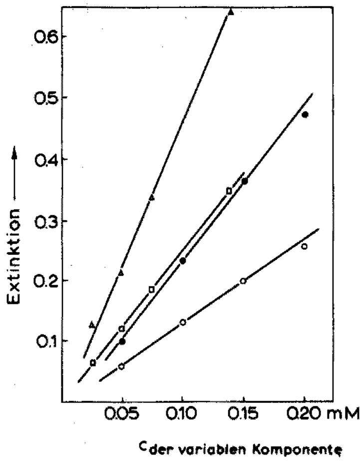
Gleiches gilt für die Extinktionen, die sich aus dem Extinktionsbeitrag des gebildeten Komplexes und aus einem konstanten Anteil der jeweiligen Überschusskomponente zusammensetzen. Trägt man die Extinktion als Funktion der variablen Konzentration auf, werden Geraden mit den Steigungen

$$s_1 = \varepsilon_{\mathrm{Komplex}} \cdot d/m \qquad s_2 = \varepsilon_{\mathrm{Komplex}} \cdot d/n$$

erhalten.

Aus dem Verhältnis der Steigungen (Neigungsverhältnis) $s_1 : s_2$ kann die Komplexzusammensetzung direkt bestimmt werden.

Wie die Auswertung zeigt, kann die beschriebene Methode sehr gut auf die



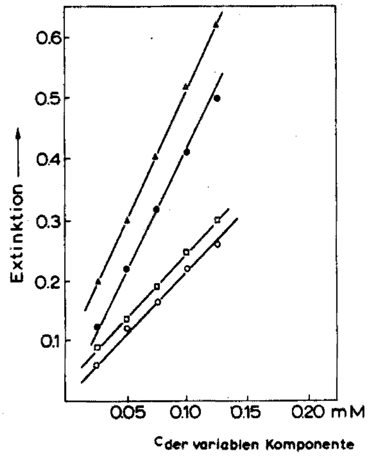


Fig. 3. Bestimmung des Zinn–Ligand-Verhältnisses im Salicylidenamino-2-thiophenolchelat nach der Neigungsverhältnismethode. (△, □) Variable Metallionenkonzentration; (○, ●) variable Ligandenkonzentration. (△) s_1, 410 nm; (□) s_1, 450 nm; (●) s_2, 410 nm; (○) s_2, 450 nm.

Fig. 4. Bestimmung des Blei–Ligand-Verhältnisses im Salicylidenamino-2-thiophenolchelat nach der Neigungsverhältnismethode. (△, □) Variable Metallionenkonzentration; (○, ●) variable Ligandenkonzentration. (△) s_1, 410 nm; (□) s_1, 450 nm; (●) s_2, 410 nm; (○) s_2, 450 nm.

interessierenden Chelate angewendet werden. Die Ergebnisse sind eindeutig. Für den Zinnkomplex (Fig. 3) werden die Verhältnisse

$$m:n = 1.3:2.5 = 1:1.9 \quad (\lambda = 410\ \text{nm})$$

$$m:n = 0.7:1.43 = 1:2.04 \quad (\lambda = 450\ \text{nm})$$

gefunden. Für das Bleichelat bestätigen die mit $m:n = 1:1$ (Fig. 4) parallel verlaufenden Geraden das Ergebnis der Molar-Verhältnis-Methode.

Der Bis(salicylidenamino-2-thiophenolato)–zinn-Komplex kann auch in Substanz dargestellt werden[3,4], ein Hinweis auf die Oxydationsstufe des Zinns ist jedoch dadurch nicht zu erhalten, da zunächst nicht bekannt ist, ob alle funktionellen Gruppen des Liganden bei der Komplexbildung beansprucht werden. Für den analogen Quecsilberkomplex Bis(salicylidenamino-2-thiophenolato)–quecksilber-(II) ist beispielsweise eine vorwiegend merkaptidartige Bindung anzunehmen[3]. Die Oxydationsstufe des Zinns wurde schliesslich mit Hilfe der Mössbauer-Spektroskopie ermittelt[10]. Die gemessene Isomerieverschiebung δ von 0.602 mm s^{-1} weist eindeutig das Vorliegen eines Zinn(IV)-Chelates mit beträchtlichen Kovalenzanteilen aus. Die relativ grosse Quadrupolaufspaltung ΔQ von 0.599 mm s^{-1} spricht für eine starke tetragonale Verzerrung des Komplexes. Die gemessene Linienbreite Γ betrug 1.04 mm s^{-1}.

METALLEXTRAKTION MIT 2-(*o*-HYDROXYPHENYL)BENZTHIAZOLIN

Die pH-Abhängigkeit der Extraktion einer Reihe von Metallen ist in Fig. 5 wiedergegeben. Aus den Kurven wird deutlich, dass für Zinn und Blei eine selektivere Bestimmungsmöglichkeit als für die übrigen Metalle erwartet werden kann. Bei dem für die Zinnextraktion günstigen pH-Wert um 2 ist bis auf Kupfer(II) noch keine Reaktion mit den übrigen Metallkationen zu befürchten, während bei pH 10.8 (Maximum der Bleiextraktion) bereits die Reextraktion der übrigen Metalle einsetzt. Ausserdem liegen die Schüttelzeiten für die quantitative Extraktion von Zinn und Blei (1 Min) niedriger als die für Kupfer (8 Min), Nickel (10 Min) und Kobalt (7 Min). Zink und Cadmium sind ohne Zusatz von Aminen nur schwierig extrahierbar.

Zinn ist ebenfalls nicht durch direkte Extraktion, d.h. durch das in der organischen Phase gelöste Reagens, abzutrennen. Hier erfolgt zunächst die Fällung des Zinnchelates in feinverteilter Form aus der wässrigen Phase und erst anschliessend wird mit Toluol extrahiert.

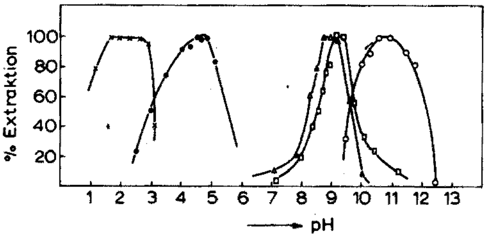


Fig. 5. pH-Abhängigkeit der Metallextraktion mit 2-(*o*-Hydroxyphenyl)benzthiazolin. (×) Zinn, (●) Kupfer, (○) Blei, (□) Nickel, (△) Kobalt.

Zur quantitativen Extraktion von Kupfer, Kobalt, Blei, sowie von Nickel und Zink in Gegenwart von Aminen, ist bereits ein geringer Ligandenüberschuss ausreichend, beim Zinn wird dagegen ein 40 facher Überschuss erforderlich.

Ein Nachteil des 2-(*o*-Hydroxyphenyl)benzthiazolins ist seine geringe Haltbarkeit in Lösung, die in der Oxydationsanfälligkeit begründet ist. Da jedoch grösserer Reagensüberschuss die Extraktion der Metalle nicht stört, kann dadurch über einige Zeit der durch Oxydation unwirksam gewordene Teil des Reagens kompensiert werden. Die Änderung der Eigenabsorption der Ligandenlösung wird durch eine entsprechende Blindprobe ausgeglichen. Untersuchungen am Beispiel der Zinnextraktion in Abhängigkeit vom Alter der Reagenslösung (s. Tabelle I) zeigen eine gute Reproduzierbarkeit der Werte innerhalb von 4 Stunden. Im festen Zustand ist das Reagens über längere Zeit haltbar.

TABELLE I

ABHÄNGIGKEIT DER ZINNBESTIMMUNG VON DER BESTÄNDIGKEIT DER REAGENSLÖSUNG DES 2-(*o*-HYDROXYPHENYL)BENZTHIAZOLINS

($\lambda = 415$ nm, Molverhältnis Zinn:Reagens = 1:40)

t (min)	*Extinktion der Reagenslösung*	*Extinktion des Zinnkomplexes*
0[a]	0.082	0.487
30	0.097	0.486
45	0.108	0.485
60	0.112	0.486
120	0.115	0.482
180	0.122	0.488
240	0.130	0.487
300	0.159	0.433

[a] Unmittelbar nach Auflösen des Reagens.

Arbeitsvorschrift zur Zinnbestimmung

Die stark saure Probelösung (10 ml) wird in einem Schütteltrichter mit 5 ml bidestilliertem Wasser, sowie 2 ml Milchsäure, versetzt und mit 2.5 *M* Natronlauge unter Kontrolle am pH-Meter auf pH 2–2.5 gebracht. Bei der Testung des Verfahrens waren dazu entsprechend der Säurekonzentration der Zinn-Standard-Lösung stets 1.35 ml 2.5 *M* Natronlauge erforderlich. Nach Zugabe von 5 ml Pufferlösung (Natriumacetat–Salzsäure-Puffer nach Walpole) fügt man 5 ml Reagenslösung zu, schüttelt kurz durch und extrahiert den feinverteilten Niederschlag nach 15 minütiger Wartezeit mit genau 10 ml Toluol. Nach der Phasentrennung wird die organische Phase mit einer Tropfpipette in die Messküvette ($d = 0.5$ cm) überführt und die Extinktion bei 415 nm gegen eine in gleicher Weise zubereitete Blindlösung gemessen.

Die Testung des Verfahrens wurde in zwei Arbeitsbereichen nach der von Gottschalk[11] angegebenen Methode durchgeführt. Das Lambert–Beersche Gesetz ist in den getesteten Bereichen erfüllt. Einige Kenngrössen der Methode sind in den Tabellen II und III enthalten.

TABELLE II

KENNGRÖSSEN FÜR DIE PHOTOMETRISCHE ZINNBESTIMMUNG IM BEREICH 0.117–1.17 μmol cm^{-3}

Extinktionskoeffizient	ε	17.043 cm^2 μmol^{-1}
Standardabweichung	S	±0.00059 μmol cm^{-3}
Variationskoeffizient	V	±(0.51–5.06) Rel.%
Fehlerbereiche	T(S = 99%)	±0.00167 μmol cm^{-3}
	T(S = 99.9%)	±0.00225 μmol cm^{-3}
Bestimmungsgrenze	b_N	0.0032 μmol cm^{-3}

TABELLE III

KENNGRÖSSEN FÜR DIE PHOTOMETRISCHE ZINNBESTIMMUNG IM BEREICH 0.021–0.210 μmol cm^{-3}

Extinktionskoeffizient	ε	16.416 cm^2 μmol^{-1}
Standardabweichung	S	±0.00028 μmol cm^{-3}
Variationskoeffizient	V	±(1.32–13.2) Rel.%
Fehlerbereiche	T(S = 99%)	±0.000786 μmol cm^{-3}
	T(S = 99.9%)	±0.001057 μmol cm^{-3}
Bestimmungsgrenze	b_N	0.00149 μmol cm^{-3}

Einfluss von Fremdionen auf die Zinnbestimmung

Die Fremdionentestung erfolgte im Bereich 0.117 μmol cm^{-3} Zinn. Zur Ermittlung der Störgrenzen wurden vor der Zinnbestimmung wechselnde Mengen an Störionen zugesetzt. Ein Fremdion stört, wenn das Analysenergebnis ausserhalb des absoluten Fehlerbereiches T(S = 99.0%) liegt. In diesem Fall muss durch Zusatz von Maskierungsmitteln oder Variation der Extraktionsbedingungen eine Veränderung des Grundverfahrens angestrebt werden.

Eine grosse Anzahl von Metallionen stört bereits ohne Zusatz von Tarnreagenzien bis zum 1000 fachen Überschuss die Zinnbestimmung nicht. Bei Anwesenheit von Thallium, Blei, Silber und Cadmium empfiehlt es sich, ab 1000 fachen Überschuss Hilfskomplexbildner zu verwenden, um Niederschlagsbildung zu vermeiden.

Erhebliche Störungen werden durch Wismut, Kupfer, Eisen, Kobalt und Quecksilber hervorgerufen.

Wismut kann bis zum 10 fachen Überschuss mit Thioharnstoff maskiert werden, grössere Mengen fallen in herrschenden Milieu als Oxidchlorid aus und reissen dabei Zinn aus der Lösung mit. Kupfer kann ebenfalls nur bis zum 10 fachen Überschuss mit Thioharnstoff unschädlich gemacht werden. Thiosemicarbazid maskiert Zinn und Kupfer, Thiosulfat verursacht störende Niederschläge. Verschiedene andere Maskierungsmittel wie Salicylaldoxim, 2-Merkaptopropanol und Thiocyanat brachten ebenfalls keine Erfolge. Kaliumcyanid scheidet als Tarnreagens im sauren Milieu aus.

Die Maskierung von Eisen gelingt hervorragend mit Thiosulfat, da Eisen(III) in die zweiwertige Stufe überführt wird, welche mit dem Reagens keine störende Reaktion zeigt.

Störungen durch Kobalt lassen sich ebenfalls durch Maskierung mit Thiosulfat und Waschen der organischen Phase nach der Extraktion mit 0.1 *M* EDTA bis zum 1000 fachen Überschuss beseitigen.

Quecksilber wird bis zum 100 fachen Überschuss durch Thioharnstoff und Thiosulfat maskiert.

Für die untersuchten Metallionen können folgende Störungen angegeben werden:

10 000 b_0: Mn^{2+}, Zn^{2+}, Ni^{2+}
1 000 b_0: Fe^{3+}, Co^{2+}, Cr^{3+}, Al^{3+}, Sb^{3+}, Pb^{2+}, Tl^{2+}, Ag^{+}, Cd^{2+}
100 b_0: Hg^{2+}, CrO_4^{2-}
10 b_0: Cu^{2+}, Bi^{3+}, Pt^{2+}

Durch komplexbildende Anionen wie Jodid, Citrat, Thioglykolat, Tartrat (in hoher Konzentration) und Äthylendiamintetraacetat wird die Bestimmung blockiert.

Anwendung von 2-(o-Hydroxyphenyl)benzthiazolin zur Bestimmung von Blei

Blei wird durch 2-(*o*-Hydroxyphenyl)benzthiazolin aus alkalischer Lösung extrahiert (Fig. 5) und kann auf diese Weise extraktionsphotometrisch bestimmt werden. Zur Durchführung der Analyse werden 5 ml der neutralen Probelösung mit 2 ml einer $2 \cdot 10^{-3}$ *M* Ammoniumtartratlösung versetzt und anschliessend mit 5 ml Borax–Natronlauge-Puffer ein pH-Wert von etwa 10.7 eingestellt. Man ergänzt das Volumen mit Wasser auf 15 ml und extrahiert dann mit einer $2 \cdot 10^{-3}$ *M* Reagenslösung in Toluol. Nach einer Schüttelzeit von 1 min wird bei 410 nm gegen eine entsprechende Blindlösung gemessen. Einige Kenngrössen für die Bleibestimmung sind in Tabelle IV zusammengestellt. Das Lambert–Beersche Gesetz ist im angegebenen Bereich streng erfüllt.

TABELLE IV

KENNGRÖSSEN[11] FÜR DIE PHOTOMETRISCHE BLEIBESTIMMUNG IM BEREICH 0.03–0.3 μmol cm^{-3}

Extinktionskoeffizient	ε	3.80 cm^2 μmol^{-1}
Standardabweichung	S	0.0038 μmol cm^{-3}
Variationskoeffizient	V	±(0.37–3.7) Rel.%
Fehlerbereiche	T(S = 99%)	0.008 μmol cm^{-3}
	T(S = 99.9%)	0.0145 μmol cm^{-3}
Bestimmungsgrenze	b_N	0.015 μmol cm^{-3}

Zur Maskierung von Störionen, die mit 2-(*o*-Hydroxyphenyl)benzthiazolin ebenfalls extrahierbare Chelate bilden, wurde Cyanid in Aussicht genommen. Die Untersuchung ergab jedoch, dass überschüssiges Cyanid mit dem Reagens selbst hellgelbe Lösungen bildet und so Fehlresultate verursacht. Ausserdem zeigen die gemessenen Extinktionswerte eine starke Zeitabhängigkeit. Es ist aber möglich den nach erfolgter Maskierung von Übergangsmetallionen verbleibenden Cyanidüberschuss mit Formaldehydlösung zu beseitigen[12,13] und so die Bleibestimmung auch neben einem 100 fachen Überschuss an Kupfer, Silber, Nickel, Kobalt und Eisen durchzuführen. Zink und Cadmium im gleichen Überschuss verursachen zu niedrige

Analysenergebnisse, Quecksilber stört auch in Gegenwart von Cyanid. Grössere Mengen Wismut können nicht mit Tartrat in Lösung gehalten werden und behindern die Extraktion des Bleis durch Niederschlagsbildung.

Dem VEB Laborchemie Apolda danken wir für gute Zusammenarbeit und grosszügige Unterstützung.

ZUSAMMENFASSUNG

Bei der Reaktion von 2-(*o*-Hydroxyphenyl)benzthiazolin mit Zinn(II)-ionen wird Bis(salicylidenamino-2-thiophenolato)–zinn(IV), mit Blei(II)-ionen (Salicylidenamino-2-thiophenolato)–blei(II), gebildet. Die Zusammensetzung der Komplexe in Lösung wurde nach der Molar-Verhältnis- und der Neigungsverhältnis-Methode bestimmt, die Oxydationsstufe des Zinns mit Hilfe der Mössbauer-Spektroskopie ermittelt. Beide Komplexe können zur extraktions-photometrischen Metallspurenanalyse genutzt werden. Der Störeinfluss zahlreicher Fremdionen wurde untersucht und Arbeitsvorschriften zur Zinn- und Bleibestimmung ausgearbeitet.

SUMMARY

The reaction of 2-(*o*-hydroxyphenyl)benzthiazoline with tin(II) gives bis-(salicylidenamino-2-thiophenolato)–tin(IV); with lead(II), (salicylidenamino-2-thiophenolato)–lead(II) is formed. The composition of the complexes in solution was determined by the molar ratio, and the gradient ratio methods; the oxidation state of tin was proved by the use of Mössbauer spectroscopy. Both complexes are suitable for the extraction-photometric determination of traces of these metals. The effects of many diverse ions were examined and procedures are given for the determination of tin and lead.

RÉSUMÉ

La réaction de la 2-(*o*-hydroxyphényl)-benzthiazoline avec étain(II) conduit à la formation de bis(salicylidènamino-2-thiophénolato)–étain(IV); avec le plomb-(II), on obtient le (salicylidènamino-2-thiophénolato)–plomb(II). L'état d'oxydation de l'étain a été déterminé par spectroscopie Mössbauer. Ces deux complexes conviennent pour un dosage photométrique, par extraction de ces métaux à l'état de traces. On examine l'influence de divers ions. Des procédés sont décrits pour le dosage de l'étain et du plomb.

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EXTRACTION-PHOTOMETRIC DETERMINATION OF URANIUM(IV) WITH CHLOROPHOSPHONAZO-III

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Chlorophosphonazo-III (2,7-bis(4-chloro-2-phosphonobenzene)-1,8-dihydroxynaphthalene-3,6-disulfonic acid) has been used for the spectrophotometric determination of many elements, including thorium[1,2] and uranium[3–6]. For the determination of uranium, the complex with hexavalent uranium has been utilized. Nemodruk *et al.*[3] reported that uranium(VI) can be determined at pH 1.0. Luk'yanov *et al.*[4] recommended 2.5–3.5 *M* hydrochloric acid for the determination of uranium(VI). Guertler *et al.*[5] proposed an extraction-spectrophotometric determination based on the extraction of the uranium(VI) complex with benzyl alcohol from dilute hydrochloric or nitric acid solution.

The present paper describes the behavior of the complex of tetravalent uranium with chlorophosphonazo-III and a new extraction-spectrophotometric method for uranium. The method is based on the fact that the chlorophosphonazo-III complex can be extracted with water-immiscible alcohol and that the absorbance in the organic phase increases remarkably compared with that in hydrochloric acid solution. The thorium complex also behaves similarly and has been utilized for the determination of thorium[2]. The sensitivity of the proposed method is much the same as that of the arsenazo-III method[7]; the molar absorptivity is over 10^5 l mole^{-1} cm^{-1}.

EXPERIMENTAL

Reagent and apparatus

Standard uranium solution. After heating U_3O_8 (National Bureau of Standards, Standard sample 950a) at 850° for 2 h, 0.236 g of U_3O_8 was dissolved in 20 ml of concentrated nitric acid and the solution was evaporated to dryness. The residue was dissolved in concentrated hydrochloric acid, and the solution was evaporated to dryness. The addition of hydrochloric acid and evaporation was repeated twice more to remove nitrate ion. The residue was finally dissolved in 200 ml of 0.1 *M* hydrochloric acid. Solutions containing 4 and 10 μg U ml^{-1} were prepared by dilution with 0.1 *M* hydrochloric acid.

Chlorophosphonazo-III (Dojindo Co., Kumamoto-shi) was used without further purification. 3-Methyl-1-butanol and other reagents were of analytical-reagent grade.

Absorbance measurements were made in 1-cm cells with a Shimadzu QV-50 spectrophotometer. An Iwaki Model KM shaker was used.

Recommended procedure

Place a sample containing 1–12 μg of uranium in a 50-ml conical beaker. Evaporate to dryness and dissolve the residue in 15 ml of 8 *M* hydrochloric acid. Add 1 g of zinc metal powder and cover with a watch glass. After the zinc has been dissolved, transfer the solution to a 100-ml separatory funnel and dilute to about 50 ml with water. Add 1 ml of aqueous 0.04% chlorophosphonazo-III solution and mix. Add exactly 10 ml of 3-methyl-1-butanol and shake for 2 min. Remove the aqueous phase, transfer the organic phase to an Erlenmeyer flask containing about 1 g of anhydrous sodium sulfate, and swirl to remove droplets of water. Measure the absorbance of the clear organic phase at 673 nm against a reagent blank as the reference. Obtain the quantity of uranium from a calibration curve, which has been prepared with known amounts (1–12 μg) of uranium.

RESULTS AND DISCUSSION

Absorption spectra

The chlorophosphonazo-III complexes of actinides (Th, U) show a green color in 3-methyl-1-butanol. Both uranium(IV) and uranium(VI) complexes have two absorption peaks (Fig. 1). The peaks occur at 625 and 673 nm for uranium(IV) and at 620 and 668 nm for uranium(VI). In 1–3 *M* hydrochloric acid, the uranium(IV) complex[6] has two peaks at 630 and 688 nm, and the uranium(VI) complex[4,6] at 620 and 670 nm. The peaks in 3-methyl-1-butanol shift to a shorter wavelength and the absorbance is much higher than that in the hydrochloric acid solution.

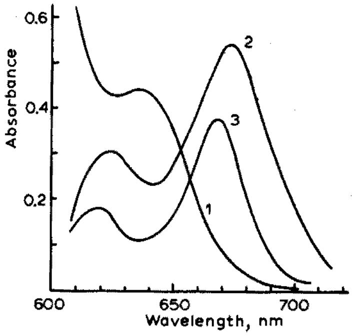


Fig. 1. Absorption spectra of uranium–chlorophosphonazo-III complexes. (1) Reagent blank in 3-methyl-1-butanol *vs.* water. (2) 10 μg U(IV) in 10 ml of 3-methyl-1-butanol *vs.* blank. (3) U(VI) in 10 ml of 3-methyl-1-butanol *vs.* blank. Extraction was made from 50 ml of 1.8 *M* hydrochloric acid containing 20 μg of U(VI).

Reduction of uranium to the tetravalent state

The zinc reduction method appears to be the most popular means of obtaining uranium(IV) in hydrochloric acid solution[8]. The hydrochloric acid concentration, the amount of zinc metal powder and the volume of the solution were examined to establish the optimal conditions. The difference in the absorbances of the blank organic phase was less than 0.01 with and without the addition of 1 g of zinc. The effect of the solution volume on the reduction step was significant; the reduction was incomplete when the volume exceeded 20 ml (Fig. 2). A hydro-

TABLE I

EFFECT OF STANDING TIME ON THE DETERMINATION OF URANIUM

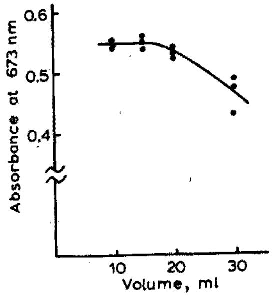
Standing time (min)	*In situ after reduction*[a]				*After dilution to 50 ml of 1.8 M HCl*[b]		
	U found[c] *(μg)*			*Average*	*U found*[c] *(μg)*		*Average*
10	9.7	9.7	10.3	9.9	10.2	10.0	10.1
30	10.2	9.5	10.1	9.9	9.4	9.6	9.5
60	10.0	9.9		10.0			

[a] Extraction was made immediately after dilution to 50 ml of 1.8 *M* hydrochloric acid.

[b] Dilution was made immediately after dissolution of zinc.

[c] Each solution contained 10.0 μg of uranium.

chloric acid concentration of 8 *M* was suitable; 1 g of zinc dissolved within 10 min in 15 ml of 8 *M* hydrochloric acid, and uranium(VI) was reduced to the lower valency state. As zinc consumes hydrochloric acid, the acidity of the aqueous phase became 1.8 *M* after dilution to 50 ml.



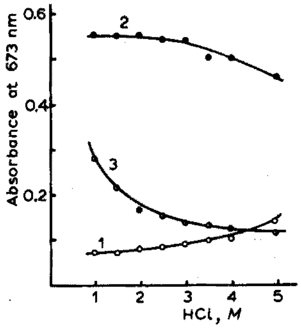


Fig. 2. Effect of solution volume at reduction step. Each solution contained 10 μg U and 10 ml of concentrated hydrochloric acid when the total volume was over 15 ml. At a total volume of 10 ml, the hydrochloric acid concentration was 8 *M*; 1 g of zinc was added.

Fig. 3. Effect of acidity of aqueous phase on absorbance of organic phase. (1) Reagent blank *vs.* water. (2) 10 μg U(IV) *vs.* blank. (3) 10 μg U(VI) *vs.* blank. Extractions for curves (1) and (2) were as in recommended procedure; curve (3) was obtained without the reduction step.

The stability of uranium(IV) was checked by allowing the solution to stand for 10–60 min and then determining the uranium by the recommended procedure. The results are shown in Table I.

Effect of acidity

The absorbance of the uranium(IV) complex in the organic phase was almost constant at an acidity of the aqueous phase in the range 1.5–3 *M* (Fig. 3); 1.8 *M* was used in further investigations. In the case of uranium(VI), the absorbance decreased with increasing acidity of the aqueous phase.

Amount of chlorophosphonazo-III

To determine the amount of chlorophosphonazo-III necessary to extract uranium(IV), 0.5–6 ml of 0.01% chlorophosphonazo-III solution was added to 50 ml of aqueous solutions that were 1.8 *M* in hydrochloric acid and contained 10 μg of uranium. Extraction was made with 10.0 ml of 3-methyl-1-butanol. The absorbance of the complex *vs.* the reagent blank was constant when the amount of 0.01% chlorophosphonazo-III solution was greater than 2 ml; 1 ml of 0.04% solution was chosen for the determination. Although this amount of chlorophosphonazo-III is not sufficient to form the complex in the aqueous phase[6], uranium can be extracted quantitatively into the organic phase. Even with 3-methyl-1-butanol containing 0.004% chlorophosphonazo-III, uranium(IV) could be extracted completely.

Extraction of the uranium(IV) complex is very rapid. Shaking for 30 s was enough to attain equilibrium.

Molar absorptivity and extent of extraction

Calibration curves prepared according to the recommended procedure showed that Beer's law was obeyed over the range 0–15 μg of uranium in about 10 ml of 3-methyl-1-butanol. The absorbance per μg of uranium was 0.055±0.001 and the absorbance of the reagent blank was about 0.07 at 673 nm. The apparent molar absorptivity was $13.1 \cdot 10^4$ l mole^{-1} cm^{-1}. When the volume change of the organic phase, owing to the slight solubility of 3-methyl-1-butanol in water, was corrected, the molar absorptivity became $12.1 \cdot 10^4$. This value is nearly triple the value obtained in aqueous 1 *M* hydrochloric solution[6]: $3.7 \cdot 10^4$ l mole^{-1} cm^{-1}. The shift of absorption peak and the increase in the molar absorptivity in the organic phase are similar to those of the thorium complex[2]. The causes of the phenomena are not yet explained. The molar absorptivity of the uranium(VI) complex is $7.86 \cdot 10^4$ (670 nm) at pH 1.0 according to Nemodruk *et al.*[3] and $7.96 \cdot 10^4$ (670 nm) in 3 *M* hydrochloric acid according to Luk'yanov *et al.*[4].

The extent of extraction of uranium was determined by the following experiment: 20 μg of uranium was extracted as in the recommended procedure, and uranium remaining in the aqueous phase was determined by the recommended procedure. The quantities of uranium found were 0.7, 0.9 and 0.8 μg, which showed that 96% of uranium was extracted. In the case of uranium(VI), only 51% of uranium was extracted from 1.8 *M* hydrochloric acid.

Stability and precision

The absorbance of the uranium(IV)–chlorophosphonazo-III complex in the organic phase does not change for at least 2 h at room temperature. The relative standard deviation was ±2.2% for 10 determinations of 10 μg of uranium.

Effect of diverse ions

Table II shows the effect of anions on the determination of uranium. Uranium could be determined in the presence of fluoride and phosphate as well as sulfate ion. Nitrate ion interfered with the reduction of uranium and could not be removed by evaporating with hydrochloric acid. Evaporation with 2 ml of 1 *M* sulfuric acid to fumes eliminated the interference of nitrate and oxalate ions.

The effect of foreign cations is shown in Table III. The permissible quantities of some cations (chromium, copper, iron), causing error less than 5%, are considerably smaller than those in the case of the determination of thorium[2]. They

TABLE II

DETERMINATION OF URANIUM IN THE PRESENCE OF ANIONS

Salt	*Amount (mmole)*	*U found*[a] *(μg)*		*Salt*	*Amount (mmole)*	*U found*[a] *(μg)*	
NaCl	5	9.9	9.9	NaF	0.2	10.0	9.7
$NaClO_4$	5	10.0	10.0		0.5	9.2	9.8
$NaNO_3$	0.5	8.9	8.3	NaH_2PO_4	2	9.8	9.8
	2[b]	9.9	9.6	$Na_2C_2O_4$	0.5	8.6	9.0
$NaHSO_4$	2	10.0	9.7		0.5[b]	9.9	9.6
	5	9.4	9.1	EDTA	0.5	10.0	9.8

[a] Each solution contained 10.0 μg of uranium.

[b] The solution was evaporated with 2 ml of 1 *M* sulfuric acid.

TABLE III

DETERMINATION OF URANIUM IN THE PRESENCE OF DIVERSE CATIONS

Ion[a]	*Amount*	*U found*[b] *(μg)*		*Ion*[a]	*Amount*	*U found*[b] *(μg)*	
Al	2 mg	9.7	9.9	Nb(V)	1 μg	9.7	9.8
Ba	10 mg	9.8	9.6		2 μg	8.9	9.1
Ca	10 mg	9.8	10.1	Ni	10 μg	9.7	9.8
Ce(III)	5 μg	10.3	9.9		20 μg	9.0	
	10 μg	8.9	10.2		100 μg	8.5	
Cr(III)	10 μg	9.2	9.5	Sc	20 μg	10.3	10.5
	100 μg	8.2	8.6	Sm	5 μg	10.3	10.5
Cu	10 μg	9.3	8.9		10 μg	11.5	11.7
	100 μg	6.6	8.7	Sr	10 mg	10.4	10.3
Fe(III)	10 μg	9.0	9.2	Th	1 μg	11.0	11.2
	100 μg	7.0	7.7	Ti(IV)	5 μg	10.0	10.1
La	20 μg	10.1	10.5		20 μg	9.5	8.0
Mg	2 mg	9.8	10.0	Y	5 μg	10.0	10.0
Mo(VI)	20 μg	10.0	9.6		10 μg	11.0	10.9
	50 μg	9.4		Zr	1 μg	12.5	12.4

[a] Valency is that before reduction with zinc.

[b] Each solution contained 10.0 μg of uranium.

must be removed by a suitable method. The interferences are due to the effects on the reduction of uranium(VI) and the stability of uranium(IV) in the presence of copper(I) and iron(II)[9], and the decomposition of chlorophosphonazo-III by strong reductants such as chromium(II) and molybdenum(III). Thorium and zirconium (1 μg) and niobium (2 μg) interfere seriously, and must be removed.

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SUMMARY

A sensitive spectrophotometric method has been developed for the determination of uranium. The uranium(IV)–chlorophosphonazo-III complex is extracted into 3-methyl-1-butanol from 1.5–3.0 *M* hydrochloric acid solution. Maximal absorbance occurs at 673 nm and Beer's law is obeyed over the range of 0–15 μg per 10 ml of the organic phase. The molar absorptivity is $12.1 \cdot 10^4$ l mole^{-1} cm^{-1}. Uranium can be determined in the presence of fluoride, sulfate and phosphate. Nitrate ion and elements (chromium, copper, iron) which affect the reduction of uranium(VI) or stability of uranium(IV) interfere.

RÉSUMÉ

Une méthode spectrophotométrique sensible est proposée pour le dosage de l'uranium. Le complexe uranium(IV)–chlorophosphonazo-III est extrait dans le méthyl-3-butanol-1, en milieu acide chlorhydrique 1.5–3.0 *M*. L'absorption maximum se trouve à 673 nm. La loi de Beer s'applique de 0 à 15 μg par 10 ml de phase organique. Le coefficient d'absorption molaire est $12.1 \cdot 10^4$ l mole^{-1} cm^{-1}. L'uranium peut être dosé en présence de fluorure, de sulfate et de phosphate. Les nitrates, ainsi que les éléments (Cr, Cu, Fe), affectant la réduction de l'uranium(VI) ou la stabilité de l'uranium(IV), interfèrent.

ZUSAMMENFASSUNG

Es wurde eine empfindliche spektrophotometrische Methode für die Bestimmung von Uran entwickelt. Aus 1.5–3.0 *M* salzsaurer Lösung wird der Uran(IV)–Chlorphosphonazo-III-Komplex mit 3-Methyl-1-butanol extrahiert. Die maximale Extinktion liegt bei 673 nm, und das Beersche Gesetz ist im Bereich 0–15 μg pro 10 ml organische Phase erfüllt. Der molare Extinktionskoeffizient ist $12.1 \cdot 10^4$ l mol^{-1} cm^{-1}. Uran kann in Gegenwart von Fluorid, Sulfat und Phosphat bestimmt werden. Nitrationen und Elemente (Chrom, Kupfer, Eisen), die die Reduktion von Uran(VI) oder die Beständigkeit von Uran(IV) beeinflussen, stören.

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THE SOLVENT EXTRACTION OF THE TERNARY COMPLEXES OF IRON(II)–RHODAMINE B WITH VARIOUS NITROSOPHENOLS

DETERMINATION OF IRON IN WATERS

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o-Nitroso derivatives of phenol and naphthol are well known as relatively selective colorimetric reagents for cobalt and iron(II). For example, 1-nitroso-2-naphthol[1], 2-nitroso-1-naphthol[1], nitroso-R salt[1], *o*-nitrosoresorcinol[1] and 2-nitroso-5-dimethylaminophenol[2] etc. have been used as analytical reagents for cobalt and iron(II).

In general, nitrosophenol, nitrosonaphthol, and their derivatives react with iron(II) to form a green complex in aqueous solution. When excess of the reagent is present, three moles of the reagent coordinate to one mole of iron(II) to form a large monovalent complex anion. These green complexes have molar absorptivities of at most $3 \cdot 10^4$.

In this work, the extraction of the ion pair formed between the large complex anion which was formed from iron(II) and nitrosophenol and a large cation, rhodamine B, was examined in detail.

In a previous paper[3], the extraction of the ternary complexes formed from the complexes of 5,7-dinitrooxine with several metal ions and rhodamine B into benzene was reported. These ternary complexes were extracted quantitatively into benzene and the molar absorptivities of the ternary complexes in benzene were very large, *ca.* $1 \cdot 10^5$; the reagent blanks were very small, because the excess of rhodamine B was extracted into benzene in the γ-lactone form. When organic solvents with large dielectric constants, such as nitrobenzene, 1,2-dichloroethane and chloroform, were used as the organic phase, the colored rhodamine B was extracted and the reagent blank was very large. Accordingly, in this work, benzene was used as the solvent.

In previous papers[4,5], the authors reported studies of the coloration of some metal ions with several *o*-nitrosophenol and *o*-nitrosonaphthol derivatives. Twenty-seven derivatives of nitrosophenol and nitrosonaphthol were examined. It was found that all these derivatives reacted with cobalt and iron(II) ions.

In the present work, the twenty derivatives shown in Fig. 1 were investigated; seven derivatives having a sulfonic group were not investigated. Of the twenty derivatives studied, the complexes of iron(II) with seven derivatives (Group 1) formed ternary complexes with rhodamine B, and these ternary complexes could be extracted quantitatively into benzene. Accordingly, the extraction of these seven ternary complexes was further investigated. These ternary complexes in benzene solution were

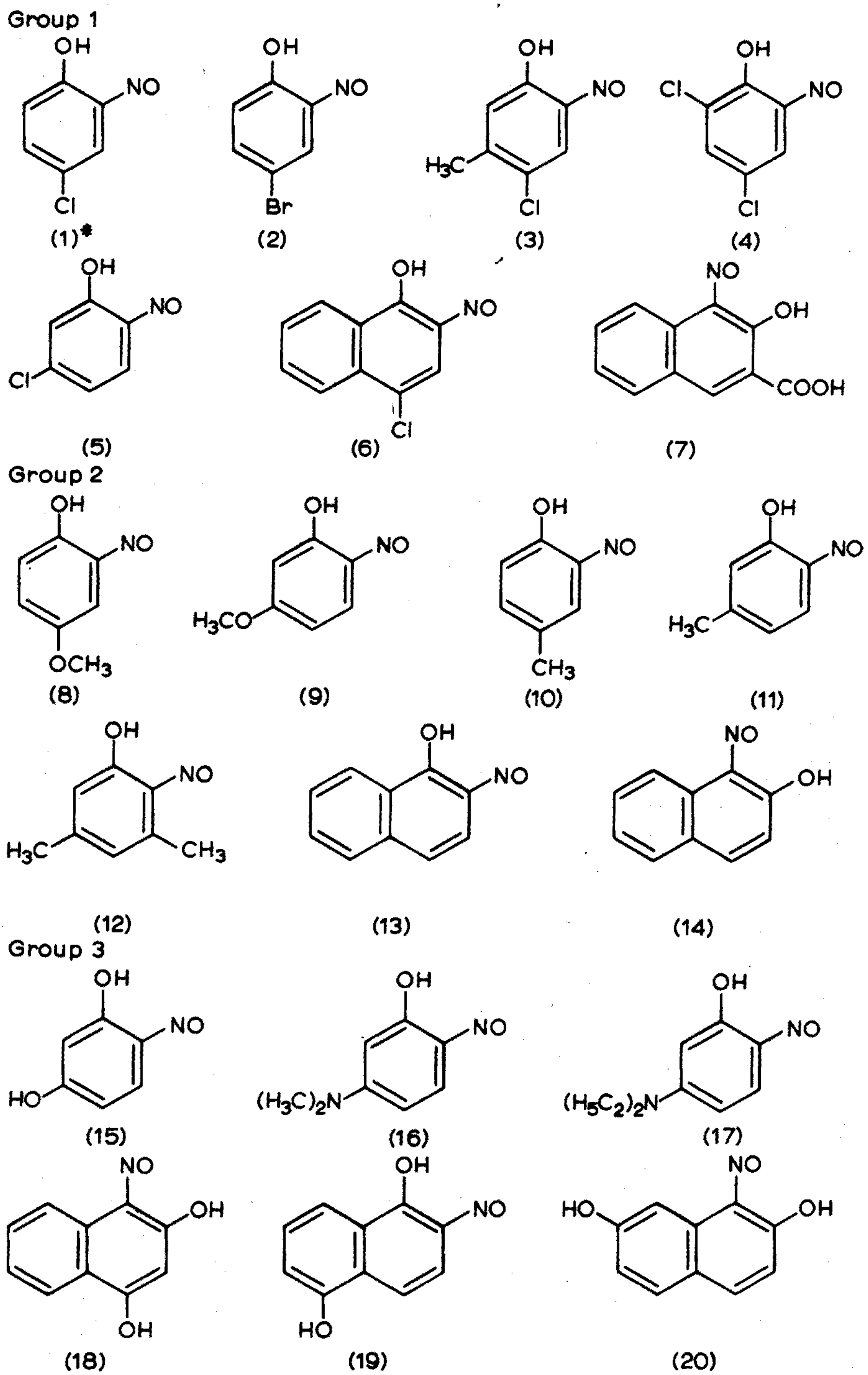


Fig. 1. Nitrosophenols and nitrosonaphthols examined. Group 1: [1]–[7], Group 2: [8]–[14], Group 3: [15]–[20]. * Reagent [1] was obtained as a sodium salt.

of 1:3:1 composition by mole ratio methods, and the calibration curves showed that Beer's law was obeyed over the range $0\text{–}1 \cdot 10^{-5}$ M iron(II). The apparent molar absorptivities of these ternary complexes calculated from their calibration curves were about $9 \cdot 10^4$ at about 560 nm. It was found that of these seven reagents, 2-nitroso-4-chlorophenol, *i.e.*, reagent [1], was superior to any of the others in the following respects: (*a*) the absorbance of the reagent blank was small and constant over a wide pH region, and (*b*) the absorbance of the ternary complex extracted into benzene was constant over a wide pH region.

The new, simple and sensitive method for the determination of trace amounts of iron recommended here is much superior to other spectrophotometric methods, such as the methods based on nitroso-R salt[6], *o*-phenanthroline[7] and 2,2'-bipyridine[7], etc. In this extraction–spectrophotometric method, iron(III) was reduced easily to iron(II) with hydroxylamine, and about 20-fold concentration was possible, hence the method could be applied to the determination of trace amounts of iron in city water and river water.

EXPERIMENTAL

Reagents

o-Nitrosophenols and o-nitrosonaphthols. The reagents were obtained by nitrosation[4,5] of the parent compounds in aqueous solution with sodium nitrite. The crude nitrosophenols and nitrosonaphthols obtained were recrystallized two or three times from suitable organic solvents. The results of elemental analysis of some of the purified nitrosophenols and nitrosonaphthols used are shown in Table I.

TABLE I

ELEMENTAL ANALYSES OF SOME NITROSOPHENOLS AND NITROSONAPHTHOLS

Reagent[a]	*Composition*	*Found (Calcd. for)*		
		C	*H*	*N*
[1]	$C_6H_3NO_2Cl \cdot Na$	39.92 (40.14)	1.60 (1.68)	7.83 (7.80)
[2]	$C_6H_4NO_2Br$	35.41 (35.67)	2.06 (2.00)	6.78 (6.94)
[3]	$C_7H_6NO_2Cl$	50.11 (49.00)	3.60 (3.53)	7.99 (8.17)
[4]	$C_6H_3NO_2Cl_2$	37.86 (37.53)	1.59 (1.57)	7.13 (7.30)
[5]	$C_6H_4NO_2Cl$	44.49 (45.74)	2.38 (2.56)	8.90 (8.89)
[6]	$C_{10}H_6NO_2Cl$	57.40 (57.85)	2.98 (2.91)	6.62 (6.75)
[7]	$C_{11}H_7NO_4$	61.35 (60.83)	3.33 (3.25)	6.49 (6.45)

[a] The reagent number corresponds to those of Fig. 1.

Reagents were dissolved in aqueous solution containing sufficient sodium hydroxide to give a $1 \cdot 10^{-3}$ M solution.

Standard iron(II) solution. Mohr's salt was dissolved in water containing a small amount of sulfuric acid and 1 wt.% of hydroxyammonium chloride to give a $1 \cdot 10^{-2}$ M solution. This was standardized by EDTA titration. This stock solution was used after accurate dilution.

Rhodamine B solution. An aqueous $5 \cdot 10^{-3}$ M solution was prepared.

Buffer solutions. The pH was adjusted with the following solutions: hydrochloric acid (pH 1–2), acetic acid–sodium acetate (pH 3–6), potassium dihydrogenphosphate–disodium hydrogenphosphate (pH 7–8), sodium bicarbonate–sodium carbonate (pH 9–11) and potassium hydroxide (pH 12–14) solutions. All the reagents used were of analytical-reagent grade.

Benzene of analytical-reagent grade was used as received.

Apparatus

A Hitachi–Perkin Elmer model 139 spectrophotometer and Hitachi model EPS-3T recording spectrophotometer were used for measuring the absorbance in glass cells of 10 mm pathlength. A Hitachi-Horiba model F-5ss pH meter equipped with a combined electrode, 6026–05T, was used for measuring the pH. An Iwaki model KM shaker was used for shaking.

General procedure

Iron(II) solution ($2 \cdot 10^{-5}$ *M*) was pipetted into a stoppered 25-ml test tube. Reagent, buffer and rhodamine B solutions were pipetted into it, in that order. After dilution to 5 ml with distilled water, and thorough mixing, the solution was left for 10 min. It was then shaken with 5 ml of benzene for 10 min. After phase separation, the absorbance of the organic phase was measured in a 10-mm glass cell. Finally, the pH of the aqueous solution was measured.

RESULTS AND DISCUSSION

Extracting solvent

When rhodamine B was extracted into organic solvents of relatively large dielectric constant, such as nitrobenzene, 1,2-dichloroethane and chloroform, the absorbance of the reagent blank was very large. When benzene or toluene was used, the reagent blank was very small. Benzene was therefore used.

Choice of reagent

Seven of the twenty derivatives examined, 2-nitroso-4-chlorophenol [1], 2-nitroso-4-bromophenol [2], 2-nitroso-4-chloro-5-methylphenol [3], 2-nitroso-4,6-dichlorophenol [4], 2-nitroso-5-chlorophenol [5], 2-nitroso-4-chloronaphthol [6] and 1-nitroso-2-hydroxy-3-naphthoic acid [7], all of which possessed electron-attracting groups, extracted iron(II) quantitatively into benzene as the ternary complex with rhodamine B (Group 1). The reagents forming Group 2 of Fig. 1 extracted only small amounts of iron(II) into benzene as the ternary complex with rhodamine B; the absorbances of these extracted ternary complexes were at most 0.01. The reagents forming Group 3 (Fig. 1), which possess strong electron-donating groups, could not extract iron(II) into benzene as the ternary complex with rhodamine B at all. The use of the seven reagents in Group 1 was therefore examined in detail.

Absorption spectra of the extracted species in benzene

The absorption spectra obtained with 2-nitroso-4-chlorophenol are shown in Fig. 2. The absorption maxima of the complex in benzene were at 420 and 558 nm. The former was the absorbance of the reagent, and the latter was the absorbance of rhodamine B. In the absorption spectrum of the reagent blank, the absorbance of the reagent at 420 nm was almost as large as in the mixture containing iron(II), and the absorbance of rhodamine B at 558 nm was very small. This small absorbance may be that of the ion pair which is formed between the reagent anion and rhodamine B cation.

The other six reagents [2]–[7] were also investigated. The absorption spectra obtained with these reagents were very similar to those of reagent [1] and their maximal absorption wavelengths are shown in Table II.

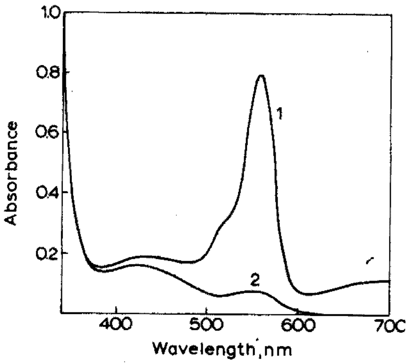
TABLE II

MOLAR ABSORPTIVITIES OF TERNARY COMPLEXES IN BENZENE

Reagent	λ_{max} *(nm)*	ε *(l mole^{-1} cm^{-1})·10^4*
[1]	558	9.00
[2]	558	8.90
[3]	556	8.70
[4]	558	8.85
[5]	554	9.00
[6]	560	9.00
[7]	561	8.90

Effect of pH

The effect of pH on the extraction of the ternary complex was studied mainly with acetic acid–sodium acetate buffer solutions. As shown in Fig. 3, for reagent [1], constant absorbances of the organic phase were obtained between pH 4.0 and 5.3, and lower constant absorbances were obtained between pH 5.7 and 6.2. The absorbances of the reagent blank were almost constant (0.07–0.08) above pH 4.3. However, they became larger below pH 4.3. The optimal pH of extraction was pH 4.3–5.3; the pH of the aqueous solution was therefore adjusted at about pH 4.8, and an acetic



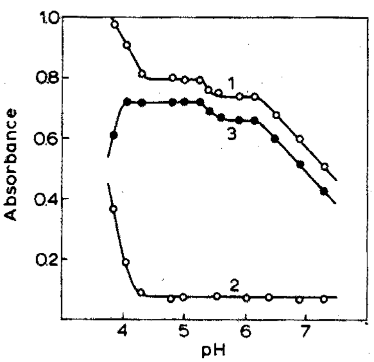


Fig. 2. Absorption spectra. Reagent, 2-nitroso-4-chlorophenol. (1) Ternary complex: $[Fe^{2+}] = 8 \cdot 10^{-6}$ *M*, $[R] = 2 \cdot 10^{-4}$ *M*, [rhodamine B] $= 1 \cdot 10^{-3}$ *M*; pH 4.8; reference, benzene. (2) Reagent blank (containing no iron); pH 4.8; reference, benzene.

Fig. 3. Effect of pH. Reagent, 2-nitroso-4-chlorophenol. (1) Ternary complex: $[Fe^{2+}] = 8 \cdot 10^{-6}$ *M*, $[R] = 2 \cdot 10^{-4}$ *M*, [rhodamine B] $= 1 \cdot 10^{-3}$ *M*; reference, benzene. (2) Reagent blank; reference, benzene. (3) Ternary complex; reference, reagent blank.

TABLE III

pH REGION OF CONSTANT ABSORBANCE

($[Fe^{2+}] = 8 \cdot 10^{-6}$ *M*, [reagent] $= 2 \cdot 10^{-4}$ *M*, [rhodamine B] $= 1 \cdot 10^{-3}$ *M*)

Reagent	*pH region*	
	Complex (Absorbance[a]*)*	*Reagent blank (Absorbance*[b]*)*
[1]	4.0–5.3 (0.72), 5.7–6.2 (0.66)	Above 4.3 (0.08)
[2]	3.9–4.9 (0.72), 5.2–6.0 (0.63)	4.7–6.9 (0.11)
[3]	3.9–5.2 (0.71), 5.5–5.8 (0.67)	Above 4.9 (0.14)
[4]	3.9–5.2 (0.71), 5.5–5.8 (0.68)	—
[5]	3.9–5.7 (0.72)	5.3–7.0 (0.08)
[6]	3.6–4.9 (0.72), 5.3–5.5 (0.67)	Above 4.3 (0.10)
[7]	3.2–5.0 (0.72)	—

[a] Reference, reagent blank. [b] Reference, benzene.

acid–sodium acetate buffer solution was used. In the case of other six reagents, [2]–[7], the effect of pH on the extraction was also studied similarly. With reagents [4] and [7], constant absorbances of the reagent blank were not obtained and the absorbances increased with decrease of pH. Even in these cases, however, constant absorbance of the complex was obtained when the reagent blank was used as the reference. These results are shown in Table III.

Standing time, shaking time and stability of color

In the presence of a small excess of the reagent, iron(II) reacted with the reagent slowly and a green water-soluble complex was produced. However, when the concentrations of iron(II), the reagent and rhodamine B were $8 \cdot 10^{-6}$ *M*, $2 \cdot 10^{-4}$ *M* and $1 \cdot 10^{-3}$ *M*, respectively, the reaction was complete immediately. In this work, a standing period of 10 min was used for safety. The shaking time was examined under similar conditions: constant absorbances were obtained by shaking for more than 5 min, and a shaking period of 10 min was used for safety.

The extracted species was very stable and its absorbance did not change for at least one week at room temperature.

Composition of the extracted species

With all the reagents examined, the iron(II): reagent ratio was found to be 1:3 by the mole ratio method, and the iron(II): rhodamine B ratio was found to be 1:1 by the mole ratio method. Therefore, the extracted ternary iron(II)–reagent–rhodamine B complexes were of the composition 1:3:1. The results obtained with reagent [1] are shown in Figs. 4 and 5, and the results obtained with the other reagents are summarized in Table IV.

Molar absorptivity

With all the seven reagents examined, the absorbances of the ternary complex in benzene obeyed Beer's law over the range 0–$1 \cdot 10^{-5}$ *M* iron(II); calibration curves with the reagent blank as reference were straight lines through the origin. The apparent molar absorptivities calculated from the slopes of the calibration curves were about $9 \cdot 10^4$ (Table II).

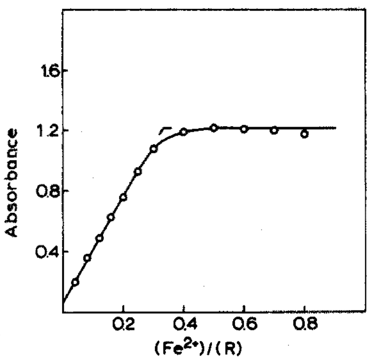


Fig. 4. Establishment of iron(II):reagent ratio by mole ratio method. Reagent, 2-nitroso-4-chlorophenol; $[\mathrm{R}] = 5 \cdot 10^{-5}$ *M*, [rhodamine B] $= 1 \cdot 10^{-3}$ *M*; pH 4.8; reference, benzene.

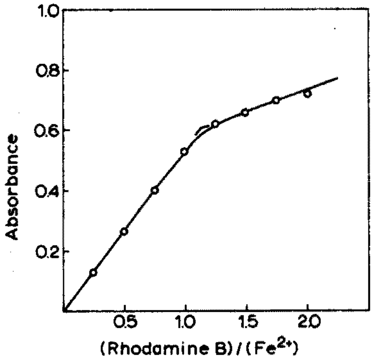


Fig. 5. Establishment of iron(II):rhodamine B ratio by mole ratio method. Reagent, 2-nitroso-4-chlorophenol; $[\mathrm{Fe}^{2+}] = 8 \cdot 10^{-6}$ *M*, $[\mathrm{R}] = 2 \cdot 10^{-4}$ *M*; pH 4.8; reference, benzene.

TABLE IV

COMPOSITION OF TERNARY COMPLEXES IN BENZENE

Reagent	*Iron(II):reagent*	*Iron(II):rhodamine B*
[1]	1:3.1	1:1.1
[2]	1:3.3	1:1.2
[3]	1:3.3	1:1.2
[4]	1:3.2	1:1.0
[5]	1:3.0	1:1.2
[6]	1:3.1	1:1.1
[7]	1:3.1	1:1.2

Extraction mechanism

As mentioned above, the mole ratio of the ternary complex was 1:3:1 iron(II):reagent:rhodamine B. The extraction mechanism can be represented as follows:

$$\mathrm{Fe}^{2+} + 3\,\mathrm{R}^- \rightleftharpoons [\mathrm{FeR}_3]^- \qquad (1)$$

$$[\mathrm{FeR}_3]^- + [\text{rhodamine B}]^+ \rightleftharpoons \{[\mathrm{FeR}_3]^-[\text{rhodamine B}]^+\}_a \qquad (2)$$

$$\{[\mathrm{FeR}_3]^-[\text{rhodamine B}]^+\}_a \rightleftharpoons \{[\mathrm{FeR}_3]^-[\text{rhodamine B}]^+\}_o \qquad (3)$$

where R is the nitrosophenol or nitrosonaphthol and subscripts a and o refer to the aqueous and organic phase, respectively.

When a large excess of the reagent reacting with iron(II) in aqueous solution was present, the univalent large complex anion $[\mathrm{FeR}_3]^-$ was easily produced as in eqn. (1). When rhodamine B solution was added, an ion pair was produced and a red precipitate was produced, which was probably the ion pair $\{[\mathrm{FeR}_3]^-[\text{rhodamine B}]^+\}$ as in eqn. (2). Owing to the formation of this ion pair, the equilibrium shown in eqn. (1) will proceed farther to the right. On shaking with benzene, the ion pair was distributed between the aqueous and benzene phases in accordance with equilibrium (3).

The excess of rhodamine B is also extracted into benzene as the colorless lactone form, so that the absorbance of the reagent blank is not influenced by rhodamine B. The absorbance of the benzene phase can probably be attributed to ion pairs of the rhodamine B cation with anions, such as the iron(II) complex anion, reagent anion, acetate, etc. However, the reagent and acetate anions are hardly extracted into benzene as ion pairs, for the absorbance of the reagent blank is very small. Consequently, iron(II) can be determined accurately and sensitively by measuring the absorbance of the benzene phase, the most satisfactory reagent being 2-nitroso-4-chlorophenol, reagent [1].

DETERMINATION OF IRON IN CITY WATER AND RIVER WATER WITH 2-NITROSO-4-CHLOROPHENOL

The amount of iron in city water and most river water is only trace, so the concentration of iron by solvent extraction with benzene was examined. When 5 ml of benzene was used and the amount of iron(II) in the aqueous phase was 2.23 μg, essentially the same absorbance was obtained whether the volume of

TABLE V

INTERFERENCE OF DIVERSE IONS

Ion	*Concentration (mole l^{-1})*	*Ratio*[a]	*Absorbance*[b]
—	—	—	0.796
Na^+	$5 \cdot 10^{-4}$	1	0.796
	$5 \cdot 10^{-3}$	10	0.791
	$5 \cdot 10^{-2}$	100	0.799
K^+	$1 \cdot 10^{-4}$	1	0.801
	$1 \cdot 10^{-3}$	10	0.793
	$1 \cdot 10^{-2}$	100	0.796
Mg^{2+}	$2 \cdot 10^{-4}$	1	0.791
	$2 \cdot 10^{-3}$	10	0.791
	$2 \cdot 10^{-2}$	100	0.793
Ca^{2+}	$5 \cdot 10^{-4}$	1	0.796
	$5 \cdot 10^{-3}$	10	0.801
	$5 \cdot 10^{-2}$	100	0.796
NH_4^+	$1 \cdot 10^{-4}$	10	0.799
	$1 \cdot 10^{-3}$	100	0.799
Cl^-	$5 \cdot 10^{-3}$	10	0.791
	$5 \cdot 10^{-2}$	100	0.793
NO_3^-	$1 \cdot 10^{-4}$	10	0.796
	$1 \cdot 10^{-3}$	100	0.796
SO_4^{2-}	$5 \cdot 10^{-3}$	10	0.799
	$5 \cdot 10^{-2}$	100	0.796
CO_3^{2-}	$1 \cdot 10^{-2}$	10	0.791
	$1 \cdot 10^{-1}$	100	0.785

[a] This ratio is the ratio of the concentration tested to the ratio normally present in city or river waters.
[b] Reference, benzene.

aqueous phase was 5, 10, 20, 50, 70 or 100 ml. Thus a 20-fold concentration by solvent extraction with benzene could be easily achieved.

Diverse ions

The interference of diverse ions was examined with particular reference to ions generally present in city water and river water. As shown in Table V, even 10-fold and 100-fold normal concentrations did not interfere with the extraction of the ternary complex.

Reduction of iron(III) to iron(II)

Iron in city water and river water exists as iron(III), hence the reduction of iron(III) with hydroxyammonium chloride was studied. Under the recommended conditions, the absorbance obtained for $8 \cdot 10^{-6}$ *M* iron was unaffected by changes in the concentration of hydroxyammonium chloride from 0.2 wt.% to 3 wt.%. Accordingly, the sample solutions were adjusted to contain about 1 wt.% of the reductant. The reduction time was also examined. Iron(III) was rapidly reduced to iron(II), and the same absorbance was obtained for $8 \cdot 10^{-6}$ *M* iron for reduction times varying from 2 min to 30 min.

Determination of total iron in city water and river water

The amounts of total iron generally existing in river water are about 100 μg l^{-1}, so that a 4-fold concentration sufficed. The following procedure is recommended.

Procedure. Transfer 25 ml of sample solution or less to a stoppered test tube, and if necessary, dilute to 25 ml with distilled water. Add 1 ml of 2-nitroso-4-chlorophenol ($1 \cdot 10^{-3}$ *M*) and 1 ml of acetic acid–sodium acetate buffer solution (pH 4.8), and mix well. After 10 min, add 1 ml of rhodamine B solution ($5 \cdot 10^{-3}$ *M*), and shake with 5 ml of benzene for 10 min. Separate the organic phase, and measure its absorbance at 558 nm, against a reagent blank, prepared by using distilled water, as reference.

Prepare a calibration curve by using 25 ml of solutions containing known amounts of iron(II).

Samples must be treated as soon as they are taken, with hydroxyammonium chloride in an amount sufficient to give about 1 wt.%. If the samples are

TABLE VI

DETERMINATION OF TOTAL IRON IN CITY WATER AND RIVER WATER

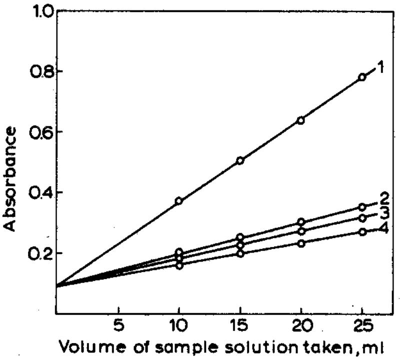
Sample[a]	*Sample taken (ml)*	*Absorbance*[b]	*Amounts of iron in 20 ml of sample solution (μg)*
1	20	0.54_9	1.7_0
2	20	0.21_0	0.65_0
3	20	0.18_2	0.56_4
4	20	0.14_1	0.43_7

[a] Sample 1: city water at Okayama City, sampled on Oct. 17, 1972. Sample 2: Yoshii River in Okayama Prefecture, sampled on Oct. 5, 1972. Sample 3: Asahi River in Okayama Prefecture, sampled on Oct. 5, 1972. Sample 4: Takahashi River in Okayama Prefecture, sampled on Oct. 21, 1972.
[b] Reference, reagent blank.

turbid, they should be filtered through a 0.45-μm Millipore filter; if the samples are clear, they can be used as received. The results obtained by the above method are shown in Table VI.

Reagent blank

To estimate any difference between the absorbance of the reagent blank in city or river water and that obtained with distilled water, and to check the quantitative extraction of iron from city or river waters, the volume of sample taken was varied from 10 ml to 25 ml and distilled water was added to each to give a constant volume of 25 ml. The results obtained are shown in Fig. 6. In all samples, linear plots were obtained and the lines could be extrapolated to the same point, which coincided with the point obtained for 25 ml of distilled water. Accordingly, distilled water can be used for the reagent blank.



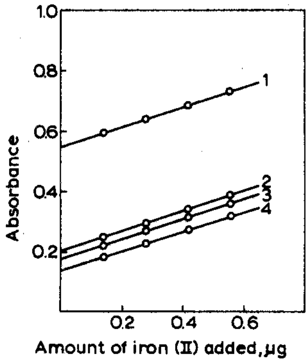


Fig. 6. Effect of volume of sample taken. Benzene phase, 5 ml; pH 4.8; reference, benzene. (1) City water, (2) Y River, (3) A River, (4) T River.

Fig. 7. Recovery of iron ion in sample solution. Sample taken, 20 ml; benzene phase, 5 ml; pH 4.8; reference, reagent blank. (1) City water, (2) Y River, (3) A River, (4) T River.

Recovery of iron

To examine the recovery of iron from the samples, known amounts of iron(II) were added to the samples and distilled water was added to give a constant volume (25 ml). The results are shown in Fig. 7. The slopes of these plots were all equal to one another and to that of the calibration curve. It therefore appears that iron in city or river water could be extracted quantitatively into benzene as the ternary complex.

CONCLUSIONS

Rhodamine B is extracted into benzene as the neutral form (lactone form) or the cation. The cation of rhodamine B can, however, be extracted only when a large anion, which can form an ion pair, is also present. Suitable large anions are metal complex anions, such as the metal complexes of 5,7-dibromooxine[8] and 5,7-dinitrooxine[3]. These chelating reagents possess electron-attracting substituents. In the case of nitrosophenols and nitrosonaphthols, only those reagents possessing electron-attracting substituents, such as chloro, bromo and carboxyl substituents,

TABLE VII

MOLAR ABSORPTIVITIES OF IRON COMPLEXES

Reagent	*Iron valency*	λ_{max} *(nm)*	ε *(l mole^{-1} cm^{-1})*	*Ref.*
1,10-Phenanthroline	II	508	$1.10 \cdot 10^4$	7
4,7-Diphenyl-1,10-phenanthroline	II	533	$2.24 \cdot 10^4$	7
2,2′-Bipyridine	II	522	$8.65 \cdot 10^3$	7
Thiocyanate	III	480	$8.3 \cdot 10^3$	7
1-(2-Pyridylazo)-2-naphthol	III	775	$1.6 \cdot 10^4$	9
4-(2-Pyridylazo)-resorcinol	II	517	$4.2 \cdot 10^4$	10
PAR + nitrilotriacetic acid	II	536	$6.04 \cdot 10^4$	11
8-Hydroxyquinoline	III	460	$4.7 \cdot 10^3$	12
Xylenol orange	III	545	$2.43 \cdot 10^4$	13
Chrome azurol S	III	630	$5.5 \cdot 10^4$	14
Pyrocatechol violet	III	610	$6.24 \cdot 10^4$	15
Pyrrollidine-N-dithiocarbamic acid	II	360	$1.14 \cdot 10^4$	16
Nitroso-R salt	II	720	$1.7 \cdot 10^4$	17
2-Nitroso-5-methoxyphenol	II	700	$3.4 \cdot 10^4$	18
2-Nitroso-4-chlorophenol + rhodamine B	II	558	$9.0 \cdot 10^4$	This work

allowed quantitative extraction of iron(II) as the ternary complex; reagents possessing electron-donating substituents, such as dimethylamino, diethylamino, hydroxyl, methoxyl and methyl substituents, did not extract iron(II).

Of the twenty nitroso compounds examined in this work, seven reagents extracted iron(II) quantitatively, and the molar absorptivities of these ternary complexes were almost equal. 2-Nitroso-4-chlorophenol, however, is recommended because of its easy synthesis and purification, the low and constant absorbance of the reagent blank over a wide pH region, and the constant absorbance of the ternary complex extracted into benzene over a wide pH region.

This new method of determining trace amounts of iron possesses many advantages, such as high sensitivity (molar absorptivity $9.0 \cdot 10^4$) as shown in Table VII, high selectivity, the possibility of concentration of iron, and the simplicity of the procedure.

In this work, the method was applied to the determination of iron in city and river waters. Iron in these sample solutions could be determined rapidly and simply.

SUMMARY

Twenty nitrosophenols and nitrosonaphthols were examined as reagents for ternary complex formation with iron(II) and rhodamine B. Only reagents containing electron-attracting substituents were satisfactory, and of these, 2-nitroso-4-chlorophenol was best. The ternary complex contains 2-nitroso-4-chlorophenol, iron(II) and rhodamine B in the ratio 3:1:1, and can be readily extracted into benzene. The red extracted complex shows maximal absorbance at 558 nm with a molar absorptivity of $9.0 \cdot 10^4$. Beer's law is obeyed over the range 0–$1 \cdot 10^{-5}$ *M* iron(II); the pH range for extraction is 4.3–5.3, and the color is stable for at least 1 week. The application of the method to the determination of iron in potable and river waters is described.

RÉSUMÉ

Vingt nitrosophénols et nitrosonaphtols ont été examinés comme réactifs pour la formation de complexes ternaires du fer(II) et de la rhodamine B. Seuls les réactifs contenant des substituants à attraction électronique ont donné des résultats satisfaisants; le nitroso-2-chloro-4-phénol est le meilleur. Le complexe ternaire est formé de nitroso-2-chloro-4-phénol, fer(II) et rhodamine B dans le rapport 3:1:1; il peut être extrait facilement dans le benzène. Le complexe extrait rouge présente une absorbance maximale à 558 nm avec un coefficient d'absorption molaire de $9.0 \cdot 10^4$. La loi de Beer s'applique pour des concentrations en fer(II) de 0 à $1 \cdot 10^{-5}$ M; le pH peut varier de 4.3 à 5.3 et la coloration est stable au moins pendant une semaine. On décrit un dosage de fer dans l'eau potable et dans l'eau de rivière.

ZUSAMMENFASSUNG

20 Nitrosophenole und Nitrosonaphthole wurden als Reagenzien für die Bildung ternärer Komplexe mit Eisen(II) und Rhodamin B untersucht. Nur die Reagenzien, die elektronenanziehende Substituenten enthielten, waren zufriedenstellend, und von diesen war 2-Nitroso-4-chlorphenol das beste. Der ternäre Komplex enthält 2-Nitroso-4-chlorphenol, Eisen(II) und Rhodamin B im Verhältnis 3:1:1 und kann leicht mit Benzol extrahiert werden. Der rote extrahierte Komplex hat eine maximale Extinktion bei 558 nm mit einem molaren Extinktionskoeffizienten von $9.0 \cdot 10^4$. Das Beersche Gesetz ist im Bereich 0–$1 \cdot 10^{-5}$ M Eisen(II) erfüllt; der pH-Bereich für die Extraktion ist 4.3–5.3, und die Färbung ist mindestens 1 Woche lang beständig. Die Anwendung der Methode auf die Bestimmung von Eisen in Trink- und Flusswasser wird beschrieben.

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TITRIMETRIC DETERMINATION OF VANADIUM(V) AND CHROMIUM(VI) ALONE AND IN MIXTURES WITH HYDRAZINE SULPHATE IN PHOSPHORIC ACID MEDIA

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Hydrazine sulphate is now available at an economic price at the purity required for an analytical reagent. It is non-hygroscopic and has a long shelf-life. Its aqueous solutions are reported to be stable for two months[1]. It has been used for the standardization of solutions of many oxidants[2–7]. In this paper, accurate and rapid titrimetric determinations of vanadium(V) and chromium(VI) at room temperature in phosphoric acid medium are reported. Hydrazine sulphate is recommended here for the standardization of vanadium(V) solutions in preference to Mohr's salt, because of its reliable composition and its stability in solution. The use of phosphoric acid as a reaction medium makes the vanadium(V)–hydrazine reaction follow a precise stoichiometry.

EXPERIMENTAL

Preparation of solutions

A 0.05 *M* solution of hydrazine sulphate was prepared from AnalaR hydrazine sulphate. A potassium bromate assay by the procedure of Kurtenacker and Wagner[8] as modified by Kolthoff[9] agreed with the weight purity to within ±0.3%. A *ca.* 0.2 *M* solution of sodium metavanadate was prepared from AnalaR ammonium metavanadate and standardized against a solution of Mohr's salt which had been standardized against potassium dichromate, the end-points in both titrations being located potentiometrically. Syrupy phosphoric acid (p.a.) was employed, as it was found to be free from manganese(II) which when present even in traces reduces chromium(VI) to chromium(III) in phosphoric acid medium[10]. It is also reasonably free from reducing impurities like phosphorous and hypophosphorous acids. All other chemicals used were of AnalaR grade.

Apparatus

The potentiometric titration assembly consisted of a "Pye" potentiometer and a Cambridge suspension galvanometer, a bright platinum rod (*ca.* 2 mm diameter) as the indicator electrode, a saturated calomel reference electrode, and a saturated potassium chloride salt bridge. This assembly served well for the individual titrations. For differential titrations of chromium(VI) and vanadium(V), a double bridge assembly was needed.

For the photometric titrations a Klett-Summerson photoelectric colorimeter with a rectangular glass cell (2 × 4 × 8 cm) was used.

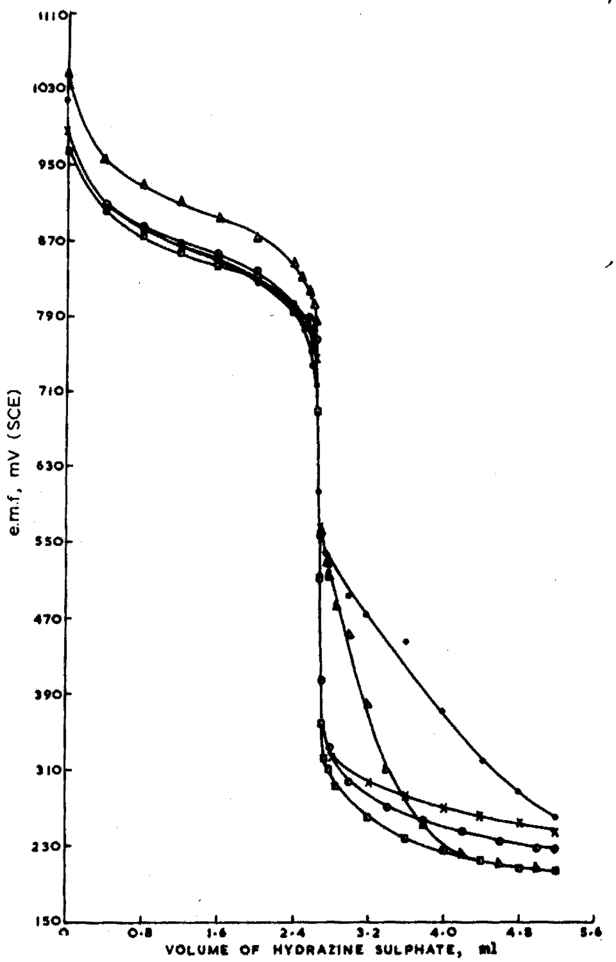

Fig 1. Effect of phosphoric acid concentration on the potentiometric titration of vanadium(V) with hydrazine sulphate. (●) 6.0 *M* H_3PO_4; (△) 7.5 *M* H_3PO_4; (⊡) 9.0 *M* H_3PO_4; (×) 10.5 *M* H_3PO_4; (⊙) 12.0 *M* H_3PO_4.

Potentiometric method

During the developmental work, photometric data showed that the reduction of vanadium(V) by hydrazine sulphate occurs rapidly in 9–12 *M* orthophosphoric acid medium. This is also shown by the potentiometric titration curves given in Fig. 1. When the phosphoric acid concentration lies between 6 and 9 *M*, the potentials take several minutes for stabilization and the potential breaks at the equivalence points are poor. In the region 9–12 *M* the potentials attain stable values within 1 min in the early stages and in 2 min near the equivalence point. The potential breaks are satisfactory, being 150–200 mV per 0.04 ml of 0.05 *M* hydrazine sulphate solution.

Recommended procedure for vanadium(V). Take 10 ml of 0.2 *M* vanadium(V) solution in a pyrex titration vessel, add enough syrupy phosphoric acid to give an overall concentration of 10–12 *M*, and titrate potentiometrically with the 0.05 *M* solution of hydrazine sulphate.

Interferences. Iron(III), copper(II), cobalt(II), nickel(II), molybdenum(VI), tungsten(VI) and chromium(III) do not interfere. Chromium(VI) interferes and is considered below. Among the anions, nitrate interferes even when present in minute amounts because it oxidizes vanadium(IV) to vanadium(V).

Photometric method

Gopala Rao and Kanta Rao[11] showed that the absorption of vanadium(IV) is appreciable in the region 600–800 nm and does not change with the concentration of phosphoric acid whereas vanadium(V) has negligible absorption in this region. Hence during a photometric titration of vanadium(V) with hydrazine sulphate, the absorption of the formed vanadium(IV) was followed with a red filter (transmission 660 nm) in the Klett-Summerson photoelectric colorimeter.

Recommended procedure. Take 5–10 ml of vanadium(V) solution (0.02 *M*–0.2 *M*) in the optical cell and treat with enough syrupy phosphoric acid to give a concentration of 10–12 *M* in a total volume of 40 ml. Place the cell in position in the colorimeter. Because of addition of phosphoric acid and dilution, the temperature of the mixture rises. Allow 15 min for cooling, and adjust the dial

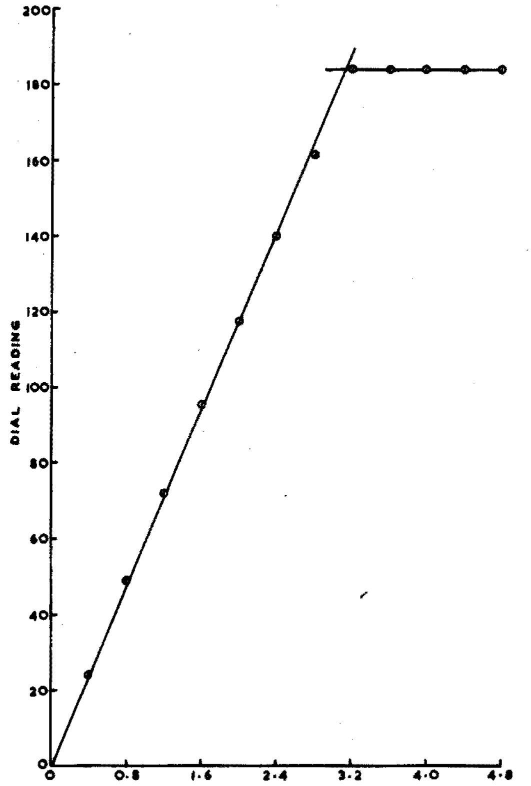

Fig. 2. Photometric titration of vanadium(V) with hydrazine sulphate in 10.5 *M* phosphoric acid medium.

reading of the instrument to "0". Titrate with the hydrazine sulphate solution (0.005–0.05 M). Mix the solution by means of a stream of carbon dioxide passing through a fine glass nozzle placed in a corner of the cell, so that it does not obstruct the optical path. Note the dial readings 30 sec after stopping the passage of carbon dioxide, otherwise gas bubbles will obstruct the light path. Correct the readings for dilution effects and plot against the volume of hydrazine sulphate. A representative titration curve is shown in Fig. 2. It consists of two straight lines meeting at a point which gives the equivalence point.

RESULTS AND DISCUSSION

Representative results of potentiometric and photometric titrations are given in Table I. The results showed that in both potentiometric and photometric titrations in phosphoric acid medium the stoichiometry of the reaction follows eqn. (2) accurately (see below). Earlier investigators of the reaction in sulphuric acid media at room or elevated temperatures stated that the reaction was not stoichiometric under any conditions[12–14]. Browne and Shetterly[13] observed that the volume of nitrogen evolved in the reaction was about 4% less than the theoretical required by eqn. (2). Cuy and Bray[14] stated that vanadate cannot be used for the determination of hydrazine. Phosphoric acid not only increases the speed of reaction but also improves the stoichiometry.

TABLE I

TITRIMETRIC DETERMINATION OF VANADIUM(V) WITH HYDRAZINE SULPHATE IN 10–12 M PHOSPHORIC ACID WITH POTENTIOMETRIC AND PHOTOMETRIC END-POINTS

Amount of vanadium(V) (mmole)			
Potentiometric		*Photometric*	
Taken	*Found*	*Taken*	*Found*
0.1388	0.1384	0.1272	0.1272
0.3322	0.3340	0.2462	0.2468
0.5862	0.5896	0.4490	0.4466
0.7440	0.7449	0.7770	0.7778
1.076	1.075	1.625	1.618
1.662	1.660	2.094	2.100

Mechanism of the oxidation

In order to explain the oxidation reactions of hydrazine with most oxidants, Browne and Shetterly[13] classified oxidants into two classes, which in modern terms can be called one-electron and two-electron acceptors. Thus the oxidation reaction follows two different paths simultaneously:

$$N_2H_5^+ \rightarrow NH_4^+ + H^+ + e^- + \tfrac{1}{2}N_2 \qquad (1)$$

$$N_2H_5^+ \rightarrow N_2 + 5H^+ + 4\,e^- \qquad (2)$$

If eqn. (1) is followed, one equivalent of oxidant is consumed per mole of hydrazine;

for eqn. (2), four equivalents will be consumed per mole of hydrazine. With different oxidants, the redox reaction follows paths (1) and (2) to varying extents. The work of Browne and Shetterly showed that with vanadium(V) the reaction follows path (1) only to the extent of 4%, while path (2) accounts for about 96%. This appears anomalous in terms of the theory of Browne and Shetterly because vanadium(V) is a one-electron abstracting agent; for the end-product of the reduction of vanadium(V) is vanadium(IV) and not vanadium(III). However, this anomalous behaviour was explained by Higginson *et al.*[15] by assuming the steps:

$$V^{5+} + N_2H_5^+ \rightarrow V^{3+} + 3H^+ + N_2H_2 \tag{3}$$

$$V^{5+} + N_2H_2 \rightarrow V^{3+} + 2H^+ + N_2 \tag{4}$$

$$2V^{3+} + 2V^{5+} \rightarrow 4V^{4+} \tag{5}$$

These add up to

$$4V^{5+} + N_2H_5^+ \rightarrow 4V^{4+} + 5H^+ + N_2 \tag{6}$$

The path of one-electron abstraction is given by eqn. (7)

$$V^{5+} + N_2H_5^+ \rightarrow V^{4+} + N_2H_3 + 2H^+ \tag{7}$$

$$2N_2H_3 \rightarrow N_4H_6 \rightarrow 2NH_3 + N_2 \tag{8}$$

Thus the occurrence of the reaction as in eqn. (7) disturbs the stoichiometry required by eqn. (6). But in the proposed titrations in phosphoric acid medium, the stoichiometry is followed accurately by eqn. (6), and the disturbing reaction of eqn. (7) does not intervene. It is suggested that even if reaction (7) occurs, the intermediate N_2H_3 is rapidly oxidized by vanadium(IV) before it can dimerize and disproportionate according to eqn. (8). This suggestion appears quite plausible because vanadium(IV) becomes a more powerful oxidizing agent in concentrated phosphoric acid medium compared with that in dilute sulphuric acid medium.

$$V^{4+} + N_2H_3 \rightarrow V^{3+} + N_2H_2 + H^+ \quad \text{(rapid in } H_3PO_4 \text{ medium)}$$

followed by the oxidation of N_2H_2 as in eqn. (4). The net result is that vanadium(V) functions as a two-electron abstracting oxidizing agent. This explanation is supported by data in Table II.

TABLE II

FORMAL REDOX POTENTIALS OF V^{4+}/V^{3+} COUPLE IN ORTHOPHOSPHORIC ACID MEDIUM[a]

Concentration of phosphoric acid	*Formal redox potential (N.H.E.) (V)*
Nil (1 *N* H_2SO_4)	0.361
1.00	0.388
2.00	0.422
6.00	0.550
8.00	0.601
10.00	0.658
12.00	0.702

[a] Adapted from Gopala Rao and Dikshitulu[16].

In view of the above considerations, the classification of Browne and Shetterly and the mechanism suggested by Higginson *et al.* to explain the major path of the reaction between hydrazine and vanadium(V) as occurring through a two-electron transfer appear reasonably valid.

Titration of chromium(VI) with hydrazine sulphate

Browne and Shetterly[13] carried out a thorough investigation of the reaction of chromium(VI) with hydrazine sulphate in acid medium, varying the acid concentration, relative concentrations of the reactants, temperature and mode of mixing the reactants. They concluded that reproducible results were not obtainable under any conditions and dismissed potassium dichromate as unsuitable for the determination of hydrazine. We have observed that the potentiometric titration of chromium(VI) with hydrazine sulphate gives capricious results even in phosphoric acid medium. Although potentials stabilize rapidly and a good break is observed in the titration curve, the equivalence point is not reproducible even for the same aliquot of chromium(VI) under the same conditions. However, when chromium(VI) was converted into its equivalent of vanadium(V) by the addition of a slight excess of vanadium(IV) and then treated with an adequate amount of phosphoric acid to give an overall concentration of 10–12 *M*, the resulting mixture of vanadium(V) and chromium(III) could be titrated with hydrazine sulphate as satisfactorily as if it were a solution of vanadium(V) alone; the stabilization of the potentials and the potential break at the equivalence point being the same. Typical results are presented in Table III.

TABLE III

POTENTIOMETRIC TITRATION OF CHROMIUM(VI) WITH HYDRAZINE SULPHATE AFTER PRIOR REDUCTION WITH VANADIUM(IV)

Chromium(VI) (mmole)	
Taken	*Found*
0.0424	0.0426
0.0500	0.0498
0.0667	0.0669
0.1000	0.1005
0.1320	0.1316

Simultaneous potentiometric titration of vanadium(V) and chromium(VI) with hydrazine sulphate in strong phosphoric acid medium

The procedure[17] involving the use of titanium(III) chloride has been reported as unsatisfactory[18]. The use of chromium(II) chloride[18] requires critical conditions in the presence of iron(III). These two reagents suffer from the disadvantage of instability of their aqueous solutions in air. A stable reductimetric reagent which does not require special storage conditions like the above two is provided by hydrazine sulphate. With this reagent, it was possible to develop differential titrations of vanadium(V) and chromium(VI) in 10–12 *M* orthophosphoric acid medium with potentiometric and photometric end-points.

When a single saturated potassium chloride salt bridge was interposed between the test half-cell and the reference half-cell, the potentials showed considerable drift with time; this is presumably due to a slow reaction between chloride ion and chromium(VI), in strong phosphoric acid medium. Replacement of the saturated potassium chloride bridge by a saturated sodium nitrate bridge also failed to give stable potentials, probably because of slow oxidation of vanadium(IV) by diffusing nitrate ion. A single salt bridge filled with a saturated solution of sodium perchlorate was unsatisfactory because the potassium ion from the reference half-cell diffused into the salt bridge and formed a blocking precipitate of potassium perchlorate. When the titration vessel was connected via a sodium perchlorate bridge and a nitrate bridge to the reference calomel electrode, stable potentials were quickly attained and two separate breaks in potential could be observed in the E–ml curve, the first break corresponding to the reduction of chromium(VI) to chromium(III) and the second to the total of chromium(VI) and vanadium(V). The potential break at the first equivalence point was about 25–40 mV and at the second about 150–200 mV per 0.04 ml of 0.05 M hydrazine sulphate. Under these conditions the potentials attained stable values within 1 min after the addition of the titrant. In view of the rather small break in potential at the first end-point, the equivalence point was established from a plot of $\Delta E/\Delta$ml against ml. A typical titration curve is given in Fig. 3. Typical results on the determination of vanadium(V) and chromium(VI) are presented in Table IV.

TABLE IV

SIMULTANEOUS POTENTIOMETRIC TITRATION OF VANADIUM(V) AND CHROMIUM(VI) WITH HYDRAZINE SULPHATE IN 10–12 M PHOSPHORIC ACID MEDIUM

Chromium(VI) (mmole)		*Vanadium(V) (mmole)*	
Taken	*Found*	*Taken*	*Found*
0.0417	0.0415	0.2479	0.2474
0.0500	0.0498	0.6308	0.6298
0.0667	0.0669	0.3968	0.3976
0.0999	0.1003	0.8114	0.8108
0.1330	0.1328	0.9990	0.9982

Differential photometric titration of chromium(VI) and vanadium(V) with hydrazine sulphate in strong phosphoric acid medium

A perusal of the absorption spectra of chromium(VI), vanadium(V), chromium(III) and vanadium(IV) in strong phosphoric acid medium as reported by Gopala Rao and Kanta Rao[10,11] shows that both chromium(III) and vanadium(IV) have considerable absorption at 660 nm while chromium(VI) and vanadium(V) have negligible absorption at this wavelength. Although both chromium(III) and vanadium(IV) have considerable absorption at 660 nm, there is a large difference in their molar absorptivities, which are 19.8 and 10.5, respectively, in 10.5 M phosphoric acid medium. Hence a red filter is quite suitable for this photometric titration.

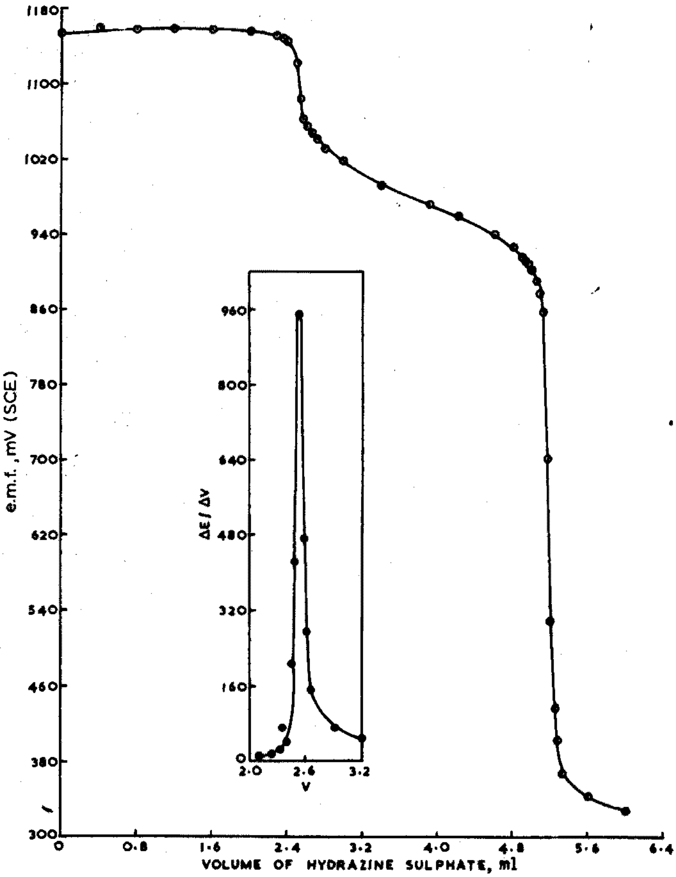

Fig. 3. Differential potentiometric titration of a mixture of chromium(VI) and vanadium(V) with hydrazine sulphate in 12 *M* phosphoric acid medium.

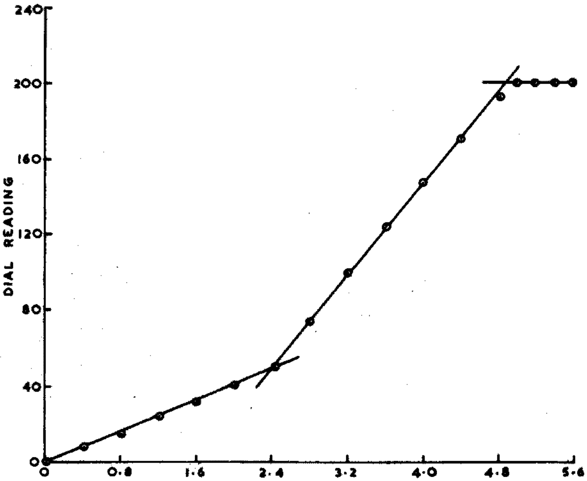

Fig. 4. Photometric titration of a mixture of vanadium(V) and chromium(VI) with hydrazine sulphate in 10.5 *M* phosphoric acid medium (660 nm).

Preliminary experiments showed that a satisfactory differential photometric titration of chromium(VI) and vanadium(V) could be made in 9–12 *M* phosphoric acid. The photometric titration is more convenient than the potentiometric titration as it requires simpler equipment and avoids the disadvantage of a low potential break at the equivalence point for chromium. The proposed procedure is to be preferred to the photometric procedure of Miles and Englis[19] which requires two reagents, arsenic(III) for chromium(VI), and iron(II) for vanadium(V). Moreover, their method involves a positive error of 0.98% for chromium(VI) and a negative error of 0.87% for vanadium(V). The proposed method is accurate for both ions. A typical titration curve is given in Fig. 4. Representative results are presented in Table V.

TABLE V

DIFFERENTIAL PHOTOMETRIC TITRATION OF CHROMIUM(VI) AND VANADIUM(V) WITH HYDRAZINE SULPHATE IN 9–12 *M* PHOSPHORIC ACID MEDIUM

Chromium(VI) (mmole)		*Vanadium(V) (mmole)*	
Taken	*Found*	*Taken*	*Found*
0.01667	0.01670	0.1196	0.1190
0.03892	0.03892	0.1840	0.1844
0.05740	0.05738	0.5520	0.5512
0.03340	0.03333	0.6876	0.6880
0.02576	0.02570	0.9920	0.9916
0.02072	0.02066	1.1960	1.1920

SUMMARY

Hydrazine sulphate is proposed as a primary standard reagent for the direct titrimetric determination of vanadium(V) and chromium(VI) alone and in mixtures with potentiometric and photometric end-points, in 9–12 *M* phosphoric acid medium. The methods proposed possess advantages over those currently available. The use of phosphoric acid as a reaction medium not only accelerates the hydrazine–vanadium(V) reaction very much but also makes it follow an accurate stoichiometric path.

RÉSUMÉ

Le sulfate d'hydrazine est proposé comme standard primaire pour le titrage direct du vanadium(V) et du chrome(VI), avec point final potentiométrique et photométrique, en milieu acide phosphorique concentré. Ce milieu acide phosphorique, non seulement accélère la réaction hydrazine–vanadium(V), mais également permet une stoechiométrie précise.

ZUSAMMENFASSUNG

Hydrazinsulfat wird als Urtitersubstanz für die direkte titrimetrische Be-

stimmung von Vanadin(V) und Chrom(VI) allein und in Gemischen bei potentiometrischer und photometrischer Endpunktsbestimmung in konzentrierter Phosphorsäure-Lösung vorgeschlagen. Die vorgeschlagenen Methoden sind vorteilhafter als die sonst üblichen. Die Verwendung von Phosphorsäure als Reaktionsmedium beschleunigt nicht nur sehr stark die Hydrazin–Vanadin(V)-Reaktion, sondern bewirkt auch, dass sie streng stöchiometrisch abläuft.

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THE COMPUTERIZED CALCULATION OF SPECTROPHOTOMETRIC TITRATION CURVES FOR COMPLEXIMETRIC TITRATIONS

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Many attempts have been made to establish reliable treatments of theoretical titration curves, and these have been summarized by Anfält and Jagner[1]. Because of the cubic expression of the absorbance, almost all spectrophotometric titration curves in compleximetry have been calculated under special conditions where some terms in the calculation, *e.g.* the concentration of the metallochromic indicator, have been neglected[2]. These approximations were, of course, useful in obtaining information about the titrations, but they were not always correct and valid for every condition in spectrophotometric titrations. The aim of the present work was to obtain complete spectrophotometric titration curves by computer calculations without neglecting any terms.

CALCULATIONS

The following symbols are used: M, L, I: the free forms of the metal ion titrated, the ligand used as titrant, and the metallochromic indicator, respectively; ML, MI: the metal chelate or complex formed with the ligand and indicator, respectively; K_L, K_I: apparent stability constants of ML and MI, respectively; C_M, C_L, C_I: total concentrations of the metal, ligand, and metallochromic indicator, respectively.

A metal (M) is titrated with a complex-forming ligand (L) in the presence of a metallochromic indicator (I). Provided that the metal gives a 1:1 ML chelate with the ligand and a 1:1 MI complex with the indicator, the following equations are valid:

$$[ML]/[M][L] = K_L \tag{1}$$

$$[MI]/[M][I] = K_I \tag{2}$$

$$C_M = [M] + [ML] + [MI] \tag{3}$$

$$C_L = [L] + [ML] \tag{4}$$

$$C_I = [I] + [MI] \tag{5}$$

Here, a titration parameter X and an index for the colour change α are defined as follows:

$$C_L/C_M = X \quad \text{and} \quad [MI]/C_I = \alpha$$

Introducing X and α into eqns. (2)–(5), we obtain:

$$[\mathrm{MI}] = K_{\mathrm{I}}[\mathrm{M}][\mathrm{I}] = \alpha C_{\mathrm{I}} \tag{6}$$

$$C_{\mathrm{M}} = [\mathrm{M}] + [\mathrm{ML}] + \alpha C_{\mathrm{I}} \tag{7}$$

$$C_{\mathrm{M}}X = [\mathrm{L}] + [\mathrm{ML}] \tag{8}$$

$$C_{\mathrm{I}} = [\mathrm{I}] + \alpha C_{\mathrm{I}} \tag{9}$$

Combination of eqns. (6) and (9) yields:

$$[\mathrm{M}] = \alpha / K_{\mathrm{I}}(1-\alpha) \tag{10}$$

and from eqns. (7) and (10), we have:

$$[\mathrm{ML}] = \frac{C_{\mathrm{M}}K_{\mathrm{I}}(1-\alpha) - C_{\mathrm{I}}K_{\mathrm{I}}\alpha(1-\alpha) - \alpha}{K_{\mathrm{I}}(1-\alpha)} \tag{11}$$

Introduction of eqns. (10) and (11) into eqn. (1) gives:

$$[\mathrm{L}] = \frac{C_{\mathrm{M}}K_{\mathrm{I}}(1-\alpha) - C_{\mathrm{I}}K_{\mathrm{I}}(1-\alpha) - \alpha}{K_{\mathrm{L}}\alpha} \tag{12}$$

From eqns. (8), (11) and (12),

$$\begin{aligned} &C_{\mathrm{M}}K_{\mathrm{I}}K_{\mathrm{L}}X\alpha(1-\alpha) = \\ &\qquad \{C_{\mathrm{M}}K_{\mathrm{I}}(1-\alpha) - C_{\mathrm{I}}K_{\mathrm{I}}\alpha(1-\alpha) - \alpha\}\{K_{\mathrm{I}}(1-\alpha) + K_{\mathrm{L}}\alpha\} \end{aligned} \tag{13}$$

Equation (13) is substantially the same as that given by Flaschka and Khalafallah[3] and can be written as follows:

$$\begin{aligned} &(C_{\mathrm{I}}K_{\mathrm{I}}K_{\mathrm{L}} - C_{\mathrm{I}}K_{\mathrm{I}}K_{\mathrm{I}})\alpha^3 \\ &+ (2C_{\mathrm{I}}K_{\mathrm{I}}K_{\mathrm{I}} + C_{\mathrm{M}}K_{\mathrm{I}}K_{\mathrm{I}} + K_{\mathrm{I}} - C_{\mathrm{M}}K_{\mathrm{I}}K_{\mathrm{L}} - C_{\mathrm{I}}K_{\mathrm{I}}K_{\mathrm{L}} - K_{\mathrm{L}} + C_{\mathrm{M}}K_{\mathrm{I}}K_{\mathrm{L}}X)\alpha^2 \\ &+ (C_{\mathrm{M}}K_{\mathrm{I}}K_{\mathrm{L}} - 2C_{\mathrm{M}}K_{\mathrm{I}}K_{\mathrm{I}} - C_{\mathrm{I}}K_{\mathrm{I}}K_{\mathrm{I}} - K_{\mathrm{I}} - C_{\mathrm{M}}K_{\mathrm{I}}K_{\mathrm{L}}X)\alpha \\ &+ C_{\mathrm{M}}K_{\mathrm{I}}K_{\mathrm{I}} = 0 \end{aligned} \tag{14}$$

If certain values of C_{M}, C_{I}, K_{I} and K_{L} are introduced into eqn. (14) and it is assumed that these values are constant in the vicinity of the equivalent point, the α parameter can be obtained by solving eqn. (14) against the titration parameter X, the variation of which is limited near the equivalent point ($X = 1$).

During a spectrophotometric titration, α at a definite wavelength varies from 1 to zero when the indicator–metal complex, MI, absorbs and the indicator, I, itself has no absorption, and *vice versa*.

COMPUTER PROGRAM

The cubic expression (14) can be easily solved with a computer. A program was written in CALPAC-3 for use with the AICOM-C3 computer by Ai Electronics Co., Ltd.

After the parameters, C_{M}, C_{I}, K_{I} and K_{L} have been read in, α is obtained at each given value of X, which is increased by increments of 0.005 starting from 0.900 and by increments of 0.001 from 0.990. When α becomes less than 0.0005, all calculation is stopped.

Differentiation of eqn. (14) with respect to α gives:

$$f'(\alpha) = 3\alpha^2 + \frac{2B}{A}\alpha + \frac{C}{A}$$

where $A = C_I K_I K_L - C_I K_I K_I$

$$B = 2C_I K_I K_I + C_M K_I K_I + K_I - C_M K_I K_L - C_I K_I K_L - K_L + C_M K_I K_L X$$

$$C = C_M K_I K_L - 2C_M K_I K_I - C_I K_I K_I - K_I - C_M K_I K_L X$$

According to Newton's method,

$$\alpha_{i+1} = \alpha_i - \frac{f(\alpha_i)}{f'(\alpha_i)}$$

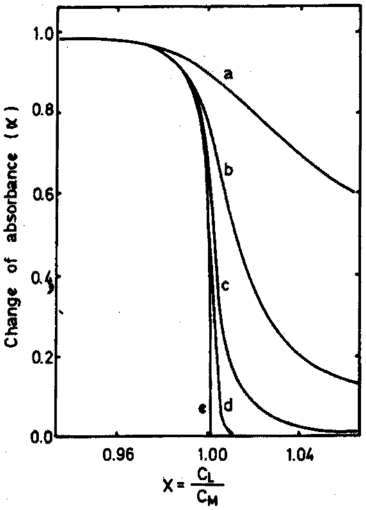
$$D = \alpha_i - \alpha_{i+1}$$

TABLE I

PART OF THE COMPUTER-CALCULATED RESULT

(K(L)=10↑(8.0), K(I)=10↑(5.0), C(I)=10↑(−5.0), C(M)=10↑(−2.0), allowance for Newton residue=0.00005, initial for Newton equation=0.9999)

X	*Alpha (A)*	*Delta (A)*	*T*	*Delta (T)*	*Log (M)*
0.9500	0.9800	0.0018	0.5232	−0.0485	−3.3094
0.9550	0.9777	0.0022	0.5827	−0.0595	−3.3561
0.9599	0.9750	0.0027	0.6575	−0.0747	−3.4083
0.9649	0.9714	0.0035	0.7542	−0.0967	−3.4677
0.9700	0.9667	0.0047	0.8843	−0.3300	−3.5366
0.9750	0.9601	0.0066	3.0683	−0.1840	−3.6183
0.9800	0.9502	0.0098	1.3485	−0.2801	−3.7189
0.9850	0.9339	0.0163	1.8256	−0.4771	−3.8496
0.9900	0.9020	0.0319	2.8122	−0.9865	−4.0359
0.9909	0.8916	0.0103	3.1487	−0.3364	−4.0846
0.9919	0.8789	0.0127	3.5732	−0.4245	−4.1391
0.9929	0.8629	0.0159	4.1238	−0.5505	−4.2010
0.9939	0.8423	0.0205	4.8622	−0.7383	−4.2721
0.9949	0.8151	0.0271	5.8943	−1.0320	−4.3555
0.9959	0.7780	0.0370	7.4108	−1.5165	−4.4551
0.9969	0.7260	0.0520	9.7687	−2.3578	−4.5767
0.9979	0.6525	0.0734	13.6157	−3.8470	−4.7262
0.9989	0.5548	0.0977	19.8598	−6.2440	−4.9044
0.9999	0.4448	0.1099	28.7806	−8.9207	−5.0961
1.0010	0.3471	0.0977	38.8466	−10.0660	−5.2742
1.0020	0.2737	0.0733	48.0414	−9.3947	−5.4236
1.0030	0.2217	0.0519	55.5632	−7.5218	−5.5451
1.0039	0.1847	0.0370	61.5031	−5.9399	−5.6447
1.0050	0.1575	0.0271	66.1905	−4.6874	−5.7280
1.0059	0.1370	0.0205	69.9341	−3.7435	−5.7991
1.0070	0.1210	0.0159	72.9706	−3.0364	−5.8609
1.0080	0.1083	0.0127	75.4723	−2.5017	−5.9154
1.0090	0.0979	0.0103	77.5635	−2.0911	−5.9641
1.0099	0.0893	0.0085	79.3344	−1.7709	−6.0081



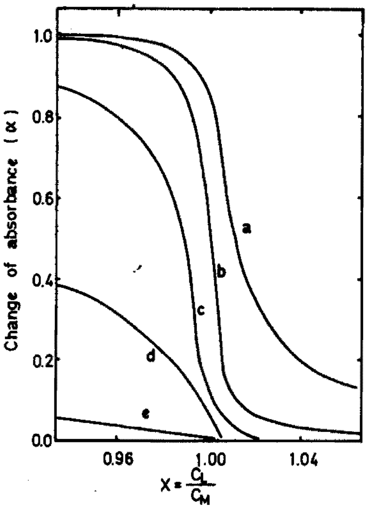


Fig. 1. An example of the dependence of titration curves on the stability constant K_L. $K_I=10^5$, $C_M=10^{-2}$ M, and $C_I=10^{-5}$ M. K_L=(a) 10^6; (b) 10^7; (c) 10^8; (d) 10^9; (e) 10^{10-12}.

Fig. 2. An example of the dependence of titration curves on the stability constant K_I. $K_L=10^8$, $C_M=10^{-2}$ M, and $C_I=10^{-5}$ M. K_I=(a) 10^6; (b) 10^5; (c) 10^4; (d) 10^3; (e) 10^2.

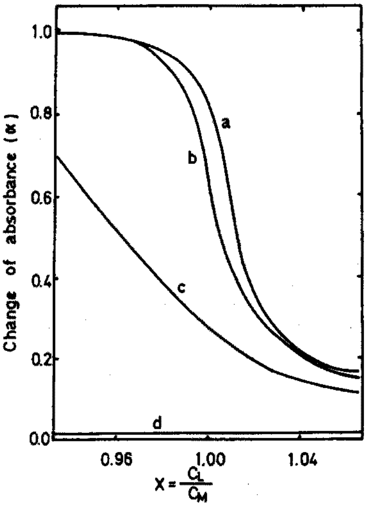


Fig. 3. An example of the effect of the indicator concentration (C_I) on the titration curves. $K_L=10^8$, $K_I=10^6$, and $C_M=10^{-3}$ M. C_I=(a) 10^{-7} and 10^{-6}; (b) 10^{-5}; (c) 10^{-4}; (d) 10^{-3} M.

When an absolute value of D converges to zero, α_{i+1} is the value of α that satisfies eqn. (14). Practically, beginning with a suitable value of α_1, a new α_2 is calculated and the iterative loop calculation for ($\alpha_i \rightarrow \alpha_{i+1}$) is continued until the absolute value of D is less than 0.00005. Then, that value α is printed.

An example of the results is shown in Table I. The difference of α between at X_i and at X_{i+1}, $\Delta\alpha$, is also printed. A transmittance index T, which is an arbitrary measure of transmittance reading, is also calculated from α, according to the equation,

$$T = \frac{10(10^{2-\alpha}-10)}{9}$$

where T varies from zero to 100 as α varies from 1 to zero. The difference of T between the points X_i and X_{i+1}, ΔT, is printed. The free metal concentration during the titration is calculated from eqn. (10), and its logarithm is recorded.

Alternative program

In a reversal of the above calculation, the value of X can be calculated against a certain value of α, as in the method used by Hannema and Den Boef[4]. Equation (13) can be rewritten as follows:

$$X = 1+X_1+X_2+X_3+X_4+X_5+X_6 \tag{15}$$

where

$$X_1 = \frac{-1}{C_M K_L}, \quad X_2 = \frac{-C_I K_I}{C_M K_L}, \quad X_3 = \frac{-C_I}{C_M}\alpha,$$

$$X_4 = \frac{C_I K_I}{C_M K_L}\alpha, \quad X_5 = \frac{-1}{C_M K_I}\cdot\frac{\alpha}{1-\alpha}, \quad \text{and} \quad X_6 = \frac{K_I}{K_L}\cdot\frac{1-\alpha}{\alpha}.$$

At a given value of α(0–1), X is calculated from eqn. (15). The calculation follows only arithmetic rules, but is tedious if done by hand, so that the use of a computer is again preferable. Both programs, of course, give the same spectrophotometric titration curve.

RESULTS

For various conditions, *i.e.* any combinations of the values of C_M, C_I, K_I and K_L, the changes of the α value during titrations are easily calculated by either of the computer programs mentioned above. Some plots of α against X are shown in Figs. 1–3. The preparation of such plots makes it possible to obtain useful information on such points as the optimal conditions for titrations and the errors involved in their execution.

The authors gratefully acknowledge the helpful suggestions of Prof. R. Kawashima and other colleagues concerning the programming and use of the computer. The authors also thank Miss M. Nambu for assistance in running the computer and making the graphs.

SUMMARY

The change of absorbance during a compleximetric titration involving a metallochromic indicator and 1:1 complexes, was calculated by means of computer; no terms were neglected. Two computer programs were developed. In addition to the absorbance, the transmittance and the free metal-ion concentration during a titration

were also calculated from the total concentrations of metal and indicator, and the stability constants of the metal–ligand and the indicator–metal complexes.

RÉSUMÉ

Le changement d'absorbance au cours d'un titrage compleximétrique, comprenant indicateur métalochromique et complexes 1:1, a été calculé à l'aide d'un ordinateur; aucun terme n'a été négligé. Deux programmes d'ordinateur sont proposés. En plus de l'absorbance, on calcule également la transmittance et la concentration de l'ion métallique libre au cours du titrage, à partir de la concentration totale du métal, et de l'indicateur, en tenant compte des constantes de stabilité du ligand métallique et des complexes indicateur–métal.

ZUSAMMENFASSUNG

Die Änderung der Extinktion während einer komplexometrischen Titration unter Verwendung eines Metallindikators und Bildung eines 1:1-Komplexes wurde mit Hilfe eines Computers berechnet. Alle Einflüsse wurden berücksichtigt. Zwei Computerprogramme wurden entwickelt. Zusätzlich zur Extinktion wurden die Durchlässigkeit und die freie Metallionenkonzentration während einer Titration aus den Gesamtkonzentrationen des Metalls und des Indikators sowie der Beständigkeitskonstanten der Metall–Ligand- und der Indikator–Metall-Komplexe ebenfalls berechnet.

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EVALUATION OF THE ACCURACY OF GRAN PLOTS BY MEANS OF COMPUTER CALCULATIONS

APPLICATION TO THE POTENTIOMETRIC TITRATION OF THE TOTAL ALKALINITY AND CARBONATE CONTENT IN SEA WATER

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During recent years, the use of Gran[1] plots to evaluate equivalence points in potentiometric titrations has become more frequent. This is probably largely due to recommendations by leading manufacturers of ion-selective electrodes to use this method in combination with their electrodes[2]. The method has, moreover, been included in text-books[3–7] and in articles concerned with chemical education[8–10]. Since it has been demonstrated that the method is based on more stringent theoretical grounds than most other methods in use[11] and since the method is, furthermore, well suited for use in automatic titration procedures[12,13], it is reasonable to assume that the Gran method will be even more frequently used in the future.

When Gran plots are used, most authors seem, however, to neglect the fact that, in the derivation of those plots originally suggested by Gran[1], it was assumed that there exists a completely dominating main reaction in all parts of the titration curve. This is, of course, never completely true in any titration curve. As pointed out by Ingman and Still[14], considerable systematic errors may arise when competing side-reactions are neglected. This drawback is particularly serious in titrations where the demand for accuracy is very high, *e.g.* in the determinaton of the total alkalinity and carbonate content in sea water by means of potentiometric titration.

The aim of this paper is to show how it is possible, by means of computer calculations, to determine the magnitude of the systematic errors associated with the plots originally suggested by Gran. It will also be illustrated how the results from the calculations can be used in the derivation of "modified" Gran plots capable of locating the equivalence points with far greater accuracy. The main features of the procedure outlined are as follows.

(*a*) The calculation of the free concentration, in each titration point, of all species involved in the particular titration solution. Such a calculation is preferably carried out with a computer program such as HALTAFALL[4,15,16], based on stability constants and total concentrations relevant to the titration under consideration.

(*b*) Conversion into e.m.f. units of that concentration which is measured potentiometrically. This is accomplished through the Nernst equation; for example, for an acid–base titration with a glass electrode

$$E_{\text{calc}} = E^0_{\text{arb}} + RT \ln 10 \log[\text{H}^+]/F \qquad (1)$$

where E^0_{arb} is chosen arbitrarily. The form of the simulated titration curve E_{calc} *vs.* v ml thus obtained, will be identical with that of the experimental curve, provided that liquid junction potentials and activity factors are kept constant and that the sensor electrode obeys Nernst's law. Shifts in the junction potential proportional to $[H^+]$ and $[OH^-]$ occur above all in very acid or basic solutions outside the pH range 2.5–11.5. The changes in activity factors during a titration are moderate in the ionic strength range 0.1–1 *M*. The total concentrations and stability constants for the species involved must also, of course, be relevant to the experimental conditions.

(*c*) Insertion of the E_{calc} and v values into the plots originally suggested by Gran, and evaluation of the equivalence point v_{extr}. The difference between v_{extr} and v_{eq}, *i.e.* the equivalence volume derived from the total concentrations fed into the HALTAFALL program, defines the systematic error associated with the Gran plot for the particular titration under consideration as

$$\% \text{ systematic error} = 100(v_{extr} - v_{eq})/v_{eq} \qquad (2)$$

(*d*) Location of the most important side-reactions in the different parts of the titration curve. This is achieved by using a plot of the concentrations of all species present in the titration solution against v ml of titrant added (*cf.* Fig. 1).

(*e*) Derivation of "modified" Gran plots which take the interfering side-reactions into account. This is done by stringent use of mass-balance conditions and equilibrium equations. An approximate knowledge of the total concentrations of the interfering substances and an approximate knowledge of the stability constants for all species involved is, however, required.

(*f*) Examination of the accuracy of the "modified" Gran plots by their application to the E_{calc} *vs.* v values of the simulated curve. Such calculations are preferably carried out with the help of a mini-computer. As mentioned above, the "modified" Gran plots contain values for stability constants and total concentrations which are only approximately known. Consequently, it is necessary to vary the values of these parameters in the "modified" Gran plots in order to test the practical significance of the "modified" Gran plots. In this way a quantitative estimation of the maximum systematic error associated with the plots when they are applied to the experimental data is obtained.

The procedure outlined above can, of course, be applied to any titration system. In this paper it is exemplified by its application to a specific titration procedure, namely the determination of the total carbonate content and alkalinity of sea water. For this titration, which is of great interest for the study of the global carbon dioxide cycle, Dyrssen and Sillén[17] have suggested the use of Gran plots. This approach has attracted considerable interest and the method can now be found in text-books of chemical oceanography[6,7]. The accuracy of the plots suggested[17] has, however, been questioned and there has been discussion as to whether or not it is possible to increase their accuracy. Consequently, the example chosen is, in itself, of interest.

THE CHEMICAL SYSTEM. HALTAFALL CALCULATIONS

The approximate concentrations of the major ionic constituents of ocean water are well known and it is also known that the relative proportions of these constituents are practically constant, regardless of the total salt content. In this respect, carbonate and hydrogen carbonate are, however, exceptions. Furthermore, the stability constants for the important acid–base equilibria occurring in sea water are well established. This is particularly true for the carbonate[18] and borate[19] systems, for which stability constants have been determined at different temperatures and salinities. Recently, the conditional constant for the protonization constant of sulphate in sea water has been determined by Elgquist and Wedborg[20] and evaluated by Dyrssen and Hansson[21]. With the HALTAFALL program it is thus possible to calculate the reactions taking place when hydrochloric acid is added to a sea-water sample contained in a closed titration vessel, which prevents the escape of carbon dioxide. In the present work, these calculations were performed as a titration of 250 ml of sea water, containing 1.2 mmoles of carbonate per kg and 1.2 mmoles of hydrogen carbonate per kg with 0.1 *M* hydrochloric acid. These calculations, which have been performed for $v = 0$, 0.2, 0.4, ... 14 ml, are closely connected to the experimental titration procedure as originally suggested by Dyrssen *et al.*[22,23]. The ratio between carbonate and hydrogen carbonate is larger than in normal sea water in order to elucidate the reactions occurring before carbonate is titrated to hydrogen carbonate. The total concentrations and stability constants for the other species contributing to the form of the titration curve are specified in Tables I and II. These values, which are assumed to be relevant to a sea-water sample of 35‰ salinity, are all expressed in the unit M_w = moles/1000 g of sea water.

The results of the calculations are shown in Fig. 1 in which the concentrations of the predominant species involved have been plotted against v ml of titrant added.

TABLE I

STABILITY CONSTANTS FOR THE HALTAFALL CALCULATIONS OF THE TITRATION OF CARBONATE IN SEA WATER WITH HYDROCHLORIC ACID

(The constants are conditional in that they include complexing between Mg^{2+} and Ca^{2+} with HCO_3^-, CO_3^{2-}, $B(OH)_4^-$, F^- and OH^- and between SO_4^{2-} and Na^+, K^+, Mg^{2+} and Ca^{2+}. The conditional constants are based on experimental values for sea water and sodium chloride given in refs. 18–21 and 24)

Equilibrium	*Notation*	*Equilibrium constant*
$H_2O + CO_2(l) \rightleftharpoons H^+ + HCO_3^-$	K_{1C}	$1.06 \cdot 10^{-6}$
$HCO_3^- \rightleftharpoons H^+ + CO_3^{2-}$	K_{2C}	$8.53 \cdot 10^{-10}$
$H^+ + SO_4^{2-} \rightleftharpoons HSO_4^-$	β_{HSO_4}	14.3
$B(OH)_3 + H_2O \rightleftharpoons B(OH)_4^- + H^+$	K_B	$1.85 \cdot 10^{-9}$
$H^+ + F^- \rightleftharpoons HF$	β_{HF}	400
$H_2O \rightleftharpoons H^+ + OH^-$	K_w	$4.84 \cdot 10^{-14}$

TABLE II

TOTAL CONCENTRATIONS OF SOME MAJOR CONSTITUENTS OF SEA WATER

Species	CO_3^{2-}	SO_4^{2-}	$B(OH)_3$	F^-
Total concn. (mM_w)	2.4	28.25	0.42	0.073

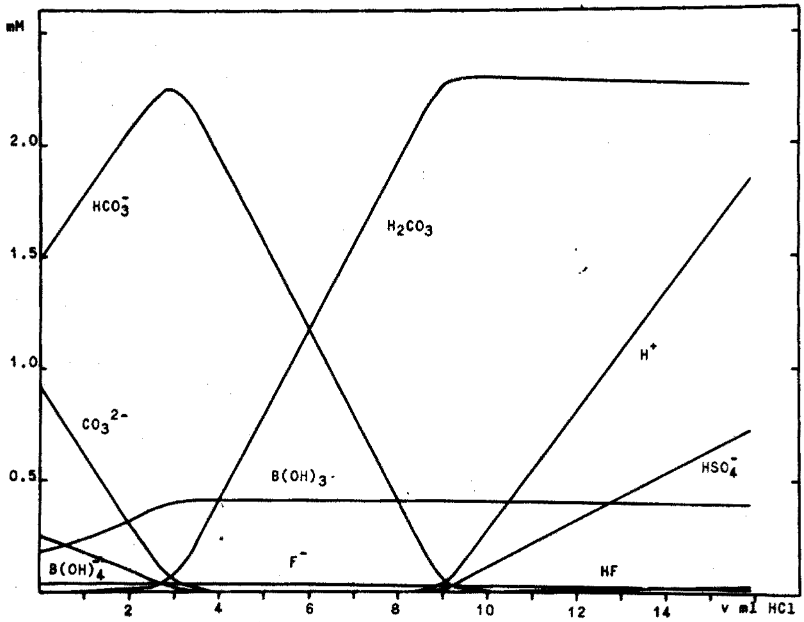

Fig. 1. The concentrations of major protolytes in sea water plotted against v ml of 0.1 M hydrochloric acid added in the titration of 250 g of sea water.

In this Figure, $v_1 = 3$ ml represents the carbonate/hydrogen carbonate equivalence point and $v_2 = 9$ ml represents the hydrogencarbonate/carbonic acid equivalence point. By definition, the total alkalinity is given by

$$\text{total alkalinity } (M_w) = v_2 \text{ (titre of HCl/g of sea water)} \tag{3}$$

and the total carbonate content is, of course, obtained from the difference between v_2 and v_1, *i.e.*

$$\text{total carbonate } (M_w) = (v_2 - v_1) \text{ (titre of HCl/g of sea water)} \tag{4}$$

The calculated values for $[H^+]$ were converted into e.m.f. units according to

$$E_{calc} = 400 + 59.16 \log [H^+]_{calc} \tag{5}$$

i.e. by using an arbitrary E^0 value of 400 mV and a temperature of 25°. The E_{calc} values were calculated with a resolution of 0.01 mV, *i.e.* $E_{calc} = 222.25$ mV when $\log [H]_{calc} = -3$.

ORIGINAL GRAN PLOTS

The Gran plots suggested by Dyrssen and Sillén[17,22] for the specific titration under consideration were derived on the assumption of completely dominating main reactions, as in the procedure outlined by Gran[1]. In their evaluation of v_2, using the function F_2 below, they assumed that all hydrogen ions added in the region $v > v_2$ form free hydrogen ions only. With this assumption the mass-balance condition for hydrogen ions can be written as

$$(v_0+v)[\mathrm{H}^+]=t(v-v_2) \qquad (v>v_2) \tag{6}$$

where v_0 is the volume of the sea-water sample and t the concentration of the hydrochloric acid titrant, here 250 ml and 0.1 *M*, respectively.

Equation (6) can be rewritten as

$$F_2=(v_0+v)\,10\exp(E/59.16)\propto(v-v_2) \tag{7}$$

since at 25°

$$[\mathrm{H}^+]\propto 10\exp(E/59.16) \tag{8}$$

If the assumption made above were correct, then F_2 would be linear for v ml of titrant added and would, furthermore, intersect the v-axis at $v=v_2$ when extrapolated to $F_2=0$.

The HALTAFALL-calculated E_{calc} values can be used to check the accuracy of F_2 in the determination of v_2. For each value of v in the volume range $v>v_2$, the corresponding F_2 value is calculated from the E_{calc} values and eqn. (7). For different sets of (v, F_2) values, the regression lines are computed and the intersection on the v-axis, $v_{2,\mathrm{extr}}$, is determined. Since F_2 only approximately expresses the mass-balance condition for hydrogen ions, $v_{2,\mathrm{extr}}$ will not be equal to v_2. This will result in a systematic error in total alkalinity. Table III lists the percentage systematic errors, $100(v_{2,\mathrm{extr}}-9)/9$, obtained when F_2 is applied to the HALTAFALL-

TABLE III

THE DEPENDENCE OF THE SYSTEMATIC ERRORS IN F_1, F_2, F_1' AND F_2' ON THE VOLUME RANGES CHOSEN TO EVALUATE v_1 AND v_2

(In sea water of normal composition the errors in alkalinity are about 1.5 times those in the Table)

Volume range used for evaluation of $v_{2,\mathrm{extr}}$	*Volume range used for evaluation of $v_{1,\mathrm{extr}}$*	*Systematic error in total alkalinity (%)*		*Systematic error in total carbonate (%)*	
		Original Gran plot F_2	*Modified Gran plot* F_2'	*Original Gran plots* F_1, F_2	*Modified Gran plots* F_1', F_2'
9.2–10	3.4–6	−1.03	0.00	−0.10	−0.01
9.2–11	3.4–6	−0.71	0.00	0.30	−0.01
9.2–12	3.4–6	−0.54	0.00	0.52	−0.01
9.2–13	3.4–6	−0.42	0.00	0.67	−0.01
9.2–14	3.4–6	−0.31	0.00	0.80	−0.01
11.2–12	3.4–6	−0.02	0.00	1.17	−0.01
13.2–14	3.4–6	0.32	0.00	1.60	−0.05
9.2–12	3.2–8	−0.54	0.00	1.38	−0.01
9.2–12	3.2–7	−0.54	0.00	0.78	−0.01
9.2–12	3.2–6	−0.54	0.00	0.78	−0.01
9.2–12	3.2–5	−0.54	0.00	1.04	−0.01
9.2–12	3.2–4	−0.54	0.00	1.70	−0.01
9.2–12	4–8	−0.54	0.00	1.68	−0.01
9.2–12	5–8	−0.54	0.00	3.27	−0.01
9.2–12	6–8	−0.54	0.00	6.86	−0.02
9.2–12	7–8	−0.54	0.00	16.77	−0.01

simulated titration curve used in this work. In the case of natural sea water where v_1 is usually small and v_2 will be close to 6 ml, the systematic error will be about 1.5 times larger.

In the derivation of the Gran plot suggested for the evaluation of v_1, it has been assumed[17] that the formation of carbonic acid from hydrogen carbonate ions is the dominating reaction in the volume range $v_1 < v < v_2$, and if this is the case then

$$[H_2CO_3] = t(v-v_1)/(v_0+v) \tag{9}$$

$$[HCO_3^-] = t(v_2-v)/(v_0+v) \tag{10}$$

Furthermore,

$$[H^+][HCO_3^-]/[H_2CO_3] = K_{1C} \tag{11}$$

and, by combining eqn. (11) with eqns. (9) and (10)

$$[H^+](v_2-v) \propto (v-v_1) \tag{12}$$

By eliminating $[H^+]$ through eqn. (8)

$$F_1 = (v_2-v)\,10\exp(E/59.16) \propto (v-v_1) \tag{13}$$

If the assumptions made in eqns. (9) and (10) were correct, then F_1 would be linear with v ml of titrant added and, moreover, would intersect the v-axis at $v = v_1$ when extrapolated to $F_1 = 0$. Of course, an accurate value of v_2 must be known. The accuracy of F_1 in determining v_1 can be checked by HALTAFALL-calculated E_{calc} values in a similar way as that outlined for F_2 above. In the present work, values of

$$F_1 = (v_{2,\text{extr}}-v)\,10\exp(E_{\text{calc}}/59.16) \tag{14}$$

were calculated in the volume range $v_1 < v < v_2$; for different sets of (v, F_1) values, the regression lines were computed and the intersection on the v-axis, $v_{1,\text{extr}}$, was determined for each regression line. The results obtained, expressed as the percentage systematic error in the total carbonate content, *i.e.* $100(v_{1,\text{extr}} - v_{2,\text{extr}} + 6)/6$, where the value of $v_2 - v_1$ is 6 ml, in the HALTAFALL calculation under consideration, are shown in Table III.

The results make it obvious that the values obtained for the total alkalinity and carbonate content are strongly dependent on the volume intervals used for F_1 and F_2. Unsuitable choices can result in systematic errors of up to 1%. A likely choice in practice would be 9.2–12 ml for v_2 and 3.4–6 ml for v_1, the corresponding systematic errors being −0.54% and +0.52% for the total alkalinity and the carbonate content, respectively. In Table III volume intervals associated with very small systematic errors are apparent, *e.g.* 11.2–12 ml for v_2. In this range, the change in e.m.f. between each successive increment of titrant is, however, rather small and, consequently, the precision will be lower than when exploiting, for example, the volume range 9.2–10 ml closer to v_2. It is therefore essential to derive modified Gran plots which can exploit experimental points over a wide volume range including points close to v_1 and v_2, and still locate these points with satisfactory accuracy.

MODIFIED GRAN PLOTS

An advantage of HALTAFALL calculations is that interfering side-reactions are easily revealed. Figure 1 shows that even at $v > v_2$ there is still some untitrated hydrogen carbonate and, moreover, that a considerable amount of hydrogen sulphate is being formed. It can also be seen that a minor part of the hydrochloric acid added for $v > v_2$ is consumed by the formation of hydrofluoric acid while the amounts of borate, hydroxide ions and carbonate are so small that they can be neglected in the mass-balance equations. Thus the amount of hydrogen ions added after v_2, $t(v-v_2)$ mmoles, is much more accurately expressed by

$$F_2' = (v_0+v)([\mathrm{H}^+]+[\mathrm{HSO}_4^-]+[\mathrm{HF}]-[\mathrm{HCO}_3^-]) \propto (v-v_2) \qquad (16)$$

$$(v > v_2)$$

than by the simpler function F_2 (*cf.* eqn. (6)).

In the volume interval $v_1 < v < v_2$, where the main reaction is the formation of carbonic acid, there are many minor side-reactions (*cf.* Fig. 1). Apart from the titration of small amounts of CO_3^{2-}, OH^- and $\mathrm{B(OH)}_4^-$, some of the hydrogen ions added form HSO_4^- and HF and an increasing excess of free hydrogen ions. The total amount of hydrogen ions added after v_1, $t(v-v_1)$ mmoles, is given by

$$F_1' = (v_0+v)([\mathrm{H}^+]+[\mathrm{H_2CO_3}]+[\mathrm{HSO}_4^-]+[\mathrm{HF}]-[\mathrm{OH}^-]- \\ -[\mathrm{B(OH)}_4^-]-[\mathrm{CO}_3^{2-}]) \propto (v-v_1) \qquad (17)$$

From eqns. (16) and (17), it follows that F_2' and F_1' are linear in v and that these lines intersect the v-axis at v_2 and v_1, respectively. However, in order to be able to use F_1' and F_2' for evaluation of v_1 and v_2 it is necessary to know not only the stability constants for all complexes given in Table I and the total concentrations for sulphate, boron and fluoride, but also an approximate value of E^0 for the electrode couple. This information is not needed when the original Gran plots F_1 and F_2 are used. As previously emphasised, the stability constants are generally only approximately known and this is also true for the total concentrations of the species interfering with the main reactions. The total concentration of carbonate as well as E^0 must be determined by iterative calculations. The initial step in such iterations is preferably based on the original Gran plots F_2 and F_1 to evaluate the first approximations of v_2 and v_1. By combination of mass-balance equations for hydrogen ions and carbonate and the equilibrium equations for the proton complexes of carbonate, one obtains:

$$F_1' = t(v-v_1) = (v_2-v)([\mathrm{H}^+]^2-K_{1\mathrm{C}}K_{2\mathrm{C}})/(K_{1\mathrm{C}}[\mathrm{H}^+]+2K_{1\mathrm{C}}K_{2\mathrm{C}})+ \\ +(v_0+v)([\mathrm{H}^+]+[\mathrm{HSO}_4^-]+[\mathrm{HF}]-[\mathrm{B(OH)}_4^-]- \\ -[\mathrm{OH}^-])([\mathrm{H}^+]^2+K_{1\mathrm{C}}[\mathrm{H}^+]+K_{1\mathrm{C}}K_{2\mathrm{C}})/t(K_{1\mathrm{C}}[\mathrm{H}^+]+2K_{1\mathrm{C}}K_{2\mathrm{C}}) \qquad (18)$$

In order to compute F_1' and F_2', eqns. (16) and (18) must be combined with eqns. (19)–(24) given below

$$[\mathrm{H}^+] = 10\exp(E-E^0)/59.16 \qquad (19)$$

$$[\mathrm{HCO}_3^-] = [\mathrm{CO}_3]_{\mathrm{tot}}/([\mathrm{H}^+]/K_{1\mathrm{C}}+1) \qquad (20)$$

$$[HSO_4^-] = [SO_4]_{tot}/(1 + 1/\beta_{HSO_4}[H^+]) \tag{21}$$

$$[HF] = [F]_{tot}/(1 + 1/\beta_{HF}[H^+]) \tag{22}$$

$$[B(OH)_4^-] = [B]_{tot}/([H^+]/K_B + 1) \tag{23}$$

$$[OH^-] = K_W/[H^+] \tag{24}$$

A flow-scheme illustrating the iterative use of F_1' and F_2' to evaluate the total alkalinity and carbonate content from experimental data is given in Fig. 2. With the aid of this flow-scheme, it should be possible, for a chemist with experience in computer programming to construct an evaluation program for his specific

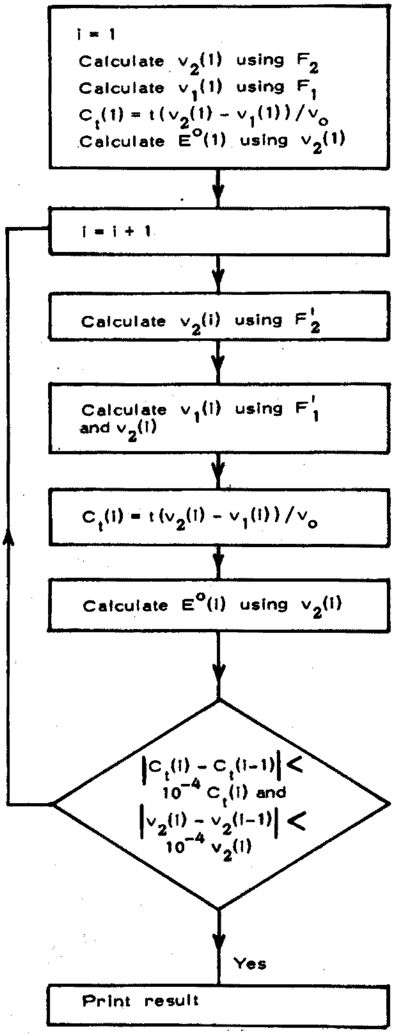

Fig. 2. Flow-scheme for the evaluation of the total alkalinity and carbonate content by means of the modified Gran plots F_1' and F_2'. The notations are explained in Table I except $h = [H^+]$ and C_t = total carbonate concentration.

computer. A complete program written in Basic can be obtained from the authors. This program could also, as in this laboratory, form part of a major program which, besides evaluating, also processes the fully computerized titration procedure.

The total alkalinity and carbonate content were evaluated according to the above flow-scheme by a computer program written in Basic for a HP 2114 B computer. The results (Table III) show that the systematic errors are small and, moreover, that they are almost independent of the volume interval used to evaluate v_1 and v_2. This means that in practice all experimental titration points with v values greater than v_1, can be used for the evaluation of either v_1 or v_2 and, consequently, both high accuracy and high precision are obtained.

Maximal systematic errors in the use of F_1' and F_2'

The stability constants for all species involved and the total concentrations are, of course, not known exactly. It is, however, usually possible to estimate the limits within which these parameters might vary. The equilibrium model suggested for sea water in Table I is still being refined, but it is unlikely that any of the stability constants involved lie outside the ranges (±20%) suggested in Table IV. By using the maximum and minimum values of these parameters in F_1' and F_2', instead of those specified in Table I, it is possible to determine the maximal systematic error caused by an uncertainty in the value of a particular parameter. This was done for all stability constants and total concentrations involved in eqns. (16)–(24). The effect of a non-Nernstian behaviour of the electrode was also computed as ±2% in the RT/F term.

TABLE IV

ESTIMATED MAXIMAL SYSTEMATIC ERRORS WHEN F_1' AND F_2' ARE USED

(In sea water of normal composition the errors in alkalinity are *ca.* 1.5 times that in the Table)

Parameter varied (cf. Table I)	*Value normally used in F_1' and F_2'*	*Expected maximum value (+20%)*	*Systematic error (%)*		*Expected minimum value (−20%)*	*Systematic error (%)*	
			Alk.	*Carb.*		*Alk.*	*Carb.*
t(°)	25	27	−0.10	0.19	23	0.10	−0.22
K_w	$4.84 \cdot 10^{-14}$	$5.8 \cdot 10^{-14}$	0.00	−0.01	$4.0 \cdot 10^{-14}$	0.00	0.00
K_{2C}	$8.53 \cdot 10^{-10}$	$10.2 \cdot 10^{-10}$	0.00	−0.20	$7.1 \cdot 10^{-10}$	0.00	0.16
K_{1C}	$1.06 \cdot 10^{-6}$	$1.27 \cdot 10^{-6}$	0.12	0.10	$8.8 \cdot 10^{-7}$	−0.10	−0.10
β_{HSO_4}	14.3	17	0.02	−0.11	11.6	−0.03	0.09
β_{HF}	400	480	−0.01	−0.03	320	0.01	−0.01
K_B	$1.85 \cdot 10^{-9}$	$2.22 \cdot 10^{-9}$	0.00	−0.09	$1.54 \cdot 10^{-9}$	0.00	0.05

Table IV shows that the most critical stability constants are K_{1C} for the total alkalinity (v_2) and K_{2C} for the total carbonate content ($v_2 - v_1$). It is clear that the stability constants for OH^- and HF have little influence on the results, and that uncertainty in the stability constant for boric acid is of moderate importance, affecting only the value of the total carbonate content. Since the total concentrations of Na^+, K^+, Mg^{2+} and Ca^{2+} decrease very slightly during the titration, the uncertainty about sulphate complexing in sea water has very little effect on the evaluation of the alkalinity and total carbonate. Possible effects fall within the range 11.6–17.0 of the conditional constant for HSO_4^-. It is also seen from Table IV that even a small change in the Nernst factor $RT(\ln 10)/F$, for instance by temperature fluctuations, causes considerable systematic errors.

Use of F_1' and F_2' at different salinities

In the future more accurate sea-water models will, no doubt, be proposed and it will then be simple to insert the new values of the corresponding stability constants into the flow-scheme of Fig. 2. The flow-scheme can also be easily modified for the titration of sea-water samples with salinities other than 35‰. As mentioned earlier, the approximate total concentrations of the major constituents can be derived directly from the salinity. The stability constants K_{1C} and K_{2C} have been determined at different salinities[18]. The stability constants for the other acid–base equilibria can still be assigned the same values without seriously affecting the accuracy.

DISCUSSION

The Gran plots originally suggested[17] for the determination of the total alkalinity and carbonate content in ocean waters are associated with systematic errors, the magnitude of which are strongly dependent on the volume ranges used for the evaluation of v_1 and v_2. The modified Gran plots F_1' and F_2', suggested here, remove this drawback and locate the equivalence points with appreciably better accuracy and precision.

The general procedure suggested for the estimation of the accuracy of Gran plots is of prime interest for analytical chemists concerned with the development of potentiometric titration procedures. It is, however, necessary to have access to HALTAFALL or to a similar computer program. Several such programs have now been published[15,25,26] and have come into routine use in many analytical laboratories. One disadvantage is that the procedure assumes an approximate knowledge of all the stability constants involved in the titration, which is not always possible, especially in non-aqueous titrations. However, the suggested procedure is of particular interest for titrations with high demands on accuracy and, in such systems, one normally has a good idea of the equilibria involved.

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SUMMARY

The use of computer calculations for the determination of the systematic errors associated with Gran plots is demonstrated. The results of such calculations are used to derive "modified" Gran plots capable of locating the equivalence point both more accurately and more precisely. The general principles are exemplified

by application to the determination of the total alkalinity and carbonate content in sea water by means of potentiometric titration.

RÉSUMÉ

On décrit l'utilisation de calculs par ordinateur pour déterminer les erreurs systématiques, associées aux courbes de Gran. On propose des modifications permettant de localiser le point d'équivalence avec plus d'exactitude et de précision. On donne comme exemple la détermination de l'alcalinité totale et de la teneur en carbonate d'une eau de mer, par titrage potentiométrique.

ZUSAMMENFASSUNG

Es wird die Anwendung von Computer-Rechnungen für die Bestimmung von systematischen Fehlern gezeigt, die mit Gran-Auftragungen verbunden sind. Die Ergebnisse solcher Berechnungen werden für die Ableitung "modifizierter" Gran-Auftragungen verwendet, die den Äquivalenzpunkt sowohl mit grösserer Genauigkeit als auch grösserer Reproduzierbarkeit festlegen. Die allgemeinen Prinzipien werden erläutert, indem die Methode auf die Bestimmung der Gesamtalkalität und des Carbonatgehaltes von Meerwasser mittels potentiometrischer Titration angewendet wird.

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THE AUTOMATIC AMPEROMETRIC AND POTENTIOMETRIC MICROTITRATION OF PHARMACEUTICALLY IMPORTANT SULFANILAMIDE DERIVATIVES BY DIAZOTIZATION WITH NITRITE

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Since the work of Ferrero and Brehain[1] on the biamperometric titration of amines by diazotization, several authors[2–10] have discussed electrometric indication for this titration. The biamperometric titration is performed in 0.15–2.5 M hydrochloric acid at room temperature; the addition of potassium bromide in concentrations varying from 0.4 to 25% (w/v) has been recommended in order to catalyze the diazotization and to enlarge the indicator current. Values of 100–600 mV have been recommended as the applied voltage across the two—usually platinum—indicating electrodes. The depolarization of the electrodes has been explained as the electro-oxidation of either nitrous acid[2,6,9] or of bromide[3,4,7] at the anode, and the electroreduction of either nitrous acid[2,3,6,9] or of nitrosyl halide[4,7,9] at the cathode.

The purpose of the investigation described here was to develop an automatic electrometric microtitration of pharmaceutically important sulfanilamide derivatives. Preliminary investigations of the biamperometric method showed that the titration branch after the end-point was slightly curved. This interfered with the accurate determination of the end-point by linear extrapolation which is necessary at low concentrations. It was to be expected that the extrapolation would be easier in a mono-amperometric titration. Furthermore, theoretical considerations[11] and experimental results[11,12] give the impression that lower concentrations may be titrated better by amperometry than by potentiometry. Accordingly, an amperometric method was developed and compared with the potentiometric titration. In order to optimize the titration, the conditions for the diazotization reaction had to be selected carefully, and the amperometric electrode processes had to be investigated.

Diazotization

In hydrochloric acid solutions stronger than 0.05 M the diazotization is catalyzed by halide ions[13]. With low concentrations of nitrous acid, in the millimolar region—as is the case during a microtitration—, nitrosyl chloride becomes the predominant reagent in hydrochloric acid solutions stronger than 0.4 M[14].

The reaction scheme can be represented as follows[13,15]:

$$\mathrm{R{-}NH_2 + H^+ \rightleftarrows R{-}NH_3^+} \qquad (1)$$

$$\mathrm{HNO_2 + H^+ + Hal^- \rightleftarrows NOHal + H_2O} \qquad (2)$$

$$R\text{-}NH_2 + NOHal \rightarrow Ar\text{-}\overset{+}{N}H_2NO + Hal^- \qquad (3)$$

$$Ar\text{-}\overset{+}{N}H_2NO \rightarrow Ar\text{-}N_2^+ + H_2O \qquad (4)$$

reaction (3) being the rate-determining step. According to this scheme, an increase in the hydrogen ion concentration will retard this reaction by diminishing the concentration of the free amine, and an increasing halide ion concentration will have an accelerating effect[14]. The overall effect is an increase of the rate of the diazotization with increasing concentration of hydrochloric acid. The diazotization rate of aniline reaches a maximum in about 5 *M* hydrochloric acid and then decreases[13]

The equilibrium indicated by eqn. (2) lies more to the right for bromide than for chloride. The concentration of nitrosyl bromide is about 40 times that of nitrosyl chloride for equal concentrations of the reactants. This can be calculated[16] from the equilibrium constants at 25°. Consequently, bromide is a much more effective catalyst than chloride.

It can be concluded that high concentrations of halide increase the rate of the diazotization. Increasing concentrations of hydrochloric acid diminish the concentration of the unprotonated amine and retard the reaction on the one hand, but on the other hand the reaction will be accelerated by an increase of the nitrosyl chloride concentration. Up to a certain, fairly high concentration of hydrochloric acid, the second effect will predominate.

Amperometric indication

Several authors[3,4,7], discussing electrometric end-point indication, published current–voltage curves of nitrite in hydrochloric acid solutions, with and without bromide. The curves give the relation between the current and the voltage across two platinum electrodes, but do not distinguish between anodic and cathodic processes. If the anode is depolarized by the oxidation of bromide, and the bromide concentration is high, then the potential of the anode will lie on the steep slope of the polarization curve of the bromide oxidation. The potential of the anode will change little with variations of the current during the titration and act as a pseudo-reference electrode. The variations of the current will be largely due to the reduction process at the cathode, which is determined by the changes in the nitrous acid concentration.

Accordingly, voltammetric studies of the oxidation of nitrite at platinum electrodes in halide-free solutions[17–20] could not be used. The papers by Schmid and Lobeck[21] on the voltammetric behaviour of nitrite and by Masek and Przewlocka[22] on the polarographic reduction of nitrite, both in sulfuric acid, are useful for the elucidation of the cathodic process, but no curves in hydrochloric acid were given. Previous work[23] did not confirm the results of Matrka and Kroupa[9]: the amperometric titration curves were straight lines, and the presentation and interpretation of the current–potential curves are different.

EXPERIMENTAL

Voltammetry

A two-electrode polarograph with electronic scan was used. The polarograph was assembled from modules of a commercially available instrumentation system based on operational amplifiers (MP-system 1000, McKee-Pedersen Instruments, Calif.). The current–potential curves were recorded with a X–Y recorder (Hewlett-Packard 7004 B). A Radiometer Type E 70 rotating platinum electrode assembly with a K 502 saturated calomel electrode (S.C.E.) was used. The platinum wire had a length of 4 mm and a diameter of 0.3 mm. The rotational speed was 1200 rev $\min^{-1}$. The scan speed was 100 mV $\min^{-1}$; the curves were recorded from 0 V to more positive potentials at room temperature.

Potentiometry

Automatic potentiometric titration curves were recorded with a Radiometer Titrator Type TTT 1 and SBR 2 Titrigraph. Titrations were carried out with a 2.5-ml Radiometer SBU 1 syringe burette in Metrohm titration vessels with a sample volume of 20 ml. The reference electrode was a saturated calomel electrode (Metrohm EA 409); the indicator electrode was a platinum disk with a diameter of 5 mm (Ingold Pt 803 NS).

Amperometry

Automatic amperometric titration curves were recorded as described previously[24]. The apparatus adds stepwise a constant volume of reagent at constant intervals. When equilibrium has been established at the electrode and the current has reached its final value, the chart motor of the recorder is activated for a constant time and the current is recorded.

A stepped titration curve is obtained. The end-point is found by linear extrapolation. The magnitude of the added volume of reagent, the length of the interval and the recording time can be chosen independently. The measuring circuit of the instrument is based on operational amplifiers. The reagent was added from motor-driven 2.5-ml (Radiometer ABU 12) or 0.2-ml (Metrohm Dosimat E412) syringe burettes. The measured current was not corrected for the dilution of the sample solution by the added reagent. The titration vessel and electrodes were the same as used for voltammetry, except that the platinum wire was 25 mm long.

Electrode pretreatment

The platinum electrodes were stored in 6 *M* nitric acid and washed with deionized water before use. The rotating electrodes were placed against the S.C.E. at 0 V in air-free 0.1 *M* perchloric acid until the current reached a small, almost constant value.

Reagents

All chemicals were of analytical grade. Deionized water was distilled from a glass still before use. Sulfanilic acid was dried for 2 h at 105° before use. The sulfanilamides used (Fig. 1) were obtained from pharmaceutical firms.

Titration procedures

Sample solutions in the millimolar range were prepared directly by dissolving accurately weighed amounts of the sulfanilamide in 10.0 ml (for potentiometry) or 15.0 ml (for amperometry) of *M* hydrochloric acid and adding 2.5 or 3 g of

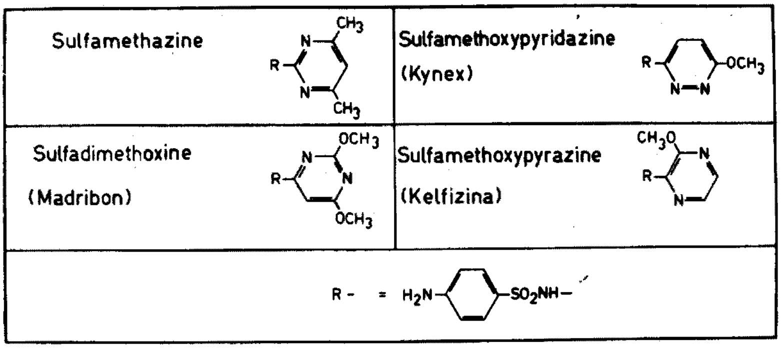

Fig. 1. Sulfanilamide derivatives used.

potassium bromide. More dilute sample solutions were prepared daily by diluting freshly prepared millimolar solutions with *M* hydrochloric acid. Of this dilution 10.0 or 15.0 ml were pipetted and titrated after adding potassium bromide. The titrations were performed at room temperature. Titration blank values were found negligible. Generally the titration took less than 20 min. The nitrite titrant was standardized daily against a sulfanilic acid solution of a concentration similar to that of the sample solution.

RESULTS AND DISCUSSION

Voltammetry

Curve A in Fig. 2 is the current–potential curve of *M* hydrochloric acid; it is limited anodically by the oxidation of chloride to chlorine at about 0.95 V. The curve of $6\cdot10^{-5}$ *M* sulfamethazine in *M* hydrochloric acid is essentially the same as curve A. Even the curve of $6\cdot10^{-5}$ *M* sodium nitrite in *M* hydrochloric acid is quite similar: no anodic or cathodic wave is observed.

Curve B was obtained after dissolving 20% (w/v) potassium bromide in *M* hydrochloric acid. This curve is limited anodically by the oxidation of bromide

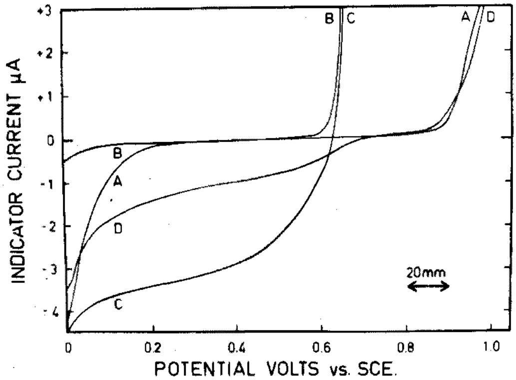

Fig. 2. Current–potential curves at the rotating platinum electrode ($l=4$ mm). (A) *M* HCl; (B) *M* HCl+20% (w/v) KBr; (C) $5\cdot10^{-6}$ *M* $NaNO_2$ in *M* HCl+20% (w/v) KBr; (D) $5\cdot10^{-6}$ *M* $NaNO_2$ in *M* HCl+20% (w/v) NaCl.

to bromine at about 0.65 V. When sodium nitrite was added to this solution and a $6 \cdot 10^{-5}$ *M* nitrite solution in *M* hydrochloric acid plus 20% (w/v) potassium bromide was scanned, curve C resulted. A large reduction wave appears. (In the Figure the anodic parts of curves B and C have been drawn as separate lines.) The unusual form of curve C suggests that two electrode reactions are involved. The anodic part represents the oxidation of bromide; the cathodic wave may be caused by the reduction of nitrosyl bromide. This interpretation of the electrode process is substantiated further by curve D, which is the polarization curve of $6 \cdot 10^{-5}$ *M* nitrite in *M* hydrochloric acid plus 20% (w/v) sodium chloride. The cathodic wave is then separated clearly from the anodic part of the curve. It has been shown[21,22] that the reduction wave of nitrous acid at positive potentials in 1 *M* and more concentrated sulfuric acid solutions is caused by the reduction of NO^+ to NO. The concentration of nitrosyl halide in *M* hydrochloric acid plus 20% (w/v) bromide or chloride should be similar to the concentration of nitrosyl hydrogensulfate in molar sulfuric acid solutions, for equal concentrations of nitrite. This is evident from a comparison of the equilibrium constants given by Schmid and Muhr[14,16] for the hydrolysis of these nitrosyl compounds. Consequently, a cathodic reduction wave of nitrosyl halide can be expected, starting at a positive potential. This wave can be attributed to the following electrode reactions:

$$NOX + e \rightarrow NO + X^- \qquad (X = Cl \text{ or } Br)$$

Lower concentrations of nitrous acid can be detected by this cathodic wave than by the oxidation wave of nitrous acid in *M* hydrochloric acid. This is apparent from a comparison of the polarization curve of $5 \cdot 10^{-6}$ *M* nitrite in *M* hydrochloric acid that showed no wave, and curve C of Fig. 2.

Amperometric titrations

The potential of the indicator electrode must be on the plateau of the cathodic wave. A potential of 0.35 V was chosen. The influence of the hydrochloric acid concentration on the limiting current, measured at 0.35 V, is shown in Fig. 3. A small platinum electrode (length, 4 mm) was used at room temperature. Initially, the

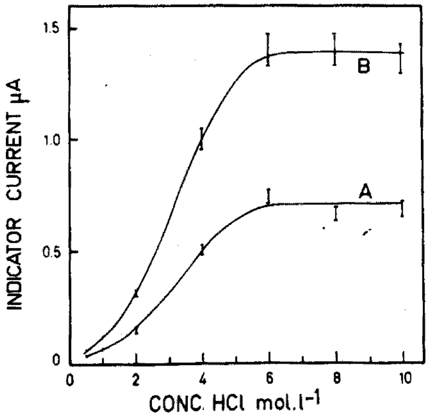

Fig. 3. Influence of the concentration of hydrochloric acid on the limiting current measured at 0.35 V *vs.* S.C.E. (A) 10^{-5} *M* $NaNO_2$; (B) $2 \cdot 10^{-5}$ *M* $NaNO_2$.

current increased with the hydrochloric acid concentration. From about 6 M no further increase of the current with the concentration was observed, most probably because all the nitrous acid has been converted to nitrosyl chloride.

The curves of Fig. 3 show a striking conformity with the curves published by Schmid and Maschka[25], which give the relation between the specific extinction of nitrosyl chloride and the hydrochloric acid concentration. This is an additional confirmation of the reduction of nitrosyl chloride at the platinum electrode. Although high hydrochloric acid concentrations catalyze the diazotization and enlarge the indicator current, such concentrations cannot be used in titrations because of the current instability, caused by decomposition of nitrous acid. At hydrochloric acid concentrations up to 2 M no decrease of the current was observed during a 4-min recording of the limiting current in a $2 \cdot 10^{-5}$ M nitrite solution at room temperature. In view of these results and the data given by Ericson and Schill[8] on current stability, a 1 M hydrochloric acid solution was selected for titrations.

The relation between the limiting current at 0.35 V and the bromide concentration is shown in Fig. 4 for $2 \cdot 10^{-5}$ M nitrite in M hydrochloric acid. The small platinum electrode was used at room temperature. In order to obtain a sufficiently high current and to catalyze the diazotization, 25% (w/v) potassium bromide was added to the sample solution (arrow in Fig. 4). The titrations were carried out at room temperature, as it was found that the current at 30° was about three times as large as the current at 0° (Fig. 5).

The results of the amperometric titrations are given in Table I. The molarity of the sodium nitrite reagent was adjusted to the concentration of the sample solution. Nitrite solutions of 0.05 M–0.001 M were used.

The following considerations determined the size of the volume of nitrite that was added at a titration step.

(*a*) The length of the chart paper corresponding to a volume step must allow

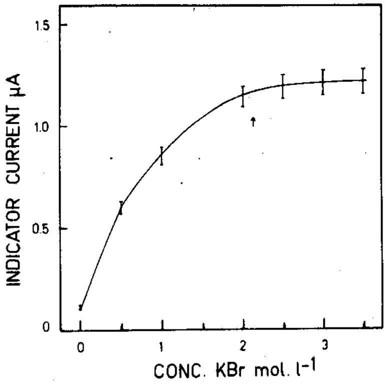

Fig. 4. Influence of the concentration of potassium bromide on the limiting current measured at 0.35 V *vs.* S.C.E. of $2 \cdot 10^{-5}$ M sodium nitrite in M hydrochloric acid.

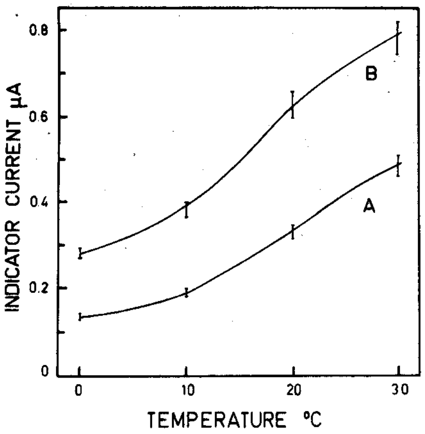

Fig. 5. Influence of the temperature on the limiting current measured at 0.35 V *vs.* S.C.E. (A) 10^{-5} M $NaNO_2$ in M HCl+20% (w/v) KBr; (B) $2 \cdot 10^{-5}$ M $NaNO_2$ in M HCl+20% (w/v) KBr.

TABLE I

RESULTS OF AMPEROMETRIC TITRATIONS

	Concentration (mol l⁻¹)	*Amount added (μg)*	*Average % found*	s_r *(%)*	*No. of detns.*
Sulfamethazine	$2.8 \cdot 10^{-3}$	$11.5 \cdot 10^{3}$	100.1	0.33	5
	$4.0 \cdot 10^{-4}$	$1.69 \cdot 10^{3}$	99.9	0.51	5
	$6.9 \cdot 10^{-5}$	289	100.0	0.60	6
	$1.8 \cdot 10^{-5}$	72.8	99.6	0.52	5
	$5.7 \cdot 10^{-6}$	23.8	99.7	0.38	5
	$2.9 \cdot 10^{-6}$	11.9	100.2	0.68	5
Sulfadimethoxine	$2.5 \cdot 10^{-3}$	$11.7 \cdot 10^{3}$	100.1	0.14	5
(Madribon)	$3.2 \cdot 10^{-4}$	$1.48 \cdot 10^{3}$	100.6	0.27	5
	$5.9 \cdot 10^{-5}$	275	99.0	0.25	10
	$1.4 \cdot 10^{-5}$	67.1	98.5	0.67	5
	$4.8 \cdot 10^{-6}$	22.4	99.9	1.02	5
	$2.3 \cdot 10^{-6}$	10.7	99.8	3.38	5
Sulfamethoxy-	$2.8 \cdot 10^{-3}$	$11.7 \cdot 10^{3}$	99.8	0.14	9
pyridazine	$3.3 \cdot 10^{-4}$	$1.38 \cdot 10^{3}$	99.8	0.05	5
(Kynex)	$7.1 \cdot 10^{-5}$	298	99.7	0.10	5
	$1.8 \cdot 10^{-5}$	74.2	99.1	1.55	8
	$5.7 \cdot 10^{-6}$	23.9	99.5	1.09	10
	$2.8 \cdot 10^{-6}$	11.9	99.5	3.04	5
Sulfamethoxy-	$3.0 \cdot 10^{-3}$	$12.7 \cdot 10^{3}$	100.3	0.10	4
pyrazine	$3.3 \cdot 10^{-4}$	$1.38 \cdot 10^{3}$	100.0	0.15	5
(Kelfizina)	$7.3 \cdot 10^{-5}$	307	99.2	0.23	5
	$1.7 \cdot 10^{-5}$	72.5	98.4	0.80	5
	$5.7 \cdot 10^{-6}$	23.9	99.7	1.50	10
	$2.9 \cdot 10^{-6}$	12.2	99.9	0.43	5

significant interpolation on the volume axis, in accordance with the precision of the burette.

(*b*) The slope of the titration curve after the end-point must be reasonably steep in order to enable a precise construction of the end-point.

The waiting period after the nitrite addition was determined by the time required for the current to become constant. Usually 30–60 s sufficed, except for the 10^{-6} *M* solutions. In order to shorten the duration of the titration of such solutions, the waiting period of 120 s before the end-point was reduced to 50 s after the end-point. The titration curve for $2.8 \cdot 10^{-6}$ *M* sulfamethazine is shown in Fig. 6. The titration had to be continued far beyond the end-point, otherwise the results would have been too low, because of systematic errors resulting from the extrapolation of a not strictly linear part of the curve; such errors may have occurred with some of the 1.4–$1.8 \cdot 10^{-5}$ *M* solutions. Residual currents were negligible or very low. The excess reagent line did not deviate from linearity within the studied concentration range, provided that sufficient excess of nitrite was added.

Titrations at lower concentrations seemed to be impractical, because of their long duration.

Potentiometric titrations

The results of potentiometric titrations of the four sulfanilamides are given in

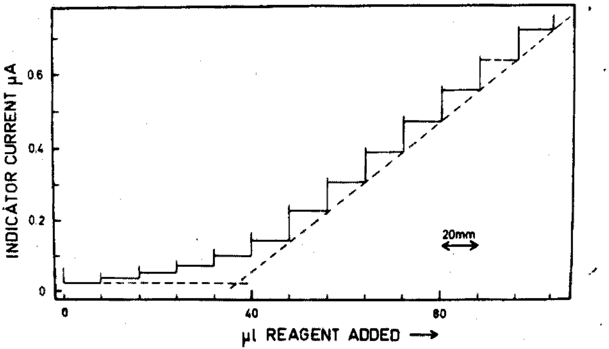

Fig. 6. Amperometric titration curve of 2.8 · 10^{-6} *M* sulfamethazine in *M* HCl + 25% (w/v) KBr. (Solid line) Recorded titration curve; (dashed line) construction of the end-point.

TABLE II

RESULTS OF POTENTIOMETRIC TITRATIONS

	Concentration (mol l^{-1})	*Amount added (mg)*	*Average % found*	s_r *(%)*	*No. of detns.*
Sulfamethazine	9.3 · 10^{-3}	25.8	100.1	0.69	5
	1.5 · 10^{-3}	4.27	100.2	0.79	4
	9.1 · 10^{-4}	2.52	99.8	0.29	5
	4.3 · 10^{-4}	1.19	101.3	1.03	5
	9.3 · 10^{-5}	0.257	100.1	1.08	5
Sulfadimethoxine	9.2 · 10^{-3}	28.4	99.8	0.20	3
(Madribon)	8.5 · 10^{-4}	2.63	100.3	0.57	5
	4.2 · 10^{-4}	1.30	99.8	1.45	5
	1.1 · 10^{-4}	0.335	99.0	0.88	5
Sulfamethoxy-	9.3 · 10^{-3}	26.1	100.8	0.30	4
pyridazine	9.4 · 10^{-4}	2.64	100.3	0.50	5
(Kynex)	4.5 · 10^{-4}	1.26	99.9	0.85	5
	1.2 · 10^{-4}	0.366	98.3	1.25	5
Sulfamethoxy-	9.0 · 10^{-3}	25.3	100.2	0.05	4
pyrazine	8.8 · 10^{-4}	2.46	99.2	0.48	5
(Kelfizina)	4.0 · 10^{-4}	1.11	99.5	0.59	5
	1.1 · 10^{-4}	0.322	99.3	0.99	5

Table II. The time taken to complete a titration was generally less than 14 min, except for the 10^{-4} *M* range, which required about 20 min. The experiments were terminated with the titration of solutions in the 1 · 10^{-4} *M* range, because the establishment of the end-point from the curves became impossible at lower concentrations. This is clear from Fig. 7, where the titration curves for 4.0 · 10^{-4} *M* and 1.1 · 10^{-4} *M* solutions of sulfamethoxypyrazine are shown. Rather large variations of the starting potentials at the beginning of the titration were observed. The end-point potentials varied to a lesser extent, but very precise titrations to a preselected end-point potential do not seem possible in this case.

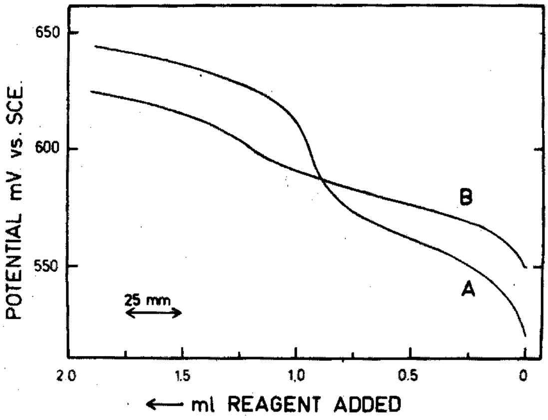

Fig. 7. Potentiometric titration curves of sulfamethoxypyrazine in M HCl + 25% (w/v) KBr. (A) $4.0 \cdot 10^{-4}$ M sulfamethoxypyrazine with 0.005 M $NaNO_2$; (B) $1.1 \cdot 10^{-4}$ M sulfamethoxypyrazine with 0.001 M $NaNO_2$.

The authors thank Hoffman-La Roche, Lederle, and Farmabo for gifts of samples.

SUMMARY

The automatic amperometric and potentiometric microtitration of pharmaceutically important sulfanilamide derivatives by diazotization with nitrite is described. Optimal conditions for diazotization and amperometric indication are discussed. A new cathodic amperometric indication of nitrite in M hydrochloric acid–25% (w/v) of potassium bromide medium is proposed; the electrode processes involved are interpreted on the basis of current–potential curves. The effects of the hydrochloric acid and bromide concentrations, and of temperature on the limiting current are described. Sulfamethazine, sulfadimethoxine, sulfamethoxypyridazine and sulfamethoxypyrazine were titrated amperometrically in the range 10^{-3}–10^{-6} M. Potentiometric titrations of these sulfanilamides were possible in the range 10^{-3}–10^{-4} M.

RÉSUMÉ

On décrit les microdosages ampérométriques et potentiométriques automatiques de dérivés de sulfanilamide importants en pharmacie; on procède par diazatation au moyen de nitrite. Les conditions optimales de diazotation et d'indication ampérométrique sont examinées; on propose une nouvelle indication cathodique du nitrite en milieu acide chlorhydrique M–bromure de potassium à 25% (poids/volume). L'interprétation de la réduction est basée sur les courbes de polarisation. Des dosages de sulfaméthazine, de sulfadiméthoxypyrimidine, de sulfaméthoxypyridazine et de sulfaméthoxypyrazine 10^{-3} à 10^{-6} M ont été effectués, par titrage ampérométrique. Les tirages potentiométriques ne peuvent pas se faire en dessous de 10^{-4} M.

ZUSAMMENFASSUNG

Die automatische amperometrische und potentiometrische Mikrotitration einiger Derivate des Sulfanilamids durch Diazotierung mit Nitrit wird beschrieben. Eine neue, kathodische amperometrische Indizierung des Nitrits in *M* Salzsäure unter 25% g/v Kaliumbromidzusatz wird vorgeschlagen. Die kathodische Reduktion wird gedeutet mit Hilfe der Strom–Spannungs-Kurven. Die Ergebnisse der amperometrischen Titrationen von Sulfamethazin-, Sulfadimethoxin-, Sulfamethoxypyridazin- und Sulfamethoxypyrazinlösungen mit Konzentrationen von 10^{-3} bis 10^{-6} *M* werden vorgelegt. Potentiometrische Titrationen dieser Sulfanilamide sind möglich im Bereich 10^{-3}–10^{-4} *M*.

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POLYMER MEMBRANE ELECTRODES

PART I. A CHOLINE ESTER-SELECTIVE ELECTRODE

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In a previous communication, a liquid membrane electrode which exhibited a Nernstian response towards choline and choline esters was described; the electrode could be employed for the determination of the activity of cholinesterases[1]. Polyvinylchloride membrane electrodes of the type described by Moody *et al.*[2] appeared to possess a number of operational advantages. The response of plasticized PVC membrane electrodes towards various organic ionic species has been briefly described by James *et al.*[3] and Higuchi *et al.*[4]. An extensive study of the response of a plasticized PVC membrane towards a wide range of onium salts was recently reported by Scholer and Simon[5]. In this report, the preparation and performance of a PVC membrane electrode containing a tetraarylborate salt of acetylcholine as the ion-exchange agent, is described.

EXPERIMENTAL

Preparation of membranes

A 5% by weight solution of acetylcholine tetra-*p*-chlorophenylborate in the solvent of choice is mixed with a finely divided PVC powder. The paste is stirred until no lumps are visible; then it is evacuated or allowed to stand for a few minutes to remove air bubbles and is carefully poured into a mold cavity. The paste is leveled and placed in an oven at 200° for 2 min.

Construction of cell and measurements of electrochemical potential

A disc is cut from the membrane film and is placed into the bottom cap of a Corning liquid membrane assembly. A small O-ring is placed behind the disc to prevent twisting when the electrode assembly is screwed together. The chamber behind the disc is filled with a saturated KCl–AgCl solution and a Ag/AgCl electrode is placed in the internal electrolyte solution. A double-junction internal reference can be used; however, all measurements described here were made with the Ag/AgCl electrode dipped directly into the internal electrolyte. All potential measurements were made against a Fisher 13-639-57 cracked bead calomel reference electrode.

Rate of change of acetylcholine concentration was monitored by recording the output from a Corning Model 12 expanded-scale pH meter on a 10-mV recorder with a zero suppression device powered by a mercury cell. All enzymic activity determinations were conducted at 25.0°. The activity was calculated from the slope in the 1–5% hydrolysis region.

Materials

The substrate solution employed was $4.0 \cdot 10^{-3}$ *M* acetylcholine bromide in phosphate buffer adjusted to pH 7.0. All PVC films were prepared from Vinyl Dispersion Resin QYOH-2 (Union Carbide). Commercial phthalate esters (Exxon Chemical Company) were used.

Membrane resistance

The resistance of the membranes was measured with an a.c. impedance bridge (General Radio Co.) at a frequency of 1 kHz. The membranes were fixed between a silver electrode in a 0.1 *M* KCl electrolyte solution and an Ag/AgCl electrode in a saturated KCl–AgCl electrolyte solution. The latter electrolyte and electrode were identical to the corresponding elements in the membrane electrode.

RESULTS AND DISCUSSION

The membrane

Several procedures for the preparation of electroactive PVC membranes have been employed by previous investigators. Plasticized PVC films may be soaked in a second plasticizer which imparts electroactivity to the membranes[6]. Alternatively, the PVC film can be cast from a solution containing the desired plasticizer and an ion-exchanger[2,7]. A more convenient procedure for the preparation of the electroactive membranes was used in the present work: the ion-exchange agent was dissolved in a suitable plasticizer, and finely divided PVC powder was then thoroughly blended into the plasticizer solution to form a plastisol which was spread in a mold and heated to form a continuous film. The films are tough, flexible and are essentially transparent. Since there are no observable particles in the visual size range these membranes are considered to be homogeneous, although under a microscope morphological variations can be observed.

The plasticizer is normally added to PVC formulations to reduce the glass transition temperature. The plasticizer functions as a nonvolatile partial solvent for the polymer. A rigid, brittle polymer is thus transformed into a rubbery material. A good plasticizer will impart high tear strength and toughness to a film. The elasticity of plasticized polymers is attributed to entanglement of the polymer chains. In time, the solvent will migrate out of the polymer-rich environment into a solvent-rich environment leading to film embrittlement.

In the initial efforts to prepare an acetylcholine-selective polymeric membrane electrode, 3-nitro-*o*-xylene was used as the plasticizer. Although a functioning electrode could be prepared, the performance deteriorated rapidly and the film became brittle. Membranes of higher quality were produced from more conventional PVC plasticizers; the effect on certain electrochemical properties of the membrane is discussed in a later section.

Some of the electrochemical properties of the polymer membrane are related to membrane thickness. Thin films (less than 6 mils) did not act as permselective membranes, *i.e.*, the observed potential across the membrane was not altered by dilution of the sample electrolyte. At the other extreme, films exceeding 30 mils in thickness exhibited extreme electrostatic sensitivity and their electrochemical characteristics could not be examined; this effect is related to the bulk resistance of the

TABLE I

D.C. RESISTANCE OF MEMBRANES

Film	*R (ohms)*
3-Nitro-*o*-xylene–PVC (no exchanger)	$5.0 \cdot 10^8$
Liquid membrane (3-nitro-*o*-xylene–X)[a]	$5.3 \cdot 10^6$
Dioctylphthalate–PVC–X	$2.9 \cdot 10^6$
NaCl-treated dioctylphthalate–PVC–X	$4.6 \cdot 10^5$

[a] X = charge carrier.

membrane. From Table I it appears that a functioning ion-selective membrane will have a resistance in the range 10^6–10^7 ohms. The membrane prepared without the charge carrier, acetylcholine tetra-*p*-chlorophenylborate, has a resistance of $5 \cdot 10^8$ ohms. The membrane appeared to loose its ion-selective character below 10^6 ohms. A plasticized exchanger-containing membrane, which was treated with a 2 *M* sodium chloride solution, no longer responded to a change in sample electrolyte concentration. Presumably salt incursion into the membrane resulted in a loss of the co-ion exclusion character of the membrane.

Cationic selectivity

The response of the phthalate ester-plasticized PVC electrodes towards univalent cations and several choline esters was examined in single electrolyte solutions. The data are shown in Fig. 1. The selectivity ratios were calculated from eqn. (1):

$$\log K = \Delta E/2.303\ B \qquad (1)$$

where ΔE is the potential difference between 10^{-1} *M* single electrolyte solutions and *B* is the observed Nernst slope factor for acetylcholine. It was assumed that the activity ratio of the solution at 10^{-1} *M* was equal to unity and the minor differences in the observed Nernst slope factors between acetylcholine and the other choline esters were ignored. These results are compared in Table II with earlier results[1] for the liquid-membrane electrodes. It can be seen that while the Nernst

TABLE II

COMPARATIVE PERFORMANCE OF MEMBRANE ELECTRODES

	Selectivity ratios[a] (slope factors[b])		
	Liquid membrane	*Plasticized PVC*	
		Dibutylphthalate	*Dioctylphthalate*
Choline	1 (45)	1 (54)	1 (58)
Acetylcholine	37.6 (53)	6.87 (56)	5.43 (59)
Acetyl-β-methylcholine	121 (59)	19.1 (60)	11.5 (55)
Butyrylcholine	407 (56)	50.0 (58)	41.7 (53)

[a] Selectivity ratios are calculated from single electrolyte measurements.
[b] Slope factors are obtained from data at 10^{-1} *M* to 10^{-3} *M* and are given as 2.303 *B* (mV).

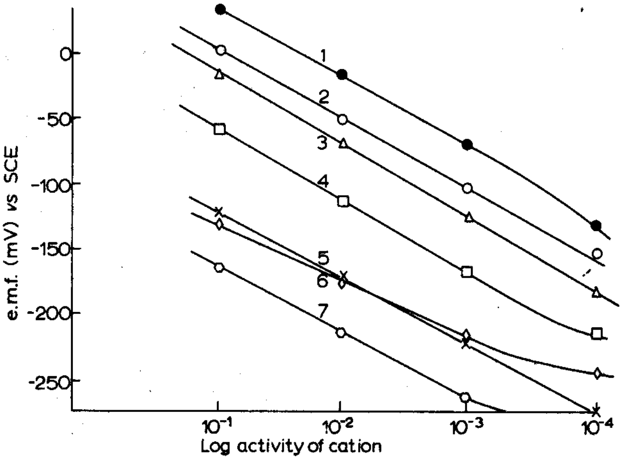

Fig. 1. Potential response curves of the polymer membrane electrode. (1) Butyrylcholine; (2) acetyl-β-methylcholine; (3) acetylcholine; (4) choline; (5) ammonium; (6) potassium; (7) sodium.

slope factors were not significantly altered by the changes in exchanger solvent and membrane form, the selectivity ratios were adversely affected. This appears to be related to the expected differences in the distribution coefficients of the choline esters between 3-nitro-*o*-xylene, the solvent used in the liquid membrane, and the phthalate esters used in the PVC membranes. The phthalate esters are expected to be better solvents for the choline esters and thus exhibit a "leveling effect".

Selectivity ratios calculated from data obtained in single electrolyte solutions are often different from ratios which are based on potential measurements of mixed electrolytes. The ratio obtained from mixed electrolyte studies is operationally more meaningful, particularly if one is concerned with the kinetic analysis of the hydrolysis of choline esters. In mixed electrolyte solutions containing the primary cation at activity a_1 and a secondary cation at activity a_2, the selectivity ratio (K) will be given by

$$E = E' + B \ln(a_1 + Ka_2) \tag{2}$$

Because dilute solutions and the ratio of the activity terms are involved, considerable simplification can be achieved with a minimal sacrifice of rigor, if concentrations are used rather than activities.

From measurements in a series of solutions where the sum of c_1 and c_2 is constant, the selectivity ratio is readily calculated from

$$E_1 - E_0 = B \ln \left[\frac{c_1 + Kc_2}{C_0}\right] \tag{3}$$

where $c_1 + c_2 = C_0$ and E_0 is the observed potential of an acetylcholine solution at C_0 concentration. Solving eqn. (3) for K gives

$$K = \frac{C_0 \operatorname{alog} \Delta E/2.303B - c_1}{c_2} \tag{4}$$

If $f = c_1/C_0$ and $S = 2.303\, B$, then

$$K = \frac{\text{alog}\,\Delta E/S - f}{1-f} \tag{5}$$

A series of solutions was prepared in which the concentrations of choline and acetylcholine were adjusted to correspond to 2.5%, 5% and 10% hydrolysis of a $4.0 \cdot 10^{-3}$ M acetylcholine solution.

In Table III, the K values calculated by means of eqn. (5) are compared to the K values obtained from data on single electrolyte solutions. At $f = 0.975$, the contribution of choline to the observed potential was so small that its effect could not be accurately measured.

TABLE III

SELECTIVITY RATIO $K_{\mathrm{ACh,Ch}}$

In mixed electrolyte	*In single electrolyte*
0.008 ($f=0.975$)	
0.36 ($f=0.95$)	0.153
0.35 ($f=0.90$)	

Assay of partially purified acetylcholinesterase

Aliquots of a stock solution containing *ca.* 0.5 mg of acetylcholinesterase per ml were assayed by the membrane electrode procedure. The activity of the solution (μ) was calculated by means of eqn. (6)*.

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* The relationship required to calculate the rate of concentration change from the experimental rate of potential change is derived as follows. Concentration rather than activity terms are used for simplicity, because only dilute solutions (10^{-3} M) are involved. If a solution contains concentration $c_1 + c_2$ of primary and secondary ion such that $c_1 + c_2 = C_0$, the observed potential is described by:

$$E = E' + B \ln(c_1 + Kc_2) \tag{1A}$$

Differentiation of eqn. (1A) with respect to time yields:

$$\frac{dE}{dt} = \frac{B}{(c_1 + Kc_2)_t}\left[\frac{dc_1}{dt} + K\frac{dc_2}{dt}\right]$$

Since $\frac{dc_1}{dt} = -\frac{dc_2}{dt}$

therefore

$$\frac{dE}{dt} = \frac{B(1-K)}{[c_1 + K(C_0 - c_1)]_t}\,\frac{dc_1}{dt} \tag{2A}$$

or

$$\frac{dE}{dt} = \frac{B(1-K)}{C_0[f_t + K(1-f_t)]}\,\frac{dc_1}{dt} \quad \text{where } f_t = \frac{c_1}{C_0} \tag{3A}$$

Rearrangement of eqn. (3A) yields:

$$\frac{dc_1}{dt} = \frac{C_0[f_t + K(1-f_t)]}{B(1-K)}\,\frac{dE}{dt} \tag{4A}$$

Because the $\log_{10}$ slope factor S which equals $2.303B$ is usually determined, and enzymic activity (μ) is defined in terms of μmoles of substrate converted, we can write

$$\mu = V\frac{dc}{dt} = \frac{2.3\,V\,C_0[f_t + K(1-f_t)]}{S(1-K)}\,\frac{dE}{dt} \tag{5A}$$

where V = volume.

$$\mu = \frac{2.3\ V\ C_0[f_t+K(1-f_t)]}{S\,(1-K)}\frac{\mathrm{d}E}{\mathrm{d}t} \tag{6}$$

In the series of assays conducted, the constants in eqn. (6) had the following values: $V=10$ ml, $C_0=4.0$ mM, $f_t=0.975$, $K=0.355$, and $S=55$.
Thus $\mu=2.57\ \mathrm{d}E/\mathrm{d}t$. (7)

The results are shown in Fig. 2. The response of the electrode is linear with the volume of enzyme solution added for over a one-decade range of volumes.

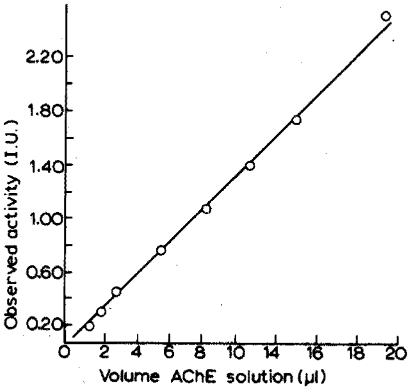

Fig. 2. Linearity of the activity measurements.

Comparison of polymer electrode, liquid-membrane electrode and colorimetric assay procedures for cholinesterase

A series of measurements was made to compare the enzymic activity data obtained by the polymer membrane electrode with those obtained by the liquid-membrane electrode and the Hestrin colorimetric procedure[8]. The activity determined by the liquid-membrane electrode was based on equations, which do not correct for the electrode response to produced choline. Results are summarized in Table IV. Both liquid and polymer membrane electrodes gave significantly higher activity values than the Hestrin procedure[8]. Kremzner and Wilson[9] have noted that initial rate activity values for acetylcholinesterase are about 20% higher than is obtained by the Hestrin method which is conducted under conditions leading to 15–40% hydrolysis. The present measurements corresponded to about 10% hydrolysis.

TABLE IV

COMPARISON OF ACETYLCHOLINESTERASE ASSAY METHODS

	Specific activity (I.U. mg^{-1})		
	Colorimetric	*Polymer membrane*	*Liquid membrane*
Average activity	110	137	141
No. of detns.	6	6	4
s_r	5.9	10.8	32.3
Coefficient of variation (%)	5.4	7.9	23

The performance of the polymer membrane electrode is markedly superior to the liquid-membrane electrode. The polymer membrane electrode has a very short recovery time between assays (1–3 min) and the start-up after an overnight storage is only about 10 min. The results obtained with the polymer membrane electrode exhibit significantly less scatter than the results obtained with the liquid-membrane electrodes.

SUMMARY

An electroactive polyvinylchloride membrane can be prepared which has a Nernstian response towards choline and choline esters. The membrane is prepared from a solution of acetylcholine tetra-*p*-chlorophenylborate in a phthalate ester which serves as the plasticizer for PVC. The membrane electrode can be used for the kinetic assay of acetylcholine esterase activity. A rate equation is derived which describes the response of the electrode towards simultaneous substrate disappearance and product formation during the enzyme-catalyzed hydrolysis of acetylcholine.

RÉSUMÉ

On propose une méthode de préparation d'une membrane polyvinylchlorure électroactive, présentant une réponse nernstienne pour la choline et ses esters. Cette membrane est préparée à partir d'une solution d'acétylcholinetétra-*p*-chlorophénylborate dans des esters phthalate, servant de plastifiant pour PVC.

ZUSAMMENFASSUNG

Es wurde eine elektroaktive Polyvinylchlorid-Membran hergestellt, die gegenüber Cholin und Cholinestern Nernstsches Verhalten zeigt. Die Membran wird aus einer Lösung von Acetylcholin-tetra-*p*-chlorphenylborat in einem Phthalatester gewonnen, der als Weichmacher für PVC dient. Die Membranelektrode kann für die kinetische Bestimmung der Aktivität von Acetylcholinesterase verwendet werden. Es wird eine Geschwindigkeitsgleichung abgeleitet, die das Verhalten der Elektrode gegenüber dem simultanen Verschwinden des Substrates und der Bildung des Produktes während der enzymkatalysierten Hydrolyse von Acetylcholin beschreibt.

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POLYMER MEMBRANE ELECTRODES

PART II. A POTASSIUM ION-SELECTIVE MEMBRANE ELECTRODE

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There has been a long sustained interest in the electrochemical properties of polymeric matrix membrane electrodes[1]. Major insights into ion-exchange characteristics of membranes were achieved by the studies of Sollner who used collodion membranes[2]. These membranes were difficult to handle and did not exhibit sufficient ionic selectivity to be of general interest. More recently, attention has shifted to plasticized polyvinylchloride (PVC) membranes which have considerable toughness and have been shown to possess, when properly formulated, a high degree of semipermeability. Dibutylphthalate-plasticized PVC membranes have moderate selectivity for calcium compared to sodium ions[3]. Tributylphosphate-plasticized membranes can support a high uranyl ion flux[4]. Dichlorodiethylether-plasticized membrânes[5] are permeable to iron(III), but not to aluminum(III).

If ion-exchange or complexing agents are present in the plasticizer, significant enhancement of ionic selectivity characteristics can be achieved. Thomas *et al.*[6,7] trapped the liquid membrane solutions supplied with commercially available calcium-(II) and nitrate ion-selective electrodes in PVC and were able to obtain polymer membrane electrodes comparable to the commercial counterparts. The complexing agent dithizone did not confer significant ion-selective character to the membrane[8]; however, the use of macrocyclic neutral carriers resulted in membrane electrodes with high selectivity for potassium compared to sodium ions[9].

The role of the plasticizer in these membrane electrodes has not been well described. Neither have there been reported investigations of the performance of these membranes over extended periods of time. Yet plasticized polymer electrodes exhibit considerable time-dependent behavior and this behavior can be related to physical and chemical factors. In this report, the plasticizer effects encountered in the preparation of a potassium-selective electrode are described. The various methods currently employed to measure the selectivity of such electrodes are also discussed. At the risk of adding further confusion into this area, yet another method of estimating the selectivity ratio of the electrode in mixed electrolyte solutions is proposed.

EXPERIMENTAL

Preparation of membranes

A solution of about 5% potassium tetra(*p*-chlorophenyl)borate in a given plasticizer was mixed with a finely divided PVC powder (Union Carbide QYOH-2). The paste was placed in a mold cavity, leveled to a desired thickness and fused at 200° for 2 min.

Screening of membranes

A Plexiglas flow-through cell with wells for 5 membranes was used to screen the many compositions examined. The capacity of the cell was about 2.3 ml. About 100 ml of new electrolyte was required to flush the cell. The cell was not thermostated; however, the solutions were at thermal equilibrium with the room. Room temperature fluctuations were about 22° ± 1°. All potential measurements were made relative to a Fisher 13-639-57 cracked-bead calomel reference electrode with a Corning Model 12 expanded-scale pH meter.

The electrochemical behavior of the membranes was compared against the relationship

$$E_{\text{obs}} = E' + 2.303\ RT/F \log a \tag{1}$$

where E' is a constant, RT/F is the Nernst slope factor and a is the mean ionic activity of the monovalent electrolyte. In this initial screening all selectivity ratios were measured in single electrolyte solutions at 0.0778 M activity. From the experimentally determined electrochemical potential values of solutions of 1:1 electrolytes containing the primary and secondary cations (a and b), the selectivity ratio is determined by the relationship[10]:

$$K_{\text{ab}} = \text{antilog}\ \frac{E_{\text{a}} - E_{\text{b}}}{2.303\ RT/F} \tag{2}$$

RESULTS AND DISCUSSION

Plasticizer selection

In PVC matrix membrane electrodes, the plasticizer must satisfy many requirements. In addition to the normal plasticizer function of reducing the glass transition temperature of the polymer, it must be immiscible in water, relatively nonvolatile, a good solvent for the ion-exchange salt, and it must promote the desired ionic selectivity. Three classes of organic compounds were examined for their effect on the semipermeability of the membrane. Membranes which did not have sufficient electrochemical stability to permit characterization will not be discussed unless some special purpose is served.

Diesters of dicarboxylic acids are commercially employed as plasticizers for PVC. Esters of phthalic acid gave good working membranes; however, the preference for potassium over sodium was much less than that exhibited by the equivalent liquid potassium(I) electrode[11]. Sebacic acid esters, $RO_2C(CH_2)_8CO_2R$, did not yield working electrodes. Organophosphates are also widely used as plasticizers for PVC. Tri(2-ethylhexyl)phosphate yielded excellent working electrodes. These membranes, surprisingly, showed anomalous selectivity ratios. The preference order was $NH_4^+ > Na^+ > K^+$. This solvent may be important in the development of an ammonium-selective membrane. Tricresylphosphate and dioctylphenylphosphonate did not yield working membranes.

Nitroaromatic compounds were found to be the most promising class of

TABLE I

EFFECT OF PLASTICIZER ON SEMIPERMEABILITY

	Selectivity ratio[a]	
	K_{KNa}	K_{KNH_4}
Esters		
Dibutylphthalate	0.08	—
Dioctylphthalate	0.08	–
Di-*i*-nonylphthalate	0.08	–
Diethoxyethylphthalate	Unstable	
Phosphorus containing solvents		
Tri(2-ethylhexyl)phosphate	6.71	19.5
Tricresylphosphate	1.0	~1
Phenyldioctylphosphonate	Unstable	
Nitroaromatics		
m-Nitrodiphenyl ether	0.027	1.18
3-*o*-Nitroxylene	0.006	
p-Hexylnitrobenzene	0.027	0.54
p-Nitrophenyloctyl ether	0.02	0.42
o-Nitrophenylbutyl ether[b]	Unstable	
Liquid membrane electrode[11]	0.01	0.5

[a] $K_{ij} < 1$, prefers i; $K_{ij} > 1$, prefers j.
[b] Provided by Dr. W. M. Wise, Corning Glass Works.

materials screened. Interestingly, 3-*o*-nitroxylene, the solvent of choice for the liquid-membrane potassium electrode, was not a suitable plasticizer for PVC and did not yield good working membranes. The *p*-hexylnitrobenzene and the octyl ether of *p*-nitrophenol were the most effective plasticizers for a potassium-selective membrane electrode. These results are all summarized in Table I. None of the plasticized polymer membrane electrodes had a selectivity ratio as favorable as the liquid membrane electrode described earlier[11].

Time-dependent studies

During the screening of various plasticizers for the PVC membrane, it became evident that some membrane compositions required a finite break-in period and that some compositions had limited life-times. Two plasticizers—*p*-hexylnitrobenzene and *p*-nitrophenyloctyl ether—were selected for an extended examination of the stability of selectivity and slope characteristics. An effort was also made to determine the influence of membrane thickness and plasticizer content on the performance characteristics of the electrode.

Four membranes plasticized with *p*-hexylnitrobenzene were prepared. Two membranes with a plasticizer content of 65% by weight with membrane thicknesses of 14 mils (curve 1, Fig. 1) and 28 mils (curve 2), one membrane with only 30% plasticizer content and of 16 mils thickness (curve 4), and one membrane with 50%

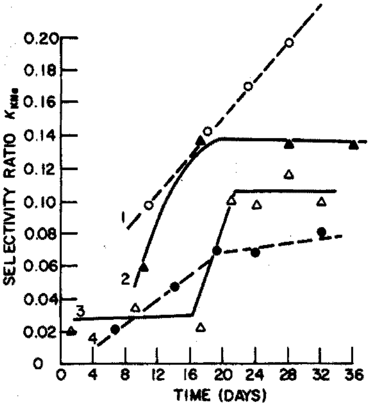


Fig. 1. Increase in selectivity ratio with time for four hexylnitrobenzene plasticized membrane electrodes. % Plasticizer, and membrane thickness (mils): (○) 65%, 14; (▲) 65%, 28; (△) 50%, 23; (●) 30%, 16.

plasticizer content and 23 mils thickness (curve 3) were examined at frequent intervals in single-electrolyte solutions for about 30 days. All four membranes exhibited about the same initial pseudo-Nernstian slopes. Although the slope values did not remain constant, no clear pattern of slope deterioration with time was evident. The K/Na selectivity of all four electrodes deteriorated with time (Fig. 1). The two membranes with high plasticizer content rapidly deteriorated in selectivity for potassium to unacceptable values; the selectivity ratio of the thicker of these two membranes did level off after 16 days. The selectivity of the relatively thin membrane with low plasticizer content deteriorated less rapidly (curve 4), and the selectivity ratio at any time up to the end of the examination period was much better than that observed for high plasticizer contents. At an intermediate plasticizer content and thickness, the membrane exhibited a low and stable selectivity ratio for about 18 days, but the selectivity ratio then rapidly deteriorated and leveled off at about 0.1 (curve 3).

It can be assumed that to some degree various time-dependent processes are operative within the membrane and at the membrane–water interface. These may include loss of plasticizer by bleeding into the aqueous phase, diffusion of water into the membrane, leaching of plasticizers from the membrane surface, diffusion of plasticizer from the interior of the membrane to the surface, and extraction of the exchange salt into the aqueous phase. Some of these processes were experimentally observed. An insufficient number of experiments was conducted to quantify the contribution of each of these processes to the deterioration of the membrane performance, but some tentative conclusions are presented.

A small amount of plasticizer loss to the aqueous solution is normally discerned by a slight yellow coloration when a new membrane is first placed in an aqueous solution. An excess of plasticizer at the membrane surface is attributed to migration of the plasticizer to the surface during the fusion step in the fabrication of the membrane. Continued plasticizer migration from the interior of the membrane to the surface and concomitant water intrusion into the membrane is believed to control the loss of electrode selectivity. In thin membranes, plasticizer is rapidly depleted from the interior of the membrane. This process appears to be diffusion-controlled since a plot of selectivity ratio against $(\text{time})^{\frac{1}{2}}$ is linear for most of the functional life-times of the thin films 1 and 4. The rate of loss of selectivity is less with the thin membrane having less plasticizer. This membrane is much stiffer than that with 65% plasticizer; consequently, diffusion rates would be expected to be much lower. However, as a thick membrane with high plasticizer content also exhibits the linear K *vs.* $t^{\frac{1}{2}}$ relationship, rapid plasticizer depletion is probably not the rate-controlling step.

An alternative suggestion is that water migration into a soft expanded polymer network could be rate-controlling. The rate of plasticizer migration is undoubtedly related to the concentration gradient between the surface and the interior of the membrane in accordance with Fick's law. An additional driving force for plasticizer migration would be the thermodynamic instability of a polymer–plasticizer composition. In a thick membrane of the intermediate plasticizer content, the selectivity ratio was essentially independent of t or $t^{\frac{1}{2}}$ until about 18 days of operation, but then rapidly deteriorated (curve 3, Fig. 1). Plasticizer migration to the surface undoubtedly occurred during the life-time of this membrane, but water diffusion into the membrane may be impeded at an optimal plasticizer content.

Membranes obtained with *p*-nitrophenyloctyl ether as a plasticizer behaved similarly (Fig. 2). An optimally plasticized thick film (50%, 22 mil) had a stable selectivity ratio up to about 28 days, after which K increased linearly with $t^{\frac{1}{2}}$.

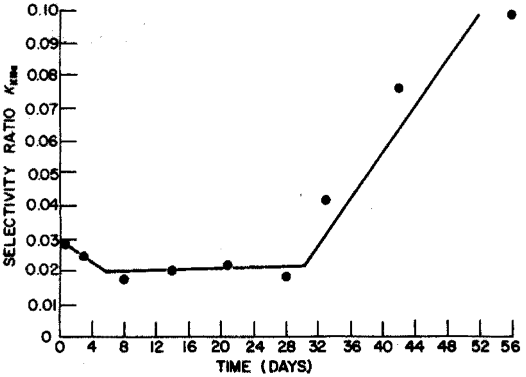


Fig. 2. Aging of nitrophenyloctyl ether plasticized membrane electrode.

Selectivity studies in mixed electrolyte solutions

The selectivity ratio obtained in studies such as those described above is not a constant and will vary with the ionic strength of the solution and the ratio of the primary to secondary ion. The selectivity ratio is related to ion-exchange equilibria at the membrane–solution interface, and any particular set of experimental conditions corresponds to a point on an ion-exchange isotherm surface. For calibration purposes, it is necessary to determine K_{ab} under solution conditions as close as possible to that of the sample. Therefore, selectivity ratios determined in mixed electrolyte solutions are of greater practical value. The several procedures in current use were recently described by Moody and Thomas[12].

A number of methods was used to examine the potential response of the potassium-selective membrane electrodes in solutions containing both sodium chloride and potassium chloride. In Fig. 3, the responses of membranes prepared with

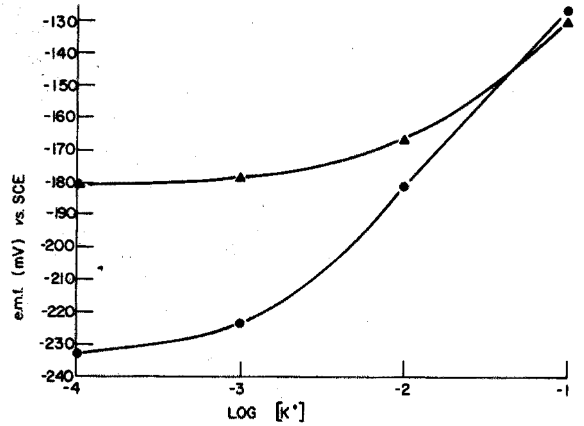


Fig. 3. Role of plasticizer in the response of membrane electrodes. [Na$^+$] = 0.10 *M*. (▲) Dibutylphthalate; (●) hexylnitrobenzene.

dibutylphthalate (poor selectivity) and *p*-hexylnitrobenzene plasticizers are compared. Measurements were made in a series of solutions which contained a constant level (0.10 *M*) of sodium chloride and decade increments of potassium chloride. The potential response curve for the dibutylphthalate-plasticized membrane is shallow, and small potential increments are obtained between decade changes of potassium concentration. The hexylnitrobenzene-plasticized membrane, by contrast, has a Nernstian-like response down to about $3 \cdot 10^{-3}$ *M* K$^+$. The liquid-membrane potassium electrode[11] was linear to nearly 10^{-4} *M* potassium. The major interest in the performance of potassium-selective electrodes is in the physiological range of serum. Thus, the present studies were mainly in the range of 10^{-2}–10^{-3} *M* potassium ion.

Of particular interest is a graphical method proposed by Srinivasan and Rechnitz[10] for membranes with low selectivity ratios (<0.1). This is the least empirical of the proposed methods; however, the relationship derived by Srinivasan and Rechnitz for monovalent cations requires two exponential terms both involving small differences between large numbers (eqn. 3):

$$a_1 - a_2 \text{ antilog}\left(\frac{E_1 - E_2}{S}\right) = K_{ab}\left[b_2 \text{ antilog}\left(\frac{E_1 - E_2}{S}\right) - b_1\right] \tag{3}$$

where E_1 and E_2 refer, respectively to a_1, b_1 and a_2, b_2, and $S = 2.303\ RT/F$.

The use of exponential functions can be avoided by an alternative treatment. The potential response of an electrode to a solution of a primary monovalent cation of activity a_1 and a secondary monovalent cation of activity b_1 can be described by the empirical equation:

$$E_1 = E' + S \log(a_1 + K_{ab} b_1) \tag{4}$$

where E' is a constant. If a second mixed electrolyte solution is prepared with cationic activities of a_2 and b_2, respectively, such that $a_1 > a_2$ and $b_2 > b_1$, the observed potential is equal to E_2.

$$E_2 = E' + S \log(a_2 + K_{ab} b_2) \tag{5}$$

When $E_1 = E_2$ and S remains constant, eqns. (4) and (5) can be combined to give:

$$\log(a_2 + K_{ab} b_2) = \log(a_1 + K_{ab} b_1) \tag{6}$$

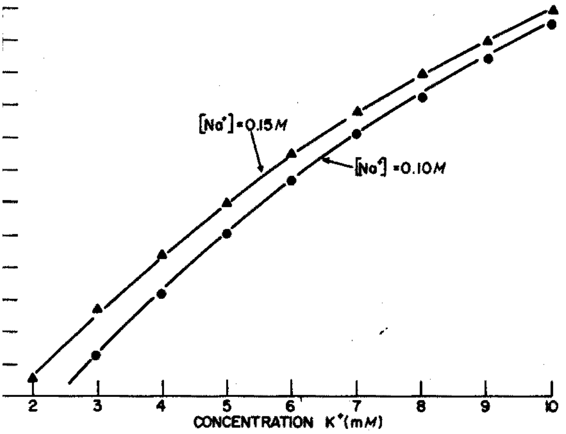
Equation 6 solved for K_{ab} gives:

$$K_{ab} = \frac{a_2 - a_1}{b_1 - b_2} \tag{7}$$

A comparison of the selectivity ratios calculated by several of the methods described is presented for the *p*-nitrophenyloctyl ether-plasticized potassium-selective polymer membrane electrode. In single electrolyte solutions, where both sodium chloride and potassium chloride are at a concentration of 0.10 *M*, the selectivity ratio is 0.018. In all of these treatments, it is necessary to assume that the slope factors (S) for both electrolytes are equal.

Two series of mixed electrolyte solutions were prepared. The potassium level in each was varied from $1.0 \cdot 10^{-3}$ *M* to $1 \cdot 10^{-2}$ *M*; the sodium background in one series was constant at 0.10 *M* and in the other at 0.15 *M*. The data obtained are plotted in Fig. 4.

The mean ionic activity coefficient of potassium chloride ($\bar{\gamma}_a$) in sodium chloride solutions will be influenced by the ionic strength of the mixed electrolyte solution and the mole fraction of potassium chloride in accordance with Harned's rule[13]. Butler and Huston[14] have calculated $\bar{\gamma}_a$ in KCl–NaCl mixed electrolyte solutions at various ionic strength and compositions. In Fig. 5, the data of Butler and Huston for $\bar{\gamma}_a$ are plotted as a function of the mole fraction (X_a) of potassium chloride at an ionic strength (I) of 0.0949. This is sufficiently close to the ionic strength of the present series of measurements at a constant background of 0.10 *M* sodium chloride, and $\bar{\gamma}_a$ values were obtained directly from this curve.



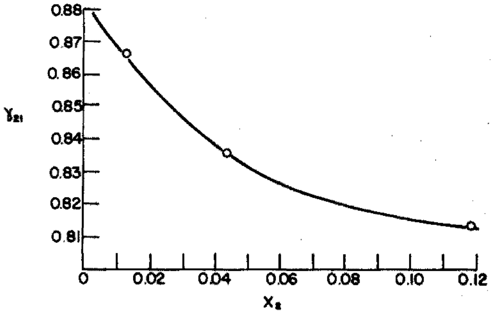


Fig. 4. Response of a plasticized membrane electrode at two levels of background sodium ion concentration.

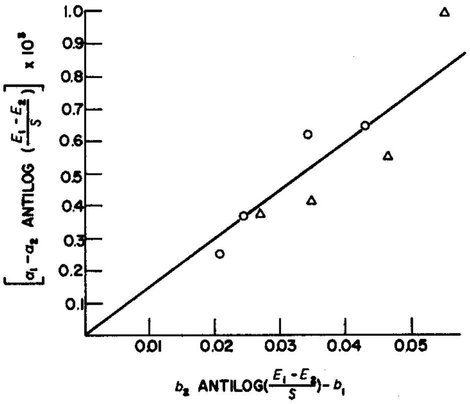
Fig. 5. Graph of data of Butler and Huston for the mean ionic activity coefficient of KCl as a function of the mole fraction of KCl.

Comparable data for the 0.15 M sodium chloride background were not available; however, by interpolation of the data of Butler and Huston for $\bar{\gamma}_a$ at several values of I, it can be estimated that $\bar{\gamma}_a$ at $I=0.15$ is 0.02 less than at $I=0.10$. The limiting form of the Debye–Hückel equation yields a change of 0.04. The values for solution composition, $\bar{\gamma}_a$, and the observed potentials are given in Table II. The data in Table II were then treated by eqn. (3) to obtain a graphical solution for K_{KNa} in accordance with the procedure of Srinivasan and Rechnitz (Fig. 6). The scatter in the data reflects the uncertainty in E_1-E_2 for solutions which are similar in

TABLE II

ACTIVITY AND ELECTROCHEMICAL POTENTIAL DATA

$m_a \cdot 10^3$	*For* $m_b=0.10$			*For* $m_b=0.15$		
	$\bar{\gamma}_a$	$a \cdot 10^3$	$-E$ *(mV) vs. S.C.E.*	$\bar{\gamma}_a$	$a \cdot 10^3$	$-E$ *(mV) vs. S.C.E.*
10	0.8175	8.18	181.0	0.806	8.06	180.2
9	0.8195	7.37	183.2	0.808	7.26	182.0
8	0.8218	6.57	185.5	0.812	6.50	184.1
7	0.8245	5.77	187.8	0.815	5.70	186.5
6	0.8285	4.96	190.7	0.819	4.92	189.1
5	0.8337	4.18	194.0	0.824	4.12	192.2
4	0.8398	3.36	197.8	0.831	3.32	195.5
3	0.8472	2.57	201.5	0.838	2.51	198.6
2	0.8577	1.72	206.5	0.845	1.69	203.0
1	0.8702	0.87	213.0	0.854	0.854	207.9



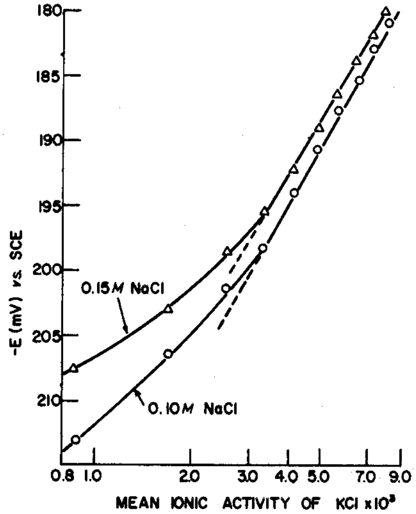


Fig. 6. Graphical solution of selectivity ratio K_{KNa} by the method of Srinivasan and Rechnitz.

Fig. 7. Graph of electrode potential *vs.* corrected mean ionic activity of potassium in NaCl–KCl electrolyte solutions.

composition. The slope of the line in Fig. 6 yields a value of 0.015 for K_{KNa} which is close to the value of 0.018 obtained in single electrolyte solutions.

The values of observed potential (Table II) were plotted against the calculated activity of potassium ion (considered as equivalent to the mean ionic activity of KCl) in the mixed electrolyte solutions (Fig. 7). The points are linear in both series of measurements down to about 0.003 *M* activity of potassium ion; below this level the interference caused by sodium ions becomes apparent. From Fig. 7 the selectivity ratio can be calculated at any portion of the curve where potential values are coincident by the use of eqn. (7). Nine such positions were selected; the potential values and the corresponding value of K_{KNa} are given in Table III.

TABLE III

SELECTIVITY RATIO CALCULATED BY $(a_1-a_2)/(b_2-b_1)$

($(b_2-b_1)=0.354$, from the mean ionic activity coefficients for NaCl solution given by Robinson and Stokes[15])

$-E$ (mV) vs. S.C.E.[a]	$(a_1-a_2)\cdot 10^3$	$K_{ab}\cdot 10^4$
206	0.67	191
202	0.62	174
198	0.65	183
194	0.50	141
192	0.60	169
188	0.60	169
186	0.55	155
184	0.65	183
182	0.70	198
	Mean	0.0174
	Standard deviation	0.0017

[a] Obtained graphically from Fig. 7.

The mean value for K_{KNa} is 0.0174 with a standard deviation of 0.0017. The mean value of K_{KNa} is essentially identical with the value obtained in single electrolyte solutions. Of interest is the nearly constant value for K_{KNa} throughout the experimental range even when significant divergence of the two sets of data points occurs.

In the present study, the selectivity ratio obtained from single electrolyte solution data and from mixed electrolyte data are almost identical; however, there are many examples in the literature where the selectivity ratio is significantly dependent upon the method of calculation and the experimental conditions employed. Examples of such studies have been reported for nitrate, chloride, and perchlorate ion-selective electrodes[10], for a polymer membrane calcium-selective electrode[6], for a lead-selective electrode[8] and for a potassium-selective electrode[9]. Studies by Huston and Butler[16] with a calcium-selective electrode demonstrated that the selectivity ratio was highly dependent on the ionic strength of the mixed electrolyte solutions. The subsequent study by Butler and Huston[14] with a potassium-selective electrode showed that at a constant ionic strength the selectivity ratio varies with the ratio of the primary to secondary ion activity.

These variations of selectivity ratio with mixed electrolyte solution compositions cannot easily be uncovered by studies in single electrolyte solutions. The method based on eqn. (7) has considerable computational simplicity although there is some ambiguity concerning the ionic strength and counter ion activity ratio and the ever-present complication of varying response slopes.

The authors acknowledge the assistance of Mr. Frank B. Ward in the experimental portions of this work.

SUMMARY

An ion-selective plasticized polymer membrane electrode of the ion-exchange type is described for potassium. The chemical nature of the plasticizer has a dominant influence on the selectivity of the electrode towards univalent cations. The selectivity ratio was examined over an extended time interval as a function of membrane thickness and plasticizer content. A simplified procedure for the determination of the selectivity ratio of the electrode in mixed electrolyte solutions is proposed and compared with several of the methods which have been described in the literature.

RÉSUMÉ

On décrit une électrode ionique sélective, à membrane polymère, de type échangeur ionique, pour le potassium. La nature chimique du plastifiant a une influence dominante sur la sélectivité de l'électrode envers les cations univalents. La sélectivité est examinée en fonction de l'épaisseur de la membrane et de la teneur en plastifiant. On propose une méthode simplifiée pour déterminer le coefficient de sélectivité de l'électrode dans des solutions de plusieurs électrolytes; elle est comparée avec plusieurs des méthodes décrites dans la littérature.

ZUSAMMENFASSUNG

Eine für Kaliumionen selektive Polymer-Membranelektrode vom Ionenaustausch-Typ wird beschrieben. Die chemische Beschaffenheit des verwendeten Weichmachers hat einen wesentlichen Einfluss auf die Selektivität der Elektrode gegenüber einwertigen Kationen. Das Selektivitätsverhältnis wurde über einen ausgedehnten Zeitraum als Funktion der Membrandicke und des Weichmachergehalts untersucht. Ein vereinfachtes Verfahren für die Bestimmung des Selektivitätsverhältnisses der Elektrode in gemischten Elektrolytlösungen wird vorgeschlagen und mit verschiedenen Methoden verglichen, die in der Literatur beschrieben worden sind.

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A STUDY OF LIQUID–MEMBRANE PERCHLORATE-SELECTIVE ELECTRODES MADE FROM AN ORGANIC RADICAL ION SALT

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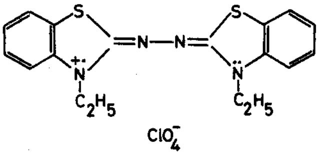
Recent efforts in this laboratory to find new sensing materials which can be used to prepare acceptable ion-selective electrodes[1] have been concentrated upon salts derived from organic radical ions[2–5]. The appreciable electrical conductivities in the crystalline states and the low solubilities which are characteristic of many of these compounds allow them to be employed with advantage in solid-state sensors intended for measurements in aqueous solutions. A wide range of cation- and anion-selective electrodes may be obtained by this approach. Accordingly, investigations have hitherto been confined, almost entirely, to such solid-state devices.

As a consequence of the above-mentioned properties and by virtue of their solubilities in organic liquids, organic radical ion salts, in contrast to many other substances which have been used in ion-selective electrodes, offer a choice of construction method. Both solid-state and liquid–membrane electrodes are readily prepared from a given salt. A closer examination of the application of the liquid–membrane technique to these substances is of importance for several reasons. In certain circumstances, *e.g.*, with radical ion salts of nitrate, sulphate or calcium which are not sufficiently insoluble in water to yield good solid-state sensors, the liquid–membrane method may be particularly useful since it should permit an extension of the operational activity range through the exploitation of extraction equilibria. In addition, direct comparisons between liquid–membrane and solid-state electrodes which are based upon a common sensing material become possible. For determinations of electrode mechanism, the presence of radical ions enables an additional sensitive method, e.s.r. spectroscopy, to be applied. Detailed information concerning the states of aggregation and solvation and the type and extent of ion-pair formation of the radical ion 'exchange sites' should thus be attainable and should thereby allow more complete interpretations of the behaviour of liquid–membrane electrodes to be given. The results of such investigations would be quite generally applicable. The present report, however, attempts to deal with only the first two of these three points for a single representative system.

In the preparation of liquid membranes, care is necessary in the choice of a suitably inert, water-immiscible, medium in which the radical ion salt may be dissolved. Particular attention must be given to the acid–base and redox properties of the solvent since these are major factors which affect the stability of a given radical ion species. As a general rule, high boiling point liquids of low permittivity which are devoid of functional groups such as $-OH$ or $-NH_2$ are to be preferred. Limited information on the chemistry of radical ions which is relevant to the selection of solvent may be found in the literature[6,7]. The choice depends heavily on the salt in question and, in the absence of definite recommendations, relies largely upon trial and error methods. In this respect, it is usually possible to obtain an assessment of the suitability of a given medium with regard to stability from prolonged spectral observations of dilute solutions of the radical ion salt.

Among the liquids examined during the present investigation, chlorinated hydrocarbons (*e.g.*, $CHCl_3$, o-$C_6H_4Cl_2$), certain ethers (*e.g.*, $(CH_2Cl \cdot CH_2)_2O$), lower ketones (*e.g.*, $CH_3 \cdot CO \cdot CH_2 \cdot CH(CH_3)_2$), nitriles (*e.g.*, C_6H_5CN), and nitro compounds (*e.g.*, CH_3NO_2, $C_6H_5NO_2$), dissolved the substance chosen sufficiently well for electrode purposes. Measurements with membrane electrodes incorporating only two of these possible solvents have, as yet, been carried out.



(I)

The perchlorate salt of N-ethylbenzothiazole-2,2′-azaviolene (I) has previously been shown to provide a solid-state electrode selective for perchlorate ions[5]. The general performance observed showed it to be a practically useful device. In order to allow a first comparison between the different methods of construction to be made in this particular instance, liquid–membrane electrodes were prepared from the above radical ion salt and studied. The results of this investigation are summarized below.

EXPERIMENTAL

Materials and membrane solutions

N-Ethylbenzothiazole-2,2′-azaviolene perchlorate (hereafter abbreviated to $NEBA \cdot ClO_4$) was prepared as described by Hünig *et al.*[8] and outlined previously[5]. The radical ion salt content of the synthesis product was found to be 70–75% (w/w) on the basis of spectral analysis in acetonitrile solution and from redox equivalent determinations[9]. The concentration values for $NEBA \cdot ClO_4$ given below were corrected accordingly.

Solutions of the above salt in 1,2-dichlorobenzene (Fluka) and in β,β'-dichlorodiethyl ether (Hopkin and Williams) were employed as liquid membranes. The solvents were used without further purification. The concentrations of $NEBA \cdot ClO_4$ used for response and selectivity parameter determinations were equal to 0.14 g l^{-1} ($3.1 \cdot 10^{-4}$ M) in both solvents. The effects of variations in the concentration of salt in the membranes upon the useful measuring ranges of the electrodes were also studied.

Electrode construction

Orion series 92 liquid–membrane electrode bodies were used in conjunction with Orion 'nitrate' porous membrane supports. The inner reference system comprised an Ag/AgCl electrode immersed in an aqueous solution containing sodium chloride and sodium perchlorate, each at a concentration of 10^{-3} *M*.

Measuring procedure

Cell potentials for the assembly

$-$Ref. electrode | NaX, aq | membrane | NaCl, $NaClO_4$, aq | AgCl | Ag+

were recorded at 25° with an Orion model 701 digital pH meter connected to an Orion model 751 digital printer. The potential of the Orion model 90–02 double liquid-junction reference electrode (outer-chamber containing aqueous 10% ammonium chloride) was +240 mV *vs.* N.H.E. No corrections for variations in liquid-junction potential were applied to the cell potential values observed. Separate, unbuffered aqueous solutions of sodium salts of the appropriate anions were employed in establishing response characteristics and interference parameters. Readings taken at 30-s intervals following immersion in the test solutions permitted an estimate of electrode response time to be made. The pH dependence of the cell potential was determined by varying the acidity of test solutions which contained a constant activity of perchlorate ions; pH values were measured *in situ* with a Metrohm EA 147 X combination glass electrode. Single-ion activities were calculated from the extended Debye–Hückel relation with the ion-size parameters of Kielland[10].

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

RESULTS

Figure 1 shows the calibration curves obtained with the NEBA·ClO_4/1,2-dichlorobenzene and NEBA·ClO_4/β,β'-dichlorodiethyl ether liquid–membrane electrodes. Table I compares the observed cell potentials with those expected on the basis of ideal membrane permselectivity to perchlorate ions. Satisfactory agreement

TABLE I

OBSERVED AND CALCULATED CELL POTENTIALS FOR LIQUID–MEMBRANE PERCHLORATE ELECTRODES IN AQUEOUS $NaClO_4$ SOLUTIONS

ClO_4^- activity (M)	*Cell potential (mV)*		
	Calc.	*NEBA·ClO_4/DCB*[a]	*NEBA·ClO_4/DDE*[b]
1	-16	-15	-15
10^{-1}	43	43	43
10^{-2}	102	101	102
10^{-3}	161	160	161
10^{-4}	220	218	219
10^{-5}	279	275	272
10^{-6}	338	322	302

[a] 1,2-Dichlorobenzene.

[b] β,β'-Dichlorodiethyl ether.

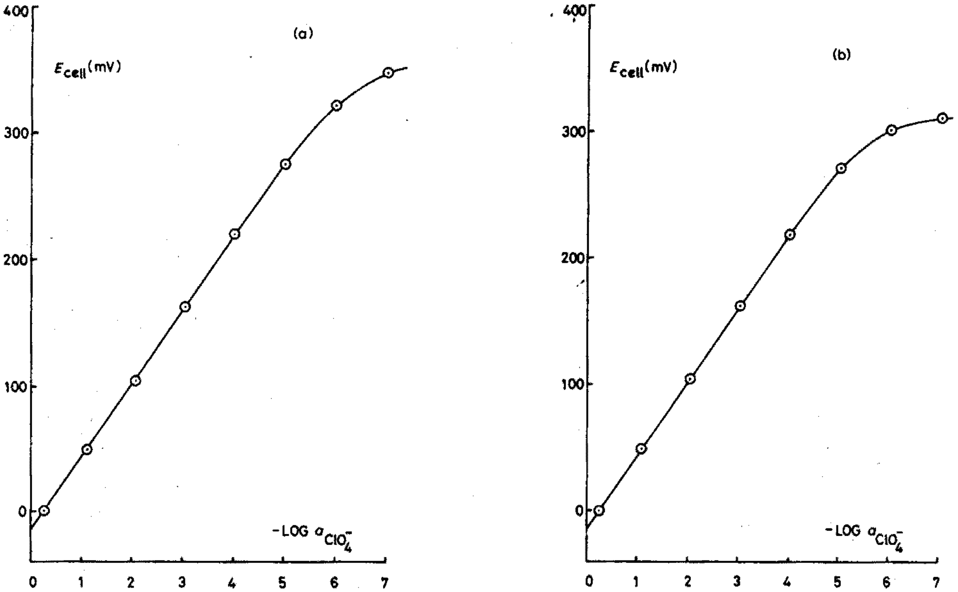


Fig. 1. Response of the NEBA·ClO_4 electrode to changes in perchlorate ion activity. The slope of the linear region was 59±1 mV decade^{-1} with 1,2-dichlorobenzene as solvent (Fig. 1a), and 58±1 mV decade^{-1} with β,β'-dichlorodiethyl ether as solvent (Fig. 1b).

is found over the activity range 1–10^{-4} *M* perchlorate for both electrodes, and essentially Nernstian slopes of 59±1 mV decade^{-1} were observed. At lower activities the response became poorer and a potential limit was approached in each case. Repeated calibrations were reproducible within ±1 mV over the range 1–10^{-5} *M* perchlorate. Somewhat greater uncertainty (*ca.* ±3 mV) existed at lower perchlorate activities.

The response times for both electrodes were short; stable potentials (±1 mV) were attained within 1–2 min of immersion in perchlorate solutions at all activities in the range 1–10^{-5} *M*. Once reached, these stable cell potentials remained constant (±1 mV) for periods exceeding 10 h (after which interval observations were discontinued) even for activities of 10^{-4} *M* perchlorate.

Potentials for the interfering ion solutions stabilized within at most 4–5 min of immersion, except for the NEBA·$ClO_4/\beta,\beta'$-dichlorodiethyl ether electrode in iodide solutions. Figure 2 illustrates the observed behaviour of the two electrodes on exposure to iodide solutions of different concentrations. Although no definite explanation for this contrast in electrode response can be offered at present, some remarks concerning possible causes are included in the discussion.

Calibration checks, which were performed with aqueous 10^{-1} *M* sodium perchlorate after potentials for each series of interfering ion solutions had been recorded, agreed with the original calibration data within ±1 mV in all cases. No permanent 'poisoning' by any of the interfering ions studied (iodide excepted) was evident during the periods required for interference parameter determinations (typically 15–20 min in each solution).

Apparent selectivity coefficients were evaluated from the cell potentials

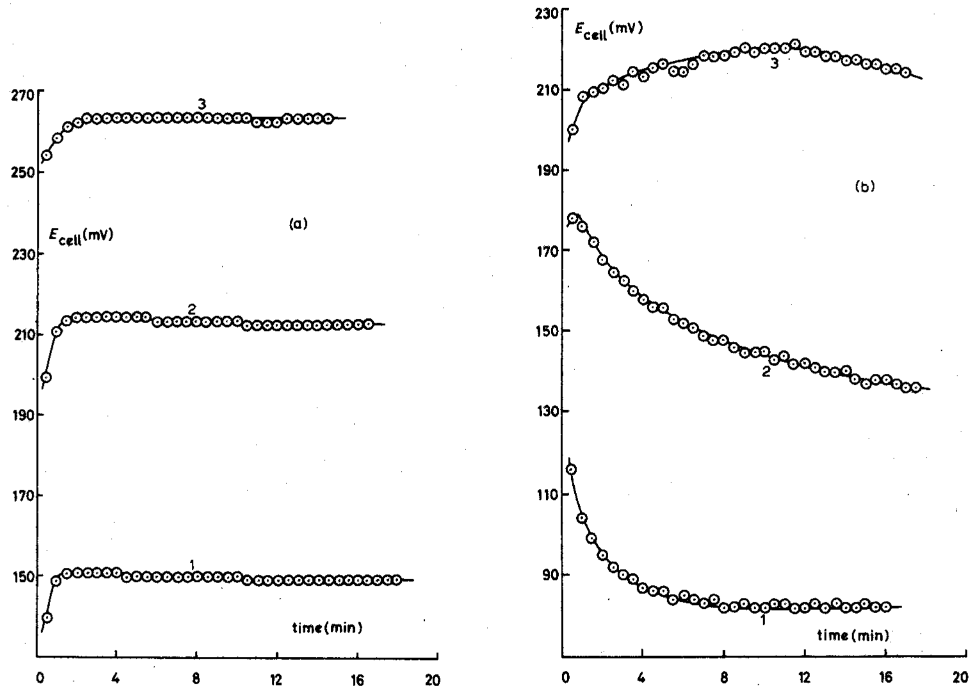


Fig. 2. Response behaviour in NaI solutions at different activities. (1) 10^{-1} *M* NaI, (2) 10^{-2} *M* NaI, (3) 10^{-3} *M* NaI with the NEBA·ClO_4/1,2-dichlorobenzene electrode (Fig. 2a) and the NEBA·ClO_4/β,β'-dichlorodiethyl ether electrode (Fig. 2b).

corresponding to reference and interfering ion activities of 10^{-1} *M* (10^{-2} *M* for sulphate) according to

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

with E_{ref} and E_{interf} given in mV. Table II contains such coefficients obtained for both liquid–membrane electrodes and for the solid-state electrode studied earlier. Ten interfering ions were studied in each case. Values of $K_{\mathrm{ClO_4^-/X}}$ less than unity indicate selectivity for the reference ion perchlorate.

The effects of variations in pH on the cell potential are illustrated in Fig. 3 for the liquid–membrane electrodes. Little change in cell potential occurred during a pH change of *ca.* 4.5 decades in the acid region, even for perchlorate activity levels of 10^{-3} *M*. Hydrogen ion activities as high as 10^{-1} *M* may thus be present in the sample solution without significant interference being caused. For alkaline solutions, the interference by hydroxide ion may be estimated from the selectivity coefficients $K_{\mathrm{ClO_4^-/OH^-}}$ given in Table II. The values observed indicate that reliable perchlorate determinations should be possible with both liquid–membrane electrodes at all activities corresponding to linear electrode response (*i.e.*, for 1–10^{-4} *M* perchlorate) for pH $\leqslant$ 12.

No thorough examination of interference by oxidizing or reducing ions has yet been performed. The electrodes (both solid-state and liquid–membrane types) were, however, unaffected by the presence of iron(II) or iron(III). The potentials recorded

TABLE II

APPARENT SELECTIVITY COEFFICIENTS, $K_{ClO_4^-/X}$, FOR LIQUID-MEMBRANE AND SOLID STATE ELECTRODES BASED ON NEBA·ClO$_4$[a]

Anion (X)	*NEBA·ClO$_4$/DCB*	*NEBA·ClO$_4$/DDE*	*Solid-state*
ClO_4^-	1	1	1
I^-	$2.4 \cdot 10^{-2}$	$3.0 \cdot 10^{-1}$[b]	$7.5 \cdot 10^{+1}$
BF_4^-	$1.2 \cdot 10^{-1}$	$1.2 \cdot 10^{-1}$	$1.2 \cdot 10^{-1}$
OH^-	$1.6 \cdot 10^{-3}$	$1.7 \cdot 10^{-4}$	$6.3 \cdot 10^{-3}$
NO_3^-	$2.0 \cdot 10^{-3}$	$1.5 \cdot 10^{-3}$	$1.1 \cdot 10^{-3}$
ClO_3^-	$1.8 \cdot 10^{-3}$	$2.1 \cdot 10^{-3}$	$8.7 \cdot 10^{-4}$
SO_4^{2-}	$1.7 \cdot 10^{-5}$	$4.4 \cdot 10^{-5}$	$2.3 \cdot 10^{-4}$
Br^-	$2.8 \cdot 10^{-4}$	$3.9 \cdot 10^{-4}$	$6.5 \cdot 10^{-4}$
F^-	$1.8 \cdot 10^{-4}$	$7.0 \cdot 10^{-5}$	$4.2 \cdot 10^{-4}$
$CH_3CO_2^-$	$4.1 \cdot 10^{-5}$	$6.0 \cdot 10^{-5}$	$3.2 \cdot 10^{-4}$
Cl^-	$2.5 \cdot 10^{-5}$	$1.1 \cdot 10^{-4}$	$7.8 \cdot 10^{-4}$

[a] Uncertainties in $K_{ClO_4^-/X}$ values estimated to be ±7%. [b] Value after 8 min.

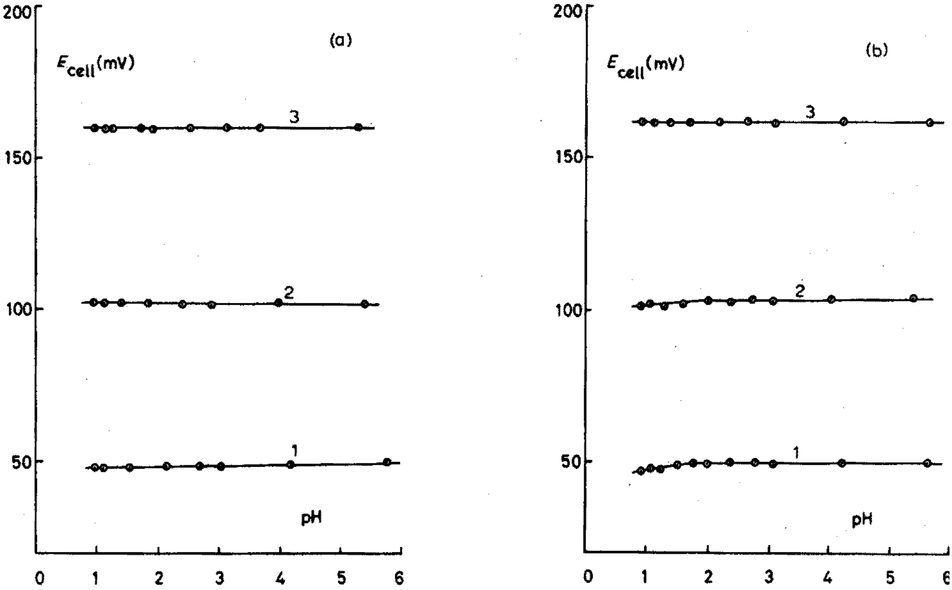


Fig. 3. Dependence of the cell potential on pH at different activity levels of perchlorate io (1) 10^{-1} *M* ClO_4^-, (2) 10^{-2} *M* ClO_4^-, (3) 10^{-3} *M* ClO_4^-, with the NEBA·ClO$_4$/1,2-dichlorobenzen electrode (Fig. 3a) and the NEBA·ClO$_4$/β,β'-dichlorodiethyl ether electrode (Fig. 3b).

for such solutions corresponded closely with response towards the anions present *e.g.*, sulphate or chloride. This result is expected on the basis of a redox potentia for the reaction

$$\text{NEBA}^{+\cdot} + e \rightleftharpoons \text{NEBA (azine)}$$

of *ca.* +690 mV *vs.* N.H.E. in aqueous media[11]. Ions which take part in redo couples with potentials lower than this value, *e.g.*, iodide in $\frac{1}{2}$ I_2/I^- ($E^\circ = +536$ mV *vs.* N.H.E.) or hexacyanoferrate(II) in $Fe(CN)_6^{3-}/Fe(CN)_6^{4-}$ ($E^\circ = +360$ mV *vs.* N.H.E.) interfere by reducing the radical ion species.

Since the lifetime of a liquid–membrane electrode is usually of the order of weeks or months (depending mainly upon mechanical loss of the membrane liquid, evaporation of the solvent and removal of active material from the membrane), the problem of regeneration is important. For the systems under discussion, the stability of the radical ion salt in the membrane solution constitutes an additional factor which must be taken into account. A moderately rapid disappearance of the exchange sites may become the predominating term controlling the duration of acceptable electrode performance. The solutions of $NEBA \cdot ClO_4$ used above were found to be stable for several months at the higher concentrations (*ca.* 10^{-4} *M*) but decomposed within 1–2 weeks at the lowest concentrations (*ca.* 10^{-6} *M*) examined. Spectral observations of the decomposed solutions showed that reduction of the radical cation, $NEBA^{+\cdot}$, had occurred. From practical considerations little advantage is to be gained by employing very low concentrations, as is shown below. Saturated solutions, which are easily prepared from the solid salt when required, provide electrodes with linear measuring ranges of at least 1–10^{-4} *M* perchlorate. In the solid state, $NEBA \cdot ClO_4$ has been found to be stable for periods exceeding six months. No difficulties were encountered in regenerating electrodes from such solutions; different examples gave calibration plots which agreed with a mean curve within ±2 mV over the range 1–10^{-5} *M* perchlorate. In applications where a precision of ±10% is acceptable, it thus appears possible to continue a series of measurements after regeneration without recalibrating the electrode.

DISCUSSION

Response behaviour

The solid-state electrode made from $NEBA \cdot ClO_4$ showed a Nernstian response to changes in perchlorate ion activity over the range 1–10^{-4} *M*[5]. At lower activities the electrode potential approached a limiting, activity-independent value. Such potential limits are a common feature of measurements with solid-state electrodes and are generally interpreted as being a consequence of the finite solubility of the sensing material itself, which imposes a lower limit upon the activity of the ion to which the electrode responds. Only in a few cases, however, has the quantitative agreement between the solubility products predicted by the response behaviour and those obtained by independent methods, been sufficiently satisfactory for such an explanation to be wholly acceptable. For the solid-state $NEBA \cdot ClO_4$ electrode the response behaviour indicated a solubility product K_{sp} ($NEBA \cdot ClO_4$), aq., 25° of $1.6 \pm 0.6 \cdot 10^{-10}$ which agreed well with a value K_{sp} ($NEBA \cdot ClO_4$), aq., 24° of $1.9 \pm 0.2 \cdot 10^{-10}$ obtained by spectral methods ($\varepsilon = 29{,}000$ for $NEBA^{+\cdot}$ at 387 nm). It thus appears justifiable to attribute the potential limit to the solubility of the sensing substance in this instance. It follows that the measuring range observed for this electrode agrees with the maximum one allowed by the construction method. No further improvements are possible.

The results presented above show that liquid–membrane electrodes may also be prepared from $NEBA \cdot ClO_4$. The response behaviour observed compares favourably with that of the solid-state sensor derived from the same substance. Linear response regions extend over more than four decades of perchlorate activity (1–10^{-4} *M*) and the slopes correspond with Nernstian values. No significant differences were found between the solid-state and liquid–membrane electrodes with regard to the stabilities and reproducibilities of the potentials recorded or with regard to the times of response. Thus, there appear to be no obvious differences in electrode function which favour one constructional method over the other. However, there exists an important controllable parameter for the liquid–membrane systems which is not present in the solid-state construction, namely the activity of NEBA·ClO_4 in the sensing phase. Since NEBA·ClO_4 is much more soluble in organic solvents than in water, it should be possible, by taking advantage of extraction equilibria, to extend the useful activity range of a liquid–membrane electrode over that found for its solid-state counterpart. In principle, this requires the use of solutions of the salt at sub-saturation concentrations as liquid membranes. Measurements were performed to confirm this possibility. Figure 4 shows the variation in limiting cell potential (which defines the lowest measureable activity level) as a function of the concentration of NEBA·ClO_4 in the membrane. Observations for both solvents are included; an increase in potential corresponds with an increase in measuring range. Markedly different behaviour was shown by the two-electrode systems. Both showed the expected improvement in measuring range during the initial stages of dilution from saturated solutions (the points for the highest concentrations in each case in Fig. 4 represent saturated solutions) but

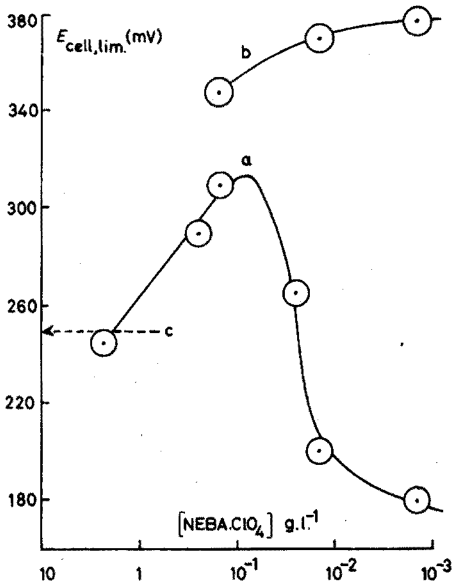


Fig. 4. Dependence of the limiting cell potential on the concentration of NEBA·ClO_4 in the membrane solution. Curves (a) and (b) refer to the NEBA·ClO_4/β,β'-dichlorodiethyl ether and NEBA·ClO_4/1,2-dichlorobenzene systems, respectively. The dotted line (c) represents the limiting potential for the solid-state electrode after appropriate adjustments to the observed potentials. The agreement between this line and the limiting potential for the saturated NEBA·ClO_4/β,β'-dichlorodiethyl ether electrode indicates that the electrodes show the same response range.

whereas an upper limit was approached by the 1,2-dichlorobenzene system, the β,β'-dichlorodiethyl ether electrode exhibited a rapid deterioration in response range for membrane concentrations of NEBA·ClO_4 below *ca.* 0.1 g l^{-1}. The behaviour of the latter is consistent with the breakdown of Donnan exclusion, whereupon co-ion transport across the membrane is permitted[12]. Similar effects were not observed for the dichlorobenzene electrode. It is clear from Fig. 5 that practically significant depressions of the perchlorate detection limits may be achieved by reducing the concentrations of NEBA·ClO_4 in the membrane phases. Dilution of saturated solutions by a factor of ten extends the measuring range by about 1 decade for the ether system and by roughly $\frac{1}{2}$ decade for the dichlorobenzene electrode. Further dilution provides little or no additional improvement.

Another aspect of the response behaviour requires comment. Thermodynamic arguments predict that solid-state and liquid–membrane electrodes which incorporate saturated solutions of NEBA·ClO_4 will show similar response ranges, irrespective of the solvent employed in the latter. Experimentally, this was found to be the case only for the saturated NEBA·ClO_4/β,β'-dichlorodiethyl ether and solid-state sensors. The limiting potential for the saturated NEBA·ClO_4/1,2-dichlorobenzene system was found to be some 90 mV higher than that for the other electrode, as shown in Fig. 5. This difference corresponds to a perchlorate activity limit which lies approximately 1.5 decades below that observed for the dichlorodiethyl ether and solid-state sensors. Two possible explanations for the 'anomalous' behaviour of the dichlorobenzene membrane may be advanced, neither of which has yet been fully explored. Firstly, the system may not be in true equilibrium. The stabilities of the potentials observed (E_{cell} constant within ± 1 mV for periods longer than 20 min at 10^{-6} *M* perchlorate), however, imply that at least a "steady-state" situation exists which can be exploited for measurements of perchlorate at lower activities. They are not sufficient to confirm the presence of equilibrium. Secondly, the state of NEBA·ClO_4 in 1,2-dichlorobenzene may differ significantly from that found in β,β'-dichlorodiethyl ether. A comparison of the visible spectra of the radical ion, $NEBA^{+\cdot}$, obtained in the two solvents showed differences which suggested that various forms of the species, *e.g.*, those resulting from aggregation, ion-pairing or specific interactions with the solvent, might arise. Without additional information, no further statement is warranted. Attempts are being made, with different physical techniques, to collect the data necessary for a reliable interpretation. On a practical basis, the dichlorobenzene electrode is superior to the other system since it offers the wider measuring range for a given membrane concentration of NEBA·ClO_4.

Selectivity

The coefficients, $K_{ClO_4^-/X}$, given in Table II show that, with the exception of the solid-state sensor in the case of iodide, all the electrodes are selective for perchlorate. Differences in selectivity behaviour do, however, exist between the three systems. Not only do the values of $K_{ClO_4^-/X}$ for a given interfering ion differ for each electrode but also a different order is shown by the ions when arranged according to decreasing interference. An examination of the selectivity differences between the two methods of construction must be confined to the NEBA·ClO_4/dichlorodiethyl ether and solid-state electrodes since the undefined state of NEBA·ClO_4 in

1,2-dichlorobenzene may invalidate such comparisons. With this restriction in mind, Table II shows that the agreement between the $K_{\mathrm{ClO}_4^-/\mathrm{X}}$ values is relatively much poorer for those ions which exhibit only slight interference, *e.g.*, SO_4^{2-}, $CH_3CO_2^-$, F^-, where differences approaching one power of ten arise, than for the major interferences, BF_4^-, NO_3^- and ClO_3^-. These larger discrepancies probably do not reflect real differences in selectivity of this magnitude between the two electrodes. For the solid-state sensor the potentials observed for ions of low interference lie close to the perchlorate detection limit and correspond to very poor response (see *e.g.*, the fluoride response curve in Fig. 2 of ref. 5, where the slope was < 8 mV decade^{-1}). Such behaviour indicates that the measurements made are not truly representative of interference by a particular ion. Upon extending the perchlorate response range by using a liquid–membrane construction, different values for the apparent selectivity coefficients of weakly interfering ions may thus be expected. This is found experimentally for ions such as SO_4^{2-}, F^-, $CH_3CO_2^-$ and Cl^- where the respective $K_{\mathrm{ClO}_4^-/\mathrm{X}}$ values are much smaller for the NEBA·ClO_4/dichlorodiethyl ether electrode than those for the solid-state system. The agreement is better between the selectivity parameters obtained for the major interfering ions, BF_4^-, NO_3^- and ClO_3^-, where measurements are expected to provide a much closer approach to "true" values. It is not possible to determine "true" interference parameters for weakly interfering ions, even from observations for the liquid–membrane electrode, since response to these ions is still not fully developed, *i.e.*, the response curves do not show slopes of 59 mV decade^{-1} at activities of 10^{-1} *M*. For all practical purposes the apparent selectivity coefficients may be regarded as upper limiting values for interference. In the light of the foregoing remarks, the selectivities shown by the two electrodes appear to be quite similar for the majority of the ions studied. Iodide, however, constitutes a clear exception where the difference in construction may exert a profound influence on both the degree and the kinetics of interference. The solid-state electrode suffers a rapid, irreversible "poisoning" of large areas of the sensing surface upon exposure to iodide-containing solutions; the radical ions at the surface are reduced by iodide according to

$$\mathrm{NEBA}^{+\cdot} + \mathrm{I}^- \rightleftharpoons \tfrac{1}{2}\mathrm{I}_2 + \mathrm{NEBA}$$

The reduction product, NEBA, forms a film upon the electrode surface which "blocks" the ion-exchange process. The same reduction reaction almost certainly occurs in the interphase regions of the liquid–membrane sensor but "blocking" to a comparable extent is eliminated by the mobility of the reactants and products within the membrane phase. As can be seen from Fig. 2(b), stable potentials were not generally obtained for the NEBA·ClO_4/β,β'-dichlorodiethyl ether electrode in iodide solutions within the periods of observation. The drift recorded for a particular iodide activity may reflect the time required for a "steady state" to be established at the electrode surface. Insufficient experimental data prohibit a more detailed interpretation of the response behaviour at present.

The NEBA·ClO_4/1,2-dichlorobenzene electrode showed selectivities for most of the ions tested which were comparable in magnitude with those obtained for the NEBA·ClO_4/β,β'-dichlorodiethyl ether and solid-state sensors. One important exception was the interference by iodide which was much lower for this electrode than for the other two systems. Figure 2(a) shows that the response to iodide was fast; stable potentials were attained after 2–3 min. This behaviour is quite different from that shown by the other liquid–membrane electrode and adds further support for the assumption of a different solute condition in dichlorobenzene. Practically, the dichlorobenzene system provides the better of the two liquid–membrane electrodes from the viewpoint of overall selectivity.

All the electrodes showed low interference by hydrogen and hydroxide ions so that perchlorate determinations should be possible with any of the three systems over wide ranges of pH.

Conclusions

From the results obtained it is finally concluded that the radical ion salt, NEBA·ClO_4, can be used to prepare practically useful liquid–membrane or solid-state electrodes which are selective for perchlorate ions. Wider response ranges can be achieved with the liquid–membrane constructions. Among the systems studied above, the NEBA·ClO_4/1,2-dichlorobenzene electrode was superior to both the solid-state and NEBA·ClO_4/β,β'-dichlorodiethyl ether sensors on the basis of its response and selectivity characteristics.

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SUMMARY

Liquid–membrane electrodes were prepared from solutions of N-ethylbenzothiazole-2,2′-azaviolene perchlorate in 1,2-dichlorobenzene and in β,β'-dichlorodiethyl ether, and their response and selectivity characteristics were examined. Perchlorate response ranges of the order 1–$10^{-6.5}$ M and 1–$10^{-5.6}$ M were shown to be attainable with the two systems, respectively. These values represent significant improvements over the range 1–$10^{-4.8}$ M found for the solid-state electrode made from the same radical ion salt. Short response times and acceptably stable potentials were observed for both liquid–membrane sensors. Both showed high apparent selectivities for perchlorate over all the ten anions tested. Iodide and tetrafluoroborate were the most serious interferences in each case. The low interference shown by hydrogen and hydroxide ions indicated that perchlorate determinations may be performed within the pH range 1–12 with both electrodes.

RÉSUMÉ

Des électrodes à membrane liquide ont été préparées à partir de solutions de perchlorate de N-éthylbenzothiazole-2,2′-azaviolène dans le dichloro-1,2-benzène et dans le β,β'-dichlorodiéthyléther; les caractéristiques de leur réponse et de leur sélectivité sont examinées. L’ordre de grandeur de la réponse est de 1–$10^{-6.5}$ M et 1–$10^{-5.6}$ M respectivement; ce qui est nettement supérieur aux valeurs trouvées pour une électrode solide. Elles présentent une sélectivité apparente élevée pour le perchlorate; dix anions étrangers ont été examinés. Iodure et tétrafluoborate constituent les plus sérieuses interférences. Hydrogène et hydroxyle n’interfèrent que très peu; les mesures peuvent par conséquent s'effectuer entre les pH 1 et 12, avec les deux électrodes.

ZUSAMMENFASSUNG

Flüssig–Membranelektroden wurden aus Lösungen von N-Äthylbenzothiazol-2,2'-azaviolen-perchlorat in 1,2-Dichlorbenzol und in β,β'-Dichlordiäthyläther hergestellt und deren Ansprech- und Selektivitätsverhalten geprüft. Bei den beiden Systemen sprach Perchlorat im Bereich $1–10^{-6.5}$ M bzw. $1–10^{-5.6}$ M an. Diese Werte stellen eine bedeutende Verbesserung gegenüber dem Bereich $1–10^{-4.8}$ M dar, in dem die aus demselben Radikalion-Salz hergestellte Festkörper-Elektrode wirksam ist. Kurze Ansprechzeiten und hinreichend beständige Potentiale wurden bei beiden Flüssig–Membransensoren beobachtet. Beide zeigten hohe scheinbare Selektivitäten für Perchlorat gegenüber allen zehn untersuchten Anionen. In jedem Fall störten Jodid und Tetrafluoroborat am meisten. Auf Grund der geringen Störungen durch Wasserstoff- und Hydroxidionen können Perchloratbestimmungen mit beiden Elektroden im pH-Bereich 1–12 ausgeführt werden.

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DETERMINATION OF HYDROFLUORIC ACID IN STRONG ACID SOLUTIONS SUCH AS STAINLESS STEEL PICKLING BATHS WITH A LANTHANUM FLUORIDE ELECTRODE AND A PERMAPLEX MEMBRANE ELECTRODE

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A stainless steel pickling bath can contain 15–25% nitric acid and 3–5% hydrofluoric acid by weight[1] and various amounts of metal ions, mostly iron. The nitric acid serves to dissolve the metal through an oxidizing attack while the hydrofluoric acid complexes the metal ions formed. The concentrations of the free nitric and hydrofluoric acids affect the pickling rate. Therefore there is a demand for rapid, direct methods to measure these concentrations.

McKaveney *et al.* have shown that semiconductor electrodes can be used both for the determination of strong acids in pickling baths[2–4] and for the determination of free hydrofluoric acid[5]. Unfortunately, these electrodes can only be used in diluted samples of pickling acids. Recently[6], it has been shown that it is possible to make direct determinations of nitric acid in stainless steel pickling baths with a Permaplex membrane electrode.

Several authors have already used the lanthanum fluoride electrode in acidic media. Frant and Ross[7] showed that the activity response of the lanthanum fluoride electrode is Nerstian from 1 to below 10^{-5} *M* fluoride in neutral aqueous solutions. Since then many authors have confirmed this observation[8–11]. Lingane[12] showed that the sensitivity limit of the electrode is a decade lower in 0.1 *M* hydrochloric acid than in 0.1 *M* sodium nitrate, and Baumann[13] found that the electrode response to free fluoride was Nernstian one to three decades below 10^{-6} *M* in the presence of complexing cations. Norén[14] showed that the response of the electrode was almost exactly Nernstian even in 4 *M* perchloric acid when the concentration of hydrofluoric acid varied within the range $4 \cdot 10^{-4}$–$2 \cdot 10^{-1}$ *M*. Baumann[15] showed that measurement of fluoride in increasing concentrations of phosphoric acid (1–10 *M*) shifted the potential in a positive direction, because of hydrogenfluoride ion formation, but at a particular acidity, Nernstian response to fluoride ion was still achieved. Srinivasan and Rechnitz[9] reported that their results, which were obtained by direct measurement of free fluoride concentration in acidic solutions, could be fully explained in terms of the species F^-, HF and HF_2^- if they assumed ideal Nernstian response of the electrode. Recently, Patel *et al.*[10] confirmed the Nernstian behaviour of the electrode in dilute acid solutions. They measured the fluoride activity in solutions containing varying amounts of hydrochloric acid and were

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able to calculate the ionization constants of hydrofluoric acid and the formation constant of HF_2^-. All these observations indicate that the lanthanum fluoride electrode functions ideally in both neutral and acidic aqueous solutions.

The main purpose of this paper is to demonstrate the usefulness of the lanthanum fluoride electrode for direct determination of hydrofluoric acid in strongly acidic solutions like stainless steel pickling baths.

Frant[16] has discussed the application of the lanthanum fluoride electrode to chromium plating baths; his method involves dilution with an acetate buffer which swamps any variation in sample ionic strength.

EXPERIMENTAL

Cell potentials were measured with a fluoride-selective electrode (Orion 94-09) and a double-junction reference electrode (Orion 90-02). The bridge solution in the reference electrode was varied as described later. Some of the measurements were made with an Ag/AgCl reference electrode.

Measurements were made to the nearest 0.1 mV with an Orion 801 digital pH meter. All measurements were made at 25.0° in a thermostatted plexiglas vessel adapted to a Penton top (Metrohm EA 615).

Series of solutions containing 0.03, 0.1, 0.3 and 1.0 *M* hydrofluoric acid, respectively, were prepared. Three series contained hydrochloric acid and three series contained nitric acid. The concentrations of strong acid were 1, 2 and 3 *M*, respectively.

All solutions were prepared by weight from the different acids used: hydrofluoric acid, 49% p.a. (Mallinckrodt), hydrochloric acid, 37% p.a. (Merck), and nitric acid, 65% p.a. (Merck). The specific gravity and the molarity of each of the concentrated acids were determined separately. Volumetric flasks made of polypropylene (500 ml) were used.

RESULTS AND DISCUSSION

Evaluation of the measurements with the fluoride-selective electrode

The species formed in acidic fluoride solutions are F^-, HF, HF_2^- and possibly the dimer $(HF)_2$. In strongly acidic solutions, the amount of HF_2^- is very small and can be neglected[17]. In the present investigation it should be less than 0.5% of the total amount of fluoride. The possible influence of the dimer will also be neglected at present. The total concentration of fluoride will then be:

$$[F_T] = [F^-] + [HF] \tag{1}$$

$$K_a = \frac{[H^+][F^-]}{[HF]}\frac{f_{H^+}f_{F^-}}{f_{HF}} \tag{2}$$

$$[F_T] = [F^-] + \frac{[H^+][F^-]}{K_a}\frac{f_{H^+}f_{F^-}}{f_{HF}} \tag{3}$$

As $[F^-]$ is 0.1% or less of $[F_T]$ in these strong acids, the $[F^-]$ term can be neglected. Taking the logarithm then gives:

$$\log[F_T] = \log[H^+] + \log f_{F^-}[F^-] + \log\frac{f_{H^+}}{f_{HF}} - \log K_a \tag{4}$$

The electrode response is given by:

$$E_{F^-} = E' - S\log[F^-]f_{F^-} + E_j \tag{5}$$

where E_j is the liquid junction potential of the reference electrode, S is an empirical factor which corresponds to $(RT/F)\ln 10$ if the electrode response is truly Nernstian, and E' is the standard potential of the fluoride electrode *versus* the Orion reference electrode when the liquid junction has been accounted for. Substitution of eqn. (5) into eqn. (4) and rearrangement gives:

$$\log[F_T] - \log[H^+] = -\frac{E_{F^-}}{S} + \frac{E'}{S} + \frac{E_j}{S} + \log\frac{f_{H^+}}{f_{HF}} - \log K_a \tag{6}$$

which can be written as:

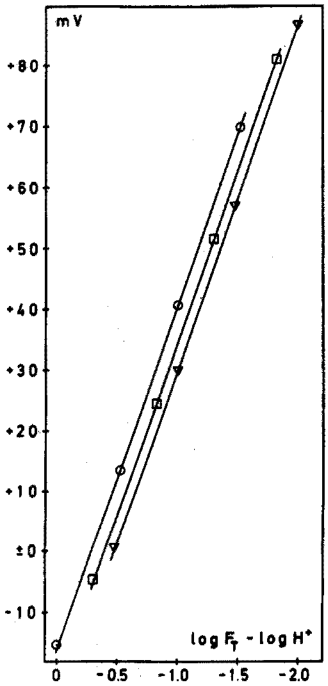
$$\log[F_T] - \log[H^+] = -\frac{E_{F^-}}{S} + K \tag{7}$$

where K varies with the concentration of the acids. K can be evaluated from a calibration procedure as follows. A set of solutions, all 1 M with respect to hydrochloric acid and 0.03–1 M with respect to hydrofluoric acid were prepared. F_T, the total amount of fluoride was equal to the number of moles of HF taken. By definition $[H^+] = 1$ M in the solutions, as the activity coefficient was included in K. The circles in Fig. 1 show a plot of E_{F^-} *versus* $\log[F_T] - \log[H^+]$. S and K can be evaluated from the slope and the intercept. Two other calibration curves were also made by the same procedure; in these, the hydrogen ion concentration was 2 M and 3 M. Figure 1 shows that the slope was the same but that different intercepts were obtained.

The intercept K contains constants by definition and concentration-dependent terms like E_j and $\log f_{H^+}/f_{HF}$. The variation of E_j with concentration will depend on the bridge solution of the reference electrode. It might therefore be possible to select a bridge solution so that the sum $(E_j/S + \log f_{H^+}/f_{HF})$ becomes independent of $\log[H^+]$. The acidity in stainless steel pickling baths will vary with time and this variation must be accounted for when calculating the total amount of hydrofluoric acid. The evaluation becomes simpler if K in eqn. (7) is a true constant for the range used.

Calibration curves, like those in Fig. 1, were made for a number of bridge solutions. It was found, as shown in Fig. 2, that with 4 M potassium chloride in the bridge the variation in E_j/S exactly cancelled the variation in $\log f_{H^+}/f_{HF}$. It may be mentioned that when potassium nitrate was used instead of potassium chloride the concentration-dependence of K became larger.

If substances other than the strong acid and hydrofluoric acid are present in appreciable amounts, K may be influenced in two ways. First, there may thus be another nonideal term in K which makes K a function of the amount of this substance; if the substance is a metal salt it is difficult to differentiate this effect from a complex formation. Secondly, the nonideal terms in K may change so that the sum $(E_j/S + \log f_{H^+}/f_{HF})$ again becomes a function of $\log[H^+]$ even when



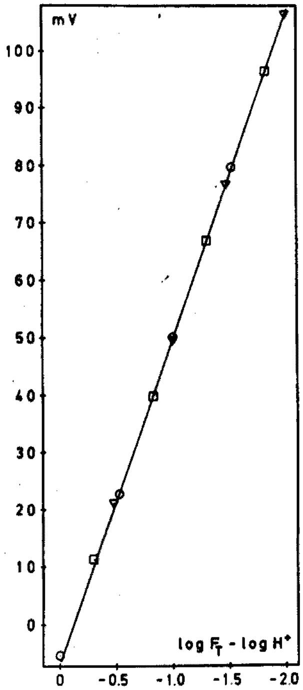


Fig. 1. Calibration curves for a lanthanum fluoride electrode in 1, 2 and 3 *M* HCl. Bridge solution in the reference electrode 2 *M* KCl. (○) 1 *M* HCl, (□) 2 *M* HCl, (▽) 3 *M* HCl.

Fig. 2. Calibration curves for a lanthanum fluoride electrode in 1, 2 and 3 *M* HCl. Bridge solution in the reference electrode 4 *M* KCl. (○) 1 *M* HCl, (□) 2 *M* HCl, (▽) 3 *M* HCl.

4 *M* potassium chloride is used as bridge solution.

A similar set of measurements was made with three series of nitric acid solutions (1 *M*, 2 *M* and 3 *M*, respectively) and varying amounts of hydrofluoric acid. The results were practically identical to those obtained for the hydrochloric acid series if the incomplete dissociation of the nitric acid solutions was taken into account. The pK_a value of nitric acid was taken to be -1.3, giving $[H^+]$ equal to 0.955, 1.83 and 2.65 in 1 *M*, 2 *M* and 3 *M* nitric acid, respectively. When 4 *M* potassium chloride was used as bridge solution, *K* became independent of log $[H^+]$ and its value was about 2 mV higher in nitric acid than in hydrochloric acid solutions. *E*, on the other hand, varied by about 1 mV between two calibrations one month apart.

If *K* and *S* have been determined as shown in Fig. 2, the total amount of fluoride in a solution can be obtained from measurements of the electrode potential E_{F^-}, provided that log $[H^+]$ can be evaluated separately.

Evaluation of the measurements with the Permaplex membrane electrode

It has been shown earlier[6] that a sulphonic acid cationic membrane made from Permaplex can be used to measure the concentration of strong acids. The interference from hydrofluoric acid and from cations in the concentrations used in stainless steel pickling baths could be neglected. When 4 *M* potassium chloride was used as bridge solution in the reference electrode, the electrode response was linear when plotted against the concentration of nitric acid. In this case the dissociation of nitric acid was not taken into account. The electrode response is thus empirically:

$$E_{HNO_3} = E'' + S'' \log[HNO_3]_T \tag{8}$$

where E'' and S'' are constants and the total amount of nitric acid is given by:

$$[HNO_3]_T = [HNO_3] + [NO_3^-] \tag{9}$$

The constants can be obtained from a calibration made in a series of nitric acid solutions. Equation (7) was shown to hold when the dissociation of nitric acid was taken into account for calculation of the $\log[H^+]$ term. To determine the $\log[H^+]$ value in an unknown solution, the potential of the Permaplex electrode, E_{HNO_3}, should be measured and $[HNO_3]_T$ calculated from eqn. (8). $[H^+]$ is then obtained from:

$$[HNO_3]_T = [H^+] + [H^+]^2/10^{1.3} \tag{10}$$

and substituted into eqn. (7).

With the 4 *M* potassium chloride bridge used in the reference electrode, there is no linear relation between the Permaplex electrode potential and log [HCl]. It should be possible to obtain a linear relation by suitable selection of bridge solution, but it would then be necessary to use two different reference electrodes in the sample solution. In most cases an empirical relation between electrode potential and $\log[H^+]$ is more convenient.

Influence of dimer formation

A conditional formation constant, $K_d = [(HF)_2]/[HF]^2$ equal to 2.7 ± 0.3 was recently reported[18]. This value is so high that an appreciable amount of the hydrofluoric acid should be present as dimer in the solutions used in pickling baths. A relation can be derived between F_T and the parameters $[H^+]$ and $[F^-]$, taking dimer formation into account. The expression for $[F_T]$ then becomes:

$$[F_T] = \frac{[H^+][F^-]}{K_a} \frac{f_{H^+} f_{F^-}}{f_{HF}} + \frac{2[H^+]^2[F^-]^2}{K_a^2} \frac{K_d f_{H^+}^2 f_{F^-}^2}{f_{HF}^2} \tag{11}$$

The formation of HF_2^- has been neglected and $F^- \ll F_T$ (*cf.* eqn. 3). The total amount of fluoride is then a quadratic function of the electrode potentials. If the influence of the second term became measurable, non-linear curves should be obtained in Figs. 1 and 2. The fact that almost linear graphs with a slope of 57 mV/decade were obtained, implies that the second term in eqn. (11) is small, and thus that K_d must be smaller than the value given by Warren[18].

S in eqn. (7) was defined so that it should only be a measure of the indicator electrode ideality and be independent of E_j. It is not possible, however, to make independent measurements of the quantities *S* and E_j. The numerical value of *S* therefore cannot be used to exclude appreciable dimer formation.

In order to avoid liquid-junction effects altogether, a series of measurements was made with an Ag/AgCl electrode immersed directly into the HCl/HF solutions in the same way as earlier described by Covington and Thain[19]. A set of solutions was prepared which were 2 M in hydrochloric acid and 0.03–1 M in hydrofluoric acid. Log$[F^-]$ can be evaluated from eqn. (11).

$$\log[F^-] = \log\frac{f_{HF}}{f_{H^+}f_{F^-}} + \log\frac{K_a}{4K_d[H^+]} + \log[(1+F_T\cdot 8\cdot K_d)^{\frac{1}{2}}-1] \qquad (12)$$

and compared with the electrode reading which is:

$$E = E''' - S'''\log([F^-]/[H^+])f_{F^-}f_{Cl^-} \qquad (13)$$

since $[Cl^-]=[H^+]$. The slopes of the fluoride and chloride electrodes were taken to be equal since they cannot be differentiated with the present experiment. At constant $[H^+]$, E in eqn. (13) should be essentially proportional to $\log[F^-]$. Figure 3 shows a plot of E *versus* $\log[F^-]$ obtained from eqn. (12) with different values of K_d. The term $\log f_{HF}/f_{H^+}\,f_{F^-}$ cannot be evaluated but it should remain almost constant within the series and it has therefore been retained in the plot as k. pK_a was taken to be 3.2, as given by Patel *et al.*[10]. Its value is not important for the discussion, because an error in K_a will appear as a slightly different value of k.

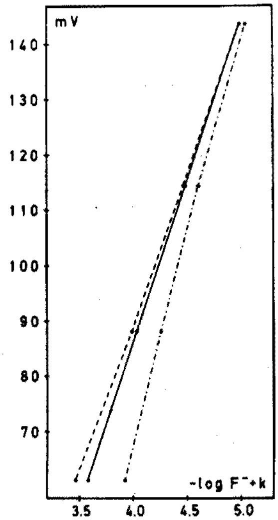


Fig. 3. Potential of the lanthanum fluoride electrode *versus* $\log[F^-]$ calculated from the last two terms of eqn. (12) with different values for the dimeric constant K_d. The reference electrode was an Ag/AgCl electrode. (------) $K_d=0$; (——) $K_d=0.25$; (–·–·) $K_d=2.7$.

The slope of the line in Fig. 3 should equal S''' if the activity coefficients are constant. It can be seen that a value of K_d equal to 2.7 results in slightly curved relationship. When S''' was fixed at 59.2 mV/decade, a value of $K_d=0.25$ was obtained.

Similar measurements were made in solutions which were 1 M and 3 M in hydrochloric acid. The same general picture was obtained. The constants obtained for $S'''=59.2$ mV/decade were 0.26 and 0.27 in 1 M and 3 M hydrochloric acid, respectively.

A small variation in the activity coefficients, as hydrofluoric acid replaces water in the solution cannot be ruled out, but it is not likely to be so large that it is compatible with a K_d value of 2.7. Since S''' cannot be measured independently in the medium, the value of a constant calculated on the assumption that it is ideal might be questioned. It should be mentioned, however, that the line for $K_d=0$ deviates from linearity. The deviation amounts to about 2 mV in the solutions 1 *M* in hydrofluoric acid. The value given by Warren[18] seems to be calculated without due consideration of variations in the liquid-junction potential and as shown above, this variation might well give large errors.

Some experiments recently discussed by Judge[20] indicate that polymeric species like $H_2F_3^-$, $H_3F_4^-$, and $H_4F_5^-$ exist in strong hydrofluoric acid. The results above indicate that the amount of these should be low compared to the amount of hydrofluoric acid. The estimate of $K_d=0.25$ is a maximum value, which might well be much lower if the polymeric species could be taken into account.

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SUMMARY

It is shown that the total amount of hydrofluoric acid in strong hydrochloric or nitric acid solutions with varying acidity can be determined directly with two ion-selective electrodes. Equations were derived and calibration procedures for both electrodes were developed. The influence of liquid junctions at the reference electrodes was investigated and it was possible to simplify the equations by the use of a suitable bridge solution. The formation constant of the dimer $(HF)_2$ was redetermined and found to be 0.26.

RÉSUMÉ

Il est démontré que la concentration totale en acide fluorhydrique dans des solutions d'acide chlorhydrique ou d'acide nitrique, à diverses acidités, peut être déterminée directement à l'aide de deux électrodes ioniques sélectives. On propose des équations et une méthode de calibrage pour ces deux électrodes. On examine l'influence du liquide de jonction des électrodes de référence. La constante de formation du dimère $(HF)_2$ est déterminée à nouveau; on arrive à la valeur de 0.26.

ZUSAMMENFASSUNG

Es wird gezeigt, dass die Gesamtmenge an Fluorwasserstoffsäure in stark salzsauren oder salpetersauren Lösungen wechselnder Acidität direkt mit zwei ionenselektiven Elektroden bestimmt werden kann. Es wurden Gleichungen abgeleitet und Eichverfahren für beide Elektroden entwickelt. Der Einfluss der Flüssig-Verbindungen mit den Vergleichselektroden wurde untersucht; durch Verwendung einer geeigneten Brückenlösung war es möglich, die Gleichungen zu vereinfachen. Die Bildungskonstante des Dimeren $(HF)_2$ wurde erneut bestimmt; der gefundene Wert ist 0.26.

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ANION SELECTIVITY STUDIES ON LIQUID MEMBRANE ELECTRODES

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A number of ion-selective liquid membrane electrodes have been described which respond selectively to anions. These include electrodes for the measurement of inorganic anions[1–8], carboxylic acid anions[2,3,9], amino acid anions[10] and anionic metal chloride complexes[11]. The liquid ion-exchange membranes of these electrodes generally consist of a large extractable cation such as a transition metal–phenanthroline complex or bulky quaternary ammonium ion dissolved in a water-immiscible organic solvent.

Although a relatively large number of usable electrodes have been reported, and a comprehensive theoretical treatment of liquid membrane electrode behavior has been presented[12,13], few experimental studies have been made of the relationship between electrode selectivity and composition of the liquid membrane. Freiser *et al.*[10,14] have found that the selectivity of amino acid anion electrodes closely parallels the solvent extraction behavior of the liquid phase as described by the relative distribution coefficients of the amino acid anion–quaternary ammonium ion pairs. Scibona *et al.*[4,5] have investigated the response of tetraheptylammonium ion–benzene electrodes to chloride, bromide and nitrate ion and have correlated electrode selectivity to ion-exchange equilibrium constants, ion-pair formation constants and ionic mobilities.

In this paper is reported a study of electrode selectivity for the common inorganic anions Cl^-, Br^-, I^-, SCN^-, NO_3^-, ClO_4^-, BF_4^- and PF_6^- as a function of the ion-exchange molecule, its concentration in the membrane phase and the organic solvent used to form the liquid membrane. The ion-exchange molecules investigated are the tris(1,10-phenanthroline)iron(II) and tris(4,7-diphenyl-1,10-phenanthroline)iron(II) complex ions and tetraheptylammonium ion. The solvents investigated are nitrobenzene, chloroform and *n*-amyl alcohol.

EXPERIMENTAL

Reagents

All chemicals used in this work were reagent-grade materials with the exception of sodium fluoroborate. Technical-grade sodium fluoroborate (Matheson, Coleman and Bell) was recrystallized from ethanol–water. Stock solutions were prepared from these chemicals with distilled water, and solutions containing 10^{-1}–

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10^{-4} *M* of the appropriate anion were prepared by serial dilution. Organic solvents were used without further purification.

Preparation of liquid ion-exchange materials

Tris(4,7-diphenyl-1,10-phenanthroline)iron(II) [$Fe(bphen)_3^{2+}$] and tris(1,10-phenanthroline)iron(II) [$Fe(phen)_3^{2+}$] liquid ion-exchange solutions were prepared as nitrate salts by the following procedure. Approximately 20 mmoles of $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$ and a threefold excess of the phenanthroline compound were dissolved in 100 ml of 0.1 *M* sulfuric acid. Aqueous hydroxylamine solution (1 ml of 10%) was added and the pH was adjusted to 5.0–5.5. The solution was transferred to a separatory funnel, and a 200-fold amount of solid sodium nitrate was dissolved in the solution. A 10.0-ml portion of the organic solvent was added, and the complex ion was extracted into the organic phase. The organic phase was separated and kept for use in the electrode. The concentration of the complex ion in the organic solvent was determined spectrophotometrically.

Solutions of tetraheptylammonium nitrate in nitrobenzene were prepared by a procedure similar to that of Scibona *et al.*[15] Successive 10–20 ml portions of 7 *M* lithium nitrate were equilibrated with 10.0 ml of a $1.0 \cdot 10^{-2}$ *M* solution of tetraheptylammonium bromide in nitrobenzene. The aqueous solution was tested after each equilibration with silver nitrate solution until no precipitate of silver bromide could be detected. The organic phase was then separated and used in the electrode.

Electrode assembly and potentiometric measurements

The body of an Orion model 92-20 calcium ion electrode equipped with Orion series 92 membranes was used as the liquid membrane electrode. The electrode was assembled as described in the manufacturer's instructions, and the internal reference and liquid ion-exchange solutions were injected into the appropriate ports in the electrode body. Each membrane was soaked in ion-exchange solution for 1 h before use in the electrode, and each assembled electrode was soaked in 10^{-2} *M* nitrate ion solution for 24–48 h before use. The internal reference solution was 10^{-2} *M* $NaNO_3$ and 10^{-2} *M* KCl.

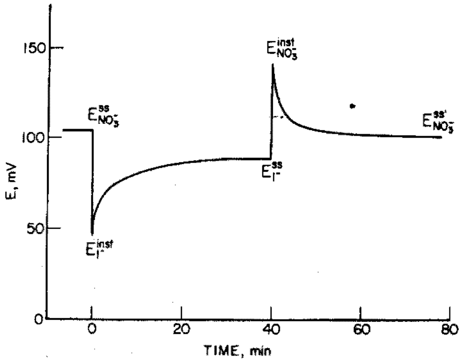

Fig. 1. Time-dependent electrode behavior on transfer between 10^{-2} *M* nitrate and 10^{-2} *M* iodide solutions. Electrode: $1.5 \cdot 10^{-3}$ *M* $Fe(bphen)_3^{2+}$ in nitrobenzene.

Potentiometric measurements were made with a Beckman Century SS pH meter. The reference electrode was a Corning model 467002 saturated calomel electrode. Measurements were made with the electrode immersed to a depth of 1 cm in the sample solution and with the solution stirred by magnetic stirring. Except for the most dilute solutions little difference (usually less than 2 mV) was observed between readings in stirred and unstirred solutions. Potentiometric measurements were made using the standard scale setting of the meter. Most readings were made directly from the face of the pH meter, but in some instances potential–time traces were recorded with a Beckman model 100500 recorder. Except in cases where the measured potential exhibited extreme time dependency, the uncertainty of these measurements was ±2 mV or better. All experimental work was carried out at ambient temperature, 22±2°.

RESULTS AND DISCUSSION

Time dependence of e.m.f. measurements

When an electrode is transferred between two solutions containing different anions a time-dependent e.m.f. is observed. Typical behavior is illustrated in Fig. 1 for an electrode containing the nitrate salt of Fe(bphen)$_3^{2+}$ in nitrobenzene. The equilibrium potential of the electrode in 10^{-2} *M* nitrate is $E^{ss}_{NO_3^-}$. Immediately after immersion in 10^{-2} *M* iodide, potential $E^{inst}_{I^-}$ is observed. After *ca.* 30 min, equilibrium potential $E^{ss}_{I^-}$ is reached in iodide solution. When the electrode is placed back in 10^{-2} *M* nitrate, potentials $E^{inst}_{NO_3^-}$ and $E^{ss'}_{NO_3^-}$ are observed instantaneously and after 30 min equilibration, respectively. E.m.f. differences $E^{inst}_{I^-} - E^{ss}_{NO_3^-}$ and $E^{inst}_{NO_3^-} - E^{ss}_{I^-}$ are instantaneous values, and the e.m.f. difference $E^{ss}_{I^-} - E^{ss}_{NO_3^-}$ is a steady-state value. Within the accuracy of the measurements, it was found that $E^{inst}_{I^-} - E^{ss}_{NO_3^-} = E^{ss}_{I^-} - E^{inst}_{NO_3^-}$; $E^{inst}_{I^-} - E^{ss}_{I^-} = E^{ss}_{NO_3^-} - E^{inst}_{NO_3^-}$; and $E^{ss}_{NO_3^-} = E^{ss'}_{NO_3^-}$, if sufficient time is allowed for equilibration of the electrode in each solution. This behavior was observed for all ions studied. The magnitude of the difference between instantaneous and steady-state values and the time required to establish steady-state potentials increase dramatically as the difference between the selectivity coefficients of the two ions increases. For example, when a nitrate-ion electrode is placed in 10^{-2} *M* hexafluorophosphate solution, $E^{inst}_{PF_6^-} - E^{ss}_{PF_6^-} = -150$ mV, and approximately four days are required to reestablish the equilibrium potential in nitrate ion solution.

The observed time-dependent electrode behavior was not studied further in this work. Similar behavior has been noted previously for both cation- and anion-sensitive liquid membrane electrodes[16–18] when an electrode is transferred between solutions of different ions or when the concentration of one ion is changed in the presence of another. Slow ion-exchange processes at the electrode–solution interface or effects arising from changes in concentration profiles within the membrane not accounted for by present theory[12,13] may offer an explanation.

Determination of selectivity coefficients

Selectivity coefficients were calculated relative to nitrate ion from the single ion calibration curves obtained from instantaneous and steady-state potential differences defined previously and shown in Fig. 1. For instantaneous readings the electrode was equilibrated in 10^{-2} *M* nitrate solution before each of four measurements in solutions containing from 10^{-4} to 10^{-1} *M* of the second ion. Steady-state readings were obtained either from the steady-state potential differences in the same experiments or by equilibrating the electrode in a 10^{-1} *M* solution of the second ion and then measuring potentials in 10^{-4}–10^{-1} *M* solutions of that ion. Equivalent results were obtained by the two methods of steady-state measurement.

Potential *vs.* log anion activity plots were prepared by means of the expression $\log f_{X^-} = -0.509\ \mu^{\frac{1}{2}}/(1+\mu^{\frac{1}{2}})$, where f_{X^-} is the activity coefficient and μ the ionic strength, to convert concentrations to activities. For all ions, these plots were linear between 10^{-1} *M* and 10^{-3} or 10^{-4} *M* for both instantaneous and steady-state measurements. The slopes of the plots, however, were generally somewhat less than the Nernstian value of −58.6 mV expected at 22°. Representative slopes are presented in Table I.

TABLE I

SLOPES OF POTENTIAL *vs.* LOG ANION ACTIVITY PLOTS FOR INSTANTANEOUS AND STEADY-STATE MEASUREMENTS WITH $Fe(bphen)_3^{2+}$ LIQUID MEMBRANE ELECTRODE[a]

Ion	*Slope (mV)*	
	Instantaneous	*Steady state*
Cl^-	−40.0	−41.7
Br^-	−47.2	−51.7
NO_3^-	−51.3	−54.2
I^-	−55.2	−53.8
BF_4^-	−50.3	−52.8
SCN^-	−57.7	−54.5
ClO_4^-	−59.3	−58.3
PF_6^-	−59.0	−53.8

[a] $1.5 \cdot 10^{-4}$ *M* $Fe(bphen)_3^{2+}$ in nitrobenzene.

Selectivity coefficients were determined by method I of Srinivasan and Rechnitz[17]. In this procedure the potential of the ion-selective electrode in a solution containing ion X^- is compared to the potential of the electrode in a solution containing nitrate at the same activity. It is assumed that the electrode response obeys the equation

$$E = E_0 - 0.0586 \log[a_{NO_3^-} + K_{X^-/NO_3^-}(a_{X^-})] \tag{1}$$

In this work the selectivity coefficient K_{X^-/NO_3^-} was calculated from two potentiometric measurements by means of eqn. (2):

$$\log K_{X^-/NO_3^-} = \frac{E_{NO_3^-}(a_{NO_3^-}) - E_{X^-}(a_{X^-})}{0.0586} \tag{2}$$

at activities $a_{X^-} = a_{NO_3^-}$ corresponding to 10^{-2} *M* concentrations in the two solutions.

Dependence of electrode selectivity on liquid membrane composition

Table II presents instantaneous and steady-state selectivity coefficients for

II

NTANEOUS AND STEADY-STATE SELECTIVITY COEFFICIENTS FOR Fe(bphen)$_3^{2+}$ ELECTRODES
TROBENZENE

s given as log K_{X^-/NO_3^-})

2.9·10⁻⁵ M Fe(bphen)$_3^{2+}$		*1.5·10⁻⁴ M Fe(bphen)$_3^{2+}$*		*1.5·10⁻³ M Fe(bphen)$_3^{2+}$*	
Inst.	*Steady state*	*Inst.*	*Steady state*	*Inst.*	*Steady state*
−1.60±0.02	−1.38	−1.70±0.02	−1.20	−1.60±0.02	−1.57
−0.62±0.06	−0.52	−0.68±0.02	−0.64	−0.72±0.02	−0.68
0.00	0.00	0.00	0.00	0.00	0.00
0.98±0.04	0.73	0.95±0.02	0.94	1.09±0.04	0.41
1.01±0.02	0.90	1.01±0.02	0.65	1.38±0.06	0.41
1.40±0.04	1.26	1.49±0.02	1.28	1.54±0.01	0.76
2.56±0.03	2.00	2.60±0.01	1.55	2.81±0.08	0.87
3.49±0.06	0.89	3.65±0.08	1.96	3.90±0.04	1.04

electrodes containing different concentrations of Fe(bphen)$_3^{2+}$ in nitrobenzene as the liquid membrane. For the instantaneous measurements the sequence of electrode selectivity is $PF_6^- > ClO_4^- > SCN^- > BF_4^- > I^- > NO_3^- > Br^- > Cl^-$. The overall range of selectivity coefficients in this sequence was *ca.* 10^5. Values of K^{inst} in Table II show a slight but detectable increase with increasing concentration of Fe(bphen)$_3^{2+}$ for the more selective ions, but changes in concentration of the ion-exchange material do not affect the selectivity order of the electrode.

With few exceptions the electrode selectivity sequence is the same for steady-state and instantaneous measurements. The most apparent difference between the two sets of measurements is that for ions for which the selectivity is better than for nitrate, values of K^{inst} are much greater than the corresponding values of K^{ss}. For chloride and bromide ions, for which selectivity is lower, K^{inst} is smaller than K^{ss}. These observations are consistent with the time-dependent behavior of the electrode shown in Fig. 1. Owing to long equilibration times for some ions it is difficult to obtain reproducible values of steady-state selectivity coefficients; therefore, primarily instantaneous values are used to characterize electrode selectivity in this work.

Instantaneous selectivity coefficients of electrodes containing Fe(phen)$_3^{2+}$ and tetraheptylammonium (THA$^+$) ion in nitrobenzene are given in Table III. The selectivity sequences and magnitudes of selectivity coefficients for these two electrodes were similar to those observed for the Fe(bphen)$_3^{2+}$ electrode. Values of K^{inst} for the Fe(bphen)$_3^{2+}$ and THA$^+$ electrodes were virtually identical for all ions. Magnitudes of K^{inst} were slightly smaller for the Fe(phen)$_3^{2+}$ electrode, indicating a smaller range of selectivity coefficients for this exchanger. Changes in selectivity order were observed only among iodide, tetrafluoroborate and thiocyanate ions. For these ions the sequence $SCN^- > BF_4^- > I^-$ was observed with the Fe(bphen)$_3^{2+}$ electrode, $SCN^- > I^- > BF_4^-$ with the Fe(phen)$_3^{2+}$ electrode and $BF_4^- > SCN^- > I^-$ with the THA$^+$ electrode. The selectivity coefficients of these three ions differed by no more than a factor of 5 under any conditions.

Instantaneous selectivity coefficients of electrodes containing Fe(bphen)$_3^{2+}$ in chloroform and amyl alcohol are given in Table IV. The selectivity sequence ob-

TABLE III

INSTANTANEOUS SELECTIVITY COEFFICIENTS OF $Fe(phen)_3^{2+}$ AND TETRAHEPTYLAMMONIUM ION ELECTRODES IN NITROBENZENE

(Results given as $\log K_{X^-/NO_3^-}$)

Ion	*$5\cdot 10^{-4}$ M $Fe(phen)_3^{2+}$*	*$1\cdot 10^{-2}$ M THA^+*
Cl^-	−0.48	−1.44 ± 0.11
Br^-	−0.21	−0.62 ± 0.08
NO_3^-	0.00	0.00
I^-	1.18	1.04 ± 0.04
BF_4^-	0.68	1.58 ± 0.09
SCN^-	1.34	1.48 ± 0.06
ClO_4^-	2.28	2.86 ± 0.11
PF_6^-	3.20	4.11 ± 0.11

TABLE IV

INSTANTANEOUS SELECTIVITY COEFFICIENTS OF $Fe(bphen)_3^{2+}$ ELECTRODES IN CHLOROFORM AND AMYL ALCOHOL

(Results given as $\log K_{X^-/NO_3^-}$)

Ion	*$2\cdot 10^{-3}$ M $Fe(bphen)_3^{2+}$ in chloroform*	*$2\cdot 10^{-3}$ M $Fe(bphen)_3^{2+}$ in amyl alcohol*
Cl^-	−1.34 ± 0.06	−0.60
Br^-	−0.18 ± 0.01	−0.21
NO_3^-	0.00	0.00
I^-	1.74 ± 0.03	0.40
BF_4^-	0.90 ± 0.05	−0.07
SCN^-	1.54 ± 0.02	0.72
ClO_4^-	2.08 ± 0.08	0.68
PF_6^-	2.90 ± 0.11	0.82

served in chloroform was $PF_6^- > ClO_4^- > I^- > SCN^- > BF_4^- > NO_3^- > Br^- > Cl^-$, which is similar to sequences observed with nitrobenzene. Relative to values in nitrobenzene, selectivities for hexafluorophosphate and perchlorate were reduced by factors of 10 and 5, respectively, and the selectivity for iodide was enhanced by a factor of 5. In amyl alcohol, selectivities for ions with values above nitrate were all diminished significantly and a very limited range of selectivity coefficients was observed. The selectivity sequence common to the other solvents was modified in amyl alcohol, wherein the sequence observed was $PF_6^- > SCN^- > ClO_4^- > I^- > NO_3^- > BF_4^- > Br^- > Cl^-$.

For electrodes containing $Fe(phen)_3^{2+}$ and THA^+ in nitrobenzene and $Fe(bphen)_3^{2+}$ in nitrobenzene and chloroform, a common sequence of anion selectivity with similar selectivity coefficients was observed: $PF_6^- > ClO_4^- > SCN^- \sim BF_4^- \sim I^- > NO_3^- > Br^- > Cl^-$. A similar sequence was observed for commercial perchlorate and nitrate ion electrodes, for which selectivity coefficients are listed in Table V. The sequence is valid for both Orion electrodes, which are liquid mem-

TABLE V

SELECTIVITY COEFFICIENTS OF COMMERCIAL ANION-SELECTIVE ELECTRODES

(Results given as log K_{X^-/NO_3^-})

Ion	*Perchlorate electrodes*		*Nitrate electrodes*	
	Orion 92-81[a]	*Beckman 39616*[b]	*Orion 92-07*[a]	*Beckman 39618*[b]
Cl^-	−1.82	−0.94	−2.22	−0.82
Br^-	−0.43	−0.40	−1.00	−0.34
NO_3^-	0.00	0.00	0.00	0.00
I^-	0.90	0.86	1.30	0.78
BF_4^-	—	1.52	—	0.96
SCN^-	—	1.60	—	1.26
ClO_4^-	2.87	2.25	3.00	1.65
PF_6^-	—	2.90	—	2.10

[a] Ref. 1, pp. 70–71.
[b] Ref. 19.

brane electrodes of the type used in this work, and Beckman electrodes, which employ an immobilized or "solid" ion-exchange membrane. It therefore appears that for anion-sensitive electrodes based on ion-association extraction systems changes in the ion-exchange material, concentration of the ion exchanger, solvent or manner of membrane construction have little effect on the selectivity of the electrode. The only significant difference is observed when amyl alcohol is used as solvent. In this case, however, the effect is to diminish rather than enhance the range of electrode selectivity.

The theory of liquid membrane electrode behavior[12,13] defines three limiting cases in which electrode selectivity may be related to the ion-partitioning process. In two cases, where the ion-exchange site and the counter ion are highly dissociated in the membrane phase or where the ion-exchange site and counter ion are highly associated but the mobility of the counter ion is much greater than that of the site, the selectivity coefficient is given by the expression:

$$K_{X^-/Y^-} = \frac{\bar{u}_{X^-} k_{X^-}}{\bar{u}_{Y^-} k_{Y^-}} \tag{3}$$

where $\bar{u}_{X^-}$ and $\bar{u}_{Y^-}$ are the mobilities of X^- and Y^- in the membrane phase, and k_{X^-} and k_{Y^-} are the single ion-partition coefficients between water and the solvent of the membrane. The ratio k_{X^-}/k_{Y^-} represents the equilibrium constant for the ion-exchange process

$$X^-(\text{aqueous}) + \overline{Y}^-(\text{membrane}) \xrightleftharpoons{k_{X^-}/k_{Y^-}} \overline{X}^-(\text{membrane}) + Y^-(\text{aqueous}) \tag{4}$$

For a membrane in which there is strong association and the sites are highly mobile relative to the counter ions, the selectivity coefficient is approximated by:

$$K_{X^-/Y^-} = \frac{\bar{u}_{RX}}{\bar{u}_{RY}} \cdot K'_{XY} \tag{5}$$

where $\bar{u}_{RX}$ and $\bar{u}_{RY}$ are the mobilities of the ion-site pairs, and K'_{XY} is the equilibrium constant for the ion-exchange reaction:

$$X^-(\text{aqueous}) + \overline{RY}(\text{membrane}) \rightleftarrows \overline{RX}(\text{membrane}) + Y^-(\text{aqueous}) \tag{6}$$

If $K_{\overline{RX}}$ and $K_{\overline{RY}}$ are the dissociation constants of the ion-site pairs in the membrane, then

$$K'_{XY} = \frac{k_X \cdot K_{\overline{RY}}}{k_Y \cdot K_{\overline{RX}}} \tag{7}$$

The extent of ion association in organic solutions corresponding to the composition of the liquid membranes used in this work is not known. Conductance studies of smaller quaternary ammonium salts in nitrobenzene[20–22] show that ion-pair dissociation constants are *ca.* $4 \cdot 10^{-2}$ and do not differ greatly among the anions studied in this work. The mobilities of the anions are typically 2 to 3 times greater than the mobilities of the quaternary ammonium ions. Ion association constants of Fe-$(\text{phen})_3^{2+}$ and Fe(bphen)_3^{2+} salts in nonaqueous solvents are not known, but it is expected that mobilities of these cations are much less than those of the anions. It therefore seems reasonable to conclude that the selectivity coefficients of both the quaternary ammonium ion and iron–phenanthroline complex electrodes can be approximated by the expression (assuming that $\bar{u}_{X^-} = \bar{u}_{Y^-}$)

$$K_{X^-/Y^-} \cong \frac{k_{X^-}}{k_{Y^-}} \tag{8}$$

Equation (8) predicts that electrode selectivity is independent of the ion-exchange molecule and its concentration in the membrane phase. To a first approximation this is demonstrated by the results of the present study. Equations (4) and (8) predict that electrode selectivity depends primarily on the relative strengths of ion–solvent interactions in the two phases. The change in solvation energy in eqn. (4) can be expressed in terms of the differences in enthalpies of hydration in the aqueous phase and enthalpies of solvation in the membrane phase of ions X^- and Y^-:

$$\Delta H^0_{X^-/Y^-} = (\Delta H^0_{\text{mem},X^-} - \Delta H^0_{\text{mem},Y^-}) - (\Delta H^0_{\text{aq},X^-} - \Delta H^0_{\text{aq},Y^-}) \tag{9}$$

Enthalpies rather than free energies of solvation are chosen because more extensive values of the former quantities are available for the purpose of comparison. In the aprotic solvents nitrobenzene and chloroform, differences in solvation energies of anions are expected to be smaller than in water. Therefore, regardless of the solvent used to form the membrane, electrode selectivity is determined primarily by differences in hydration energies in the aqueous phase. This is shown in Table VI where the enthalpies of hydration and ionic radii of ions studied in this work are presented. There is good correlation between electrode selectivity and ionic size and hydration enthalpy. The ions for which the electrodes have highest selectivity are the large hydrophobic anions having the smallest negative hydration energies. In competition with smaller, more strongly hydrated anions, these anions find themselves preferentially distributed into the membrane phase of the electrode. Similar explanations, based on relative anion hydration energies, have been advanced to explain the solvent extraction behavior of anions[28,29] and the selectivity of anion-exchange resins[30]. It, therefore, appears that unless some means of promoting strong

TABLE VI

HYDRATION ENTHALPIES AND IONIC RADII OF UNIVALENT ANIONS

Ion	$\Delta H^0_{aq,X^-}$ *(kcal mole^{-1})*	*Reference*	*Radius (Å)*	*Reference*
Cl^-	−87.6	23	1.81	25
Br^-	−79.8	23	1.95	25
NO_3^-	−74.5	24	1.96	26
I^-	−69.7	23	2.16	25
BF_4^-	−71.2	23	2.26	23
SCN^-	—		—	
ClO_4^-	−57.1	23	2.45	23
PF_6^-	—		3.00	27

selective interactions in the membrane phase can be found, the selectivity of liquid membrane electrodes for common inorganic anions cannot be greatly altered from the order predicted by hydration energies. Possible evidence of stronger interactions in the membrane phase exists in the case of the $Fe(bphen)_3^{2+}$–amyl alcohol electrode, but the result is to decrease the range of electrode selectivity. Because amyl alcohol is an hydroxylic solvent, it is expected to solvate anions to a degree more nearly equal that of water. As a result, differences in solvation energies between the aqueous and membrane phases are minimized and more nearly equal selectivity coefficients are observed.

The factors influencing electrode selectivity appear to be the same as those governing solvent extraction processes[14]. Unfortunately there are few data on which quantitative comparisons of selectivity and extraction behavior can be made. One instance in which a quantitative comparison can be made is illustrated in Fig. 2. The instantaneous selectivity coefficients of a $Fe(phen)_3^{2+}$–nitrobenzene electrode are

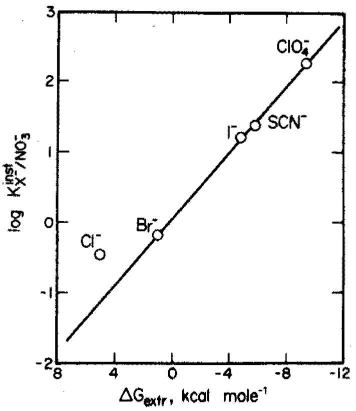

Fig. 2. Plot of log $K^{inst}_{X^-/NO_3^-}$ *vs.* free energy of extraction of $Fe(phen)_3^{2+}$ salts into nitrobenzene according to equilibrium 2 of ref. 31. Electrode: $5 \cdot 10^{-4}$ *M* $Fe(phen)_3^{2+}$ in nitrobenzene.

compared to the free energies of extraction of the corresponding $Fe(phen)_3^{2+}$ salts into nitrobenzene[31]. Good correlation is obtained for the five ions studied. Other solvent extraction studies show an order of anion extractability qualitatively similar or identical to the order of selectivity found in this work. Such similar sequences are found in systems employing quaternary ammonium ions in toluene and dichloromethane[32,33], triphenyltetrazolium salts in chloroform[34] and quaternary phosphonium, arsonium and stibonium salts in chloroform, dichloromethane, 1,2-dichloroethane and 2,2′-dichlorodiethyl ether[29].

SUMMARY

Selectivity coefficients of liquid-membrane electrodes for common inorganic anions were measured in electrodes containing tris(1,10-phenanthroline)iron(II), tris(4,7-diphenyl-1,10-phenanthroline)iron(II) or tetraheptylammonium ion in nitrobenzene, and tris(4,7-diphenyl-1,10-phenanthroline)iron(II) ion in nitrobenzene, chloroform or *n*-amyl alcohol as the liquid membrane. With the exception of the amyl alcohol electrode, selectivity coefficients were relatively independent of membrane composition and followed a common sequence of decreasing selectivity: $PF_6^- > ClO_4^- > SCN^- \sim I^- \sim BF_4^- > NO_3^- > Br^- > Cl^-$. This sequence parallels the order of increasing anion hydration energy, suggesting that aqueous phase solvation energies play a predominant role in determining electrode selectivity for these ions. Time-dependent behavior of liquid-membrane electrodes on transfer between solutions containing different ions also is described. Instantaneous e.m.f. readings were used to determine selectivity coefficients.

RÉSUMÉ

Des mesures de coefficients de sélectivité d'électrodes à membrane liquide ont été effectuées pour des anions inorganiques courants, à l'aide d'électrodes contenant: tris-(1,10-phénanthroline)fer(II), tris-(4,7-diphényl-1,10-phénanthroline)fer(II) ou ion tétraheptylammonium, dans le nitrobenzène, et tris-(4,7-diphényl-1,10-phénanthroline)fer(II), dans le nitrobenzène, le chloroforme, ou l'alcool n-amylique comme membrane liquide. A l'exception de l'électrode à alcool amylique, les coefficients de sélectivité présentent des valeurs décroissantes, dans l'ordre: $PF_6^- > ClO_4^- > SCN^- \sim I^- \sim BF_4^- > NO_3^- > Br^- > Cl^-$, laissant supposer que les énergies de solvatation jouent ici un rôle prédominant. On examine également l'influence du temps. La détermination des coefficients de sélectivité a été faite avec lecture f.e.m. instantanée.

ZUSAMMENFASSUNG

Selektivitätskoeffizienten von Flüssig-Membran-Elektroden für die üblichen anorganischen Anionen wurden mit Elektroden gemessen, die Tris-(1,10-phenanthrolin)eisen(II)-, Tris-(4,7-diphenyl-1,10-phenanthrolin)eisen(II)- und Tetraheptylammonium-Ion in Nitrobenzol und Tris-(4,7-diphenyl-1,10-phenanthrolin)eisen-(II)-Ion in Nitrobenzol, Chloroform oder *n*-Amylalkohol als Flüssig-Membran enthielten. Mit Ausnahme der Amylalkohol-Elektrode waren die Selektivitätskoeffizien-

ten relativ unabhängig von der Membranzusammensetzung und folgten einer normalen Reihenfolge kleiner werdender Selektivität: $PF_6^- > ClO_4^- > SCN^- \sim J^- \sim BF_4^- > NO_3^- > Br^- > Cl^-$. Diese Reihenfolge entspricht der Reihenfolge zunehmender Anionen-Hydratationsenergie und weist darauf hin, dass die Solvatationsenergien in der wässrigen Phase eine dominierende Rolle spielen bei der Bestimmung der Elektrodenselektivität für diese Ionen. Das Zeitverhalten der Flüssig-Membran-Elektroden beim Übergang zwischen Lösungen, die verschiedene Ionen enthalten, wird ebenfalls beschrieben. Die e.m.k.-Werte wurden momentan aufgezeichnet, um die Selektivitätskoeffizienten zu bestimmen.

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DOSAGE POTENTIOMÉTRIQUE DU COBALT APRÈS SÉPARATION SUR RÉSINES ÉCHANGEUSES D'IONS

APPLICATIONS À L'ANALYSE DES ACIERS ET ALLIAGES

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Dans un article récent, Boulin *et al.*[1] ont montré qu'il est possible d'étendre le domaine d'application de la méthode de dosage spectrophotométrique du cobalt aux faibles teneurs en cet élément dans les aciers. Après avoir comparé les propriétés des principaux réactifs, ils ont adopté l'isonitrosomalonylguanidine ou NMG, qui, par son coefficient d'extinction spécifique élevé, permet de déterminer des teneurs inférieures à 0.02%. Une telle application intéresse les aciers pour réacteurs nucléaires qui ne doivent pratiquement pas contenir de cobalt. La mesure spectrophotométrique est utilisable pour des concentrations comprises entre 0.01 et 5%. Au-delà, il est nécessaire d'opérer des dilutions préjudiciables à la précision du dosage. S'agissant de nombreux produits industriels à fortes teneurs en cobalt (Stellite, Maraging, etc.), une méthode de mesure électrochimique semble appropriée, telle que la méthode potentiométrique; elle peut s'appliquer sans dilution et éventuellement en présence de nickel.

Les méthodes électrochimiques de dosage du cobalt font, en général, appel aux propriétés oxydo-réductrices de ses complexes hexacoordonnés (cobaltiamines), avec l'ammoniaque, l'hydrazine, l'hydroxylamine ou les amines organiques. Ces complexes sont nombreux, Duval[2] en cite un nombre voisin de 2300; de plus, ils sont facilement réductibles et on suit aisément la réaction d'oxydation ou de réduction par potentiométrie:

	E_0 (E.C.S.)	
$Co(OH)_2 + 2e^- \rightleftarrows Co + 2\,OH^-$	-0.73 V	(1)
$[Co(NH_3)_6]^{2-} + 2e^- \rightleftarrows Co + 6\,NH_3$	-0.42 V	(2)
$Co^{3+} + e^- \leftrightarrows Co^{2+}$	$+1.84$ V	(3)
$Co(OH)_3 + e^- \leftrightarrows Co(OH)_2 + OH^-$	$+0.17$ V	(4)
$[Co(CN)_6]^{3-} + e^- \rightleftarrows [Co(CN)_6]^{4-}$	-0.83 V	(5)
$[Co(NH_3)_6]^{3+} + e^- \rightleftarrows [Co(NH_3)_6]^{2+}$	$+0.10$ V	(6)

La polarographie utilisée pour le dosage des traces de cobalt fait appel à ces diverses réactions. Par exemple, en milieu tartrique, le cobalt (III) est réductible à -1.40 V et à -1.36 V (E.C.S.) dans un électrolyte alcalin (normal en hydroxyde et en chlorure d'ammonium).

La mesure potentiométrique selon la réaction (6) est utilisée d'abord par Tomicek et Freiberger[3], Dickens et Maassen[4], puis précisée par Lingane[5]. Lingane utilise comme agent d'oxydation l'hexacyanoferrate(III) de potassium, en milieu fortement ammoniacal suivant la réaction:

$$Co(NH_3)_6^{2+} + Fe(CN)_6^{3-} \rightleftarrows Co(NH_3)_6^{3+} + Fe(CN)_6^{4-}$$

et dose ainsi des quantités de cobalt comprises entre 18 et 200 mg avec une erreur relative inférieure à 1%. Des variantes font intervenir certaines amines telles que la diéthylènediamine, la triéthylènetetramine, la triméthylènediamine et la propylènetetramine[6]. Ainsi, Diehl et Butler[7] utilisent l'éthylènediamine; le milieu résultant présente les inconvénients d'une oxydation spontanée des complexes du cobalt par l'air, et de difficultés pour complexer les ions ferriques.

C'est donc à partir des résultats de Lingane que la présente méthode, applicable aux aciers alliés contenant environ 5% de cobalt, et au-delà, a été étudiée.

CONDITIONS DE MESURE

Le montage comporte une électrode de référence (électrode au calomel saturée), une électrode indicatrice (Pt) et un millivoltmètre à haute impédance d'entrée (environ 10^{12} Ω). Différents appareils automatiques comportent une burette automatique dont le débit est asservi à la pente de la courbe de titrage par l'intermédiaire d'un dispositif électronique, un millivoltmètre et un enregistreur permettant d'obtenir la courbe directe et en général la courbe dérivée.

On a vérifié la stoechiométrie de la réaction à l'aide d'une solution étalon de cobalt préparée à partir de cobalt métallique pur (99.999 de Johnson Matthey).

La solution titrante d'hexacyanoferrate(III) est fraîchement préparée et le titre confirmé par un dosage au moyen de la solution titrée de thiosulfate de sodium, elle-même vérifiée par titrage par la solution titrée d'iodate de potassium. Nous avons montré que les volumes de solution titrée de $Fe(CN)_6K_3$ théoriquement requis pour le titrage des ions cobalt(II) (à 30 et 3 mg) correspondent à ceux que l'on a préalablement introduits (écart 1%).

La Fig. 1 montre qu'à pH voisin de 9.5, en milieu citrique, le cobalt(II) est bien oxydé quantitativement en cobalt(III), comme l'avait constaté Lingane[5] en milieu NH_4Cl (1 *M*) et NH_4OH (3 *M*). Pour éviter certains inconvénients, dus à l'instabilité des réactifs, à l'influence de l'oxygène de l'air, on a choisi d'opérer par titrage en retour.

En vue d'établir l'influence du pH, peu précisée par les données dans la littérature[8], nous avons ajouté en milieu citrique sensiblement *M*, des quantités d'ammoniaque telles que l'on obtienne avant le titrage les pH: 8.9—9.5—10—10.5. Il ressort du Tableau I qu'un pH situé entre 9.5 et 10.5 est à recommander; on l'a fixé à 9.7, assurant ainsi une complexation totale du fer, une réaction quantitative, et une variation importante de potentiel (environ 250 mV). De plus, l'influence de l'oxygène de l'air est peu marquée si le titrage est effectué en retour et ceci pour des concentrations en cobalt et en hexacyanoferrate(III) de potassium comprises entre $5 \cdot 10^{-3}$ et 10^{-1} *M*.

Il semblerait, d'après Diehl et Butler[7], que l'influence du pH soit plus ou moins marquée suivant que l'on emploie l'ammoniaque ou une amine pour com-

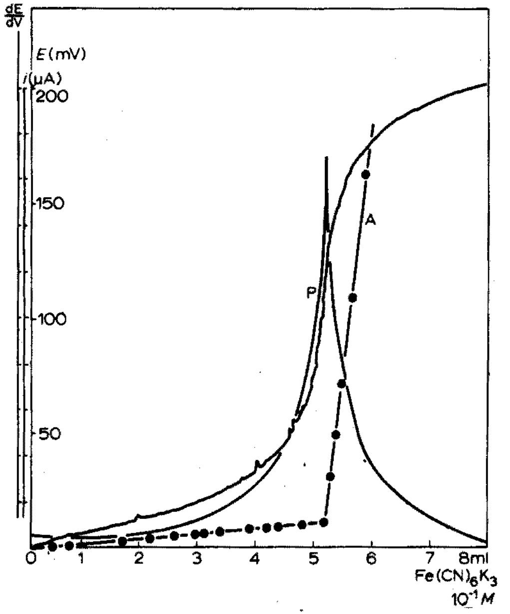


Fig. 1. Etalonnage 5 ml Co 10^{-1} N. (A) Ampérométrie; (B) potentiométrie.

plexer le cobalt; on peut formuler une réserve à ce sujet car en présence d'une quantité notable d'amine, le pH est mesuré dans un milieu non totalement aqueux.

Influence des éléments

Le fer peut être complexé au pH optimal de 9.7 par les milieux pyrophosphoriques, salicyliques, oxaliques et citriques. Les derniers ont été retenus en raison de leur constante de stabilité élevée et de leur pouvoir tampon favorable. Le fer(III) ne peut perturber le dosage que si la quantité de citrate est insuffisante, car il précipite avant la formation du complexe sous forme d'hydrate ferrique dès que le pH est voisin de 3. Les essais montrent, dans les conditions opératoires choisies, qu'une masse de fer inférieure à 1 g est acceptable; au-delà, il est très difficile de maintenir les ions ferriques en solution (Tableau II). Le choix de l'acide pyrophosphorique aurait peut-être permis de tolérer des quantités de fer plus importantes; les essais n'ont pas été concluants.

Le manganèse est oxydé quantitativement par l'hexacyanoferrate(III) en milieu citrique ammoniacal au stade d'oxydation trivalent[4,9] suivant une réaction analogue à celle du cobalt. Les potentiels normaux apparents des deux réactions d'oxydation étant très voisins (0.10 V), la mesure conduit à la somme $Co+Mn$ (Tableau III). Il a été proposé d'éliminer l'influence du manganèse par précipitation à l'aide du chlorate de sodium selon Hampe *et al.*[10], ou par précipitation au persulfate en solution sulfurique selon Knorre[11]. Il est plus facile de le séparer en même temps que d'autres éléments gênants comme on le verra ultérieurement.

Le nickel n'existe pratiquement qu'à la valence II sauf dans des conditions très particulières[12]; en solution ammoniacale, il n'est pas oxydé par l'hexacyanoferrate(III)[13]. L'intérêt du titrage potentiométrique réside dans le fait qu'il est pos-

TABLEAU I

L'INFLUENCE DU pH

ΔE (mV)	*pH*	*Observations*
Le potentiel augmente d'une façon continue	8	Pas de point d'inflexion. Réaction non quantitative. Difficultés de formation des complexes.
Environ 100	9	Réaction incomplète.
Environ 200	9.5	Réaction stoechiométrique.
Environ 250	9.7	Réaction stoechiométrique. Fe^{3+} est complexé.
Environ 250	10	Réaction stoechiométrique.
Environ 250	10.5	Oxydation de $Co(NH_3)_6^{2+}$ par l'air.

TABLEAU II

INFLUENCE DE FER(III)

(Conditions de mesure: pH 9.7. Citrate d'ammonium (25 ml sol. à 250 g l^{-1})+NH_4OH. Volume final ~150 ml)

mg Co introduit	*mg Fe[a] introduit*	*mg Co trouvé*
3.00	1920	↓ hydroxyde ferrique
3.00	960	début ↓ hydroxyde ferrique
6.01	960	6.02
6.01	960	6.03
12.02	960	12.34
30.06	960	29.84
30.06	960	30.42

[a] Fer pur attaqué par le mélange $HCl+HNO_3$.

TABLEAU III

INFLUENCE DU MANGANÈSE(II)

mg Co initial	*mg Mn initial*	*mg (Σ Co+Mn) trouvé*	*Ecart (mg)*
30.06	54.93	86.10	+1.11
30.06	54.93	86.35	+1.36
60.12	54.93	116.10	+1.05
60.12	54.93	110.55	−4.50
Néant	54.93	58.40	+3.47
Néant	54.93	56.10	+1.17

sible de doser le cobalt en présence de nickel quel que soit le rapport Ni/Co (alliages simples Co–Ni par exemple) (Fig. 2).

De même, le cuivre, l'aluminium, le titane qui ne possèdent qu'une valence

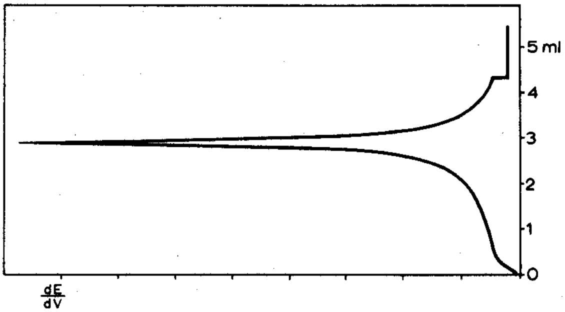


Fig. 2. Alliage nickel–cobalt, Co% = 81.80. Titrage en retour, $Fe(CN)_6K_3 = 0.103$ *N*; Co = 0.100 *N*; prise d'essai et dilution = 2 g→200 ml→5 ml; point equivalent = 2.88 ml; pH = 9.7.

stable, dans le milieu choisi, ne modifient pas la position du point équivalent. Le chrome trivalent n'est pas oxydé par l'hexacyanoferrate à froid mais il y a bien oxydation de Co^{2+} en Co^{3+} en présence de Cr^{6+}. Le tungstène, en milieu phosphorique, ne perturbe pas le titrage. Le vanadium pentavalent peut être réduit par le citrate d'ammonium en milieu acide. Si la neutralisation a lieu avant l'addition de citrate, la présence de cet élément ne modifie pas la position du point d'inflexion.

En résumé, dans les conditions opératoires choisies, les ions gênants sont ceux pour lesquels on observe un changement de valence, à un potentiel voisin de celui du système:

$$[Co(NH_3)_6]^{2+} \rightarrow [Co(NH_3)_6]^{3+} + e^-$$

Ce sont manganèse(II) et chrome(VI).

Les ions Ni^{2+}, Cu^{2+}, Al^{3+}, Ti^{4+}, Mo^{5+}, Fe^{3+} ne modifient pas la position du point d'inflexion. Pour Ti^{4+} et Mo^{5+} comme pour Fe^{3+}, la concentration doit être telle qu'elle n'entraîne aucune précipitation dans les conditions de l'essai.

SÉPARATION DU COBALT PAR ÉCHANGE D'IONS

L'emploi des échangeurs d'ions a paru mieux adapté à la séparation des masses relativement importantes de cobalt requises par le dosage, que l'extraction, laquelle convient plus particulièrement à la séparation des traces.

La séparation du cobalt par échange d'ions est facile à mettre en oeuvre et a donné des résultats satisfaisants. Elle permet d'isoler le cobalt non seulement du fer, du manganèse, du chrome, du vanadium, du molybdène, du tungstène et du titane mais aussi de nombreux autres éléments (Zr, Sn, Nb, Ta, etc.) et peut ainsi être adaptée à différents cas particuliers.

La plupart des modes opératoires décrits dans la littérature concernent la séparation du cobalt en présence de fer, de cuivre, de nickel et de manganèse. Les auteurs, dans leur majorité, utilisent des séparations sur résines anioniques, soit en milieu acide chlorhydrique concentré, dérivées de la méthode décrite par Kraus et Nelson[14], soit en milieu acide minéral–solvant organique tels acide chlorhydrique–éthanol, acide chlorhydrique–méthanol, acide chlorhydrique–acétone, etc. Les séparations sur résines cationiques sont moins nombreuses. Elles sont généralement effectuées en milieu chlorhydrique, nitrique ou sulfurique[15,16] ou bien dans des mélanges d'acide chlorhydrique et d'acétone [17,18] ou d'acide chlorhydrique et d'éthanol[19].

Dans le cas présent, ces séparations conviennent mal car, d'une part elles exigent des colonnes d'assez grandes dimensions, et d'autre part le fer est fixé sur la résine dans les conditions convenant également à la rétention du cobalt; or il est du plus grand intérêt de choisir des conditions de séparation telles que le fer, principal constituant des aciers, soit directement entraîné dans l'effluent. On peut alors opérer sur des prises d'essai suffisamment importantes pour ensuite doser le cobalt dans de bonnes conditions, tout en conservant les avantages que présente l'utilisation des colonnes de petites dimensions (faibles volumes de solution d'où gain de temps et dilution réduite des échantillons).

Le milieu fluorhydrique satisfait à ces conditions; il a été très étudié pour les séparations sur résines anioniques[20,21] mais beaucoup moins avec les résines cationiques. Le travail de Fritz *et al.*[22] ne donne aucun coefficient de partage mais les conditions d'élution indiquées permettent de prévoir les séparations possibles; en particulier, en milieu fluorhydrique 0.1 M et 1 M le cobalt, le nickel et le chrome sont retenus dans une résine du type Dowex 50W-X8.

Afin de déterminer les conditions de séparation, l'on a tracé les courbes de coefficient de partage d'un certain nombre d'éléments dans l'acide fluorhydrique, à différentes concentrations, puis procédé à des essais de séparation dans des colonnes, d'abord sur des solutions synthétiques, enfin sur des solutions obtenues à partir d'aciers.

Les solutions employées ont été préparées par dissolution de métaux purs dans un mélange d'acides fluorhydrique, nitrique et chlorhydrique, évaporation à sec et reprise par l'acide fluorhydrique. On utilise la résine cationique BioRad AG 50W-X8, 100–200 mesh, forme H^+, et la résine anionique BioRad AG 1 X8, 100–200 mesh, forme Cl^-. Les colonnes sont constituées d'un tube de polyéthylène de 10 mm de diamètre intérieur et de 100 mm de longueur. Un réservoir de 30 ml environ, également en polyéthylène est fixé à la partie supérieure de la colonne. Un tube plus fin (diamètre intérieur 0.5 à 1 mm) est emboîté à la partie inférieure. Le débit qui dépend de la hauteur du lit de résine et de la nature des solutions est en moyenne de l'ordre de 1 ml min^{-1}. Il peut être facilement ajusté par l'emploi d'une pompe péristaltique. Le fond des colonnes est garni d'un tampon de chlorofibre Rhovyl. Un autre tampon placé sur le lit de résine évite le mélange des couches d'échangeur à l'introduction des solutions.

Pour la détermination des coefficients de partage, nous avons utilisé la méthode statique qui consiste à mettre une masse connue de résine sèche (1 g) au contact d'une solution (50 ml) contenant une quantité déterminée (5 mg) de l'élément étudié. Lorsque l'équilibre est atteint, on dose le soluté dans la phase aqueuse. La concentration dans la résine est calculée par différence. Connaissant ces valeurs, on calcule le coefficient de partage P:

$$P = \frac{\text{masse d'élément dans la résine}}{\text{masse d'élément dans la solution}} \times \frac{\text{volume de solution}}{\text{masse de résine sèche}}$$

On a étudié le comportement des éléments suivants: cobalt, fer, nickel, manganèse, vanadium(IV), vanadium(V), titane, molybdène, tungstène et chrome. Les

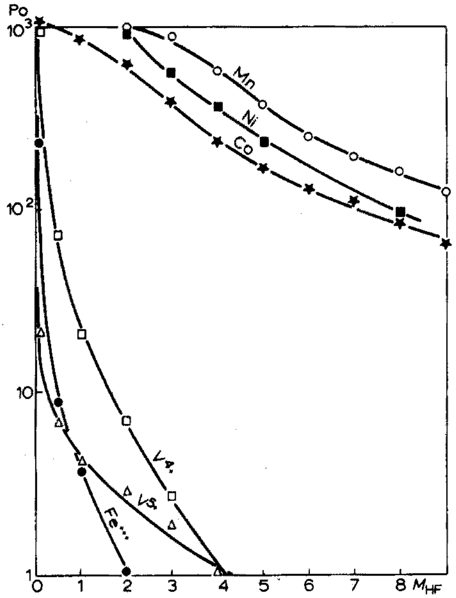


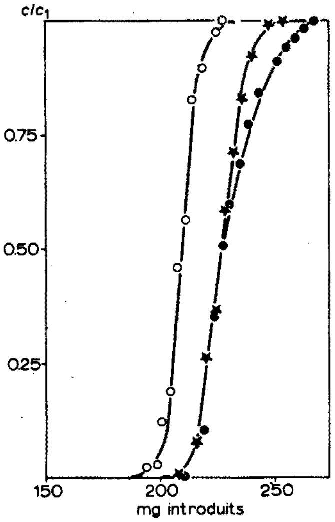
Fig. 3. Coefficients de partage en milieu HF, resine AG 50W-X8.

valeurs obtenues des coefficients de partage (résine cationique AG 50W-X8) sont reportées sur les courbes de la Fig. 3 (les concentrations de l'acide fluorhydrique sont portées en abscisses et les coefficients de partage en ordonnées).

Il en résulte que les coefficients de partage du cobalt, du manganèse et du nickel diminuent lentement lorsque la concentration de l'acide fluorhydrique augmente et restent grands dans tout le domaine étudié; mais ils sont voisins, ce qui rend difficile la séparation de ces éléments en milieu fluorhydrique; et également que les affinités du vanadium(IV), du vanadium(V) et du fer diminuent très rapidement lorsque la concentration en acide fluorhydrique augmente. Les coefficients de partage du molybdène, du tungstène et du titane sont inférieurs à 10, quelle que soit la concentration de l'acide. En milieu acide fluorhydrique environ 2 *M*, la séparation en deux groupes ne présente donc pas de difficultés. Le cobalt, le manganèse et le nickel sont fixés dans la résine et séparés ainsi des autres éléments; le cobalt devra toutefois être séparé du manganèse et du nickel selon les conditions différentes.

La séparation sur résine cationique a été étudiée avec des colonnes contenant 4 ml de résine cationique en milieu acide fluorhydrique 2 *M*. Comme le laissent prévoir les courbes de coefficients de partage, le cobalt, le nickel et le manganèse sont retenus quantitativement dans la résine. Les courbes de saturation d'une colonne de 4 ml indiquent (Fig. 4) que ce volume d'échangeur permettant de fixer 150–200 mg de ces éléments est suffisant dans la majorité des cas. A noter que ces résultats sont en désaccord, en ce qui concerne le manganèse, avec ceux de Fritz *et al.*[22] qui indiquent, en effet, que le manganèse n'est pas fixé en milieu fluorhydrique 1 *M*.

Le comportement du fer a été étudié à l'aide de prises d'essai de 1 g. La Fig. 5 montre qu'il est rapidement élué et qu'il est éliminé dans sa quasi totalité par



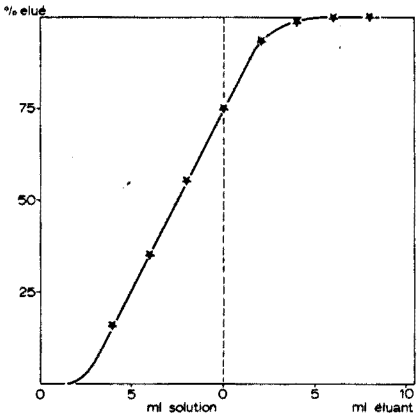
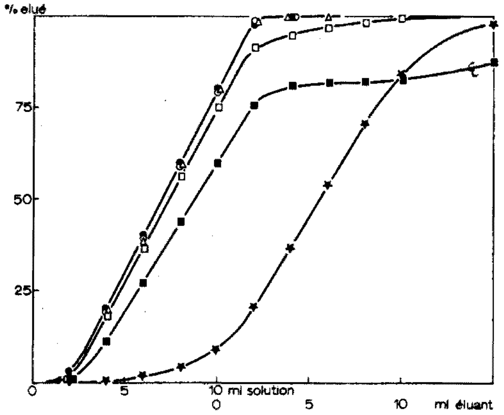


Fig. 4. Courbes de saturation en milieu HF 2 *M*. Resine AG 50W-X8 colonne de 4 ml; solutions influentes 4 mg ml^{-1}; (c_1) concentration dans l'influent, (c) concentration dans l'effluent. (○) Mn; (●) Ni; (★) Co.

Fig. 5. Elution de lg fer par HF 2 *M*. Resine AG 50W-X8 colonne de 4 ml.



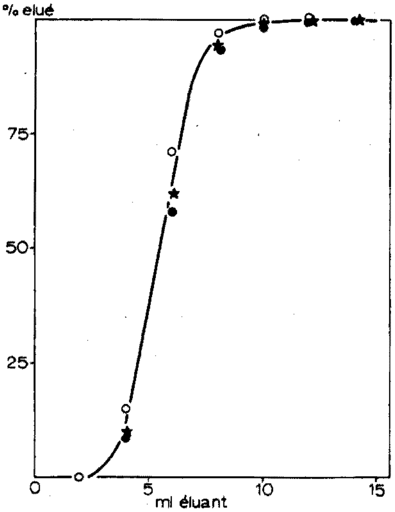


Fig. 6. Elution par HF 2 *M*. Resine AG 50W-X8 colonne de 4 ml. (★) V^{4+}; (□) V^{5+}; (●) Ti; (○) Mo; (△) W; (■) Cr^{3+}.

Fig. 7. Elution par HCl 3 *M*. Resine AG 50W-X8 colonne de 4 ml. (○) Mn, 10 mg; (●) Ni, 10 mg; (★) Co, 10 mg.

lavage de la colonne avec 10 ml d'acide fluorhydrique. L'élution directe du fer permet donc d'utiliser des prises d'essai égales ou supérieures à 1 g, tout en conservant un volume réduit à la colonne.

Les éléments vanadium, titane, molybdène et tungstène ayant en milieu fluorhydrique 2 M des coefficients de partage très petits, leur élution est rapide et complète lorsque la résine a été lavée avec 10–15 ml d'acide (Fig. 6). Cette Figure montre aussi que le vanadium(V) est plus rapidement élué que le vanadium(IV). Le comportement du chrome est moins net que celui des autres éléments. Tout se passe, en effet, comme si le chrome existait en solution sous différentes formes. La plus grande partie est éluée lors du passage des solutions en milieu fluorhydrique (Fig. 6) mais dans tous les cas, une certaine fraction reste retenue dans la résine et n'est éluée qu'en même temps que le cobalt, le nickel et le manganèse.

Nous avons essayé d'éluer sélectivement le cobalt en appliquant la méthode proposée par Fritz et Rettig^{17} mais la taille des colonnes rendant son emploi délicat, l'on a préféré éluer simultanément le cobalt, le manganèse et le nickel et les séparer ensuite sur résine anionique.

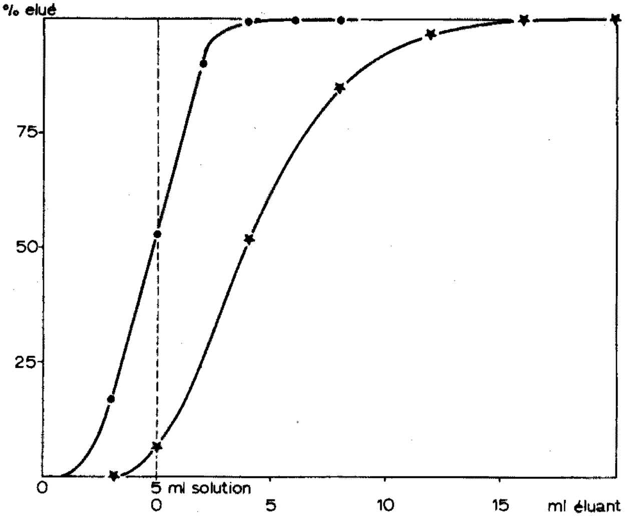


Fig. 8. Elution par HCl 10 M. Résine AG1-X8 colonne de 4 ml. (★) Mn, 10 mg; (●) Ni, 10 mg.

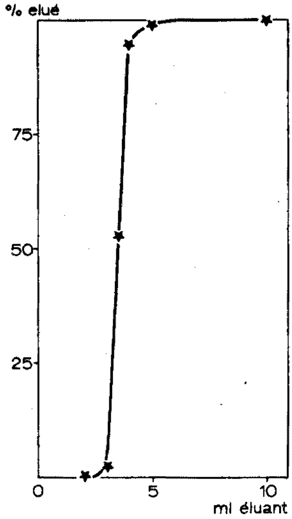


Fig. 9. Elution de 10 mg de cobalt par HCl 1 M. Résine AG1-X8 colonne de 4 ml.

Les coefficients de partage donnés par Strelow^{15} montrent que l'élution est rapide en milieu acide chlorhydrique 3 M. Celle-ci est effectivement complète lorsque la colonne a été lavée avec 15 ml d'éluant (Fig. 7).

La séparation sur résine anionique permet d'isoler le cobalt du nickel et du manganèse; elle est effectuée en milieu chlorhydrique 10 M. Cette séparation est bien connue et couramment utilisée^{14}. Le cobalt est retenu sous forme de complexes chlorures. Le nickel, le manganèse (et le chrome) sont quantitativement élués après lavage de la colonne avec 20 ml d'acide (Fig. 8). Le cobalt est ensuite élué au moyen d'acide chlorhydrique dilué (Fig. 9).

L'ensemble des séparations sur résine cationique et anionique peut être schématisé selon la Fig. 10.

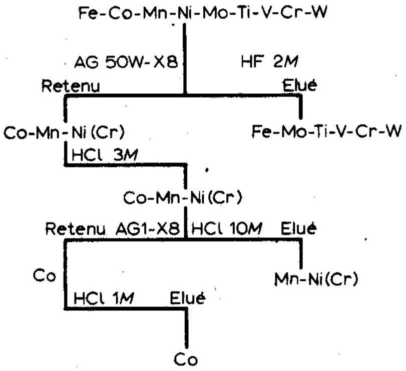


Fig. 10. L'ensemble des séparations.

RÉSULTATS

Nous avons soumis aux calculs statistiques les résultats obtenus par application de cette technique à des séries de 10 dosages sur 4 alliages. Les résultats obtenus figurent dans le Tableau IV.

TABLEAU IV

APPLICATION À DES ALLIAGES

(10 dosages sur chaque alliage)

Échantillon	*Valeurs trouvées en Co (%)*		*Écart type* s	*Écart type de la moyenne* s_m	*Erreur relative*[a,b]
	Moyenne, $\bar{X}$	*Médiane*			
Alliage 10.122.3T[c]	4.80_7	4.82	0.073_5	0.023_2	1.075
Échantillon-type 209.1[d]	4.850	4.86	0.058_5	0.018_5	0.85
Acier maraging 10015[e]	10.22[f]	10.23	0.20_5	0.065	1.42
Alliage Co–Ni (80:20)	81.95[f]	81.95	0.39_7	0.125	0.33_9

[a] Erreur relative sur la moyenne(%): $(s_m \cdot t)/\bar{X} \cdot 100$.

[b] $t = 2.228$ pour 10 déterminations au niveau 95%.

[c] Composition(%): C 0.014; Mn 6.15; Ni 6.35; Cr 18.60; Co $\sim$5.

[d] Composition(%): C 0.80_0; Si 0.25_6; Mn 0.23_4; S 0.007_5; P 0.027; Cr 4.16; W 18.72; V 1.83; Mo 1.13; Co 4.95.

[e] Composition(%): C 0.007; Si 0.020; P 0.003; S 0.005; Mn 0.020; Ni 18.40; Cr 0.024; Mo 4.85; Ti 0.70; Co $\sim$1

[f] Sans séparation sur résines.

APPLICATION À L'ANALYSE DES ACIERS ET DES ALLIAGES

Appareillage

Colonnes en polyéthylène contenant respectivement 4 ml de résine anionique AG 1 X8 et 4 ml de résine cationique AG 50W-X8. Tampons en ouate de chlorofibre Rhovyl.

Dispositif de mesure. Burette au 10^{-2} ml, millivoltmètre à haute impédance d'entrée (*ca.* $10^{12}\cdot\Omega$), électrode de référence (E.C.S.), électrode indicatrice (platine), ou système de titrage automatique avec enregistreur.

Mode opératoire

Mise en solution. Introduire la prise d'essai (0.2–1 g contenant au maximum, dans le cas d'une séparation, 25 mg de cobalt) dans un bécher en "Téflon" de 250 ml. Ajouter 5 ml d'acide fluorhydrique ($d = 1.13$), 5 ml d'acide nitrique ($d = 1.4$) et éventuellement 5 ml d'acide chlorhydrique ($d = 1.19$). Chauffer jusqu'à dissolution complète. Évaporer à sec. Reprendre le résidu par 10–20 ml d'acide fluorhydrique (2 *M*) et chauffer au voisinage de l'ébullition jusqu'à dissolution complète des sels. Ramener à la température ambiante.

Séparation du cobalt. Introduire la solution dans la colonne de résine cationique préalablement traitée avec 10 ml d'acide fluorhydrique 2 *M**. Après écoulement complet, rincer le bécher et la colonne avec 4 fractions de 5 ml du même acide puis laver la colonne avec 10 ml d'eau distillée. Rejeter l'effluent. Éluer le cobalt, le manganèse, le nickel et les traces de chrome fixés dans la résine au moyen de deux fractions de 10 ml d'acide chlorhydrique 3 *M*. Evaporer l'éluat à sec et reprendre le résidu par 5 ml d'acide chlorhydrique 10 *M*. Tiédir pour redissoudre les sels et ramener à la température ambiante. Introduire la solution dans la colonne de résine anionique préalablement lavée avec 10 ml d'acide chlorhydrique 10 *M*. Après écoulement complet, rincer le bécher et la colonne avec 4 fractions de 5 ml du même acide.

Éluer le cobalt fixé dans la résine par 3 fractions de 5 ml d'acide chlorhydrique 1 *M*. Évaporer pour chasser la majeure partie de l'acide. Reprendre par 50 ml d'eau.

Dosage. Ajouter à la solution 25 ml de citrate d'ammonium (250 g l^{-1}), amener à pH 9.7 avec l'ammoniaque au demi ($d = 0.9$) ajoutée par petites fractions afin d'éviter l'échauffement de la solution. Ajouter un volume connu de solution titrée d'hexacyanoferrate(III) potassium 0.01 *N* ou 0.1 *N* en excès et titrer en retour au moyen de la solution de sulfate de cobalt 0.01 *M* ou 0.1 *M*. L'agitation doit être maintenue pendant toute la durée de l'opération.

La résine cationique est régénérée par passage dans la colonne de 10 ml d'eau puis de 10 ml d'acide fluorhydrique 2 *M*. La résine anionique est régénérée par passage dans la colonne de 10 ml d'acide chlorhydrique 10 *M*.

L'électrode de platine est nettoyée par lavage dans l'acide chlorhydrique concentré et chaud, suivi d'une calcination dans la flamme d'un bec Mecker.

CONCLUSIONS

La présence de plus en plus fréquente de fortes teneurs de cobalt dans les aciers alliés (Maraging) nous a amenés à en étudier le dosage à forte concentration. Après avoir rappelé le principe de quelques méthodes (spectrophotométrie, polarographie), nous avons signalé les avantages et les inconvénients présentés par chacune d'elles.

Nous proposons une adaptation de la méthode potentiométrique à courant

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* Acide fluorhydrique ($d = 1.13$) = 90 ml et eau en quantité suffisante pour 1 litre.

nul décrite par Lingane. L'étude de différents facteurs: pH, composition du milieu, nous a permis de préciser les conditions optimales de mesure; le dosage en retour évite l'oxydation anticipée de Co^{2+} en Co^{3+} et n'implique plus l'emploi d'un dispositif permettant d'opérer sous gaz inerte. Le montage utilisé est très simple, la mesure peut être accélérée, si cela est nécessaire, par l'emploi d'un dispositif de titrage automatique.

L'influence de quelques éléments a été étudiée, le plus gênant est le manganèse qui doit être éliminé obligatoirement avant la mesure tandis que le chrome doit être ramené à la valence III. Le fer, le titane et le molybdène n'interfèrent que si leur concentration dans la solution entraîne leur précipitation. Le nickel est sans influence et le cobalt peut être dosé en sa présence à toute concentration.

Nous préconisons l'emploi de résines pour isoler le cobalt. L'échange d'ions permet en effet de le séparer non seulement du manganèse mais aussi de nombreux autres éléments; il rend ainsi la méthode de dosage applicable à des matrices très diverses, évite l'addition d'agents complexants supplémentaires (ions pyrophosphoriques, amines) et ramène la mesure au cas le plus simple. Étant très générale, la séparation proposée peut être utilisée avec des systèmes de mesure autres que la potentiométrie (ampérométrie, spectrophotométrie).

Nous pensons que, par son exactitude, cette méthode peut servir de référence pour l'étalonnage de divers procédés physiques d'analyse.

RÉSUMÉ

Les principales études relatives au dosage du cobalt dans les alliages et les aciers sont revues. Une méthode électrochimique basée sur l'oxydation d'un complexe aminé par l'hexacyanoferrate(III) de potassium a été adaptée. Les différents facteurs pouvant modifier les mesures sont examinés: pH, influence de quelques éléments. Le fer, le vanadium, le manganèse, le molybdène, le tungstène etc. sont séparés sur résine cationique en milieu acide fluorhydrique. Un mode opératoire est proposé.

SUMMARY

The main methods for the determination of cobalt in alloys and steels are briefly reviewed. An electrochemical method based on the oxidation of cobalt–ammine complexes by hexacyanoferrate(III) is applied. The various factors which could affect the measurements are examined, particularly pH and interferences. Iron, vanadium, manganese, molybdenum, tungsten, etc. are separated on a cationic resin in a hydrofluoric acid medium. Cobalt is further separated from manganese and chromium on an anionic resin from which it is eluted with hydrochloric acid. A procedure suitable for application to alloys and steels containing 4–80% cobalt is described.

ZUSAMMENFASSUNG

Es wird ein Überblick über die wesentlichen Methoden für die Bestimmung von Kobalt in Legierungen und Stählen gegeben. Es wird eine elektrochemische

Methode angewendet, die auf der Oxidation von Kobalt–Ammin-Komplexen durch Hexacyanoferrat(III) beruht. Die verschiedenen Faktoren insbesondere pH und Störungen, die die Messungen beeinflussen könnten, werden geprüft. Eisen, Vanadin, Mangan, Molybdän, Wolfram etc. werden an einem Kationenharz in fluorwasserstoffsaurem Medium abgetrennt. Kobalt wird weiterhin von Mangan und Chrom an einem Anionharz abgetrennt, von dem es mit Salzsäure eluiert wird. Ein Verfahren, das sich für Legierungen und Stähle mit 4–80% Kobalt eignet, wird beschrieben.

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DIRECT DETERMINATION OF BISMUTH AND ANTIMONY IN SEA WATER BY ANODIC STRIPPING VOLTAMMETRY

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Bismuth and antimony are known to be present in sea water at very low concentrations: of the order of 0.03 and 0.3 μg kg^{-1} respectively. For the determination of bismuth, Brooks[1] used an ion-exchange concentration step taking 100 days, followed by emission spectrography of the evaporated eluate and the ashed resin. Portman and Riley[2] developed a procedure involving concentration by ion exchange from a 10-l sample, followed by extraction and spectrophotometric determination with dithizone and radiometric correction for losses in the chemical procedure. The same workers[3] determined antimony by coprecipitation from a 5-l sample with manganese dioxide, separation by solvent extraction and colorimetric measurement with rhodamine B, again with radiometric correction. The most extensive study on antimony was done by Schutz and Turekian[4] by neutron activation analysis of freeze-dried samples. All of these methods are time-consuming, most require large samples and extensive handling, and none are adapted to on-shipboard use.

The present investigation was prompted by a desire to develop alternative methods for the determination of bismuth and antimony in sea water which would be rapid, simple, direct, of high enough sensitivity to eliminate the need for preconcentration or chemical separation, and be adaptable to shipboard use. The technique of anodic stripping voltammetry with the mercury-coated graphite electrode (MCGE) of Matson *et al.*[5] suggested itself as offering the largest number of these virtues. This electrode has been shown by Fitzgerald[6] and by Seitz[7] to be suitable for the direct determination of copper, lead and cadmium in sea water, and to be superior to the conventional hanging mercury drop electrode for such applications. Fitzgerald has demonstrated the adaptability of the technique to shipboard use, and Carter and Hume[8] have discussed the factors governing electrode characteristics. The behavior of bismuth and antimony at the hanging drop electrode has been described by a number of authors[9–16]. Bismuth in 0.5–1.5 *M* hydrochloric acid is reported to give good stripping peaks. Antimony requires higher concentrations of hydrochloric acid for electroactivity and, because its stripping peak is very close to that of bismuth, has offered a difficult problem in resolution. Seitz[7] in a preliminary investigation observed that bismuth added to sea water at the 10^{-8} *M* level gave sharp, symmetrical stripping peaks with the MCGE if the sample were acidified to 1.0 *M* with hydrochloric acid, but that antimony under the same conditions was rapidly deactivated, presumably by hydrolysis.

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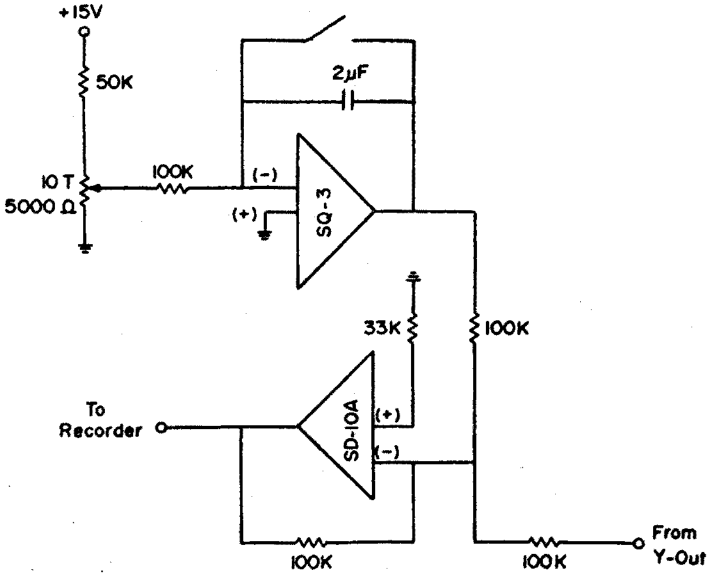
EXPERIMENTAL

Apparatus and materials

Plating and stripping were carried out with a three-electrode operational-amplifier controlled potentiostatic polarograph of conventional design. The instrument is designed to apply up to ±2.0 V *vs.* a reference potential, with a continuously variable potential scan rate of up to 100 mV s^{-1} and a maximum current output of 15 mA. A Houston HR-97 X-Y recorder served as the readout device. In order to diminish the effect of the steeply rising background current (about 0.1 μA s^{-1}) on the measurement of small bismuth and antimony stripping peaks, a simple compensating circuit was devised (Fig. 1). This device sums the "Y-OUT" signal with a linearly increasing voltage of opposite sign generated by an integrating operational amplifier.

The cell (Fig. 2) was fabricated from quartz tubing 25 mm in diameter, chosen for its relative inertness with respect to adsorption or release of trace metals when in contact with sea water. Before use, each cell was conditioned by soaking with portions of acidified sea water for several days. The stopper was machined from Teflon and drilled to hold the various electrodes and a fine Teflon delivery tube



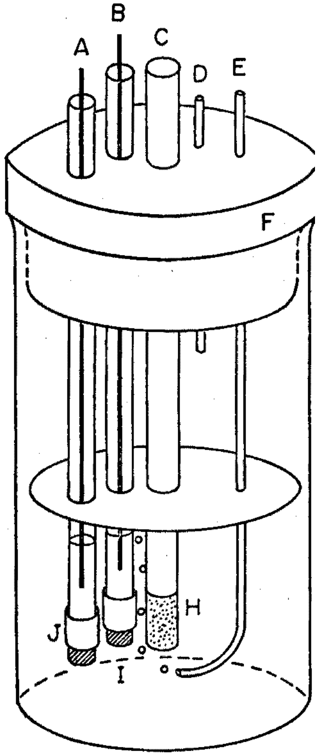


Fig. 1. Background current compensating circuit.

Fig. 2. Electrolysis cell. (A) Platinum counter electrode; (B) silver/silver chloride reference electrode; (C) wax-impregnated graphite rod; (D) nitrogen vent; (E) nitrogen inlet; (F) Teflon stopper; (G) quartz cell; (H) mercury coating on graphite electrode; (I) unfused Vycor plugs; (J) Teflon tubing.

for purified nitrogen. The stream of gas served both to purge oxygen from the sample and cell, and to provide stirring during the plating step. The reference electrode consisted of a silver wire previously anodized in sea water and held in a borosilicate glass tube containing a small portion of the untreated sample being analyzed, separated from the sample under analysis by a plug of unfused Vycor held in place by a short piece of Teflon tubing. This sea-water silver reference electrode (SWSE) is convenient to use, and for 35‰ sea water has a potential of about +5 mV *vs.* the saturated calomel electrode. The variation in potential as a function of salinity is small, at 35‰ salinity being less than 1 mV for a 1‰ change.

A mercury-covered graphite electrode (MCGE) similar to that described by Matson *et al.*[5] was utilized. Graphite rods 6 mm in diameter were impregnated with molten ceresine wax under vacuum, allowed to cool slightly and dipped repeatedly into the molten wax to build up an insulating coating. The electrode surface was prepared by scraping the wax from one end of the rod and up its side for a distance of 1 cm. The exposed surface was polished with fine (410) emery paper and buffed with a wad of absorbent paper (Kimwipe) until smooth. The active surface was plated with mercury from 10 ml of sea water acidified to pH 2.5, to which sufficient mercury(II) nitrate solution had been added to give a mercury coverage of $5.0 \cdot 10^{-7}$ moles cm^{-2}. Care was taken to plate at a potential more negative than −0.5 V *vs.* SWSE to assure the plating of all the exposed graphite sites, a precaution previously shown necessary[8]. The use of only $2.5 \cdot 10^{-7}$ moles cm^{-2} of mercury, which is advantageous in sea-water samples of lower acidity, led to some loss of precision as observed in the analysis of the Bahia Honda samples for antimony (Table II). In sea water made 1–4 *M* in hydrochloric acid, traces of oxygen may convert a significant amount of the mercury to calomel, hence the heavier mercury coverage is recommended. When not in use, the electrode was stored in the cell filled with pH 2.5 sea water and held at a potential of −0.1 V.

Sampling

Samples were collected at a depth of 2 m near Boston Light-Ship, 42°20′N, 70°46′W in preconditioned 1-l polyethylene bottles containing sufficient hydrochloric acid to make the samples about 0.1 *M* in free acid. Samples were collected at a depth of 1 m near Bahia Honda Key, Florida, 24°40′N, 81°15′W and, unless otherwise noted, made 1 *M* in hydrochloric acid within 3 days. An aliquot of Pacific Deep sample collected between 2530 and 2570 m at 28°13′N, 121°42′W and immediately acidified with hydrochloric acid to pH 1.67 was made available to us by Dr. Derek W. Spencer as part of an interlaboratory intercalibration study[17]. Two aliquots of a sample of Caribbean Deep water, a composite of three samples collected at 3000 m in the East Cayman Basin, the East Venezuela Basin and the Columbia Basin, and acidified to pH 2.54 were also made available from the same source.

Aliquots of the sample were taken by pouring small portions into preconditioned polyethylene beakers and the desired volume was transferred to the electrolysis cell, also preconditioned and rinsed with the sample, by means of a conditioned polyethylene syringe equipped with a Teflon "needle". As an additional precaution against contamination, sample transfer and manipulation were carried out in a glove bag under nitrogen.

Procedure for bismuth

Make the sea water sample in its storage container, unless already acidified, 1 *M* in hydrochloric acid by addition of gaseous hydrogen chloride until the proper weight increase has been achieved. This is most conveniently done with the container on the pan of a top-loading direct reading balance of suitable sensitivity. Allow the sample to cool for 2 h or more after acidification, and then sub-sample the well-mixed solution, transferring 20.0 ml to the electrolysis cell with a well rinsed disposable polyethylene syringe and a Teflon "needle". Purge the sample with a nitrogen stream for 10 min, insert the electrode assembly and continue purging for another 10 min to remove oxygen. For bismuth concentrations above $3 \cdot 10^{-10}$ *M* (0.06 μg kg^{-1}), plating for 15 min at −0.40 V *vs.* SWSE with agitation by nitrogen flowing at 1 ml s^{-1} is sufficient. Lower concentrations require correspondingly longer plating times.

At the end of the plating period, stop the agitation and allow the solution to rest for 20 s. Then scan the MCGE potential to −0.10 V *vs.* SWSE at a rate of 1000 mV min^{-1}, and record the resulting current–voltage curve at an appropriate current sensititivity such as 2 or 5 μA full scale. Shortly after the anodic scan is begun, activate the background current compensating circuit. In order to determine the optimum voltage ramp and actuation potential, preliminary scans with the MCGE in 1.0 *M* hydrochloric acid–sea water need to be made. Select the proper ramp potential to be applied to balance the background change in "Y-OUT" signal at the potential of the bismuth stripping peak by means of the 10-turn 5000-ohm precision potentiometer. Slight adjustments are usually necessary for each new series of runs or recoating of the electrode.

Determine the bismuth concentration by the standard addition technique using 10-μl additions of a 10^{-6}–10^{-7} *M* bismuth solution in 1 *M* hydrochloric acid prepared fresh daily by dilution of a $1.5 \cdot 10^{-4}$ *M* solution of Bi_2O_3 in 1 *M* hydrochloric acid. A Grunbaum pipet was found to be most convenient for the additions. Run each point twice to check reproducibility, and plot peak height against added bismuth.

Procedure for antimony

Acidify the remaining sample while still in the original storage container to 4.0 *M* with gaseous hydrogen chloride. After cooling and thorough mixing, transfer a 20.0-ml sample to the cell as before and purge with nitrogen. Carry out the plating at −0.5 V *vs.* SWSE for 10 min with nitrogen flowing at 1 ml s^{-1}, stop the agitation and allow the solution to rest for 20 s. Record the antimony stripping peak by scanning to −0.20 V at a rate of 1000 mV min^{-1} with an appropriate current sensitivity (*e.g.* 5μA full scale) and a compensating voltage ramp selected to balance out most of the background current rise during the stripping peak. Determine the antimony concentration by use of the standard addition technique using additions of a 10^{-5}–10^{-6} *M* antimony(III) solution in 2 *M* hydrochloric acid. Prepare the addition solution fresh daily by dilution of a millimolar stock solution prepared by dissolving weighed antimony oxide in concentrated hydrochloric acid and making up to volume in a 2 *M* hydrochloric acid medium. Lingane and Nishida[18] have shown that at the plating potential used here, both antimony(V) and antimony(III) are reduced to elemental antimony in a 4 *M* hydrochloric acid medium, so that the original oxidation state of the antimony is immaterial. Trivalent antimony was used for the standard as a matter of convenience. A plot of peak area (rather than height) against added antimony gives, on extrapolation, the total of antimony and bismuth, and correction for the previously determined bismuth gives the value for antimony. The increase in sample volume resulting from addition of hydrogen chloride in the pretreatment must be taken into consideration in the calculations.

RESULTS AND DISCUSSION

Representative current–voltage curves for bismuth and antimony stripping in sea water samples are shown in Figs. 3 and 4. The bismuth peak-width at half-height was 25–28 mV, consistent with a reversible three-electron oxidation. Standard addition plots were linear for both peak height and peak area as a function of concentration over the range 10^{-10}–10^{-7} M. The limit of detection for bismuth for a 20-min plating time appears to be about 0.004 μg kg^{-1}, or $2 \cdot 10^{-11}$ M. The peaks for antimony at natural levels in sea water were broader than the theoretical, the result of the concurrent stripping of bismuth with a slightly different peak potential. Successive standard additions of antimony, which greatly increased the Sb/Bi ratio in the amalgam, usually gave stripping peaks which were progressively sharper and narrower and more closely approximated the theoretical shape for a three-electron oxidation. Calibration curves for antimony based on peak heights tended to curve

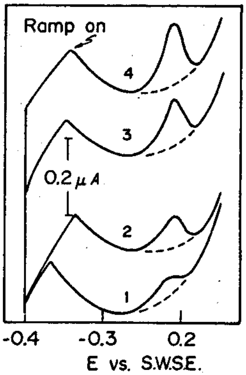


Fig. 3. Anodic stripping curves of bismuth in Pacific Deep. Sample made 1 M in HCl. 20-min plating. Curves 2–4, additions of standard in $2 \cdot 10^{-10}$ M Bi increments.

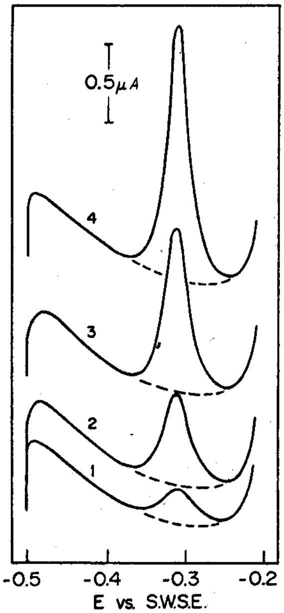


Fig. 4. Anodic stripping curves of antimony in Boston Light-Ship water made 4 M in HCl. Curves 2–4, additions of standard in $3 \cdot 10^{-9}$ M increments.

upward while calibrations based on peak area were linear over the concentration range of 10^{-9}–10^{-7} *M*. The limit of detection is somewhat dependent on the amount of bismuth present but is in the vicinity of 0.01 μg kg^{-1}.

Typical results for the determination of bismuth and antimony in samples of sea water from various sources are shown in Tables I and II. Each sample was analyzed in triplicate; the results shown are the averages of triplicates and the 95% confidence limits used to indicate the precision of the measurements are in each case 130% of the range of the three independent results.

The determination of bismuth in 1 *M* acid without interference by antimony is made possible by the extensive hydrolysis of the antimony species present. Both

TABLE I

BISMUTH CONTENT OF SEA WATER

Location	*Bi (μg kg^{-1})*	*95% Confidence limits (n=3)*
Boston Light-Ship	0.015	±43%
Pacific Deep	0.040	±42%
Bahia Honda Key		
Sample 1	0.090	± 6%
2	0.086	±31%
3	0.094	± 4%
4	0.080	±25%
5	0.075[a]	± 9%
6A	<0.008[b]	—
6B	0.04[c]	—

[a] Acidified after 6 weeks storage at natural pH, then analyzed.
[b] Transferred to new bottle after 8 weeks storage at natural pH, then acidified and analyzed.
[c] Empty bottle from 6A extracted with 1 *M* HCl and analyzed.

TABLE II

ANTIMONY CONTENT OF SEA WATER

Location	*Sb (μg kg^{-1})*	*95% Confidence limits*
Boston Light-Ship	0.18	±45%
Caribbean Deep		
Sample 1	0.48	±15%
2	0.39	±19%
Bahia Honda Key		
Sample 1	0.40	±16%
2	0.48	±20%
3	0.43	±28%
4	0.44	±13%
5	0.32[a]	±14%
6A	0.27[b]	± 8%

[a] Acidified after 6 weeks storage at natural pH, then analyzed.
[b] Transferred to new bottle after 8 weeks storage at natural pH, then acidified and analyzed.

bismuth and antimony in raw sea water would be expected to be present in the form of highly hydrolyzed and probably polymerized hydroxy chloro complexes or as colloidal hydrous oxides. Sillén[19] has suggested that antimony in sea water which is in equilibrium with the atmosphere ($E=0.75$ V *vs.* S.H.E., pH$=8$) should be in the pentavalent state. Whatever the species present may be, they are electroinactive at a mercury electrode unless the sample is fairly strongly acidified. To test the validity of determining bismuth in the presence of antimony by using 1 *M* acid as in the present procedure, a large sample of raw sea water from the vicinity of Boston Light Ship was divided into two portions in polyethylene bottles and each was made $9.0 \cdot 10^{-9}$ *M* in bismuth. One portion was also made $80 \cdot 10^{-9}$ *M* in antimony. After 15 h, each was acidified to 1 *M* with hydrogen chloride gas as in the recommended procedure and the bismuth concentrations were measured after 1, 2 and 10 days of storage. The concentrations of bismuth in the two solutions determined after 1, 2 and 10 days were 9.3, 8.7 and 8.7 $M \cdot 10^9$ in the sample without added antimony and 8.3, 9.6 and 8.5 $M \cdot 10^9$ in the sample with added antimony. From this it may be concluded that there is no interference by a 9-fold excess of antimony, and also that 10^{-8} *M* bismuth is stable in the acidified solution for at least a 10-day period.

To examine the possibility that bismuth and antimony might be lost in significant amounts during storage of raw sea water in polyethylene bottles, an experiment was performed with six bottles of water taken simultaneously at Bahia Honda Key in Florida. Bottles 1–4 were acidified to 1 *M* with hydrogen chloride within 2 days of sample collection. Bottle 5 was acidified only after 6 weeks of storage. The contents of bottle 6 were transferred to a new bottle eight weeks after collection and then acidified (sample 6A). The emptied bottle was leached for 24 h with 1.0 *M* hydrochloric acid and the bismuth content of the leachings determined and corrected to the original volume of sea water (Sample 6B). From the results presented in Tables I and II, it is seen that most of the bismuth in sea water is adsorbed on the walls of a polyethylene container as a result of lengthy storage of unacidified solutions, a result confirming the observation of Portman and Riley. The loss is not irreversible as shown by the results on Sample 5 and Sample 6B. That the tendency toward loss is much less for antimony is shown by comparison of Samples 3 and 6A, an observation in agreement with Robertson's report of no adsorption of antimony from raw sea water by polyethylene containers[20].

Under the conditions of plating used in the procedure, silver and copper would be the elements most likely to constitute interferences in the determination. A sea water sample $5 \cdot 10^{-10}$ *M* in bismuth showed no interference when made $5 \cdot 10^{-7}$ *M* in copper or $3 \cdot 10^{-9}$ *M* in silver. Similarly neither a 4000-fold excess of copper nor a 200-fold excess of silver had any effect on the size of the stripping peak of $1.9 \cdot 10^{-9}$ *M* antimony in sea water. A 4000-fold excess of silver resulted in a sharply rising background current at the stripping potentials of bismuth and antimony, making accurate peak measurement difficult. This would seem to pose no practical problem, however, as the silver : antimony ratio in sea water does not normally exceed 10 at the most.

Because of the large amounts of hydrogen chloride gas used, particularly in the antimony procedure, it is necessary to run blanks on each tank of gas and apply a correction if necessary. In our experience the blank values were satisfactorily low, being less than $4 \cdot 10^{-11}$ *M* (0.008 μg.kg^{-1}) for bismuth and less than $2 \cdot 10^{-10}$ *M* (0.02 μg kg^{-1}) for antimony. For exact analysis, it should be noted that addition of hydrochloric acid gas to sea water produces a 3% increase in volume on acidification to 1 *M* and a 9% increase on acidification to 4.1 *M*, so that corresponding allowances should be made in the calculation of the analytical results.

The results in Tables I and II for samples of Massachusetts coastal water, Gulf Stream water from the Florida Keys and Pacific Deep water from the Baja California Seamount Province show bismuth values ranging between 0.015 and 0.094 μg kg^{-1}, which are comparable with those of Portman and Riley[2] who observed a range of 0.024–0.042 in the Irish Sea and English Channel, and the single value of 0.017 obtained spectrographically by Brooks[1] after ion-exchange concentration of 250 l of South African coastal water. The antimony results ranging from 0.18 to 0.48 μg kg^{-1} are in good agreement with the 0.18–0.40 values found by Portman and Riley[3] and the regional averages corresponding to 0.25, 0.38 and 0.47 μg kg^{-1} for the Caribbean, Northwest Atlantic and Gulf of Mexico reported by Schutz and Turekian[4], who used neutron activation analysis of freeze-dried samples. Of particular interest is the comparison of the present results for antimony in the Caribbean Deep with those of the two laboratories which determined antimony in the intercalibration study[17]. Using two sub-samples of the master sample, we found 0.39 and 0.48 (average 0.44) μg kg^{-1}. The other laboratories, each using three sub-samples of the same master sample, found 0.48, 0.39 and 0.46 (average 0.44) and 0.57, 0.58 and 0.58 (average 0.58) μg kg^{-1} by means of neutron activation analysis of the freeze-dried sea salts. The anodic stripping technique would appear to give very satisfactory results with a considerable advantage in simplicity and economy as well as the option of shipboard use.

The authors wish to express their appreciation to Dr. D. W. Spencer for supplying samples of Caribbean Deep and Pacific Deep water and to Mr. H. W. Kim and the crew of the R. V. Shrock for assistance in obtaining samples. This work was supported in part by the U.S. Atomic Energy Commission under Contract AT(30-1)-905, and the National Science Foundation under grant GP33950.

SUMMARY

A method based on anodic stripping voltammetry at the mercury-coated graphite electrode has been developed for the direct determination of bismuth and antimony at their natural levels in sea water. Bismuth plated at -0.4 V from sea water made 1 *M* in hydrochloric acid gives a stripping peak proportional to concentration at -0.2 V without interference from antimony or other metals normally present. Antimony may be plated from sea water made 4 *M* in hydrochloric acid and gives a stripping peak at -0.2 V proportional to the sum of bismuth and antimony. By use of the standard addition technique, satisfactory results were obtained for sea water samples with concentration ranges of 0.02–0.09 μg kg^{-1} for bismuth and 0.2–0.5 μg kg^{-1} for antimony.

RÉSUMÉ

Une méthode, basée sur la voltammétrie strippante anodique à électrode de graphite, revêtue de mercure, est mise au point pour le dosage direct du bismuth et de l'antimoine dans l'eau de mer. Le bismuth déposé à -0.4 V, d'une eau de mer 1 M en acide chlorhydrique, donne un pic proportionnel à la concentration, à -0.2 V, sans interférence d'antimoine ou d'autres métaux normalement présents. L'antomoine est déposé d'une eau de mer 4 M en acide chlorhydrique et donne un pic à -0.2 V, proportionnel à la somme bismuth et antimoine. La technique avec addition d'étalon permet d'obtenir des résultats satisfaisants pour des échantillons d'eau de mer dont la concentration va de 0.02 à 0.09 μg kg^{-1} pour le bismuth et 0.2 à 0.5 μg kg^{-1} pour l'antimoine.

ZUSAMMENFASSUNG

Es wurde eine Methode für die direkte Bestimmung von Wismut und Antimon in den natürlichen Konzentrationen in Meerwasser entwickelt. Sie beruht auf der Voltammetrie nach dem anodischen Stripping-Verfahren mit einer mit Quecksilber beschichteten Graphitelektrode. Wismut wird aus Meerwasser, das mit Salzsäure auf 1 M angesäuert worden ist, bei -0.4 V abgeschieden und ergibt einen Stripping-Peak bei -0.2 V, der der Konzentration ohne Störung durch Antimon oder andere normalerweise vorliegende Metalle proportional ist. Antimon kann aus Meerwasser (4 M Salzsäure) abgeschieden werden und ergibt einen Stripping-Peak bei -0.2 V, der der Summe von Wismut und Antimon proportional ist. Durch Anwendung der Standardzumischmethode wurden zufriedenstellende Ergebnisse bei Meerwasserproben erhalten, deren Konzentrationen zwischen 0.02 und 0.09 μg kg^{-1} Wismut und 0.2 und 0.5 μg kg^{-1} Antimon lagen.

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SHORT COMMUNICATION

Improved apparatus for determination of mercury by flameless atomic absorption

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A widely used method for the measurement of trace amounts of mercury is the cold-vapor atomic absorption procedure of Hatch and Ott[1]. The application of a highly efficient purging technique, which is simple and inexpensive, and increases sensitivity while reducing analysis time, is described here.

Experimental

Apparatus. The essential components of the apparatus are a regulated source of purge gas, such as prepurified tank nitrogen; a flowmeter for the 100–1000 ml min^{-1} range; a Pyrex Büchner-type funnel with a fine frit; and a 10–15 cm absorption cell with windows transparent at 253.7 nm (Fig. 1). A three-hole rubber stopper is used atop the funnel to allow the addition of reagents without disassembling the apparatus. An 11-cm drying tube filled with anhydrous magnesium

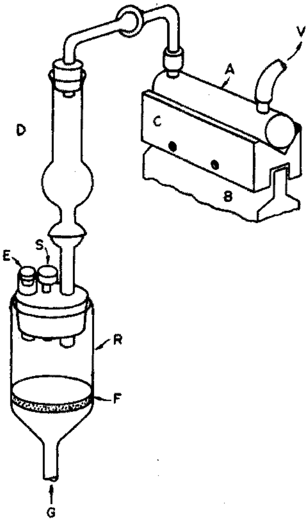

Fig. 1. Apparatus. (A) Absorption cell; (B) burner; (C) wooden cell holder; (D) drying tube; (E) sample entry port; (F) glass frit; (G) gas inlet; (R) reaction cell; (S) serum cap; (V) vent.

perchlorate was used to keep water vapor from condensing in the absorption cell. Alternatively, an infrared heating lamp may be positioned just above the absorption cell to prevent the condensation, but droplets of solution may reach the cell and leave residues on the windows, especially at high carrier-gas flow rates. No circulating pumps or special by-pass valves were required.

Most commercially available atomic absorption instruments can be used for cold-vapor measurements. To simplify the changeover from flame to flameless mode an absorption cell holder of wood is made to fit over the head of the air–acetylene burner. The controls used to adjust the burner head orientation can then also be used to align the absorption cell in the light beam. Preliminary studies were made with an Instrumentation Laboratory Model 153 atomic absorption spectrophotometer so modified. In the experiments described here a Coleman MAS-50 mercury analyzer altered to vent the mercury vapor directly from the absorption cell was used, and absorbance measurements were recorded on a Brown model 153Y strip-chart recorder.

Reagents. Standard mercury(II) solutions: a 1000-p.p.m. stock in 0.3 *M* hydrochloric acid was prepared by dissolving mercury(II) chloride in concentrated hydrochloric acid and diluting to the appropriate volume with distilled deionized water. A 2-p.p.m. standard was prepared weekly by dilution of the stock, and a 0.1-p.p.m. solution daily by dilution of the 2-p.p.m. stock. A 15% tin(II) chloride solution prepared fresh daily and purged for several minutes with nitrogen to remove any free mercury was employed as the reducing agent.

Procedure. To insure that all the mercury in the sample is present in the reducible mercury(II) state, some preliminary treatment is often required, *e.g.* the addition of permanganate[2] or persulfate[3] to an aqueous sample, or its irradiation with ultraviolet[4] to destroy organomercury compounds. For animal tissue, sludge, marine sediments, and other highly organic samples, a hot acid digestion is usually employed[5].

The desired volume of treated sample is placed in the funnel, which should be no more than two-thirds filled. An appropriate amount of the tin(II) reducing agent is added, the funnel quickly stoppered and the purging gas and recorder turned on. After the pen returns to base line, the gas flow is turned off and either the funnel emptied and a new sample added, or a known volume of dilute mercury(II) chloride standard injected into the reduced sample through the serum cap by means of a calibrated hypodermic syringe. The purging gas is again turned on and absorbance peak is measured. In this manner a calibration curve based on absorbance peak height may be constructed which is applicable to a given sample matrix.

Results and discussion

In the original Hatch and Ott apparatus, the sparging gas enters a sample volume of about 130 ml in a 250-ml flask through a 5-mm i.d. glass tube and is recirculated by a pump until an absorbance maximum is reached. Hwang and Ullucci[6] showed that with a gas washing bottle with a fritted glass disperser as the reaction cell, the absorption peak observed as the mercury was swept out of the sample and vented through the absorption cell could be used for quantitative measurements. By either method the sensitivity is limited by dilution of the mercury vapor passing through the absorption cell and it is evident that a minimum of purging gas used with maximum efficiency in purging should be aimed for. The apparatus described here, which is an adaptation of that developed by April and Hume[7] for use in plasma emission spectrometry of mercury, was designed with that objective. By making the entire bottom of the reaction cell a fritted-glass gas disperser, using a rapidly-acting reductant and minimizing dead volume between the reaction cell and the absorption cell, the sensitivity by peak height measurement is optimized.

With the method described, 25 ng of mercury in a 100-ml sample with 5 ml of reductant purged at a gas flow rate of 16 ml s^{-1} in a 150-ml Büchner funnel gave a signal which reached maximum in 10 s and returned to base line in about 75 s. This peak height was 50% greater than the steady-state maximum (reached in about 1 min) obtained on an identical sample when the recirculation pump system and 300-ml BOD bottle sample holder supplied with a MAS 50 was used. For samples containing greater than 0.1 μg of mercury, the two techniques show essentially equivalent reproducibility, but for very small amounts of mercury, going down to a few nanograms, peak height reproducibility was distinctly superior to that of steady state or slowly falling values close to background. Comparison of 100-ml samples containing 25 ng of mercury by the two methods showed standard deviations by the present method to be one half to one third those given by the recirculation technique, with a corresponding improvement factor of 2–3 in the detection limit (Table I). With small sample volumes, the mercury eluted faster, allowing slower purge gas flow rates. The signal from 25 ng of mercury in a 10-ml sample returned to base line in about 40 s with a nitrogen flow rate of 6 ml s^{-1}.

Funnels of 30-, 60- and 150-ml capacity were used for sample sizes of 2–100 ml. Over this range several trends were observed: the smaller the sample, the better the absolute sensitivity of the system. The detection limit for a 5-ml sample was 0.6 ng, but for a 50-ml sample, 2 ng (Table I). These values illustrate another general trend: that the larger the sample volume the better the relative sensitivity

TABLE I

DETECTION LIMITS

Sample volume (ml)	*Volume 15% $SnCl_2$ added (ml)*	*Hg detection limit*[a]	
		ng	*p.p.b.*
5	2	0.6	0.1
10	2	0.8	0.08
25	3	2.0	0.06
50	5	2.0	0.05
75	5	3.0	0.04
100	5	4.0	0.04

[a] The detection limit is here defined as the amount or concentration corresponding to a peak height above background equal to twice the standard deviation of measurement. Standard deviation values were observed not to be concentration dependent for 2–10 ng in 5-ml samples. The variability in peak height for 25-ng additions was also independent of sample volume from 10–100 ml although the peak height diminished as the concentration decreased with increasing sample volume.

of the technique, from a 0.12-p.p.b. detection limit for a 5-ml sample to 0.04 p.p.b. for a 100-ml sample.

When the recirculation to maximum signal technique is not used, it must be remembered that the flow rate of mercury vapor through the absorption cell affects the size and shape of the mercury peak. Generally, the faster the nitrogen flow rate, the narrower the absorbance peak (see Fig. 2) although with progressively faster rates the peak sharpens up at a slower rate. Similarly the peak height increased with increased flow rate, but only slightly at very fast flow rates. To achieve good sensitivity and reasonably short analysis time, a flow rate should be selected which is on or near the plateau of the peak height curve where small fluctuations have little effect either on peak width or height. The optimal flow rate is governed by the size of the funnel used and must be determined experimentally. For a 60-ml funnel, a flow rate of 6 ml s^{-1} is satisfactory (Fig. 2). Linearity of response with the amount of mercury in the sample was excellent in the range of 1 ng–1 μg in a 25-ml volume. Larger amounts overtax the optical capacity of the instrument and require use of a smaller sample.

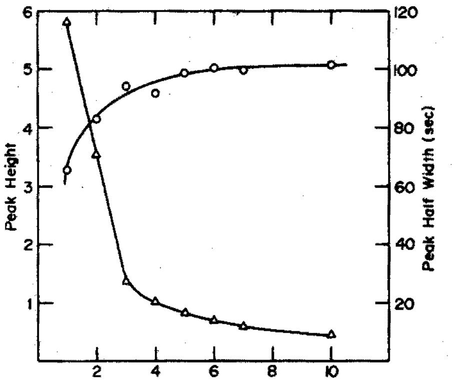

Fig. 2. Peak height and peak width as a function of flow rate for a 60-ml reaction cell and a 10-ml sample containing 25 ng of mercury. (○) Peak height; (△) peak half width.

In practical use, the funnel frit may require some routine maintenance depending on the nature of the samples. If the product of a hot acid digestion is being analyzed, the cell can be reused with only a water rinse between runs. For less acidic samples, such as untreated environmental waters, the frit may become clogged with tin(IV) salts after repeated use, resulting in reduced gas flow for the same gas pressure. If permanganate is used in sample pretreatment, manganese dioxide precipitate may also clog the frit. In either case the frit can be cleaned by allowing a small portion of concentrated hydrochloric acid to stand in the funnel a few minutes, then rinsing out the cell with deionized water. Although a fine frit is more susceptible to clogging than a coarse or medium grade, it is less likely to allow the sample to seep out when the gas flow is off, and a simple deionized water rinse between samples leaves no cell "memory" for mercury.

The procedure described makes use of inexpensive equipment to measure sub-part-per-billion concentrations of mercury rapidly and over a wide range of sample sizes. Practical application has been made to measuring mercury present in sea water, marine sediments, fish and other marine organisms, and clothing material.

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SHORT COMMUNICATION

Spectrophotometric determination of vanadium in sea water

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Most spectrophotometric methods for vanadium in sea water, in which it occurs at the 2-p.p.b. level, require preconcentration of vanadium by coprecipitation[1–4] or ion exchange[5]. Okabe and Morinaga[6] used a catalytic method[7]. Recently, Yotsuyanagi *et al.*[8] reported that 4-(2-pyridylazo)resorcinol (PAR) reacts selectively with vanadium in the presence of 1,2-cyclohexanediaminetetraacetic acid (CyDTA); the vanadium–PAR complex is extracted into chloroform by coupling with tetradecyldimethylbenzylammonium chloride (zephiramine)[9].

The present authors tried to apply this PAR method to a direct determination of vanadium in sea water, but the chloroform layer became turbid, and also some cations in sea water were not completely masked with CyDTA. These difficulties were overcome by adding potassium cyanide as well as CyDTA and by washing the chloroform layer with sodium chloride solution. A simple spectrophotometric method for vanadium in sea water then became possible.

Reagents

Standard solution of vanadium (200 μg V ml^{-1}). Dissolve 0.230 g of ammonium metavanadate in 25 ml of 1.8 *M* sulfuric acid and dilute to 500 ml with water.

PAR, 0.1% 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 water.

CyDTA, 0.5 M solution. Dissolve 45.5 g of 1,2-cyclohexanediaminetetraacetic acid in 125 ml of 4 *M* sodium hydroxide solution, and dilute to 250 ml with water.

Phosphate buffer. Mix 5 volumes of 0.5 *M* sodium monohydrogen phosphate solution with one volume of 0.5 *M* sodium dihydrogen phosphate solution.

Procedure

Place 500 ml of a sea-water sample in a 1-l separatory funnel, and add 2 ml of the CyDTA solution, 2 ml of aqueous 0.5 *M* potassium cyanide solution and 4 ml of the PAR solution. Adjust the pH to 6.8 by addition of the required amount of buffer, and mix. After 5 min, add 20 ml of aqueous 0.05 *M* zephiramine solution and 20 ml of chloroform, and shake for 3 min. Transfer the chloroform to a 200-ml separatory funnel, and add 1 ml of the CyDTA solution and 50 ml of 3% sodium chloride solution to depress foaming. Adjust the pH of the solution to 6.5 with the phosphate buffer, shake for 3 min, and filter the chloroform through a filter paper. Measure the absorbance of the chloroform solution in a 2-cm cell at 560 nm against water. Subtract the blank which is determined by using a vanadium-free artificial sea-water solution.

Analytical conditions

Analytical conditions were examined with artificial sea-water solutions which were either vanadium-free or contained 4 μg V l^{-1}.

Constant absorbances were obtained in the pH range 6.5–7.0 for the extraction, and 6.3–6.8 for the washing. Absorbances were unaffected by addition of 17–21 ml

TABLE I

EFFECT OF DIVERSE IONS

Ion	*Concentration in sea water (μg l^{-1})*[a]	*Added (μg l^{-1})*	*V found (μg l^{-1})*[b]
Ag^+	0.1	0.5	4.0
Al^{3+}	5	490	4.1
Cd^{2+}	0.05	10	3.9
Co^{2+}	0.08	5	3.9
Cu^{2+}	3	15	4.0
F^-	1400	10000	4.0
Fe^{3+}	3	50	3.9
Hg^{2+}	0.05	3	4.0
Mo^{6+}	10	50	4.1
Mn^{2+}	2	20	4.1
Ni^{2+}	2	50	4.0
Pb^{2+}	0.03	5	4.0
Ti^{4+}	1	6	4.1
U^{6+}	3	15	4.1
W^{6+}	0.1	1	3.9
Zn^{2+}	5	100	4.0

[a] Data from Riley and Chester[10].

[b] 4.0 μg V l^{-1} taken.

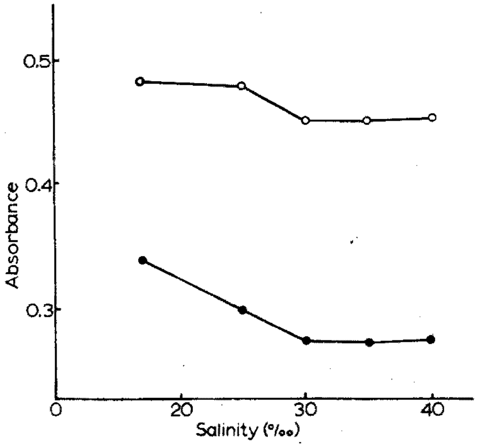

Fig. 1. Effect of salinity of sea-water sample. (○) 4 μg V l^{-1}, (●) reagent blank.

of the zephiramine solution or 0–3 ml of the cyanide solution. Shaking for more than 1 min in the extraction and washing steps sufficed. No interferences were found from various ions when they were present in concentrations 5–100 times their usual concentrations in sea water (Table I). Vanadium(IV) showed the same coloration with PAR and the same molar absorptivity with vanadium(V). Variation of salinity between 30 and $40^0/_{00}$ gave the same result (Fig. 1).

The sensitivity of this method was 0.025 μg V l^{-1} of sea water for 0.001 absorbance. The relative standard deviation of 5 replicate determinations was 8% at the 1 μg V l^{-1} level and 3% at the 3 μg l^{-1} level.

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SHORT COMMUNICATION

Separation of polyphosphates by paper chromatography with a new solvent

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Ascending paper chromatography is one of the most accurate methods of determining condensed phosphate species in their mixtures. Individual species can be identified qualitatively by their position on the chromatogram or by predetermined R_F values. The analysis can be made quantitative by cutting the chromatogram in strips on the boundaries of the developed color and determining total phosphorus in each strip after hydrolysis to orthophosphate.

Ebel's[1] comprehensive paper on the chemistry of oxyphosphoric acids and his suggested methods of separation of the species has been regarded as a classical investigation, and the acid solvent No. 1 (pH 1.9) he suggested has been the standard solvent used by most workers who separate the different species of linear polyphosphates.

Huhti and Gartaganis[2] modified Ebel's solvent only slightly, but they did make a significant change in the shape of the chromatographic paper that made possible a much cleaner separation of species (ortho- to nonapolyphosphate) in superphosphoric acid. Huhti and Gartaganis also recommended maintaining the temperature of the chamber at 17° to decrease the hydrolysis of the condensed phosphates during the separation.

Mixtures of phosphoric acids in nearly equilibrium distribution can be successfully separated chromatographically by the method of Huhti and Gartaganis with either their solvent or that of Ebel. Chromatograms of relatively pure materials such as sodium tripolyphosphate or hexaammonium tetrapolyphosphate, however, show a blue front that makes it difficult to identify species less highly condensed than the major phase. This phenomenon indicates that the major species hydrolyze to some extent during the separation.

Three factors—time, temperature, and pH of the solvent—affect the extent of the hydrolysis of polyphosphates during the chromatographic separation. Time and temperature are interdependent factors in the separation by a given solvent, and if one is changed the other must be changed also to obtain satisfactory results. Only the pH of the solvent can be changed without affecting either of the other factors. The present study was made to determine the extent to which adjustment of the pH affects the hydrolysis of polyphosphates during the chromatographic separation.

Experimental

The initial chromatograms in this study were developed by ascending chromatography for 16 h at 17°. The paper used was Whatman's 31 Thick, cut in the shape described by Huhti and Gartaganis[2].

The solvents used in the separations of sodium tripolyphosphate and hexaammonium tetrapolyphosphate were Ebel's solvent and an alkaline solvent that had been developed at this laboratory. This solvent consisted of 12.5 g of monochloroacetic acid, 250 ml of isopropanol, 350 ml of acetone, 350 ml of water, and 15 ml of concentrated ammonium hydroxide; its pH was 8.7. The results of the separations Table I) shows that there was significant hydrolysis of both of the polyphosphates in Ebel's acidic solvent.

Monochloroacetic acid is much weaker than trichloroacetic acid, so that substitution of the mono- for the trichloroacetic acid in Ebel's solvent would raise the pH. With this substitution, however, polyphosphates more highly condensed than tetrapolyphosphate were not separated.

After several trials, a new solvent consisting of 50 g of monochloroacetic acid,

TABLE I

CHROMATOGRAPHIC ANALYSES OF POLYPHOSPHATES WITH EBEL'S AND ALKALINE SOLVENTS AT 17°

Material	*Solvent*	*Distribution (%) of phosphate*				
		Ortho	*Pyro*	*Tri*	*Tetra*	*Other*
$Na_5P_3O_{10} \cdot 6H_2O$	Ebel's	1.9	2.3	94.0	—	1.8[a]
	Alkaline	1.2[b]	—	98.2	—	0.6[a]
$(NH_4)_6P_4O_{13} \cdot nH_2O$	Ebel's	1.2	2.6	3.8	92.2	0.3
	Alkaline	0.5[c]	—	—	97.1	2.4

[a] Includes tetra.
[b] Includes pyro.
[c] Includes pyro and tri.

TABLE II

R_F VALUES OF NEW AND EBEL'S SOLVENTS

Phosphate species	*R_F values*	
	New solvent	*Ebel's solvent*
Ortho	0.81	0.87
Pyro	0.67	0.61
Tripoly	0.59	0.58
Tetrapoly	0.52	0.40
Pentapoly	0.46	0.33
Hexapoly	0.41	0.26
Heptapoly	0.36	0.21
Octapoly	0.32	0.16

250 ml of isopropanol, 350 ml of acetone, 300 ml of water, 100 ml of 0.25% EDTA solution, and 15 ml of concentrated ammonia liquor was developed that had a pH of 4 and gave distinct separation of the nine species from ortho- to nonapolyphosphate. This solvent did not give the blue front observed in the chromatograms of sodium tripolyphosphate and hexaammonium tetrapolyphosphate that were developed in Ebel's solvent. In addition, the R_F values of the new solvent were somewhat higher than most of those with Ebel's solvent and were more conveniently distributed (Table II).

Chromatograms of three pure materials and three pilot-plant ammonium polyphosphates were developed in Ebel's solvent and the new solvent; the results are presented in Table III. The major species of the sodium tripolyphosphate and the hexaammonium tetrapolyphosphate in the chromatograms developed in the new solvent are in good agreement with those in the chromatograms obtained with the alkaline solvent shown in Table I. Hydrolysis during the separation was less for both compounds with the new solvent than with Ebel's solvent, the result of raising the pH of the solvent.

TABLE III

CHROMATOGRAPHIC ANALYSES OF AMMONIUM POLYPHOSPHATES WITH EBEL'S SOLVENT AND THE NEW SOLVENT AT 17°

Material	*Solvent*	*Distribution (%) of phosphate*				
		Ortho	*Pyro*	*Tri*	*Tetra*	*Other*
$(NH_4)_3HP_2O_7$	Ebel's	0.5	99.0	—	—	0.4
	New	0.2	99.6	—	—	0.2
$Na_5P_3O_{10}\cdot 6H_2O$	Ebel's	1.9	2.3	94.0	—	1.8
	New	0.8	0.5	98.4	—	0.3
$(NH_4)_6P_4O_{13}\cdot nH_2O$	Ebel's	1.2	2.6	3.8	92.2	0.3
	New	0.6	1.4	0.3	97.7	0.0
APP[a]	Ebel's	20.9	78.3	—	—	0.8
	New	20.3	79.4	—	—	0.4
APP[a]	Ebel's	13.2	16.2	70.6	—	0.0
	New	12.9	15.3	71.8	—	0.0
APP[a]	Ebel's	8.7	10.4	80.7	—	0.2
	New	8.1	9.3	82.5	—	0.0

[a] The three ammonium polyphosphates were prepared in the pilot plant by ammoniation of three different electric-furnace polyphosphoric acids.

Two electric-furnace superphosphoric acids also were separated with both solvents. The results (Table IV) showed that hydrolysis was again less with the new solvent than with Ebel's solvent.

After the new solvent had been used for several years, a brief study was made to determine whether hydrolysis would increase significantly if the separation were made at room temperature, about 25°, instead of at 17°. Chromatographic separation of sodium tripolyphosphate and an impure hexaammonium polyphosphate were made in Ebel's solvent at 15°, the newly developed solvent at 25°, and

TABLE IV

CHROMATOGRAPHIC ANALYSES OF SUPERPHOSPHORIC ACIDS AT 17°

Distribution (%) of phosphate	*80.0% P_2O_5 acid*			*83.5% P_2O_5 acid*		
	Ebel's solvent	*New solvent*		*Ebel's solvent*	*New solvent*	
Ortho	17.2	16.0	16.3	5.8	4.6	5.0
Pyro	41.5	40.4	40.4	18.3	14.7	14.7
Tripoly	22.1	23.6	23.7	18.9	16.3	16.2
Tetrapoly	11.1	11.5	11.4	17.1	14.6	14.6
Pentapoly	4.9	5.1	4.9	14.1	12.6	12.5
Hexapoly	1.9	2.1	2.0	11.7	9.8	9.9
Heptapoly	—	0.8	0.8	—	7.5	7.4
Octapoly	—	—	—	—	6.7	5.2
Higher	1.2	0.5	0.5	14.2	13.2	14.5

TABLE V

CHROMATOGRAPHIC ANALYSES OF POLYPHOSPHATE SALTS WITH DIFFERENT SOLVENTS AND AT DIFFERENT TEMPERATURES

Material	*Solvent*	*Temp. (°)*	*Distribution (%) of phosphate*				
			Ortho	*Pyro*	*Tri*	*Tetra*	*Other*
$Na_5P_3O_{10} \cdot 6H_2O$	Ebel's	15	5.2[a]	—	94.0	—	0.7[b]
	New	25	0.3	—	99.7	—	—
	Alkaline	25	0.5	—	99.5	—	—
$(NH_4)_6P_4O_{13} \cdot nH_2O$	Ebel's	15	6.6	6.7	4.4	82.0	0.3
	New	25	5.8	6.1	2.9	84.9	0.3
	Alkaline	25	6.0	6.3	2.4	84.4	0.9

[a] Includes pyro.
[b] Includes tetra.

the alkaline solvent at 25°. All separations were made for 16 h. The results are shown in Table V.

The major species determined with the alkaline solvent and the new solvent at room temperature are in excellent agreement. These results also show that the polyphosphates hydrolyze significantly in Ebel's solvent, even at low temperature.

Excellent separation of polyphosphates can be obtained at room temperature on Orange Ribbon 589 chromatographic paper which is thinner than Whatman No. 31. With the thinner paper the wet oxidation of the strips described by Woodis[3] is carried out more expeditiously.

The new solvent is markedly superior to Ebel's highly acidic solvent. With the new solvent, more species can be determined because of better resolution between migrating bands, hydrolysis is significantly decreased, and the separations can be carried out on a thinner paper and at room temperature and so do not require refrigeration.

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SHORT COMMUNICATION

The colour reaction of N-glycylcomenamic acid with iron(III)

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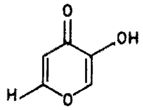
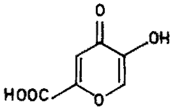
Reactions of iron(III) with a variety of compounds based on pyromeconic acid (I) as skeleton have been reported[1–3]. This note reports experiments in which the heteroatom of the pyrone ring is replaced by nitrogen. The conversion of comenic acid (II) to comenamic acid (III) by reaction with ammonia is known[4,5] but a cleaner reaction with better yield has been reported when glycine is used, giving N-glycylcomenamic acid (IV)[6].



I



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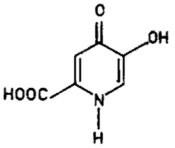
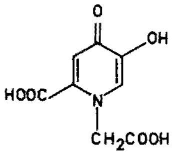
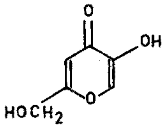


III



IV



V

Experimental

The reagent was prepared as described by Kleipool and Wibaut[6]. Meconic acid (Nutritional Biochemicals Corp.) was purified by the method of Garkusha[7] to give a product which assayed 91% by titration compared to 60% for the material received. Glycine from the same supplier was used as received. The product of the sealed tube reaction between 20 g of meconic acid and 17 g of glycine in 400 cm^3 water in a 2000-cm^3 tube heated for 10 h at 115° was recrystallized four times from water. The reaction was carried out at both pH 7 and 9, and microanalysis of the product showed that avoiding alkaline conditions was critical. At pH 7, the product melted at 224.4–226° (lit. 225.5–227°) and gave a satisfactory analysis. Found, 43.06% C, 3.50% H, 46.57% O, 6.24% N; calculated for the semihydrate, 43.24% C, 3.63% H, 46.82% O, 6.31% N.

Other reagents used were of ACS or comparable grade, and all water was deionized.

Stock solutions of both iron(III) perchlorate and of the ligand were prepared at exactly known concentrations near $5 \cdot 10^{-3}$ M in 0.1 M perchloric acid as solvent, and then mixed in various proportions and diluted with further 0.1 M perchloric acid to give a constant total molarity for metal plus ligand of $2 \cdot 10^{-3}$ M in samples of varying composition. Separate series of samples were made up by omitting first one, and then the other, of the stock solutions. Spectra of the three series of samples were recorded on the Cary 14 spectrophotometer, and digitized at 5-nm intervals from 700 to 350 nm.

The digital data were submitted to the matrix reduction technique of Varga and Veatch[8] with RANK and CONTOUR programs[9]. At an estimated absorbance error level of 0.030, RANK indicated one absorbing complex, and CONTOUR indicated a metal:ligand ratio of 1:1.

Results and discussion

The spectrum of the red complex showed a broad peak at 495–500 nm with a shoulder at 420–430 nm. At 500 nm, the molar absorptivity was estimated to be 960. Extrapolation of terminal tangents to the continuous variations curve allows the formation constant to be estimated in the case of a 1:1 complex, and gave in this case, $k_1 = [\mathrm{ML}][\mathrm{H}]/[\mathrm{HL}][\mathrm{M}] = 7.8 \cdot 10^3$. It seems likely, since both give a red colour at low pH, that complexation occurs at the same sites as in the γ-pyrone reagents: kojic, meconic, and comenic acids; *i.e.*, at the oxygens on ring positions 4 and 5. Thus, to convert the estimated k_1 value to an estimated $K_1 = [\mathrm{ML}]/[\mathrm{M}][\mathrm{L}]$, the acidity constant for the proton on the hydroxy group at the 5 position is needed. This was determined by potentiometric titrations of a solution millimolar in the ligand and 0.1 M in sodium perchlorate. From calculations made at 21 points in the buffer region, a mean value for $\mathrm{p}K_a$ of 7.41 was obtained. Upon insertion in the following equation, this gave $\log K_1 = \log k_1 + \mathrm{p}K_a = 11.30$.

TABLE I

COMPARISON OF REAGENTS

Reagent			*Complex with iron(III)*		
Compound	*Ref.*	*$\mathrm{p}K_a$ (5-OH)*	*$\log K_1$*	*λ_{max} (nm)*	*ε*
Comenic acid	10	7.12	12.4	580	680
Kojic acid	2	7.78	10.16	495	946
N-Glycylcomenamic acid		7.41	11.30	500	960

Table I presents a comparison of these results with measurements for two of the γ-pyrone reagents. The similarity of the new results to those for kojic acid (V) is considerable. In view of the availability of kojic acid, and the lengthy preparation of comenamic acids, this similarity makes the former preferable as a reagent.

This work was supported by a National Research Council of Canada grant, which is gratefully acknowledged.

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Analytica Chimica Acta, 65 (1973) 477–480

SHORT COMMUNICATION

Square-wave-polarographische Bestimmung von Barium in Eisenoxid

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(Eingegangen den 6. August 1972)

Photometrische Verfahren zur Bestimmung von Bariumspuren können wegen ihrer Störanfälligkeit und ihres unspezifischen Verhaltens nicht auf eine Eisenoxidmatrix mit stark schwankenden Gehalten an Wismut und Calcium angewendet werden. Die Forderung eines hohen Wertebedarfes bei einfacher Arbeitsweise, geringer Probenmasse und geringem Chemikalienaufwand lässt den Einsatz polarographischer Verfahren zweckmässig erscheinen. Für praktische Messungen werden dafür im wesentlichen folgende Grundelektrolyte verwendet (Tabelle I).

TABELLE I

GRUNDELEKTROLYTE FÜR POLAROGRAPHISCHE VERFAHREN

Grundelektrolyt	*Literatur*	*Bemerkungen*
$(C_2H_5)_4NJ$, 0.1 *M* 80% Isopropanol	1	Nicht bei Anwesenheit von Ca.
$(C_2H_5)_4NJ$, 0.1 *M*	2	Erste Ca-Stufe stört stark.
$(C_2H_5)_4NJ$, 0.1 *M* 20% CH_3OH	3	Ca-Doppelstufe, schlechte Trennung, Ba-Stufe gestört.
$(C_4H_9)_4NJ$, 0.5–1.0 *M*		Tensammetrischer Peak bei 1.8 V und Wechselspannungsverfahren.
$CaCl_2$, 0.25 *M*	4	Gut auswertbar und getrennt, R_z für Wechselspannungsverf. zu gering, pH-Einstellung schwierig.
$CaCl_2$, 1 *M* $Ca(OH)_2$ sat.		Gute Stufenausbildung und Trennung bei 0.25–2 *M* $CaCl_2$.
Indirekte Verfahren	5	Geringe Selektivität
LiCl		Ähnlich $CaCl_2$- Grundelektrolyt, LiOH-Zusatz verbessert die Stufenausbildung geringfügig.

Durchführung der Messung

Geräte. Square-wave-Polarograph OH 104 (Fa. Radelkis, VR Ungarn); Mikrobürette 0.25 ml (Fa. Radiometer, Kopenhagen); Mikropipette 100 μl, Ansaugsystem Temperaturstabilisiert (Selbstanfertigung).

Messzelle (Abb. 1). (*a*) Eine Schliffhülse NS 12.5 wird abgeschmolzen. Die Spannungszuführung erfolgt über einen Pt- oder W-Stift.

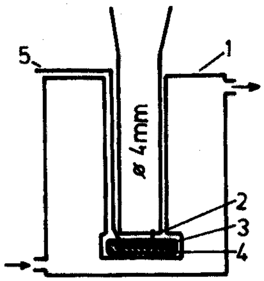

Abb. 1. Messanordnung. (1) Silikonisierter Cu-Block zur Abschirmung; (2) Einschmelzung Pt oder W; (3) Ag/Cd-Platte; (4) PTFE-Isolierung; (5) Anschluss Polarograph.

(*b*) *Vorbehandlung der Kapillare.* Um ein "Rinnen" des Quecksilbers bei stark negativen Potentialen zu vermeiden, wurden Mikrorisse an der Austrittsöffnung durch Wärmebehandlung (Propan, 0.8 mm Injektionskanüle) unter dem Stereomikroskop verschmolzen. Silikonisierte Kapillaren arbeiten schon nach kurzer Einsatzzeit auf Grund des stark alkalischen Grundelektrolyten unregelmässig. "Kapillare-response" wurde bei "verschmolzenen" Kapillaren nicht beobachtet.

Bestimmung von Barium in Eisenoxid. Je nach BaO-Gehalt werden 1–5 g lufttrockenes Fe_2O_3 in möglichst wenig konz. HCl unter Zusatz von 2–3 ml über Austauscher gereinigtem, 30%igem H_2O_2 gelöst, auf Raumtemperatur abgekühlt und im Schütteltrichter mit 10 ml Methylisobutylketon (zur Extraktionsanalyse) versetzt. Die Phasentrennung wird durch Zuspritzen von Wasser erreicht. Bei Einwaagen bis zu 1 g wird nochmals, bei grösseren Einwaagen weitere zwei Mal extrahiert. Die wässrige Phase wird anschliessend in einem Teflon-Becher zur Trockne eingedampft, der Becher auf Zimmertemperatur abgekühlt, mit Argon gespült und mit 1 ml Grundlösung (1 *M* $CaCl_2$ in gesättigter $Ca(OH)_2$-Lösung) versetzt. Zur Bestimmung werden 0.5 ml in die Messzelle überführt und ohne Schutzgasspülung polarographiert.

Ba-dotiertes Eisenoxid. Die Einwaagen werden nach den zu erwartenden Bariumgehalten von 1–10% zwischen 1–0.1 mg gewählt oder entsprechende Aliquote einer höherkonzentrierten Probenlösung eingesetzt. Die Verwendung von Aliquoten ist empfehlenswerter; Inhomogenitäts- oder Entmischungserscheinungen bleiben dadurch weitgehend ohne Einfluss. Bei Inhomogenitätsuntersuchungen wird die Einwaage auf 1–0.1 mg verringert, mit 2 ml HCl/H_2O_2 gelöst, die Eisenmatrix durch zweimaliges Extrahieren mit je 3 ml Methylisobutylketon entfernt und wie bereits angeführt, weiter verfahren. Bei geringen Einwaagen wird die Eindampfungsoperation direkt in der Messzelle durchgeführt. Bei ungenügender Reinheit des Extraktionsmittels (tensidische Begleitstoffe) behandelt man den Rückstand nach Entfernen des HCl/H_2O_2-Gemisches nochmals mit 1 ml 30% H_2O_2.

Messbedingungen
Gegenelektrode: Bodenquecksilber oder S.C.E.
Widerstand S.C.E.: 120 Ω.
Y-Wert der Kapillare[6]: 0.952 ($Y = t^{\frac{1}{6}} m^{-\frac{1}{3}}$).
Tropfensynchronisation automatisch.
Wechselspannung: 10 mV.
Anfangspotential: -1.60 V.

Auswertung: nach Eichzusatzmethode.

Bei Verwendung eines inneren Standards kann Pb^{2+} als Bezugselement zugesetzt werden.

Ergebnisse

Es wurden systematisch die aus der Literatur bekannten Grundelektrolyte auf ihre Anwendbarkeit zur Bariumbestimmung überprüft. Ergebnisse ergänzender Untersuchungen wiesen aus, dass eine pH-Änderung durch $Ca(OH)_2$ bis zur gesättigten Lösung bei $CaCl_2$ als Grundelektrolyt keinen wesentlichen Einfluss auf die Halbwertsbreite und Stufenausbildung im Konzentrationsbereich 10^{-3} bis 10^{-5} *M* Barium ausübt. Das Optimum der $CaCl_2$-Konzentration wurde zu 1 *M* für Wechselspannungsverfahren ermittelt. Der Ba-Peak tritt bei $E_{\frac{1}{2}} = -1.856$ V auf.

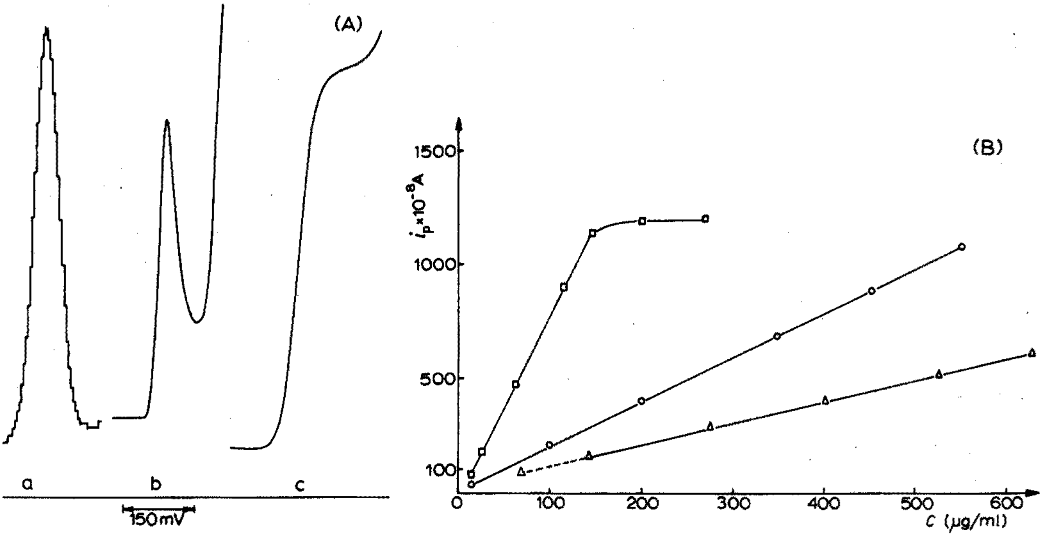

Abb. 2. (A) Kurvenformen bei polarographischen Verfahren zur Bariumbestimmung. Grundelektrolyt 1 *M* $CaCl_2$ in sat. $Ca(OH)_2$. (a) Square-wave, $C_{Ba} = 5 \cdot 10^{-4}$ *M*; (b) sine-wave (Rapidverfahren), $C_{Ba} = 1 \cdot 10^{-3}$ *M*; (c) d.c.-polarographisch (Rapidverfahren), $C_{Ba} = 5 \cdot 10^{-3}$ *M*. (B) Eichkurven für Ba und Pb. Grundelektrolyt: 1 *M* $CaCl_2$, $Ca(OH)_2$ sat. (○) Ba; (□) Pb; (△) Ba (d.c.-Polarographie).

Die Bestimmung ist mit Wechselspannungs- und Rapid-Gleichspannungsverfahren durchführbar (Abb. 2). Die Halbwertsbreite[7] (50 mV) weist auf eine schwach irreversible Reaktion hin. Die theoretische Spitzenstromstärke wurde unter Zuhilfenahme von rechnerisch ermittelten V-Werten[8] für einen gerätespezifischen β-Wert von 0.905[7] nach

$$i_P(\text{theor.}) = 21.27 \cdot 10^2 \frac{n^2 F^2}{RT} m^{\frac{2}{3}} t^{\frac{2}{3}}$$

$$C \Delta U_R (D/\vartheta \bar{u})^{\frac{1}{2}} \sum_{\vartheta \bar{u}}^{\infty} (-1)^m (\beta + m)^{-\frac{1}{2}}$$

ermittelt. Die experimentell bestimmten Peakströme bei C_{Ba} $5 \cdot 10^{-5}$–$5 \cdot 10^{-4}$ *M* ergaben, auf die theoretische Spitzenstromstärke bezögen, Werte zwischen 80 und 83%, was die Aussage der Halbwertsbreite bestätigt. Square-wave-polarographische Bariumbestimmungen an Eichproben mit BaO-Gehalten von 1–10% ergaben Variationskoeffizienten (aus 10 Einzelbestimmungen) von 1.8–2.5%.

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ANNOUNCEMENTS

European Symposium of the International Association of Forensic Toxicologists

Ghent 31st August–1st September 1973

The European Symposium of the International Association of Forensic Toxicologists, will be held at the State University of Ghent, Belgium, Faculty of Pharmaceutical Sciences, Department of Toxicology, on 31st August–1st September 1973.

This meeting was decided at the last International Meeting of Forensic Sciences in Edinburgh. The language of the Symposium, as at the previous meetings, will be English.

Additional information can be obtained at the following address: Department of Toxicology, State University of Ghent, Hospitaalstraat 13, 9000 Ghent, Belgium.

The society for analytical chemistry

Centenary Celebrations 1974

The Society for Analytical Chemistry (SAC) has great pleasure in announcing that the Centenary of its formation will be celebrated in London from July 16th to 19th, 1974.

The Society was founded in 1874 by a group of Public Analysts as a means of exchanging information on methods of analysis. As the applications of analytical chemistry became more widespread, the Public Analysts were joined in the Society by other consultants and by analytical chemists employed by industrial concerns, and the original name of "The Society of Public Analysts" (SPA) was modified to "The Society of Public Analysts and Other Analytical Chemists". In 1954, the Public Analysts, although retaining their membership of the Society, formed a separate professional association; and the Society again changed its name to "The Society for Analytical Chemistry". In 1971, the Society was granted Armorial Bearings by the Royal College of Heralds. On January 1st, 1972, the Society became, for a trial period of three years, the Analytical Division of the new Chemical Society. During this period the Society will retain its identity and this will permit the celebration in 1974 of the Centenary of its founding.

The Celebrations will commence on Tuesday July 16th with a Grand Opening Ceremony at the Royal Institution, Albemarle Street, London. This will be followed by the Presentation of fraternal greetings by kindred Societies from home and overseas. The Centenary Lecture will then be presented by Professor H. M. N. H. Irving. The theme of the lecture will reflect the progress of analytical chemistry during the past one hundred years. Following the plenary lecture of each day, three streams of invited papers will be held simultaneously.

In conjunction with the Science Museum of London, there will be a major

Exhibition that will depict the progress and development of analytical techniques and apparatus over the last one hundred years.

A full Social Programme will be arranged, including a Centenary Banquet probably in London's historic Guildhall, and a reception by the Chemical Society at Burlington House, Piccadilly.

Accommodation will be provided in two Halls of Residence, one at Imperial College, South Kensington, and the other at Halliday Hall (Kings College), Clapham Common. Coach transport for all occasions will be arranged. Intending delegates will of course be free to make their own arrangements at London hotels if they so prefer.

During the years, the Society has formed close ties with the Chemical Societies of many countries all over the world, and on this historic occasion, the Society very much hopes that it will have the opportunity to act as host to delegates from all these countries.

Further information will be published as it becomes available, but if you hope to attend the Celebrations and would like the information sent to you personally, please contact:

The Secretary, Society for Analytical Chemistry, 9/10 Savile Row, London W1X 1AF.

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BOOK REVIEWS

Analytical Chemistry of Phosphorus Compounds, Edited by M. Halmann, Wiley–Interscience, New York, 1972, x + 850 pp., price £ 16.80.

The *Chemical Analysis* series of monographs, of which the present book is volume 37, has already provided comprehensive texts on the analytical chemistry of nitrogen and sulphur compounds. Comparing these books with the present one, the analytical chemist may be rather taken aback to realise just how few unequivocal methods are available for phosphorus compounds, once one leaves the well-trodden area of phosphate determinations. The editor has selected specialist authors—a truly international collaboration—to give a full survey of all the analytical techniques which have in any way proved of value in dealing with phosphorus compounds.

After introductory sections on the general role of phosphorus, and on the determination of total phosphorus, the text is divided into 4 parts. Separation methods (Part I) based on gas chromatography and solution chromatography are discussed in detail. The identification methods described in Part II include high-resolution nuclear magnetic resonance, vibrational spectroscopy and mass spectrometry; identification and analysis of minerals are considered separately. In Part III, different classes of substances are discussed: elemental phosphorus, phosphorus(III) compounds, phosphorus halides, phosphorus oxides and oxo acids, phosphorus–nitrogen compounds, cyclophosphazenes, phosphorus–sulphur compounds, phosphoranes, sugar phosphates and nucleotides, lipids and natural C–P compounds. Part III includes a good deal of general chemistry, and much of the information is concerned with structural analysis rather than conventional analytical methods. In Part IV, the determinations of phosphorus in soils, natural waters, fertilizers, feedstuffs and insecticides are described in detail.

The editor has done very well in homogenizing the offerings of 22 diverse groups of authors, and there is remarkably little overlap between the different sections. Indeed, in some sections, a little overlap would be welcome, for some information appears in unexpected places, and the index is not always very helpful in finding it.

The book, like others in this series, is beautifully produced, and can be strongly recommended for library purchase. It will prove of great value to chemists presented with a problem involving any type of phosphorus compound.

A. M. G. Macdonald (Birmingham)

J. Haslam, H. A. Willis and D. C. M. Squirrell, *Identification and Analysis of Plastics*, Iliffe Books, London, 2nd Ed., 1972, vi+749 pp., price £18.

When producing the first edition of this book in 1965, the authors testified as to their enthusiasm for a combination of chemical and physical methods in the analysis of polymers and the resultant work was evidence of the close professional association between spectroscopist and analytical chemist. The expanded second edition incorporates further instrumental techniques such as n.m.r., pyrolysis gas chromatography and X-ray fluorescence into this integrated approach.

The first chapter on instrumental methods deals in a general way with the techniques but is perhaps most valuable for the descriptions of sample preparation and interpretation of the data obtained and should be regarded as a supplement to the standard texts given in the references. The second chapter on qualitative analysis predominantly contains material from the first edition, with the addition of a short section on qualitative analysis from n.m.r. spectra. The next eight chapters describe analytical procedures for particular polymer types and show evidence of full revision and incorporation of new techniques since the first edition. The final chapter deals with the analysis of plasticizers, fillers, pigments and solvents and an atlas of over 300 infrared spectra is provided as an appendix.

This edition will be as welcome as the first to all who have to analyse plastics, but the increased cost of book production makes it less likely that it will be found in the libraries of teaching laboratories where it could be a source of inspiration to general analytical chemists. However, one can hope that teachers of analytical chemistry will add the first two chapters of this book to the reading lists they give to their students since they provide a practical exposition of applied analytical chemistry.

P. G. W. Cobb (Aldermaston)

A. D. Baker and D. Betteridge, *Photoelectron Spectroscopy, Chemical and Analytical Aspects*, No. 53 of International Series of Monographs in Analytical Chemistry, Pergamon, London, 1972, x+178 pp., price £3.50.

There is a wide variety of spectroscopic techniques, all of them of some interest to some chemists. The early development of most of these has been in the hands of spectroscopists, a curious breed of scientist, part physicist, part chemist, part experimentalist, part theoretician. A *few* of these techniques, such as n.m.r., have been widely accepted by chemists and particularly by those interested in structural analysis. Fewer still have become generally useful to analytical chemists. Since this book appears in a series on Analytical Chemistry, the unwary analyst may be misled into supposing that photoelectron spectroscopy is a new but tried technique likely to be of use in his immediate problems. A reading of this book will show that this is not so.

In terms of practical use, the two branches of the technique, one using X-rays and often called e.s.c.a., the other using ultraviolet photons, are at different stages. It is unfortunate that e.s.c.a., which has been tried for many practical problems, and has been found to be of some use in some of them, is given the smaller part of the book. Ultraviolet photoelectron (u.v.p.e.) spectroscopy is being explored as an analytical tool by the group associated with the authors but has not yet found acceptance elsewhere. The book gives details of some of their interesting explorations carried out so far, but so much of this refers to necessary further work that it is in no sense a prescription for the present analytical use of u.v.p.e. spectra.

However, the subtitle includes chemical aspects as well as analytical aspects. Much of the book is intended as a general introduction to u.v.p.e. spectroscopy, since the authors consider that chemists are "put off by the theoretical treatments which are a staple ingredient of most papers in the field". This is probably true, though the amount of theory is hardly surprising for a technique whose main use so far has been for comparison with the qualitative and quantitative predictions of molecular orbital theory. It may also be true that the technique "is of fundamental importance to chemists"; so is molecular orbital theory, but many chemists manage their daily affairs without either. For those who nevertheless would like to know something of the technique, the authors provide a readable account of the theory, though with some unevenness; on an early page unitary transformations appear without explanation, but later on it is thought necessary to define electronegativity and to give an elementary account of the bonding in molecular nitrogen. The central chapter gives a good account of the application of qualitative ideas to the interpretation of the u.v.p.e. spectra of a variety of organic molecules containing hetero atoms, and includes a collection of original spectra and some correlation diagrams summarising data on many spectra.

As is appropriate in a book at this level, an outline of the apparatus and some general notes on the use of it are included for both techniques. Some experimental aspects of u.v.p.e. spectra are covered in surprising detail; discussions of photon linewidths, calibration details and even of some apparatus of essentially historical interest could well have been left as references to the original work. On the other hand there is no explicit indication in the text that the majority of u.v.p.e. spectrometers, including those used for the spectra shown, have a sensitivity which varies sharply across the spectrum. There are a few statements which while not necessarily incorrect could be confusing, such as "resolution is affected by reactions in the target chamber" to introduce a discussion of thermal broadening of lines.

The coverage of e.s.c.a. is short, but includes an account of chemical shifts and some indication of the uses and potential uses for analytical work. The use of e.s.c.a. in surface analysis is mentioned, but the converse, that the use for bulk analysis assumes that the chemical composition of the surface and immediately sub-surface layers is the same as that of the bulk, is given insufficient emphasis. This is of particular importance since estimates of the observation or sampling depth of e.s.c.a. have decreased recently from the authors' quoted 100 Å. In conclusion, the book fills a gap between the shorter reviews and the detailed monographs for spectroscopists, but the techniques are not yet at the stage of routine analytical use.

D. R. Lloyd (Birmingham)

Wolfgang Leithe, *Die Analyse der organischen Verunreinigungen in Trink-, Brauch- und Abwässern*, Wissenschaftliche Verlagsgesellschaft mbH, Stuttgart, 1972, xii + 172 pp., Preis DM 48.–.

Cet ouvrage est destiné aux scientifiques et ingénieurs intéressés par la caractérisation et le contrôle des eaux potables, naturelles et usées. Il s'intéresse plus spécialement à l'analyse des polluants organiques. Cet ouvrage est l'un des premiers qui traite de ce sujet d'une façon générale tout en proposant diverses techniques qui jusqu'à l'heure actuelle étaient encore relativement dispersées dans des traités, mémoires et revues. Sont intérêt est donc de faciliter le travail de laboratoire en évitant la recherche d'une documentation et les mises au point fastidieuses.

Dans une introduction (33 p.) l'auteur expose l'origine des polluants organiques, l'influence de ceux-ci sur le milieu et les techniques d'épuration des eaux usées. Ces généralités doivent permettre au non spécialiste de se documenter rapidement sur les problèmes posés d'une part, et de se faire l'interprète des résultats obtenus d'autre part.

Un premier chapitre (35 p.) propose des dosages caractérisant les "propriétés colligatives" des constituants organiques d'une eau (p. ex. C-organique, oxydabilité au $KMnO_4$, D.B.O., D.C.O., N-organique). Dans un second chapitre (63 p.) sont décrits les dosages "spécifiques" de diverses espèces organiques (p. ex. cyanures, phénoles, détergents, hydrocarbures, pesticides). Des techniques instrumentales d'analyses de traces de particules sont proposées (p. ex. chromatographies, spectroscopie i.r., u.v. et de fluorescence). Dans une dernière partie (10 p.), l'auteur traite les méthodes de détermination de constituants spéciaux (p. ex. urochrome, urée, acide urique, coprostérol, acides humiques, lignine). Plus de 300 références bibliographiques sont citées.

Ce livre donne une impression sérieuse et nous paraît constituer un manuel de base à recommander à tout chimiste intéressé par l'importance toujours croissante de l'eau dans l'économie humaine.

Werner Haerdi (Genève)

Fritz Feigl and Vinzenz Anger, *Spot Tests in Inorganic Analysis*, Translated by R. E. Oesper, Elsevier Scientific Publishing Co., Amsterdam, 1972, xxix + 669 pp., price Dfl125,00 (*ca.* £39.00).

One of the privileges of being an analytical chemist is that the opportunity occasionally arises to review an edition of Feigl's "Spot Tests". Even though it is almost fifteen years since the previous edition of "Spot Tests in Inorganic Analysis" was prepared, this new edition has been eagerly awaited, and at last it has appeared. There can be no doubt about its being overdue, but unquestionably it is well worth the waiting. Sadly, it is the first Feigl text to appear posthumously and remind us of his death early in 1971. However, Dr. Anger to whom Professor Feigl entrusted the updating of the fifth English edition has carried out his task faithfully and expertly, and the result is a new volume which maintains all the high standards and traditions of the earlier editions which Feigl himself prepared.

It is, perhaps, difficult to compare this new sixth edition with its immediate predecessor. Fourteen years of developments in analytical chemistry have led to many new reagents and tests, and even new ways of carrying out spot test reactions. The result is a completely reorganised and revised text in which most of the significant new material has been incorporated. The text has also been reorganised in that Chapter 4 (the main bulk of the text) contains tests for the elements, their ions and compounds in alphabetical order, each element section being subdivided to provide tests for the particular form in which the element is present, be it free element, cation, anion, non-ionic or organic compound. Thus, the section dealing with Iron, contains tests for Fe^{2+}, Fe^{3+}, $Fe(CN)_6^{4-}$, $Fe(CN)_6^{3-}$, nitroprussides and ferrocene. This certainly makes for easier and quicker reference. At the end of each sub-section is to be found a reference list which includes a useful bibliography of appropriate quantitative procedures where these have been developed. This is certainly a worthy addition to the Feigl volumes. Containing some 900 individual tests and 130 applications of spot reactions to various technical materials and minerals, it is one of these books which few practising chemists can afford to be without. The information it contains is incomparable with any other book, and those who feel that the cost is excessively high may take some comfort from the excellent Elsevier presentation, and the relative cheapness of the individual items of chemical information so provided. Dr. Ralph Oesper has, once again, been responsible for the translation of the authors' German text and has done this so unobtrusively that the reader is quite unaware that the text was ever in anything but excellent English.

W. I. Stephen (Birmingham)

N. N. Greenwood and T. C. Gibb, *Mössbauer Spectroscopy*, Chapman and Hall Ltd., London, 1971, xii+659 pp., price £12.

This book attempts to summarise virtually the whole of the published literature on the Mössbauer effect from its discovery 15 years ago up to 1970. This task has been accomplished satisfactorily. The result is a source of references which will be especially valuable to analytical chemists just entering the field with the new relatively cheap and reliable spectrometers now commercially available.

The basic theory of the effect is described in 15 pages "without extensive use of mathematical formalism"; experimental methods and the information which can be derived from them are covered in a further 70 pages. The analyst will find this section very straightforward and sufficient for most of his requirements. The remainder of the book summarises the experimental observations on the 72 isotopes of 42 elements in which the Mössbauer effect has so far been observed. Since 75% of all Mössbauer literature has been concerned with measurements of ^{57}Fe it is not surprising that about half the book is devoted to this element, and these chapters reveal the wealth of structural detail which can be obtained in favourable circumstances. In contrast the section on silver has one reference and requires only 8 lines. In between these extremes the chapters on tin, the rare earths and the actinides occupy nearly 100 pages and a further 22 elements are covered in a similar space. At present only about 12 elements give Mössbauer results suitable for chemical applications. No doubt, this number will be extended and the technique become more widely accepted as another valuable weapon in the armoury of the analyst in general, and the molecular spectroscopist in particular. The book will be equally useful to both.

H. I. Shalgosky (Harwell)

H. D. Beckey, *Field Ionisation Mass Spectrometry*, Pergamon Press, 1971, xvi+344 pp., price £9.50.

This book devotes one third of its contents to a discussion of the instrumental techniques required for the production of mass spectra by field ionisation. Essentially, a sample in the gaseous state is subjected to the high gradient electrical field around a sharp pointed anode when an electron is removed from the molecule. Another section of the book deals with the application of this technique to physicochemical problems. A third section discusses the application of this technique to qualitative and quantitative analysis. The main advantage of field ionisation over electron impact mass spectrometry is that stronger molecular ions are produced and there is much less fragmentation. This makes the analysis of mixtures much simpler when the field ionisation technique is used. Several pages are devoted to the analysis of petroleum mixtures using this technique. Transfer of solids to the gaseous state for mass spectral analysis can be a problem. With the field ionisation technique this can be avoided by adsorption of the sample on to an activated surface which is used directly as anode in the field ionisation emitter.

Commercial equipment for the production of field ionisation mass spectra is becoming available, so this book, written by a pioneer in the field, is timely; much of the information is otherwise only available in original papers. It should help to stimulate interest in the use of this technique.

J. Grimshaw (Belfast)

W. J. Price, *Analytical Atomic Absorption Spectrometry*, Heyden and Son Ltd., London, 1972, xii+239 pp., price £5.80.

This book is written for the practical chemist. In this respect it is very much in the same mould as the first book written on atomic absorption spectrometry (a.a.s.), by Elwell and Gidley. It is six years since the second edition of the latter was published, and the present text can thus be considered as a worthy successor. It is full of information for the analyst; most if not all aspects of a.a.s. relevant to its practical application are described clearly yet concisely, whereas the more abstruse theoretical aspects are firmly relegated to a supporting role. The book also often provides a historical perspective of many of the developments.

The book begins with a brief chapter on basic principles, followed by a description of instrumental requirements—flames, non-flame systems, nebulizers, radiation sources, optics, detectors, read-out systems and automation are dealt with comprehensively, with additional information on emission and fluorescence instrumentation where this differs from the requirements of a.a.s. General analytical methodology is also described at some length, and the applications of a.a.s. to a wide variety of samples are summarized. Finally, details of the atomic absorption characteristics of each element are summarized in alphabetical order of the elements. There is no author index, but there is an alphabetically arranged list of 464 references.

A. Townshend (Birmingham)

Mass Spectrometry: Techniques and Applications, Edited by G. W. A. Milne, Wiley–Interscience, 1971, x + 521 pp., price £11.75.

This book is a collection of critical reviews of various areas of organic mass spectrometry. In all there are twelve chapters each written by an acknowledged expert in the area covered. Each chapter assumes from the reader some prior knowledge of mass spectrometry, and sets out to give an account of the present state of the subject, with extensive references, and of possible future developments.

The chapter on application of mass spectrometry to problems in medicine and biochemistry discusses many applications of m.s. to problems in analytical chemistry. Also of direct interest to analytical chemists is the chapter on gas chromatography–mass spectrometry which discusses in detail the main types of interfacing for these techniques. Applications of m.s. to the solution of structural and analytical problems in peptide and protein chemistry are also discussed. A chapter on stable isotopes in chemistry and biochemistry gives examples of the use of m.s. for isotope composition analysis. Other chapters deal with instrumental techniques, computer-assisted interpretation of mass spectra, fragmentation pathways and aspects of metastable transitions.

The book is well produced and a high degree of uniformity in style has been achieved in the various chapters, in spite of there being nineteen individual contributors. The title does not clearly indicate that it is a book on organic mass spectroscopy. Other important aspects of mass spectrometry, such as spark ionisation of metal samples, are not discussed.

J. Grimshaw (Belfast)

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ERRATUM

F. Ingman, A. Johansson, S. Johansson and R. Karlsson, Titration of mixtures of acids of nearly equal strength, *Anal. Chim. Acta*, 64 (1973) 113–120.

On p. 115, the heading of the third column of Table I should read $-j$ and not j.
On p. 119, Figure 2 has unfortunately appeared as a mirror image; the vertical axis should read pH.

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