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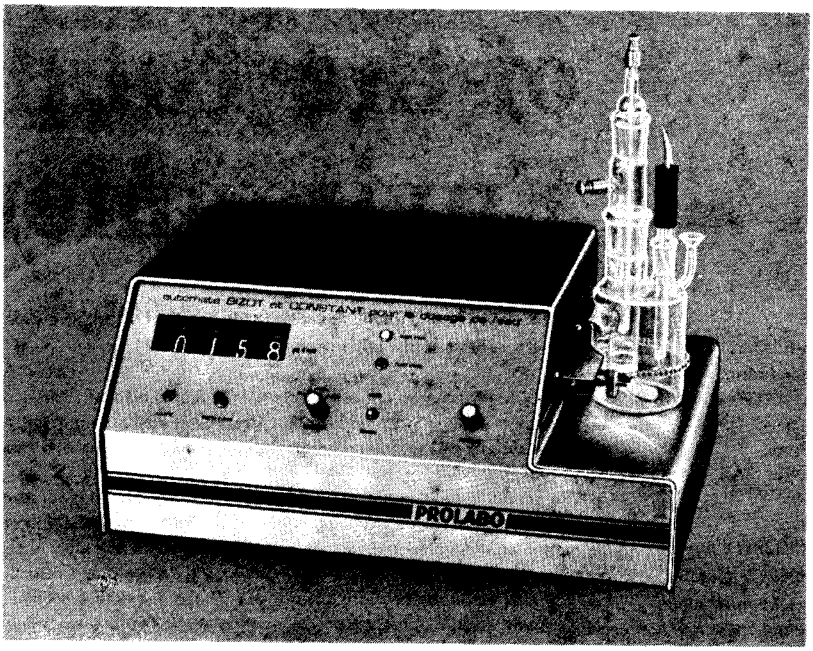

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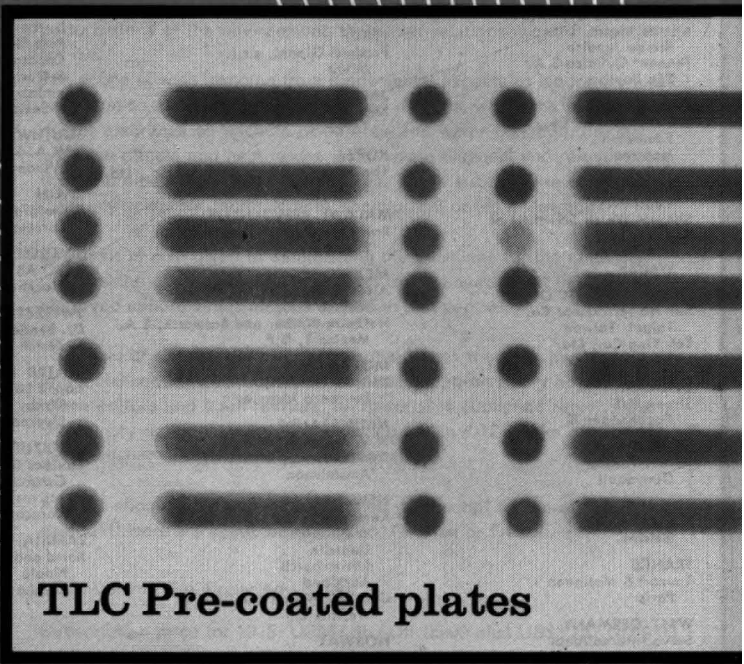

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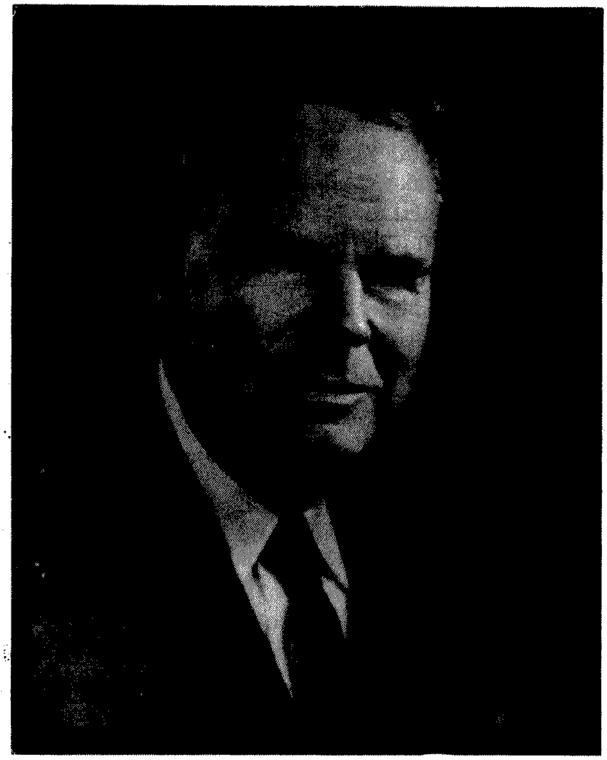

HOBART H. WILLARD
1881–1974

On May 7, 1974, Professor Hobart H. Willard died in Ann Arbor, Michigan, after an illustrious career in chemistry, largely at the University of Michigan Chemistry Department, during the course of which he contributed so greatly to the development of analytical chemistry as a scientific discipline.

As measures of Professor Willard's influence on analytical chemistry as a teacher and as an investigator, mention need only be made of the Willard–Winter method for the isolation and determination of fluoride, the Willard–Greathouse methods for the photometric determination of manganese, the appearance in 1974 of the fifth edition of his textbook on physical methods of analysis, and the contributions of his students and of their students to analysis. His contributions to analytical chemistry were many and varied, often being among the pioneering efforts in the areas concerned. It is interesting to note that in the period between 1920 and 1928 three women received Ph.D. degrees with Willard, and that their collaborative research with him ultimately resulted in thirty four publications.

Of major importance was his work on the preparation and utilization of perchloric acid and perchlorates, which his student, G. Frederick Smith, has done so much to publicize and to make available to analytical chemists. With N. Howell Furman of Princeton, he initiated the use of cerate oxidimetry. With M. Guy Mellon of Purdue, he introduced 1,10-phenanthroline as a photometric reagent for iron. He pioneered in and contributed greatly to the area of kinetically controlled precipitation (precipitation in homogeneous solution). He was one of the pioneers in the use of organic reagents for the determination of inorganic ions, introducing the use of phenylthiohydantoic acid and of tetraphenylarsonium chloride and its phosphorus and antimony analogs. Other areas to which he contributed in an influential manner included atomic weights for lithium, silver and antimony, bimetallic electrode pairs, periodate chemistry, important methods for early alloying elements in steels such as chromium, vanadium, tungsten and zirconium, etc.

Professor Willard was born in Erie, Pennsylvania, on June 3, 1881, but spend his boyhood in Michigan. In 1899, he came to the University of Michigan with which he remained connected for the remainder of his life and upon which he had such great impact as a teacher and investigator, receiving in 1946 the Henry Russell Lectureship which is the highest distinction given by the University to a member of its faculty. Receiving his A.B. degree in 1903, he began to teach at Michigan but interrupted his stay for several years to go to Harvard in order to work with Theodore W. Richards on problems in atomic weight determination; on receiving his Ph.D. degree in 1909, he returned to Michigan. Professor Willard's doctoral research involved perchlorates, which had, as indicated, a strong impact on his early research studies.

In 1951, he reached the mandatory retirement age of 70 at Michigan and became Professor Emeritus. However, for the next decade, he taught for one or more semesters at each of a number of other universities and continued his consulting activities, often spending extended periods of time at the Oak Ridge and Los Alamos Laboratories of the U.S. Atomic Energy Commission.

Professor Willard's scientific contributions include one hundred and thirty research papers, three textbooks on analytical chemistry which have had a major impact on the nature of analytical chemistry texts, a number of book chapters, a monograph on precipitation in homogeneous solution, and – last but certainly by no means least – a major impact on students of analytical chemistry for over half of the twentieth century. As an example of the latter, one should mention some of his former graduate students and collaborators who have and still are contributing so greatly to the development of analytical chemistry: G. Frederick Smith, R. D. Fowler, Ross W. Moshier, Harvey Diehl, Lynne L. Merritt, Taft Y. Toribara, Carl W. Zuehlke, Arno Heyn, Harry Freund, Louis Gordon, Richard B. Hahn, A. L. Wooten, John A. Dean and Charles A. Horton.

Professor Willard's accomplishments were recognized by many groups associated with analytical chemistry. A detailed biography and analysis of his research investigations was published by Harvey Diehl (*Talanta*, *7*, 135 (1961)); a list of Professor Willard's publications is given on pages 316–22 of the same issue of that journal. A good summary of Professor Willard's view of analytical chemistry, as well as of the development of analytical chemistry, is given in his Fisher Award address (*Anal. Chem.*, *23*, 1726 (1951)).

On behalf of the Editors and the Editorial Board of *Analytica Chimica Acta*, the writers express the sorrow and regret of the Board on the passing of Professor Willard and extend its sympathies to his family: Mrs. Margaret Willard, his wife, Mrs. Ann Korfhage and Mrs. Nancy Lindbloom, his daughters, and their husbands and children.

Charles L. Rulfs
Philip J. Elving

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APPLICATION OF INDUCTIVELY COUPLED PLASMAS TO THE ANALYSIS OF GEOCHEMICAL SAMPLES

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(Received 10th September 1974)

Inductively coupled plasmas have been shown to be promising sources for the optical emission spectrometric analysis of trace elements in solution[1,2]. The technique offers excellent sensitivity and is comparatively free of chemical interferences[2,3].

Various degrees of ionization interferences in the plasma, in the form of ionization suppression of easily ionized elements owing to the presence of high concentrations of easily ionized concomitants, have been reported[4–6]. The magnitude of these specific interferences depends partly on the ionization potentials of the elements concerned, their relative concentrations in the sample solution, the aerosol flowrate and the observation height in the plasma. It has been shown previously[4] that by selecting an aerosol flowrate of 1.0 l min^{-1} and an observation height of 20 mm above the load coil, these interferences are small or insignificant for reasonable changes in the concentrations of easily ionized elements. The elements of interest in the present study, Cu, Zn, Ni, Co and Pb, have first ionization potentials of 7.72, 9.39, 7.63, 7.86 and 7.42 eV, respectively. Since these potentials are all relatively high, it was considered that ionization suppression due to reasonable changes in the concentration of an easily ionized element would be negligible.

Recent studies of the inductively coupled plasma have included the measurement of some fundamental parameters[7–9], establishment of favourable operating conditions[2,4,10], and the application of the technique to the analysis of trace elements in various matrices such as oils, organic compounds and biological fluids[2,11–13]. Microliter sampling techniques for the plasma have also been developed[12–14].

The present study deals with the practical application of a modern plasma system to the analysis of geochemical soil samples.

Sampling and analysis of soils is extensively used in geochemical mineral exploration. According to Hawkes and Webb[15], the elements most commonly associated with sought-after sulphide ores are S, Cu, Zn, Pb, Fe, Ag, Au, Hg, Cd, In, Se, Te, As, Sb, Bi, Ni, Co, Mo and the platinum-group metals. Of these the most common analyses are for Cu, Zn, Ni, Co and Pb, mainly owing to their relative ease of analysis by atomic absorption spectrometry.

The flame atomic absorption technique is probably the most widely employed method for analysing soil solutions in geochemical prospecting[16]. Nevertheless, one of its major disadvantages is that it is a single element method. Furthermore, it has been shown by Govett and Whitehead[17] that errors in the atomic absorption determination of Pb, Zn, Ni and Co may be caused by the presence of Fe, Al, Ca, Mg, Na and K in the sample solution. The magnitudes of these errors are dependent on the concentrations of the analyte and concomitants in the solution. The authors conclude that the standard analytical practice of varying sample weight and dilution of the sample solution to suit the expected element concentration and the capabilities of the analytical procedure must be used with extreme caution in atomic absorption spectrometry.

The use of the inductively coupled plasma multi-element technique for analysing geochemical samples would enable rapid analyses to be performed. Furthermore, certain interference effects common to the atomic absorption technique may be reduced or eliminated. The large analytical range of the plasma technique[7,18] means that fewer, if any, dilutions of the sample solution need be performed.

This paper presents a comparison of results obtained by the plasma emission and conventional flame atomic absorption spectrometric techniques.

EXPERIMENTAL

Inductively coupled plasma system

Radio-frequency generator and coupling unit. The radio-frequency generator (International Plasma Corporation, Hayward, Calif., Model 140–27) is of a similar design to that described previously[18], apart from the following: output power can be increased up to a maximum of 4 kW, although an output power of 1 kW was used throughout the present study; the output power is stabilized by the incorporation of electronic control circuits and monitored by forward-power and reflected-power meters. The coupling unit is of somewhat different design to that described in ref. 18 but serves the same purpose. Output power is obtained via a 1.5-turn coil consisting of 6 mm o.d. water-cooled copper tubing.

Plasma torch. A schematic diagram of the plasma torch is shown in Fig. 1. A previous design[18] had the disadvantage that desolvated aerosol droplets coalesced at the injection orifice of the aerosol injector after prolonged spraying of a highly concentrated solution. The present aerosol injector tube consists of a 50 mm long capillary tube with constant bore diameter of 1.4 mm. The tip of the injector is 5 mm lower than the top of the concentric inner (plasma) tube. This resulted in less heating of the tip and consequently negligible coalescence of desolvated aerosol droplets. No difficulty was experienced in injecting the aerosol into the plasma, possibly because the aerosol flow from the capillary is less turbulent than for the previous design.

Nebulizer, sample chamber and flow controller. (The last from Brooks Instruments Division, Emersion Electric Co., Model 8943.) A low flowrate teflon and glass right-angle nebulizer and a sample chamber of the type described previously[18] were used. No aerosol desolvation system was used. The argon flowrate to the nebulizer was held constant at 1.0 l min^{-1} by the incorporation of a flow control device in the gas supply line. This device holds the flowrate constant for any downstream pressure between atmospheric pressure and the constant upstream pressure of 400 kPa (above atmospheric pressure). The downstream pressure (nebulizer

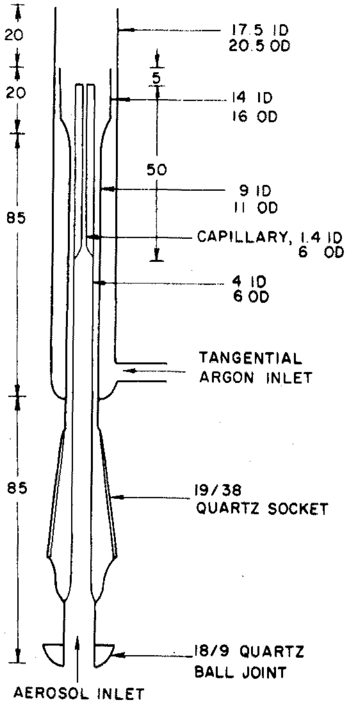


Fig. 1. Schematic diagram of plasma torch (all measurements in mm).

pressure) was monitored by a pressure gauge. A deposition occurring at the nebulizer orifice could thus be immediately detected by an increase in pressure.

A satisfactory diameter for the argon capillary tube orifice was found to be 0.22 mm. This produced a pressure of 100 kPa between the flow controller and the nebulizer for an argon flowrate of 1.0 l min^{-1}. The orifice of the solution uptake capillary was also 0.22 mm. A smaller diameter for the latter orifice presumably produces smaller aerosol droplets[19], which is favourable, but the orifice easily becomes clogged by small particles unless the sample solutions are filtered. The present choice is considered to be a practical one. The solution uptake rate could be varied between 0 and 4.5 ml min^{-1} by adjusting the position of the uptake capillary orifice relative to the argon capillary orifice. An uptake rate of 3 ml min^{-1} was used in the present study.

Spectrometer and readout system. The spectrometric instrumentation is summarized in Table I. Although a monochromator was used for the determinations of the various elements, the experimental conditions were not optimized for any one element and remained unchanged throughout this study. This was done to assess the capability of the source for true simultaneous multi-element analysis. The pertinent conditions are listed in Table II. Readout was effected by recording the reading on the digital voltmeter (connected to the recorder output of the amplifier) every 5 s. A damping time constant of 3 s was used.

Atomic absorption system

A Varian Techtron atomic absorption spectrophotometer Model AA-5

TABLE I

SPECTROMETRIC INSTRUMENTATION FOR PLASMA STUDY

Spectrometer	
Ebert mount, 0.5 m	0.5-m focal length (Jarrel-Ash Division, Fisher Scientific Co., Model No. 82000)
Unilateral slit assembly	25 μm entrance; 25 μm exit
Grating	1180 rulings mm^{-1}, blazed at 300 nm; first order
Reciprocal linear dispersion	1.6 nm mm^{-1}; first order
Photomultiplier	Hamamatsu type R106, S-19 photo cathode response
Optics	Plasma imaged in 1:1 ratio onto entrance slit with 16-cm focal length × 5 cm diameter fused quartz lens.
Photomultiplier power supply	High voltage supply (Keithley Instruments, Model No. 244)
Amplifier	Linear picoammeter with built-in pre-amplifier, zero suppression and variable damping (Keithley Instruments, Model No. 417)
Damping time constant	3 s
Readout	Digital voltmeter (Systron Donner, Model 7004); Strip chart recorder (Hitachi, Model QPD 54)

TABLE II

PLASMA OPERATING PARAMETERS

Frequency	27 MHz
Forward power	1000 W
Reflected power	<20 W
Argon coolant flowrate	9.5 l min^{-1}
Argon flowrate to nebulizer	1.0 l min^{-1}
Nebulizer pressure (above atm)	100 kPa
Observation height in plasma	20 mm (above coil)

TABLE III

ATOMIC ABSORPTION OPERATING PARAMETERS

(Air–acetylene flames were used in all cases.)

Element	*Wavelength (nm)*	*Lamp current (mA)*	*Spectral band pass (nm)*
Cu	324.7	5	0.3
Pb	217.0	5	1.0
Zn	213.9	5	0.3
Co	240.7	5	0.2
Ni	232.0	5	0.2

was used. Typical operating conditions are shown in Table III. The fuel and support gas pressures were usually 130–170 kPa for air, and 7–30 kPa (above atmospheric pressure) for acetylene. The acetylene pressure was in all cases adjusted for maximal sensitivity.

Samples and standards preparation

The soil samples were air-dried at ambient temperature and screened through an 80 mesh sieve. The material passing through the sieve was split several times through a chute riffler similar to that described by Allen and Khan[20] to ensure maximal homogeneity. Up to 8 replicate 1-g samples were weighed and transferred into 140-mm test-tubes in stainless steel racks. These racks were designed in such a way as to allow the test-tubes to fit into holes bored in refractory bricks placed on a thermostatically controlled hot-plate.

By means of an automatic dispensing pipette, 3 ml of a 9:1 mixture of concentrated (analytical-grade) perchloric and nitric acids was added. The acidified samples were maintained at a temperature of 180°C for 1 h and then allowed to cool. Sample solutions were then transferred to 50-ml Grade A volumetric flasks and made up to volume with distilled water. After the sediment had been allowed to settle, the supernatant liquid was decanted into clean 50-ml screw-top bottles. No further dilution was necessary for the plasma study.

Standard pure analyte solutions were prepared from pure metals dissolved in analytical-grade nitric or hydrochloric acid.

RESULTS AND DISCUSSION

Copper

The plasma technique has proved to be a very successful method for the analysis of copper in soils. No significant interferences were experienced at the 324.7-nm emission line. This conclusion is based on the facts that the plasma results compare favourably with those obtained by the atomic absorption technique and that the freedom of interferences for the latter technique has been well established[21,22]. A graphical comparison of results between the plasma and a.a.s. techniques for a total of 29 soil samples, ranging in copper content from approximately 5 to 2000 p.p.m. is shown in Fig. 2. (The copper concentrations in the solutions fell in the range 0.1–40 p.p.m.)

It was found that the plasma instrumentation could be calibrated with just one aqueous standard (and a blank solution) for all the determinations, because

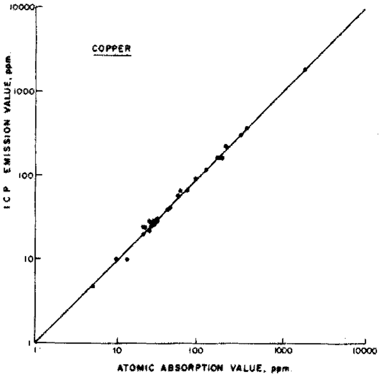
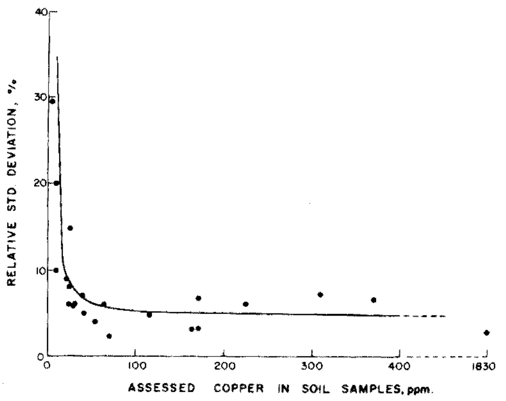


Fig. 2. Comparison between atomic absorption and plasma results for copper.

a linear response was obtained for aqueous standards over the full concentration range. A dynamic range of the readout instrumentation of 10^4 was required for precise measurement of the values. This was easily achieved with the amplifier and digital voltmeter system.

The instrumentation was calibrated with an aqueous 37.5 p.p.m. copper standard. This technique was facilitated by the fact that the background signal at 324.7 nm was extremely low. At 0.5 p.p.m. copper in aqueous solution, the spectral line-to-background intensity ratio was found to be 3.0.

The relative standard deviations of the plasma results for a number of samples are plotted against the assessed copper concentrations in Fig. 3. The relative standard deviations were calculated from the pooled results obtained for up to 10 repeat analyses of each of up to 8 replicate solutions. It is seen that in most cases a precision of better than 10% was achieved for copper concentrations in excess of 20 p.p.m. in the soil samples (or 0.4 p.p.m. in the soil solutions). It should be noted that the reported values of the precision are estimates of the overall precision of the analytical method, including the dissolution process.



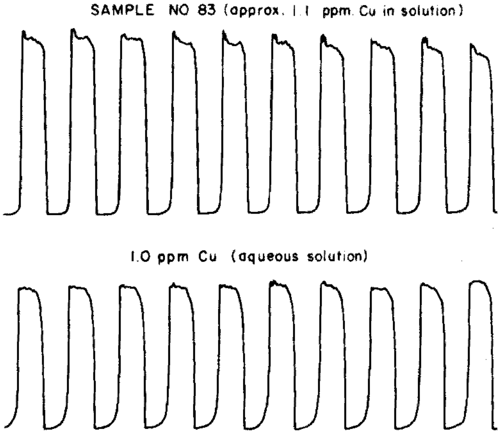


Fig. 3. The relative standard deviations of the assessed copper content of soil samples *versus* the assessed value for replicate determinations by the plasma technique.

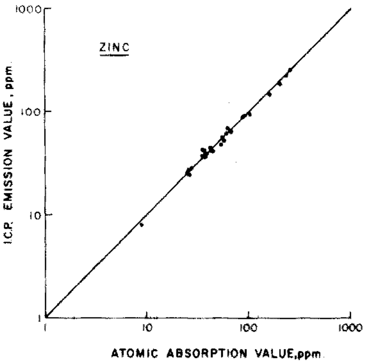
Fig. 4. Recorder tracings showing the reproducibility of measurements over a period of 20 min.

The reproducibility of an individual run is shown graphically in Fig. 4. In the upper trace, the signals are for copper in a typical soil sample and in the lower trace, for a 1-p.p.m. aqueous copper standard. Analyte and blank solutions were run alternately at 1-min intervals in each case.

The plasma detection limit (defined as the concentration necessary to produce a signal equal to 3 times the standard deviation of the background signal at the wavelength of the analysis line) for copper in pure aqueous solution was 0.002 p.p.m.

Zinc

The zinc line at 213.8 nm was found to be suitable for the determination of zinc in soils with the plasma source. As for copper, the readout signal was linearly proportional to the concentration over the full concentration range. Comparative results for the plasma study and the atomic absorption study are illustrated in Fig. 5. It can be seen that the results compare favourably. Since no serious interference effects have been reported for the atomic absorption determination of zinc in geological materials[17,22], it is reasonable to think that the plasma can be used with success for such determinations.



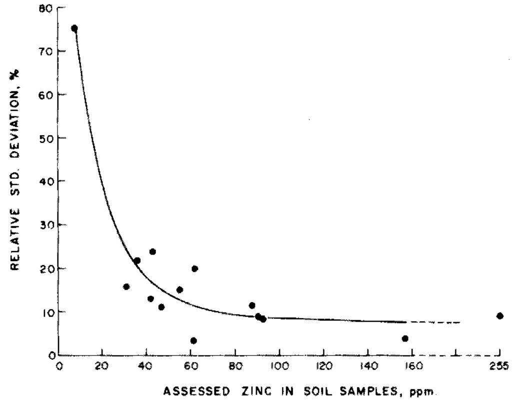


Fig. 5. Comparison of results, as in Fig. 2, for zinc.

Fig. 6. Relative standard deviations, as in Fig. 3, for zinc.

The line-to-background intensity ratio for zinc was rather poor; for an aqueous solution containing 0.5 p.p.m. Zn, the line-to-background ratio was only 0.10. The background signal, however, remained very stable. The plasma detection limit (as defined above) for zinc was 0.05 p.p.m. in pure aqueous solution.

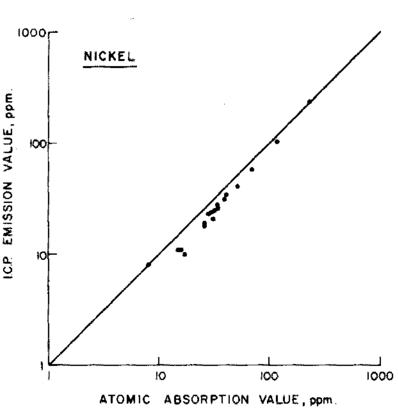
Figure 6 shows the relative standard deviations of the plasma results for various soil samples.

Nickel

Nickel concentrations in the soil solutions ranged from 0.14 p.p.m. to 4.8 p.p.m. A linear calibration curve was obtained for the nickel emission at 351.5 nm. Comparative results are illustrated in Fig. 7.

It can be noted that the concentration values obtained by the plasma technique are generally lower than those obtained by atomic absorption spectrometry. Nickel interferences have been reported in atomic absorption[17,22]. Govett and Whitehead[17] have shown that for low nickel concentrations, the presence of reasonably high concentrations (1000–5000 p.p.m.) of K, Na, Mg, Al, Ca and Fe in the solutions causes interferences. At 0 and 1 p.p.m. nickel, they showed that 3000 p.p.m. calcium gave an apparent nickel concentration of about 0.6 and 1.6 p.p.m. respectively, whereas at 10 p.p.m. nickel, the apparent concentration dropped slightly to 9.8 p.p.m.

Since most of the above elements are present in soil solutions in reasonably high concentrations, similar interferences very probably occurred in the atomic absorption nickel determinations.



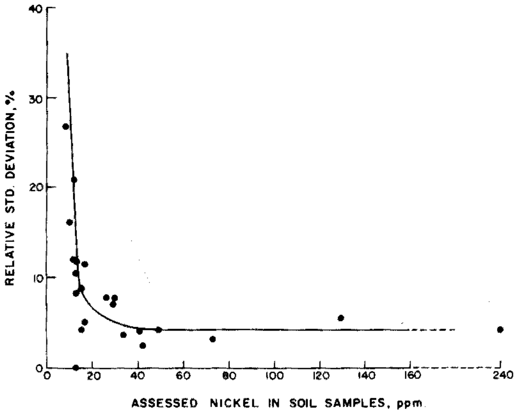


Fig. 7. Comparison of results, as in Fig. 2, for nickel.

Fig. 8. Relative standard deviations, as in Fig. 3, for nickel.

The plasma detection limit for nickel in pure aqueous solution was 0.01 p.p.m. The line-to-background intensity ratio for 0.5 p.p.m. nickel in aqueous solution was 1.0.

The precision of the plasma technique for the determination of nickel is shown in Fig. 8.

Cobalt

The cobalt line at 345.3 nm was used for the plasma study. Cobalt concentrations in the soil samples were in the range 4–40 p.p.m. (0.08–0.8 p.p.m. in the solutions). Linearity of instrumental response *versus* cobalt concentration was tested and confirmed.

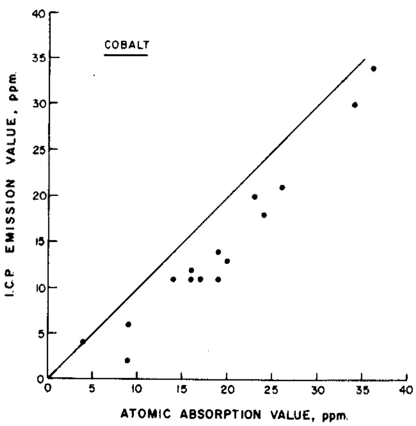
The results obtained by the atomic absorption and plasma emission methods are compared in Fig. 9. Although the atomic absorption technique has received wide acceptance as a suitable method for cobalt determinations in soils, it has nevertheless been shown that extraneous elements such as calcium and aluminium cause erroneous results for cobalt levels in the range 0–5 p.p.m. in solution[17,23]. As in the case of nickel, the differences between the plasma and atomic absorption values are probably caused by the presence of these elements in the soil solutions.

The precisions for the cobalt determinations with the plasma source are given in Fig. 10.

The plasma line-to-background intensity ratio for 0.5 p.p.m. cobalt in pure aqueous solution was 0.43, and the detection limit was 0.02 p.p.m.

Lead

This study commenced with the analysis of the soil samples at the 405.8-nm Pb line which appeared sufficiently sensitive for the determinations with the plasma source. The initial plasma values for the lead concentrations in the samples, however, were all higher than the atomic absorption values. In the worst case, where the atomic absorption value was very low (10 p.p.m.), the plasma value was higher by



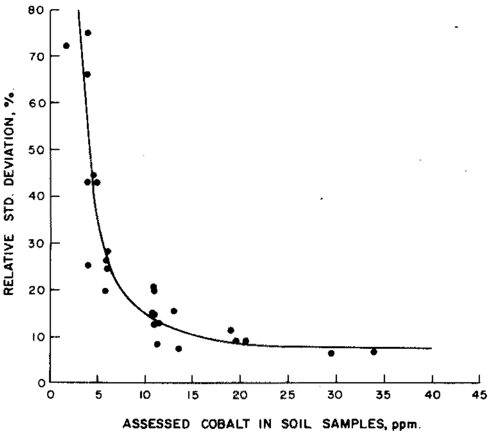


Fig. 9. Comparison of results, as in Fig. 2, for cobalt.

Fig. 10. Relative standard deviations, as in Fig. 3, for cobalt.

nearly 800%. Govett and Whitehead[17] have shown that lead is more subject to interferences by K, Na, Mg, Al, Ca and Fe in atomic absorption than any other trace element studied. (The order of interference of major elements was given as Fe > Ca > Al > Mg > Na > K). However, the reported interferences for lead in the concentration range of the solutions used for the present atomic absorption study are all enhancements. The fact that the plasma results were higher than the atomic absorption results showed that an even greater interference was present in the plasma study.

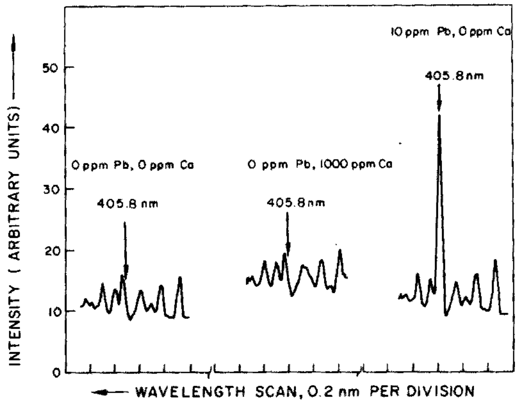
In further tests, the spectral interference of magnesium on lead due to the weak Mg line at 405.76 nm was examined, and the apparent lead concentration at 405.78 nm was assessed with Mg and Pb standards. It was found that the apparent lead content increased linearly from 0 to 1.2 p.p.m. as the magnesium concentration increased from *ca.* 30 to 800 p.p.m. When a correction was applied to the initial plasma lead values (which entailed analysing the soil solutions for magnesium), the plasma lead values decreased somewhat, but were still higher than the atomic absorption values.

No significant spectral interferences from iron or manganese could be found.

Several of the soil samples were then analysed by the standard addition method to assess whether any form of chemical interference was taking place in the plasma. Results of this study were, within experimental error, the same as before. The standard addition solutions were also run in atomic absorption, with similar results.

It was subsequently found that when a soil solution was sprayed into the plasma, the spectral background in the vicinity of the 405.8-nm emission increased relative to that of a pure aqueous standard. The background level was found to depend on the calcium concentration in the solution. Figure 11 shows the influence of 1000 p.p.m. calcium on the background intensity at 405.8 nm. The reason for this effect is not clear. To our knowledge, there is no calcium-band in the vicinity of 405.8 nm (a CaO band-head at 408.43 nm is degraded to the red), and the effect was not caused by second-order interference. This was established by placing a glass filter in front of the entrance slit to absorb the shorter wavelength radiation.

The apparent lead concentration in solution caused by the presence of calcium was measured for various concentrations; in this case, the apparent lead content increased almost rectilinearly from 0 to 2 p.p.m. as the calcium concentration increased from 0 to 1000 p.p.m. Then the calcium content of the soil solutions was measured (by the plasma method) in order to make the necessary corrections to the lead values. Final plasma lead values, after corrections for the above interferences, are compared to the atomic absorption values in Fig. 12. In some cases where the lead values are very low, the results obtained by this correction procedure may be meaningless. This undesirable situation may arise when the corrected lead concentration falls within the standard deviation of the apparent lead concentration.



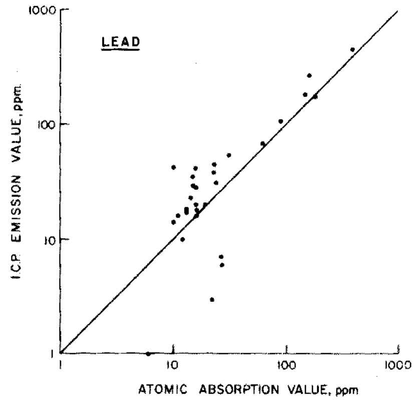


Fig. 11. Recorder tracings showing the influence of 1000 p.p.m. Ca on the spectral background intensity at 405.8 nm. Concentrations given are for aqueous solutions.

Fig. 12. Comparison of results, as in Fig. 2, for lead.

Attempts to use other lead spectral lines met with limited success. The 364.0, 283.3, 217.0 and 220.4-nm lines were investigated. The line-to-background ratios of these lines and the 405.8-nm lines are given, together with the detection limits, in Table IV. The sensitivities at the 283.3, 217.0 and 220.4-nm lines were too low for most of the soil samples, and only a few selected samples with higher atomic absorption lead values than the rest were analysed for comparison purposes. The results of this study are given in Table V. All the plasma results, except for two low (corrected) results at the 450.8-nm line, are higher than those obtained by atomic absorption. These differences are most likely caused by spectral interferences in the plasma study, owing to the inability of the 0.5-m monochromator to resolve nearby interfering matrix lines.

Comparison of results for the analysis of Co, Ni and Pb in synthetic samples

To examine the effect of various major elements on the determinations of cobalt, nickel and lead by the plasma and atomic absorption methods, synthetic "soil" solutions containing known concentrations of Co, Ni, Pb, Ca, Mg, Fe and Al of the

TABLE IV

LINE-TO-BACKGROUND RATIOS AND DETECTION LIMITS FOR VARIOUS LEAD SPECTRAL LINES

(Average values)

Wavelength (nm)	*Pb concentration (p.p.m.)*	*Line-to-background ratio*	*Detection limit*[a] *(p.p.m.)*
405.8	1.0	0.40	0.02
364.0	1.0	0.12	0.03
283.3	1.0	0.12	0.08
217.0	10.0	0.18	0.7
220.4[b]	10.0	0.64	—

[a] Detection limit defined as the concentration necessary to produce a signal equal to 3 times the standard deviation of the background signal at the wavelength of the analysis line.

[b] At an observation height of 10 mm in plasma. This decrease was necessary to increase the sensitivity at the 220.4-nm ion line. This was the sole exception to the earlier statement that experimental conditions remained unchanged throughout the study.

TABLE V

RESULTS FOR LEAD AT VARIOUS SPECTRAL LINES

(Average values)

Sample no.	*Plasma (p.p.m.)*					*A.a.s. (p.p.m.)*
	405.8 nm[a]	*364.0 nm*	*283.3 nm*	*217.0 nm*	*220.4 nm*[b]	
74	28	42	—	—	—	16
76	100	124	200	320	160	90
78	180	145	210	250	210	145
79	3	50	80	220	—	22
83	45	46	—	—	—	23
84	460	410	560	660	440	390
85	7	29	—	—	—	27
86	270	250	250	350	320	160

[a] Value corrected for Ca and Mg interference.

[b] At 10 mm observation height in plasma.

order found in the actual soil solutions were analyzed. The compositions of these synthetic solutions are given in Table VI.

Results of this investigation are given in Table VII. No significant interferences occurred in the plasma study in the cases of cobalt and nickel, whereas in the atomic absorption study, enhancements of up to 56% occurred for cobalt and up to 18% for nickel. The atomic absorption values for lead were also enhanced, but by no more than about 13%. The most serious interferences in the plasma study occurred in the case of lead, where 4 spectral lines were investigated in an attempt to find a suitable line free of interference. The 217.0-nm Pb line was not sufficiently

TABLE VI

COMPOSITION OF SYNTHETIC SOIL SOLUTIONS

Sample no.	*Concentration (p.p.m.)*						
	Co	*Ni*	*Pb*	*Ca*	*Mg*	*Fe*	*Al*
1	0.50	0.5	10.0	500	500	750	500
2	0.50	1.0	1.5	50	250	1000	750
3	0.50	5.0	2.5	750	250	0	500
4	0.25	0.5	2.5	1000	250	500	500

TABLE VII

RESULTS FOR THE ANALYSIS OF SYNTHETIC SOIL SOLUTIONS

(Average values; see Table VI for the actual values)

Sample no.	*Assessed concentration (p.p.m.)*								
	Plasma						*A.a.s.*		
	Co	*Ni*	*Pb*	*Pb*	*Pb*	*Pb*	*Co*	*Ni*	*Pb*
	345.3 nm	*351.5 nm*	*405.8[a] nm*	*217.0 nm*	*283.3 nm*	*364.0 nm*	*240.7 nm*	*232.0 nm*	*217.0 nm*
1	0.51	0.50	9.8	12.0	11.6	10.3	0.60	0.56	10.3
2	0.52	1.00	1.4	—	3.2	1.9	0.63	1.02	1.7
3	0.48	5.0	2.3	—	2.8	2.6	0.57	5.0	2.6
4	0.25	0.50	2.2	—	3.3	2.9	0.39	0.59	2.7

[a] Values corrected for Ca and Mg interference.

sensitive for the analysis of samples 2, 3 and 4. The line that produced the most accurate results without corrections was found to be 364.0 nm.

The corrected lead values obtained with the 405.8-nm line differed from the actual values by not more than 12%, which was considered to be a satisfactory result. It is apparent that iron and aluminium did not cause any significant interferences at 405.8 nm. The high lead values obtained with the 283.31-nm line could possibly be explained as having been due to a spectral interference by the iron line at 283.34 nm. Similarly, the reason for the incorrect values obtained for samples 2 and 4 with the 363.96-nm Pb line was probably an interference by the 364.04-nm Fe line. This latter interference was not as severe as the former. Measurements indicated that 1000 p.p.m. iron in solution produced an apparent lead concentration of 0.4 p.p.m. at 363.96 nm. This interference was negligible in the case of sample 1.

The above findings show that the differences between the plasma and atomic absorption values for nickel and cobalt in the various soil samples were mainly due to enhancement effects which occurred in the atomic absorption determinations, whereas the differences for lead were mainly due to spectral interferences in the plasma study.

CONCLUSION

The inductively coupled plasma has proved to be a suitable spectrometric source for the direct determination of Cu, Zn, Ni and Co in solutions of geochemical soil samples. A spectrometer with greater resolving power than that used for the plasma study is probably necessary in order to reduce spectral interferences in the case of lead, or spectral interference corrections have to be made. The latter procedure involves measuring the concentration of the interfering element(s) in the soil sample, depending on which analysis line is chosen. This can easily be accomplished if a multichannel spectrometer is used. Cu, Zn, Ni, Co, Pb and the interfering element(s) could thus be determined simultaneously.

The precision of the plasma technique could possibly be improved by the use of signal integration instead of the present readout system, and also by using a lower sample dilution factor for simultaneous multi-element analyses, where a smaller volume of sample solution would suffice. The use of an integrator could also result in a lowering of the detection limits of the elements studied.

The authors wish to thank Mr. S. Geldenhuis of McLachlan and Lazar (Pty) Ltd for providing some of the soil samples and the atomic absorption analyses thereof.

SUMMARY

The application of the inductively coupled plasma as an emission source for the spectrometric determination of Cu, Zn, Ni, Co and Pb in geochemical soil samples is presented. Comparative results obtained by the flame atomic absorption technique are given. Values compare favourably in the case of Cu and Zn, but not in the case of Ni, Co and Pb. Interference effects in atomic absorption may account for some of these differences.

REFERENCES

1 V. A. Fassel, *XVI Colloquium Spectrosc. Int., Reprints*, Plenary Lectures, Hilger, London, 1972, p. 63.
2 S. Greenfield, I. L. Jones, H. M. McGeachin and P. B. Smith, *Anal. Chim. Acta, in press.*
3 P. W. J. M. Boumans and F. J. de Boer, *Spectrochim. Acta, Part B*, 27 (1972) 391.
4 G. F. Larson, V. A. Fassel, R. H. Scott and R. N. Kniseley, *Anal. Chem.*, (1974), in press.
5 F. J. de Boer and P. W. J. M. Boumans, *XVII Colloquium Spectrosc. Int., Reprints*, Vol. 1, 1973, p. 107.
6 R. H. Scott, *Rep. Fis. 51*, National Physical Research Laboratory, CSIR, Pretoria, South Africa, 1974, p. 1.
7 P. W. J. M. Boumans, H. Wagenaar and F. J. de Boer, *XVII Colloquium Spectrosc. Int., Reprints* Vol. 1, 1973, p. 114.
8 D. J. Kalnicky, R. N. Kniseley and V. A. Fassel, *Spectrochim. Acta*, in press.
9 J. F. Alder and J. M. Mermet, *Spectrochim. Acta, Part B*, 28 (1973) 421.
10 P. W. J. M. Boumans and F. J. de Boer, *Spectrochim. Acta*, in press.

11 R. M. Dagnall, D. J. Smith, T. S. West and S. Greenfield, *Anal. Chim. Acta*, 54 (1971) 397.
12 S. Greenfield and P. B. Smith, *Anal. Chim. Acta*, 59 (1972) 341.
13 R. N. Kniseley, V. A. Fassel and C. C. Butler, *Clin. Chem.*, 19 (1973) 807.
14 D. E. Nixon, V. A. Fassel and R. N. Kniseley, *Anal. Chem.*, 46 (1974) 210.
15 H. E. Hawkes and J. S. Webb, *Geochemistry in Mineral Exploration*, Harper and Row, New York, 1962, p. 19.
16 N. H. Brundin, *The Spex Speaker*, 18 (1973) 3.
17 G. J. S. Govett and R. E. Whitehead, *J. Geochem. Explor.*, 2 (1973) 121.
18 R. H. Scott, V. A. Fassel, R. N. Kniseley and D. E. Nixon, *Anal. Chem.*, 46 (1974) 75.
19 E. Kranz, *Spectrochim. Acta, Part B*, 27 (1972) 327.
20 T. Allen and A. A. Khan, *Chem. Eng. (London)*, May (1970) CE 108.
21 B. Farrar, *At. Absorption Newslett.*, 4 (1965) 325.
22 W. Slavin, *Atomic Absorption Spectroscopy*, Interscience, New York, 1968, p. 103.
23 A. M. Ure and R. L. Mitchell, *Spectrochim. Acta*, Part B, 23 (1967) 79.

Analytica Chimica Acta, 70 (1975) 271–279

ÉTUDE DES INTERFÉRENCES DANS UN PLASMA INDUIT PAR HAUTE FRÉQUENCE

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Nous travaillons en analyse par émission atomique à partir de solutions aqueuses en utilisant comme source d'excitation un plasma induit par haute fréquence[1–4]. Cette source conduit en général a de bonnes limites de détection[5,6] aussi bien sur les éléments facilement excitables que sur les éléments réfractaires ou donnant des oxydes réfractaires, notamment sur les terres rares. Ces limites sont généralement meilleures que celles obtenues par l'absorption atomique classique.

Cela nous a conduit à étudier les interférences (déviation systématique d'un signal due à la présence d'un corps) qui peuvent se produire dans le cas de mélanges de plusieurs éléments. Ces interférences peuvent être classées en deux grandes catégories: d'une part les interférences spectrales qui ont lieu lorsqu'on ne peut séparer une raie de l'élément à analyser d'une raie ou bande due à la source ou à un autre élément, et d'autre part les interférences dues à l'effet de matrice qui se divisent en deux groupes:

(1) interférences chimiques dues à la formation d'un complexe suffisamment stable pour n'être détruit qu'en partie au cours du passage dans la flamme;

(2) interférences d'ionisation dues à la présence d'éléments de faible énergie d'ionisation, présence qui a pour effet, en principe, d'augmenter la densité électronique du milieu, donc de modifier la répartition entre atomes ionisés et neutres ce qui change l'intensité des raies d'analyse.

C'est à ces deux derniers types d'interférences que nous nous sommes intéressés.

PARTIE EXPÉRIMENTALE

Appareillage

La générateur haute fréquence est de marque S.T.E.L. de 6 kW de puissance appliquée fonctionnant à une fréquence de 5,4 MHz.

Le four à plasma est composé d'une bobine d'induction de trois spires en tube de cuivre de 4 mm de diamètre extérieur, refroidie par circulation d'eau et qui sert à fournir l'énergie nécessaire à ioniser le gaz plasmagène qui la traverse grâce à une tête d'injection. Celle-ci est composée de deux tubes concentriques en silice de diamètre extérieur et intérieur respectivement de 30 et 27 et de 22 et 18 mm. L'alimentation en gaz plasmagène (argon) se fait tangentiellement.

Optique. Monochromateur SOPRA, type Ebert–Fastié, de 2 m de longueur focale, réseau holographique Jobin–Yvon de 160 mm de diamètre et de 2400 traits par mm. Photomultiplicateur EMI 6256 S. Zone d'observation comprise entre la sortie du tube extérieur et 1 cm au dessus.

Introduction d'échantillons

Les solutions aqueuses sont nébulisées par ultrasons[7] puis séchées par passage dans un four infrarouge et déssolvatées lors de la traversée d'un réfrigérant qui recondense le solvant[2,5]. L'échantillon pénètre dans le plasma à l'aide d'un injecteur métallique refroidi par eau, de 2 mm de diamètre intérieur.

Debits de gaz. 7 l min^{-1} au démarrage, 20 l min^{-1} en fonctionnement normal, pour le débit extérieur, 6 l min^{-1} pour le débit intérieur et 1,5 l min^{-1} pour le débit d'injection.

INTERFERENCES CHIMIQUES

De nombreux auteurs ont montré que la température atteinte dans un plasma h.f. et le temps de séjour élevé des particules avaient pour effet de rendre négligeable ce type d'interférence. Fassel[8] dans un article de présentation sur les flammes électriques a fait les comparaisons entre les différents auteurs sur les interférences du phosphate sur le calcium et de l'aluminium sur le calcium. Souilliart[2] sur notre appareillage, confirme l'absence d'influence de l'aluminium sur le calcium. Nous même n'avons observé qu'une légère influence du phosphate sur le barium (Fig. 1). C'est donc un des avantages du chalumeau à plasma h.f. de rendre négligeable ce type d'interférences.

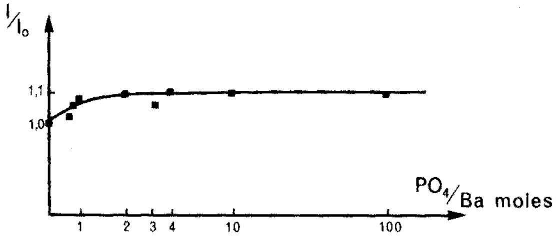


Fig. 1. Interférence de l'ion phosphate sur le barium.

INTERFERENCES D'IONISATION

Les quelques auteurs qui ont étudié l'influence d'éléments tels que le césium, le potassium et le sodium sur l'émission d'autres éléments à énergie d'ionisation plus élevée, ont constaté qu'il y avait généralement interférence, celle-ci étant variable suivant le type de générateur à plasma utilisé.

Schirrmeister[9] a constaté dans un plasma arc du type Kranz[10] que la présence d'ions potassium, qui devrait avoir pour effet d'augmenter la densité électronique, modifie le rapport nombre d'atomes neutres sur nombres d'atomes ionisés du magnésium dans le sens d'une diminution de la densité. La température mesurée par rapport d'intensité des raies du cuivre ne varie pas avec la teneur en potassium. Valente et Schrenk[11] indique une influence non précisée du potassium sur le calcium. Kliska et Marinkovic[12], également sur un plasma arc, a étudié l'influence du potassium et du sodium sur l'aluminium et le lithium. L'émission passe par un maximum et décroit. A ce maximum correspond un minimum d'émission de l'argon plasmagène. Polatbekov et coll.[13] toujours sur un plasma arc, constate une diminution de la température et une modification de la répartition des atomes de chrome en présence de sodium. Murayama[14] sur un plasma 2450 MHz a noté une influence du sodium sur l'émission des terres rares. Il observe une augmentation importante du signal, qui est interprétée par une variation de la température et une diffusion des particules. Kitagawa et Takeuchi[15] a constaté, également sur un plasma 2450 MHz, que le barium, le strontium et le calcium abaissent le degré d'ionisation du manganèse. Kirkbright et coll.[16] sur un plasma h.f. a étudié l'interférence de plusieurs éléments sur le phosphore. Il a constaté que le potassium, le magnésium, le sodium et le zinc n'ont pas d'influence alors qu'il observe une augmentation du signal avec l'aluminium, le calcium, le cobalt, le fer, le nickel et le zinc. Boumans et coll.[17] a remarqué une légère influence du lithium sur la densité électronique d'un plasma h.f. d'argon, la température ne variant pratiquement pas. Il est donc difficile de donner une règle générale de variation: celle-ci semble dépendre, dans une large mesure, de l'appareillage utilisé.

Théorie

L'intensité d'une raie atomique est une fonction de la densité d'atomes dans l'état d'ionisation considéré et de la température. Nous avons mesuré cette dernière[18], aussi bien sur l'argon que sur des éléments excités (fer et titane). Nous obtenons dans les deux cas, une température de 6000 ± 500 K dans la zone d'observation. Pour connaitre la densité d'atomes, on utilise habituellement l'équation de Saha qui donne la relation entre la densité électronique n_e et les densités n_q et n_{q+1} des atomes dans deux états d'ionisation successifs q et $q+1$:

$$\frac{n_e n_{q+1}}{n_q} = 4{,}825 \cdot 10^{15} \frac{Z_{q+1}}{Z_q} T^{\frac{3}{2}} \mathrm{e}^{-((E_i - \Delta E_i)/kT)}$$

Z_q et Z_{q+1} étant les fonctions de partition, T la température absolue, k la constante de Boltzmann, E_i l'énergie d'ionisation entre l'état q et $q+1$ et ΔE_i la correction due aux microchamps électriques dans le plasma[19].

Dans le cas d'un mélange de plusieurs constituants dans plusieurs états d'ionisation successifs, il est nécessaire d'écrire une relation plus générale que nous avons établie avec Jarosz[20]. En appliquant l'équation de conservation de la matière, celle de la neutralité électrique et en définissant le rapport R_α comme étant celui des densités des atomes de l'élément α par rapport à l'élément 1, nous obtenons une relation de la forme suivante, pour v constituants ayant L_α états d'ionisation i à la pression P:

$$n_e = \frac{P}{kT} \frac{\sum_{\alpha=1}^{v} R_\alpha (B_\alpha/(1+A_\alpha))}{\sum_{\alpha=1}^{v} R_\alpha + \sum_{\alpha=1}^{v} R_\alpha (B_\alpha/(1+A_\alpha))}$$

avec

$$A_\alpha = \sum_{i=1}^{L_\alpha} n_e^{-i} \prod_{u=1}^{i} S_{u.\alpha}$$

$$B_\alpha = \sum_{i=1}^{L_\alpha} i n_e^{-i} \prod_{u=1}^{i} S_{u.\alpha} \quad \text{ou} \quad S_{u.\alpha} = \frac{n_{u.\alpha} n_e}{n_{u-1.\alpha}}$$

Cette mise en équation plus générale permet d'accéder aux densités des particules neutres $n_{0.\alpha}$ et ionisées $n_{i.\alpha}$:

$$n_{0.\alpha} = \left[\frac{P}{kT} - n_e\right]\left[\frac{R_\alpha}{\sum_{\alpha=1}^{v} R_\alpha}\right]\left[\frac{1}{1+A_\alpha}\right]$$

$$n_{i.\alpha} = \left[\frac{P}{kT} - n_e\right]\left[\frac{R_\alpha}{\sum_{\alpha=1}^{v} R_\alpha}\right]\left[\frac{n_e^{-i} \prod_{u=1}^{i} S_{u.\alpha}}{1+A_\alpha}\right]$$

Le calcul de n_e, puis des densités de particules, se fait de façon itérative à l'aide d'un programme Fortran sur IRIS 80.

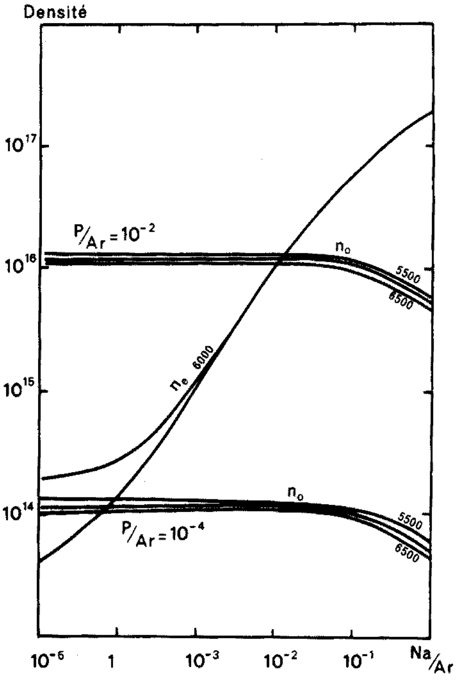


Fig. 2. Densités théoriques des particules neutres du phosphore et densité électronique dans le mélange Ar–Na–P.

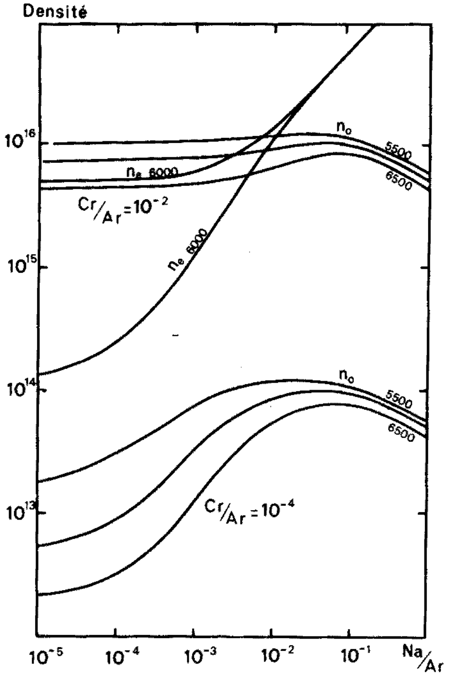


Fig. 3. Densités théoriques des particules neutres du chrome et densité électronique dans le mélange Ar–Na–Cr.

Calcul

Nous avons pris le sodium ($E_i = 5,14$ eV) comme élément interférant sur le phosphore ($E_i = 10,49$ eV) et sur le chrome ($E_i = 6,76$ eV) avec des rapports R_α pour P/Ar et Cr/Ar compris entre 10^{-2} et 10^{-4}, l'élément $\alpha = 1$ étant l'argon. Ces rapports encadrent la concentration expérimentale qui est de l'ordre de grandeur de 10^{-3} en pulvérisant une solution à 1 μg ml^{-1} à 0,5 ml min^{-1}. Nous avons fait les calculs pour 5500, 6000 et 6500 K. Sur les Figs. 2 et 3, nous avons tracé les courbes des densités qui nous interéssaient, en fonction de la concentration en sodium, c'est à dire la densité électronique et la densité des atomes neutres, l'intensité d'une raie I étant proportionelle à cette dernière densité, à température constante. Nous voyons donc sur ces graphes qu'il devrait y avoir augmentation de la densité électronique quand la teneur en sodium augmente. De plus l'influence sur l'émission du phosphore devrait être négligeable. Par contre celle sur le chrome devrait se traduire par une augmentation du signal.

Résultats expérimentaux

Nous avons fait varier la concentration en sodium de 10^{-2} à 10^{3} μg ml^{-1} pour un débit d'aérosol de 0,5 ml min^{-1}. Nous avons travaillé sur la raie 4254,3 I du chrome et 2535,6 I du phosphore (dans le second ordre du réseau pour cette dernière). Sur la Fig. 4 nous indiquons les résultats trouvés pour deux concentrations du phosphore (100 et 500 μg ml^{-1}) et du chrome (50 et 500 μg ml^{-1}) en indiquant la variation relative du signal par rapport à l'intensité mesurée en l'absence de sodium. Nous pouvons observer que si l'influence du sodium sur le chrome est faible, elle est par contre plus importante (multiplication du signal par 2,4) dans le cas du phosphore, ce qui est contraire aux calculs obtenus à partir de l'équation de Saha.

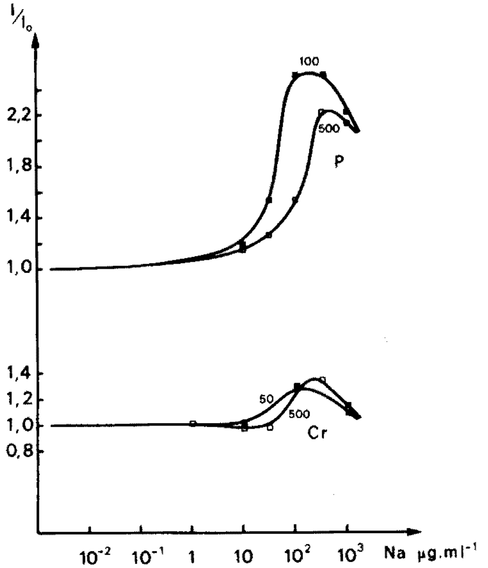


Fig. 4. Variations du signal de la raie 2535 I du phosphore et de la raie 4254 I du chrome en fonction de la concentration en sodium.

Etude de la densité électronique et de la température. Du fait de ce désaccord nous avons voulu savoir si la présence de sodium avait une action sur la densité électronique et sur la température. Pour étudier la variation de la densité, nous avons utilisé le magnésium (1 μg ml^{-1}) comme élément test en mesurant le rapport de deux raies dans deux états d'ionisation successifs (raies 2852 I et 2802 II), la densité électronique étant proportionnelle à ce rapport. De même, pour suivre l'évolution de la température, nous avons utilisé le titane (10 μg ml^{-1}) en mesurant le rapport de deux raies dans le même état d'ionisation (3222 II et 3224 II), la température étant une fonction de ce rapport. Les résultats obtenus en fonction de la concentration en sodium figure sur le Tableau I.

TABLEAU I

LES RAPPORTS DE DEUX RAIES EN FONCTION DE LA CONCENTRATION EN SODIUM

Concentration de Na (μg ml^{-1})	$\frac{I_{2852}}{I_{2802}}$	$\frac{I_{3222}}{I_{3224}}$
0	0,065	2,61
0,01	0,061	
0,1	0,063	2,56
0,5	0,066	
1	0,064	2,52
5	0,060	
10	0,062	2,52
100	0,064	2,62
200	0,060	
500		2,40
1000	0,063	2,64

Nous observons d'une part que la variation de température n'est pas significative en fonction de la concentration en sodium (la différence entre 2,4 et 2,6 représentant 160 K) et d'autre part que la variation du rapport du nombre d'atomes neutres sur le nombre d'atomes ionisés est également très faible. Cela signifie qu'en pratique, au moins jusqu'à 10^3 μg ml^{-1} de sodium, cet élément ne modifie pas de façon appréciable la densité électronique et la température du milieu plasmagène. L'équation de Saha ayant les deux paramètres densité et température ne variant pas, ne peut plus être appliquée dans ce cas. Ce qui explique qu'il n'y ait pas concordance entre les résultats calculés par cette équation et les résultats expérimentaux.

Nous avons également vérifié (Fig. 5) que l'influence du sodium sur l'émission d'argon était peu sensible, en utilisant la raie 4259 I. L'intensité figurant sur le graphe est l'intensité radiale obtenue par l'inversion d'Abel à partir de l'intensité expérimentale[21]. On sait en effet que du fait du gradient élevé de température, l'intensité mesurée expérimentalement n'est qu'une intensité moyenne et qu'il faut effectuer un traitement mathématique pour remonter à l'intensité en un point.

Nous avons également vérifié que la variation du signal ne provenait pas d'un changement dans la répartition des particules dans le plasma. Nous donnons sur les Figs. 6, 7, l'étude sur le phosphore. Sur la Fig. 6 nous indiquons l'évolution de l'intensité expérimentale en fonction de la concentration en sodium et sur la Fig. 7,

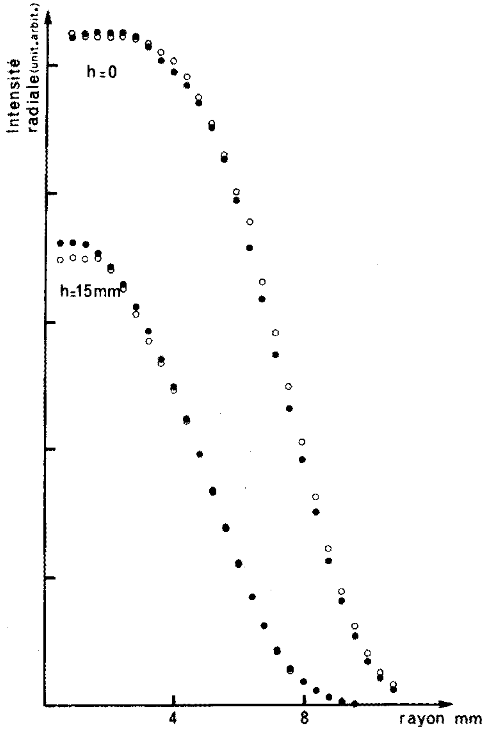
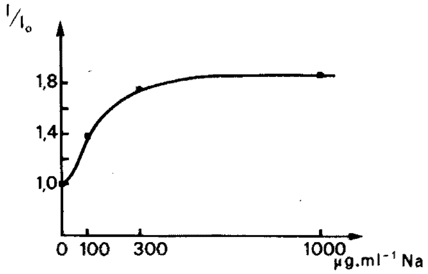


Fig. 5. Étude de l'interaction du sodium sur la raie 4259 Ar I. (○) Ar; (●) Ar + $10^3 \mu g$ Na ml^{-1}.



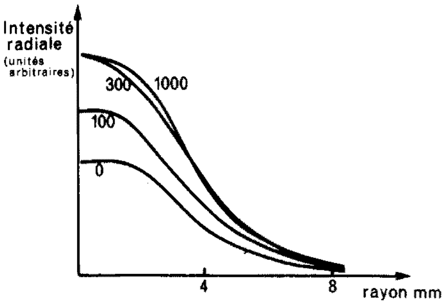


Fig. 6. Influence du sodium sur l'intensité expérimentale avant inversion de la raie 2535 I.

Fig. 7. Répartition radiale à la sortie du tube de la raie 2535 I en fonction de la concentration en sodium.

la répartition de l'émission de la raie 2535 dans le plasma en fonction du rayon. Nous pouvons observer que l'augmentation du signal se retrouve sur toute la largeur du plasma et qu'il n'y a donc pas modification de la répartition des particules.

CONCLUSION

A la différence d'une source classique comme la flamme chimique, nous n'avons pas constaté que la présence d'un élément électrophile modifie la densité électronique du milieu plasmagène, et de ce fait, qu'il soit la cause de l'évolution des raies de certains éléments (nous n'avons trouvé aucune influence expérimentale sur le cuivre, l'aluminium, le barium et sur les terres rares comme le samarium).

Ces résultats sont à rapprocher des mesures de températures et de densité électronique effectuées par ailleurs[18] et qui montrent que l'équilibre thermodynamique local (e.t.l.) n'est pas vérifié dans la source utilisée. De ce fait, il n'est pas surprenant que le comportement des mélanges étudiés ne puisse être interprété quantitativement à l'aide de l'équation de Saha, puisque, en toute rigueur, celle-ci ne peut être appliquée que dans les conditions de l'e.t.l.

Les seules variations possibles de la densité électronique que nous ayons obtenues avec notre appareillage, et encore dans une faible mesure, proviennent de modifications du champ électrique et non de la composition du milieu plasmagène.

RÉSUMÉ

Une étude des interférences chimiques et d'ionisation a été réalisée dans un plasma induit par haute fréquence utilisé comme source d'excitation en spectroscopie atomique. Du fait de la température élevée (6000 K), les interférences chimiques sont négligeables. Les interactions produites par la présence de sodium (exaltation du signal du phosphore et plus faiblement du chrome, non influences sur d'autres éléments) ne peuvent s'expliquer par un changement de l'équilibre des particules dans le plasma (loi de Saha), la densité électronique et la température mesurées en fonction de la concentration en sodium ne variant pas de façon appréciable.

SUMMARY

Chemical and ionization interferences were studied in a high-frequency induction plasma, used as spectroscopic source. As the temperature is high (6000 K), chemical interferences are negligible. Some interactions caused by sodium (enhancement of the phosphorus line and, more weakly, the chromium line, no influences on other elements) cannot be explained by a change of particle equilibrium in the plasma (Saha's equation): electronic density and temperature, measured against concentration of sodium do not vary appreciably.

BIBLIOGRAPHIE

1 J. M. Mermet et J. Robin, *XIV Colloq. Spectrosc. Intern., Debrecen*, 2 (1967) 715.
2 J. C. Souilliart, Thèse, Lyon, 1972.
3 N. Rosa-Brussin, Thèse, Lyon, 1971.
4 J. F. Alder et J. M. Mermet, *Spectrochim. Acta, Part B*, 28 (1973) 421.
5 J. C. Souilliart et J. P. Robin, *Analusis*, 1 (1972) 427.
6 R. H. Scott, V. A. Fassel, R. N. Kniseley et D. E. Nixon, *Anal. Chem.*, 46 (1974) 75.
7 J. M. Mermet et J. P. Robin, *Anal. Chem.*, 40 (1968) 1918.
8 V. A. Fassel, *XVI Colloq. Spectrosc. Intern., Heidelberg, Conférence plénière*, (1971) 63.
9 H. Schirrmeister, *Spectrochim. Acta, Part B*, 23 (1968) 709.
10 E. Kranz, Thèse, Iéna, 1967.
11 S. E. Valente et W. G. Schrenk, *Appl. Spectrosc.*, 24 (1970) 197.
12 M. Kliska et M. Marinkovic, *Spectrochim. Acta, Part B*, 25 (1970) 545.

13 P. P. Polatbekov, K. B. Zhukov et I. A. Mukatov, *Vop. Obshch. Prikl. Fiz. Tr. Respub. Konf.*, (1967) 197.
14 S. Murayama, *Spectrochim. Acta, Part B*, 25 (1970) 191.
15 K. Kitagawa et T. Takeuchi, *Anal. Chim. Acta*, 67 (1973) 453.
16 G. F. Kirkbright, A. F. Ward et T. S. West, *Anal. Chim. Acta*, 62 (1972) 241; 64 (1973) 353.
17 P. W. J. M. Boumans, H. Wagenaar et F. J. de Boer, *XVII Colloq. Spectrosc. Intern., Florence*, 1(1973) 114.
18 J. M. Mermet, *Spectrochim. Acta, Part B*, à paraître.
19 H. W. Drawin et P. Felenbock, *Data for plasmas in local thermodynamic equilibrium*, Gauthier–Villars, Paris, 1965.
20 J. Jarosz, J. M. Mermet et J. Robin, *C.R. Acad. Sci. Ser. B*, 278 (1974) 885.
21 J. M. Mermet et J. Robin, *Rev. Int. Hautes Temp. Refract.*, 10 (1973) 133.

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THE DETERMINATION OF MERCURY AT PICOGRAM/LITRE LEVELS IN WATER WITH A MICROWAVE-INDUCED ARGON PLASMA EMISSION SYSTEM

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The accurate determination of mercury in trace and ultra-trace quantities has recently attained considerable importance as a result of the establishment of the toxic nature of this element. Because it is now often necessary to establish mercury levels in unpolluted areas for base line studies, extreme sensitivity of the analytical technique is required. During recent years, methodology for mercury determination has centred around variations of the cold vapour technique of Hatch and Ott[1].

Gilbert and Hume[2], Brandenburger and Bader[3] and Robinson *et al.*[4] have all attempted to increase the sensitivity of this technique. Kalb[5] reported a method for collecting the mercury liberated from solution, after reduction with tin(II) chloride on silver foil. This mercury is subsequently released by heating the foil in an induction furnace. Head and Nicholson[6] modified this process for geological samples by using gold wire clippings and a resistance furnace to liberate the amalgamated mercury. Long *et al.*[7] used silver wool to collect mercury from ambient air, again using a resistance furnace to liberate the mercury. In each case mercury vapour was passed into an absorption cell to be measured.

The analytical technique developed during the course of this study is based on a microwave-induced argon plasma emission system. This system was combined with a collection stage where mercury, released by tin(II) chloride reduction of water samples, was amalgamated onto silver wool, contained in quartz amalgamation tubes.

PRELIMINARY STUDIES

Calibration

Initial experiments to determine the sensitivity of the method used by Kalb[5] were carried out with a Varian-Techtron Atomic Absorption Spectrometer, Model AA 1200 with a mercury analysis accessory. Known quantites of mercury-saturated air were injected into an absorption cell, by a hypodermic syringe, the flow rate of the carrier gas being optimized. At its most sensitive this system was able to detect 2 ng of mercury. However, the difficulty of injecting similar small amounts of mercury led to low precision at these values. When the analytical limit for calibration had been determined by the injection method, it was necessary to compare this with a preconcentration method based on quartz amalgamation tubes. These 12 cm long tubes (QAT's) were prepared from 9 mm o.d., 7 mm i.d. quartz tubing; 250 mg of silver wool was packed in a central 2-cm constricted zone. A 20% tin(II) chloride solution in (1+4) hydrochloric acid was used as the reducing agent.

For initial calibration, known concentrations of mercury standards were added to 100 ml of deionized water and 5 ml of tin(II) chloride solution contained in a Dreschel bottle. This mixture was allowed to react for 1 min, after which time the solution was passed through a QAT where the mercury was amalgamated. The amalgamation tube was disconnected after 2 min and the procedure repeated. In this way a series of amalgamation tubes for calibration was built up.

The amalgamation tubes were subsequently connected to the inlet side of the Varian mercury absorption cell in the optical path of the spectrometer, and heated with a Meker burner (a resistance furnace was used for later experiments). Mercury was released from the silver wool and flushed with the carrier argon into the absorption cell. Peak absorption measurements were recorded on a chart recorder. It was again found that flow rate was very critical. Too fast a flow through the cell gave calibrations similar to those of Fig. 1(A). However, a 600 ml min^{-1} flow was found to be optimal (Fig. 1(B)).

The analytical limit of this method was approximately 0.5 ng of mercury.

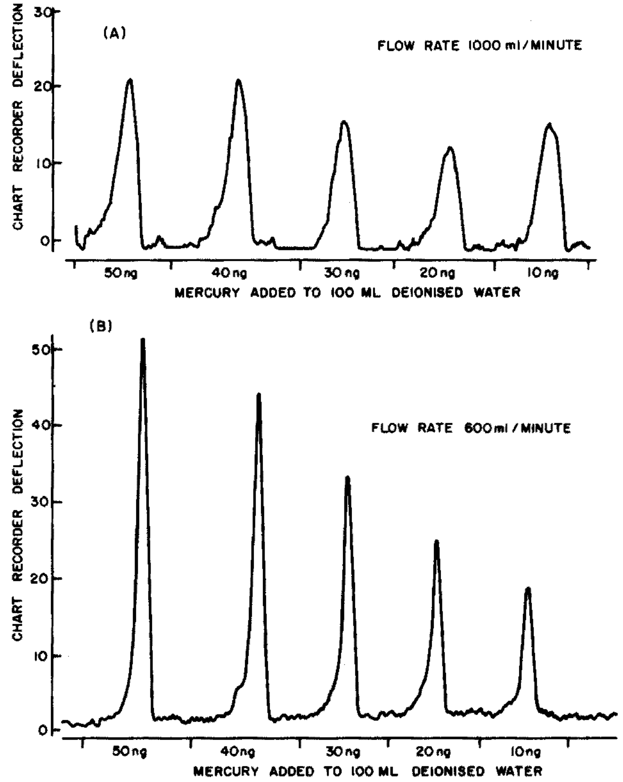


Fig. 1. Effect of argon flow-rate on mercury calibration.

Mercury collection

In order to obtain evidence as to the effectiveness of silver wool as an amalgamating agent, the two calibration methods of direct injection and amalgamation followed by heating to release the mercury, were compared. Because there was a difference in the time required for each analysis between the two methods it was decided to compare the calibrations on the basis of integrated peak area rather than peak height. Figure 2 illustrates this comparison; it is clear that at amounts below 15 ng, collection of the mercury by the silver is 100% efficient, but at 30 ng, amalgamation appears to be only 73% efficient. The efficiency could be increased by increasing the amount of silver in each QAT and by increasing the path length over which the mercury was in contact with the silver. If high levels are expected, it is also possible to arrange QAT's in series with each other and combine analyses for the final values. However, for these experiments the given size of each QAT was found to be optimal, and silver wool was considered an excellent mercury collector.

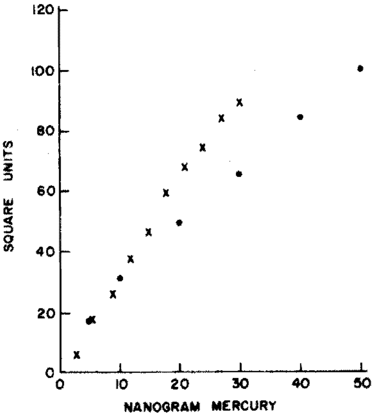


Fig. 2. Effectiveness of silver wool as a mercury amalgamator. Calibration based on peak areas. (×) Pulse. (●) Amalgamation.

Storage of standards

Extensive research has been undertaken to determine the effect of storage on dilute mercury solutions. Benes and Rajman[8] studied mercury adsorption onto polythene and found that a 5-day old mercury(II) solution lost 85% of its original 6 μg Hg l^{-1}. Benes[9] found considerable adsorption on a sial glass surface. Rosain and Wai[10] also tested several containers. Feldman[11] tested various media (HNO_3, $H_2SO_4+KMnO_4$, $K_2Cr_2O_7$, and $HNO_3+K_2Cr_2O_7$) for keeping mercury(II) solutions at strength. The author has also experimented with three solutions in Pyrex containers: (i) 10% HNO_3; (ii) 0.05% $KMnO_4+1\%$ H_2SO_4; (iii) 0.05% $KMnO_4$.

The results of these tests over a 12-day period are summarized in Fig. 3. The mechanisms for the behaviour seen in Figs. 3(B) and 3(C) have been discussed by Feldman[11]. On the basis of these experiments, 10% nitric acid was used to store dilute mercury solutions. It is worth noting that a 100 μg Hg l^{-1}

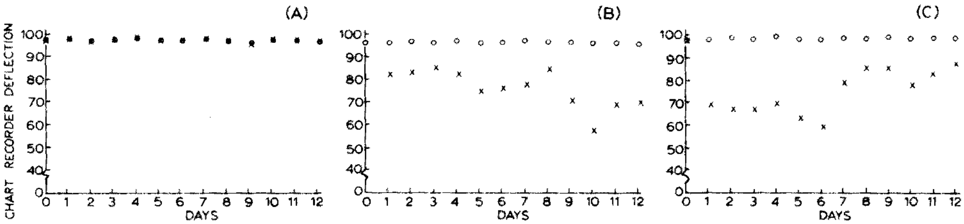


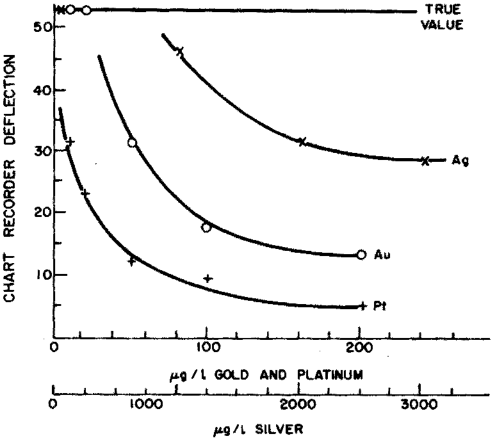
Fig. 3. The effect of three storage media on dilute mercury solution. (A) 10% HNO_3; (B) 0.05% $KMnO_4 + 1\%\ H_2SO_4$; (C) 0.05% $KMnO_4$. (○) Fresh 100 μg/l standard in 10% HNO_3, (×) stored 100 μg/l standards in A, B and C.

solution thus stored gave readings identical to those of a freshly prepared standard after 162 days.

During this investigation several metals were tested for interference on mercury release from solution. Iron, copper, zinc, manganese, lead, potassium, sodium, calcium and magnesium showed no interference on a 10 $\mu g\ Hg\ l^{-1}$ solution when present in quantities varying from 10 to 10^5 $\mu g\ ml^{-1}$. However, silver, gold and platinum had a marked effect. Figure 4 shows the effect of the interference of these metals on mercury release.

The tin(II) chloride probably reduces both the gold and platinum compounds to their respective metals with consequent adsorption or amalgamation of part of the released mercury. Silver, on the other hand, forms colloidal silver chloride, which adsorbs some of the mercury. However, the likelihood of such concentrations of gold, platinum or silver occurring in natural waters is considered negligible.

By using the method described in association with atomic absorption techniques, it was possible to obtain reproducible values down to levels of 0.5 ng Hg l^{-1} in both sea and fresh water. This level was, however, not sensitive enough for background monitoring in unpolluted areas and consequently a more sensitive technique was developed.



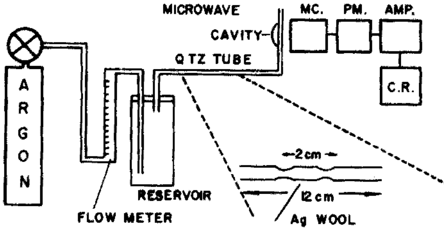


Fig. 4. Interference of gold, platinum and silver on mercury release from solution after tin(II) reduction.

Fig. 5. Microwave plasma flow diagram.

THE MICROWAVE PLASMA

Lichte and Skogerboe[12] describe a method based on a microwave plasma where mercury reduced by tin(II) chloride is passed, after drying, into a plasma flame and the emission signal is recorded. Their method gives a detection limit, defined as the amount of mercury required to produce a signal twice the standard deviation of the background, of $6 \cdot 10^{-11}$ g. This is one order of magnitude better than the atomic absorption values already described, and although this represents a significant increase in the detection limit, it was not considered sufficiently sensitive for our analytical requirements.

The microwave plasma system subsequently developed produced a flame-like plasma by using a 200-W medical microwave generator of the type generally used for electrodeless discharge lamps.

A 1/4-wave Evenson cavity was positioned on the optical axis of a Varian-Techtron spectrometer. A 16-cm quartz tube, 5 mm o.d. and 3 mm i.d., was placed at the discharge point and connected to the QAT as shown in Fig. 5. A sharp flame-like plasma could be ignited from the front of the tube when argon was passed through the tube. This plasma has an extremely high electron temperature in spite of its relatively low gas temperature. When mercury vapour passes into this plasma, the mercury spectrum is excited.

A spectral scan was made of the mercury emission from 200–600 nm when a steady stream of mercury vapour was passed through the system. The Hg 253.65-nm line was found to be sharp and free of background. The discharge was also found to be extremely constant with a variation of peak deflection of only ±1% over 30 min and ±2% over 1 h.

Calibration of the argon plasma flame

A similar procedure to that used for calibrating the atomic absorption system was used for the plasma flame. The carrier gas flow was once again found to be critical (650–700 ml min^{-1}). Once the system had been optimized, however, excellent calibration graphs were obtained (Fig. 6).

Because of the very low concentrations measured, exceptional steps were taken to clean glassware and to purify reagents, *e.g.* triply distilling all acids. Extreme precautions were taken to clean the tin(II) chloride solution as reagent blanks from this are in many cases as high as sample concentrations. The tin(II) chloride solutions were purged with air for 48 h at a flow rate of 2 l min^{-1}. The air was stripped free of any entrained mercury by passage over glass wool impregnated with 5% palladium(II) chloride. The solution was subsequently purged for 24 h with argon at a rate of 1 l min^{-1}. The argon was similarly freed of all mercury beforehand. It was essential that the purging process was carried out in the dark glass containers in which the tin(II) solution was to be stored, thus removing further risk of contamination from glassware. Blank values even at 0.01 ng l^{-1} levels of calibration were consequently reduced to a minimum.

Amounts above 200 ng of mercury on the silver wool caused the emission graph to curve from linearity. The most likely cause for this is self-absorption in the flame, but as concentrations seldom reach such a high level, this phenomenon is not considered important in this context. Calibration studies indicated that

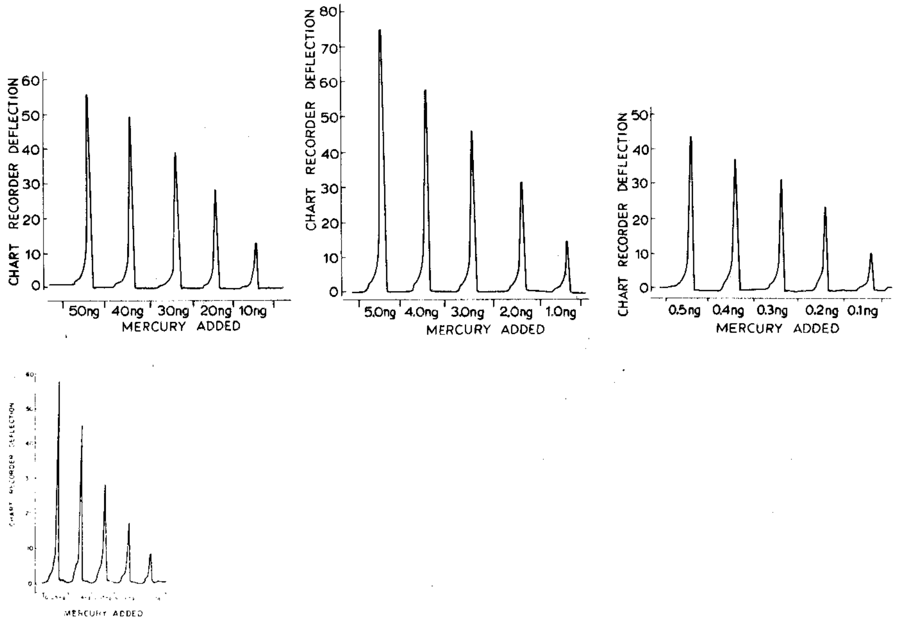


Fig. 6. Mercury calibration graphs. The amounts of mercury indicated were added to 100 ml of deionized water.

linearity was obtainable from 0.0001 ng to 200 ng. However, the majority of samples fell within the 0.01–10-ng range. The calculated detection limit of the system was $3 \cdot 10^{-17}$ g of mercury according to the accepted definition outlined above. However, a realistic lower analytical limit for actual practice is 10^{-14} g, a figure well below that normally required even in baseline studies.

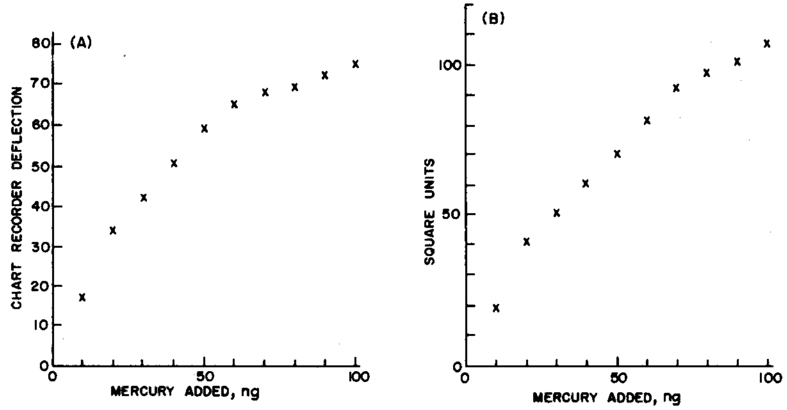


Fig. 7. Comparison of peak height (A) and peak area (B) calibration for mercury release. The amounts of mercury indicated were added to 100 ml of deionized water.

A study was again carried out to ascertain whether peak height or integrated emission gave better values. Figure 7 shows the calibration graphs for both methods, but as the integration method was more onerous it was decided to use peak height.

The effect of slit width

The effect of slit width on the emission over a wide range of concentrations was studied; a graph of relative intensity against slit width for a standard concentration is shown in Fig. 8. Owing to the freedom from spectral interference, a slit width of the same order as an interference filter can be tolerated, indicating that a filter detector can be used for measurement of the mercury radiation rather than a monochromator.

RESULTS

A series of experiments was carried out on fresh and sea waters spiked with mercury solutions in order to obtain information about the accuracy of the

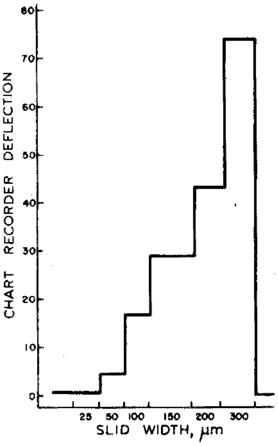


Fig. 8. Chart recorder trace of effects of changing slit widths of a monochromator on signal produced by a standard concentration of mercury passing through the plasma.

TABLE I

RESULTS FOR FRESH AND SEA WATERS SPIKED WITH MERCURY[a]

Hg added (ng)	*Hg found (ng)*	*Hg added (ng)*	*Hg found (ng)*	*Hg added (ng)*	*Hg found (ng)*
0.01	0.011	0.3	0.31	5.0	5.03
0.02	0.018	0.4	0.40	10.0	10.10
0.03	0.029	0.5	0.49	20.0	15.21
0.04	0.041	1.0	1.00	30.0	21.66
0.05	0.050	2.0	2.00	40.0	29.31
0.1	0.10	3.0	3.00	50.0	35.50
0.2	0.19	4.0	4.02		

[a] Each spike was added to 1 l of sample water.

method. Each result given in Table I represents the mean of three values; as results for sea water and fresh water were identical no distinction is made between them. Calibration was done by the direct injection technique; values below 10 ng were calculated by comparison to the projected line of this graph.

Concentrations below those given were not attempted by this method because of the inaccuracies inherent in extrapolating a syringe calibration graph to lower levels.

It can be seen from these results that the combination of the mercury collection on silver and the plasma emission technique provides an extremely sensitive and practical method for the determination of mercury at ultra-trace levels. A particular advantage is that the initial process of mercury extraction may be carried out at the sample site without the need to preserve the sample with the consequent possibility of mercury adsorption onto the walls of the container during storage. It is also unnecessary to transport large volumes of acidified or frozen water samples for the duration of field work, as the QAT, once prepared, can be stored for at least one week. Experiments are at present taking place to determine the time limit of storage of these QAT's, if any, without loss of mercury. Results will be reported in a subsequent paper. Because of the high sensitivity and low sample volume needed, it is possible to do duplicate or triplicate analyses and thus produce a statistically more useful result.

The author wishes to acknowledge the staff of the Applied Spectroscopy Division of NPRL for their useful comments and criticisms, especially Drs. L. R. P. Butler and C. W. F. T. Pistorius who also read the manuscript.

SUMMARY

The need for accurate determinations of mercury at sub-ng l^{-1} levels in sea water has led to the development of a microwave-excited argon plasma emission method. The system utilizes an amalgamation stage where mercury released from water samples by tin(II) chloride reduction is amalgamated onto silver wool. The wool is subsequently heated and the mercury thus released is flushed by argon into a plasma where it is excited. The emission signal thus produced results in a detection limit of $3 \cdot 10^{-17}$ g and an analytical range of $1 \cdot 10^{-14}$–$1 \cdot 10^{-7}$ g.

REFERENCES

1 W. R. Hatch and W. L. Ott, *Anal. Chem.*, 40 (1968) 2085.
2 T. R. Gilbert and D. N. Hume, *Anal. Chim. Acta*, 65 (1973) 461.
3 H. Brandenberger and H. Bader, *At. Absorption Newslett.*, 6 (1967) 101.
4 J. W. Robinson, P. J. Slevin, G. D. Hindman and D. K. Wolcott, *Anal. Chim. Acta*, 61 (1972) 431.
5 G. W. Kalb, *At. Absorption Newslett.*, 9 (1970) 84.
6 P. C. Head and R. A. Nicholson, *Analyst (London)*, 98 (1973) 53.
7 S. J. Long, D. R. Scott and R. J. Thompson, *Anal. Chem.*, 45 (1973) 2227.
8 P. Benes and I. Rajman, *Collect. Czech. Chem. Commun.*, 34 (1969) 1375.
9 P. Benes, *Collect. Czech. Chem. Commun.*, 35 (1970) 1349.
10 R. M. Rosain and C. M. Wai, *Anal. Chim. Acta*, 65 (1973) 279.
11 C. Feldman, *Anal. Chem.*, 46 (1974) 99.
12 F. E. Lichte and R. K. Skogerboe, *Anal. Chem.*, 44 (1972) 1321.

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NEW SOLID STANDARDS FOR THE DETERMINATION OF TRACE IMPURITIES IN METALS BY FLAMELESS ATOMIC ABSORPTION SPECTROMETRY

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A special advantage of flameless atomic absorption analysis is that it may be applied directly to solid samples. However, when metals in the solid state are analysed for trace impurities by instrumental methods, problems are often encountered with standards, as these are usually required to match the chemical and physical characteristics of the sample.

This paper describes two new types of solid standards and their application to the flameless atomic absorption analysis of solid material. The case of p.p.m.-traces of thallium in pure aluminium is chosen as an example.

One of these two types of solid standards has a sample-matching metal matrix and is used as a primary standard, while the other has a urea matrix and is used as a secondary standard. The primary standards are made by the method of ion implantation following a proposal by Gries and Rautenbach[1].

The less expensive and more easily prepared secondary standards are solid solutions of the desired trace element in urea and are the ones used in all routine analyses. These primary and secondary standards will subsequently be referred to as implantation standards and urea standards, respectively.

Implantation standards

The most direct method by which trace quantities of an element can be introduced into a metallic matrix is by ion implantation[2]. The element is atomized and ionized in the ion source of a heavy ion accelerator. The resulting ions are accelerated to an energy of several tens of KeV and then shot into the matrix. The ionic charge transferred to the matrix is registered, requiring the matrix to be electrically conductive, and is used to calculate the amount implanted to a high degree of accuracy. The matrix then becomes an implantation standard.

A computation model for implantation standards has been developed by one of the authors (W.H.G.) and will be published shortly. The following are the important points.

(i) The implantation standards are limited to trace elements with a higher mass number than that of the matrix element. This limitation has been introduced to avoid significant back-scattering of trace element ions from the matrix surface which would complicate measurement of the implantation dose. Theoretical corrections are not yet sufficiently reliable to correct for this limitation.

(ii) Matrix sputtering is a result of the ion bombardment and leads to surface erosion in direct proportion to the ion dose. Because the stopping probability for trace element ions in amorphous and polycrystalline matrices is quasi-Gaussian with a mean penetration depth of the order of 10 nm, matrix sputtering will soon lead to re-sputtering of some of the earlier implanted atoms of the trace element. The re-sputtered trace element forms an increasing percentage of the total dose, and an upper limit is thereby placed on the retainable amount of implanted trace element. This upper limit is of the order of several μg cm^{-2} of irradiated matrix surface and decreases with increasing sputtering efficiency. The limit value (known as saturation value) and intermediate retention values can only be calculated approximately, since at present not enough is known about secondary effects such as dose-induced changes of sputtering efficiency and trace element diffusion. In the absence of experimental data the ion dose for implantation standards is therefore usually restricted to below 10% of the theoretical saturation value to ensure good accuracy. Because of the limitation on ion dose, implantation standards are typically single-element standards with a sub-microgram content of the trace element for each cm^2 of irradiated surface. This content is higher for slow-sputtering matrices than for fast-sputtering matrices.

(iii) By using as matrix a thin metal foil of mg cm^{-2} thickness, the average trace element concentrations may be up to several hundred p.p.m. for slow-sputtering matrices. The emphasis is on average here, because the depth distribution (perpendicular to the irradiated surface) is non-uniform and most of the implanted trace element is situated within a few tens of nm of the irradiated surface. The surface distribution can be made uniform.

It is clear from the foregoing that implantation standards are well suited for use in flameless atomic absorption analysis which by its nature is a single-element determination method in which milligram quantities of sample are analysed for p.p.m.-traces.

The work reported here proves the validity of this claim for the case of traces of thallium in an aluminium matrix. A manufacturing procedure was adopted which may be developed for the economic mass production of implantation standards. The experimental section includes a brief description of this procedure.

As an independent check on the implantation standards a set of comparison standards was prepared by a method which is also described in the experimental section.

Urea standards

The conditions of analysis under which implantation standards have been used for calibration must be maintained during further analysis. The supervision consists of the detection of sample-independent changes in the absorbance signal from one analysis or set of analyses to the next and can be carried out by use of less costly secondary standards for which precision rather than accuracy is of importance.

Solid urea standards have proved to be very satisfactory for this purpose for several reasons. Urea, in the molten state at 133°C, is an excellent solvent for many inorganic compounds and can also be readily ashed, being a simple organic compound. High-purity urea is cheap, and therefore suitable for the bulk production of standards down to very low trace concentrations. Urea standards are free from adsorption losses to receptacle walls, are stable at room temperature, and have an unlimited shelf-life if protected from excessive air humidity (in excess of 80%). The fact that the standards can be weighed is an advantage, especially for small samples of low concentrations. These properties make urea standards very reliable and contribute to a high analytical precision.

The preparation and use of these standards is described below.

EXPERIMENTAL

Preparation of the implantation standards

An electromagnetic mass separator was used to supply beams of 40-keV ions of the two thallium isotopes of masses 203 and 205. These beams were admitted, one at a time, through the slit aperture of a special implantation camera (not described here) onto a film of high-purity aluminium foil of thickness 2 mg cm^{-2}. The film was oscillated under the ion beam at constant speed, in such a way that a uniform exposure of the irradiated area was obtained. The ion dose was registered on a current integrator. The film was exposed to the two isotopic beams of thallium in the proportion of their natural abundances because the atomic absorption lines of this element exhibit a large isotopic shift which necessitates a natural isotopic composition of the trace element in the standard. The essential details of implantation are shown in the upper half of Fig. 1. The film was then cut into smaller pieces of equal size and equal irradiated area as

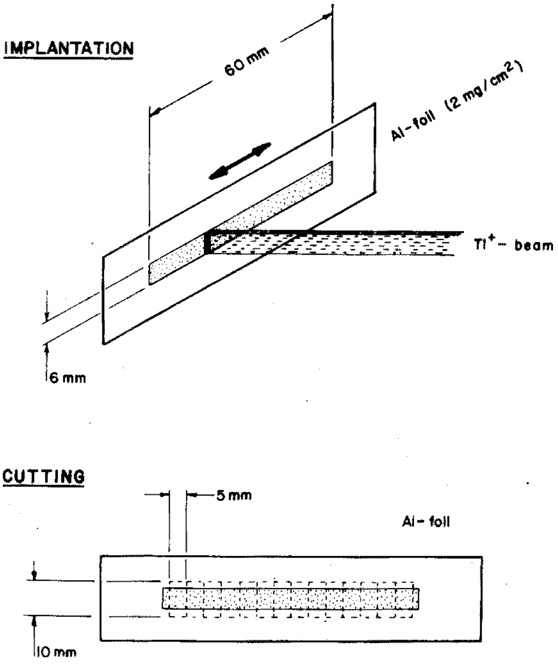

Fig. 1. Essentials of the manufacture of several identical implantation standards in one operation. The shaded area is uniformly irradiated. A stack of equally spaced razor blades is used for cutting.

shown in the lower half of Fig. 1. Standards of equal thallium content and equal matrix mass of 1 mg were obtained in this way. Implantation standards were made which contained doses of approximately 30, 60 and 90 ng Tl cm^{-2} of irradiated area, or about 9, 18 and 27 ng of thallium per final standard. The matrix mass of each standard was adjusted to 1 mg to within 2% by clipping the unexposed ends when necessary.

Preparation of the comparison standards (dip standards)

These standards were used only for confirmation of the implantation standards. The standards were made by a process in which thallium as thallium sulphate was deposited on pieces of aluminium foil by dipping into an aqueous 5 p.p.m. standard solution of the salt, and are therefore called dip standards. The pieces of aluminium foil were identical to the implantation standards, but were given a conical shape to enable them to hold more solution. The quantity of solution transferred varied between 1 and 10 mg, and was measured as mass-loss of the solution.

The solution was contained in a narrow Teflon beaker of 1-ml capacity on the weighing pan of a semimicro balance of which the weighing compartment was pre-saturated with water vapour to cut evaporation losses. The time for a dip and complete mass-loss determination was typically about 30 s, and the evaporation loss for this period was only about 0.01 mg.

After dipping, each standard was immediately dried in hot air and directly loaded into a graphite tube for analysis.

Preparation of the urea standards

A large amount of an approximately 20 p.p.m. master standard was prepared by dissolving a known quantity of thallium sulphate in an appropriate quantity of

A large amount of an approximately 20 p.p.m. master standard was prepared by dissolving a known quantity of thallium sulphate in an appropriate quantity

of urea which had been melted at 140°C. The mixture was not stirred mechanically, but the molten phase was maintained for 30 min, during which time a stirring action was provided by the slow evolution of ammonia and carbon dioxide, the gaseous decomposition products of urea. The actual concentration was determined by weighing after rapid cooling and the solid cake was then ground to a fine powder. Standards with lower concentrations were prepared by fusing some of the master standard with pure urea and following the abovementioned procedure.

Portions of 2 mg of the urea standards were weighed into a small smooth stainless steel spoon and loaded into clean tubes. The urea was removed by ashing in a muffle furnace for 5 min at 250°C after which the temperature was rapidly raised and kept at 450°C for another 5 min. Ashing tests with the radio isotope ^{204}Tl showed the thallium loss to be negligible ($<0.5\%$ for 1 h at 450°C).

Analyses were performed on the residues after ashing. A calibration curve was established with urea standards of different concentrations. As will be explained later, this curve was used as the norm for all further analyses.

Apparatus and analysis

The principal features of the apparatus are given in Table I.

TABLE I

APPARATUS

Spectrometer	Zeiss PMQ II
Absorption cell	Massmann type tubes of vitreous graphite of the dimensions shown in Fig. 2. Tube supports of metal lined with graphite at the contact surface. The whole enclosed by a glass gas chamber with slow argon flow
Line source	Thallium hollow-cathode lamp
Background correction	Similar to that of Koirtyohann and Pickett[3]
Continuum source	Hydrogen hollow-cathode lamp
Signal registration	Recorder and integrator in series
Current source	Variable resistance transformer capable of supplying a current of 400 A
Current regulator	Parallel-switched type, stabilizing the current within 1%

A current of 230 A was used for vaporization, giving a temperature ceiling of 1900°C. The tubes were cleaned with a current of 250 A. The chief advantages of the vitreous graphite tubes used were their negligible permeability, high specific resistivity, rapid temperature rise (10 s to 1900°C) and good agreement on maximum temperature between the individual tubes of a series. The latter point was of particular importance, since a fresh tube was used for each determination in a series, so that a number of tubes was used for each experiment in this study. This is, however, not a requirement of the method. The tubes were kept in covered stainless steel containers. The lids were removed when the urea was ashed. The tube dimensions are given in Fig. 2.

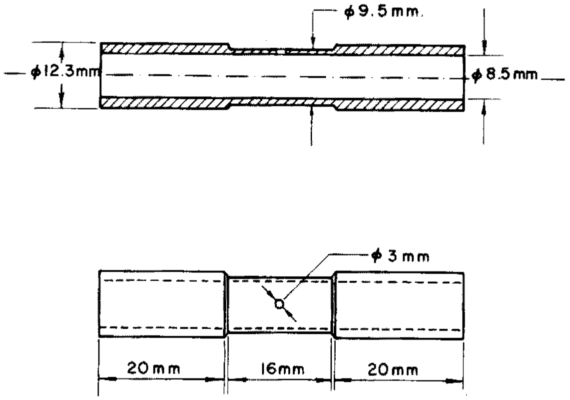

Fig. 2. The graphite tube used for flameless atomic absorption analysis.

In the case of the implantation standards the calibration curve was derived as the nearest fit to three specific points, each representing the average of the absorbance values obtained for a number of identical standards of the 9-, 18- and 27-ng thallium sets. In the case of the dip standards, the concentrations were all different and the absorbance values were therefore plotted standard by standard. The calibration curve was then derived by the method of best fit to this scatter of points.

The urea standards were used for normalization of the absorbance signals from different sets of analyses, and also for correction of drift within a set. Best results were obtained when each standard (implantation or dip) in a set was alternated with a urea standard. The average absorbance value for all urea standards in a set was used to calculate the normalization factor with respect to a once-established urea standards calibration curve which was used as the norm.

RESULTS AND DISCUSSION

Implantation and dip standards

The results obtained with implantation and dip standards are shown in Fig. 3. The calibration curve obtained with the implantation standards is shown as a smooth solid line through three specific points and through the origin. The excellent fit is an indication of the high precision of the implantation standards.

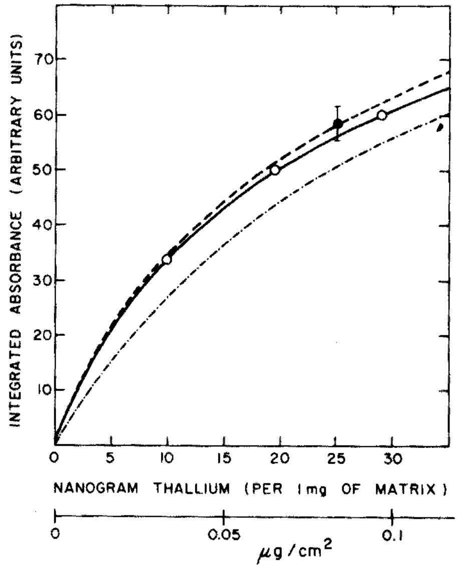

Fig. 3. Calibration curves obtained with (a) implantation standards (—, Al matrix), (b) dip standards (---, Al matrix; —·—, Cd matrix).

Proof of the accuracy of the implantation standards comes from three sources, of which the theoretical model is one. The second is the calibration curve of the dip standards which is shown as a broken line (with the vertical bar representing the standard deviation) which runs in close proximity to the implantation standards calibration curve. Because fewer dip standards were available for the higher concentrations, it is not certain that the deviation of the former from the latter curve is real. The implantation standards curve is also in closer agreement with the Lambert–Beer law. Final confirmation of the accuracy comes from earlier work by Gries[4] which proved that krypton ions of 40 keV implanted in aluminium can be measured accurately to within 1% by coulomb measurement of the ionic charge up to a dose of 0.75 μg per cm^2 of irradiated surface. This is 20 times higher than the highest dose (in atoms cm^{-2}) used for the implantation standards of the present work.

The bottom curve in Fig. 3 represents another calibration curve for otherwise identical dip standards with a cadmium matrix. It may be concluded that the matrix effect was responsible for the difference between the two curves.

Urea standards

The calibration curve obtained with urea standards is shown in Fig. 4 as a solid line. A calibration curve obtained with aqueous standards of thallium sulphate is shown as a broken line for comparison. Typical values for the relative standard deviations obtained with 2 mg quantities of 5 p.p.m. thallium in urea standards (*i.e.* 10 ng Tl) were 2.6, 3.1, 3.3 and 3.7%. This is excellent for flameless atomic absorption analysis considering that a different graphite tube was used for each sample. It is proof both of the uniformity of the urea standards and of the high precision attainable by their use. The precision is better than for aqueous standards. Ample justification for the extensive use of the urea standards was provided by the normalization factors found for different sets of analyses. These varied by as much as 30%. Significant drift within a set of analyses was also occasionally observed.

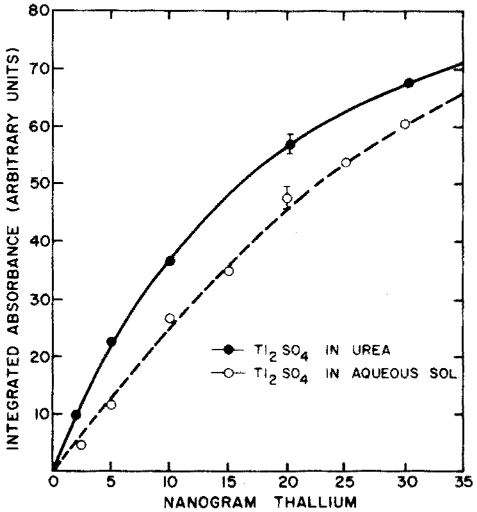

Fig. 4. Calibration curves obtained for thallium sulphate standards in urea (—) and with aqueous solution standards (---).

CONCLUSIONS

The work reported here demonstrates the analytical possibilities of two new types of solid standards for flameless atomic absorption analysis.

The implantation standards have the advantages of a contamination-free preparation, a wide concentration range, and good accuracy and reproducibility. The inhomogeneous distribution of the implanted trace element is of no importance in this method of analysis as shown by the observation that the difference between dip standards (having all the Tl on the surface) and implantation standards (having all the Tl in the bulk) is not significant. The implantation standards may be found useful also in other direct micro-methods of analysis in which an inhomogeneous distribution of the trace element in the matrix is of little concern (*e.g.* in activation analysis). Homogenization of the standards, such as by dissolution, can further extend the field of application. Implantation standards should prove very useful for the quality control of high-purity metals, metal alloys and graphite. It must, however, be emphasized that theoretical predictions regarding the accuracy of implantation standards must for most combinations of trace element and matrix still be confirmed by experiment (*e.g.* dip standards or radioactive implantation standards).

The more easily prepared and less expensive urea standards have been shown to be excellent secondary standards. The facts that urea is a simple matrix material and is also a very good solvent for many trace elements, thus yielding a uniform distribution of the solute, make this type of standard ideal for flameless atomic absorption spectroscopy as well as for other methods of analysis. In particular, urea standards seem to have potential as general reference materials which could be used in interlaboratory comparison tests. These standards can be prepared with high precision and remain unchanged for long periods if stored in hermetically sealed containers. Being in solid solution, there is little chance that the low concentration metals will adsorb onto the walls of containers.

SUMMARY

Two new types of solid standards are described for the direct determination of trace impurities in metals by flameless atomic absorption. One of these, a primary standard, has a metal matrix and can be tailor-made to the required size and concentration by the technique of ion implantation. The other, a secondary standard, has a urea matrix into which trace elements are introduced by dissolution. Upper concentration limits are in the 100–1000 p.p.m. range. Both types of standard, the secondary in particular, are suitable for application in other methods of trace analysis.

REFERENCES

1 W. H. Gries and W. L. Rautenbach, *VIth International Symposium on Micro-techniques, Graz, September 1970, Preprints Vol. E,* Verlag der Wiener Medizinischen Akademie.
2 G. Carter and J. S. Colligon, *Ion Bombardment of Solids*, Heineman Educational Books, London, 1968, p. 354.
3 S. R. Koirtyohann and E. E. Pickett, *Anal. Chem.*, 37 (1965) 601.
4 W. H. Gries, *VIth International Symposium on Micro-techniques, Graz, September 1970, Preprints Vol. E,* Verlag der Wiener Medizinischen Akademie; and further unpublished work.

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A METHOD FOR THE DETERMINATION OF MERCURY IN SEDIMENTS BY THE AUTOMATED COLD VAPOR ATOMIC ABSORPTION TECHNIQUE AFTER DIGESTION

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Recently, mercury in sediments has been of interest because of its low environmental mobility[1] and its effects on the environment. Because of this, many laboratories have been involved in its determination in sediments. For programs where the analysis of a large number of samples is required, a simple rapid and reliable method is necessary. The intention of this work was to obtain a comprehensive digestion procedure and adapt it to an automated cold vapor technique of mercury analysis as reported by Goulden and Afghan[2,3], and Bailey and Lo[4]. Basically, these methods involve the digestion of water samples, and the oxidation of mercury to mercury(II), in a closed system. The mercury is then reduced to the metal with tin(II) and the mercury vapor is swept from the solution with a stream of air and through a quartz cell for determination by flameless atomic absorption spectrometry. Sediment samples have to be predigested before mercury is determined by the above technique. The automated system, designed originally for water samples, was modified to suit digested sediment extracts.

Irrespective of the form of mercury introduced into the aqueous environment, it ends up adsorbed on fine-grained inorganic and organic particles[5]. The forms of mercury in sediments have been shown by many workers[5–8] to be adsorbed on iron oxides, on sulfide surfaces and on clay particles, and to be present as inorganic phosphorus complexes, in humate complexes, and as methyl- and dimethyl-mercury as produced by microbial activity. It has been shown[7,9,10] that there exists a high correlation between mercury and organic matter content in lake sediments.

From the above, it is clear that for the determination of mercury in sediments, it is necessary to extract the inorganic mercury and to liberate mercury from organomercurials by oxidation of the organic matter. Methods to achieve this have been proposed by many workers. Hatch and Ott[11] used sulfuric acid and hydrogen peroxide for rock samples. Cranston and Buckley[12] used sulfuric and nitric acids for sediments. Jonasson *et al.*[13] used nitric and hydrochloric acids for rocks. Klein[14] used nitric acid and potassium permanganate for soils. Head and Nicholson[15] used sulfuric acid and potassium permanganate for geological material. Melton *et al.*[16] used sulfuric and nitric acids and potassium persulfate for soils; Iskander *et al.*[17] and Muscat *et al.*[18] used sulfuric and nitric acids with potassium permanganate and potassium persulfate.

The digestion procedure required was one which would extract all forms of inorganic mercury and which would oxidize the most resistant organic matter. The digestion procedure of Iskander *et al.*[17] was chosen since this method is applicable to a wide variety of sediment types, particularly those with high organic content. It has good precision and simplicity for routine application.

In adopting this procedure[17], a problem was encountered with the decomposition of permanganate to produce precipitated MnO_2, which adsorbed some mercury and caused inhomogeneities in solutions. A solution of hydroxyammonium sulfate and sodium chloride served to reduce the MnO_2 and excess permanganate without reducing mercury(II), and made it possible to analyse the prepared solution automatically.

This paper describes a procedure for the automatic determination of mercury in sediments after manual digestion.

EXPERIMENTAL

Apparatus

Samples were digested in 100-ml volumetric flasks in a temperature-controlled shaker bath (Model 75, Precision Scientific Co.).

The equipment used for the analysis consisted of (a) an automatic sampler (Technicon AutoAnalyzer II sampler with 20-1/5 cam), (b) proportionating pump (Carlo Erba, Model 08-59-10202), (c) Technicon AutoAnalyzer tubing of specified dimensions (Fig. 1), (d) gas separator as used by Goulden and Afghan[2,3], (e) mercury monitor (Pharmecia Fine Chemicals), and (f) strip chart recorder (Hewlett Packard, Model 7101B).

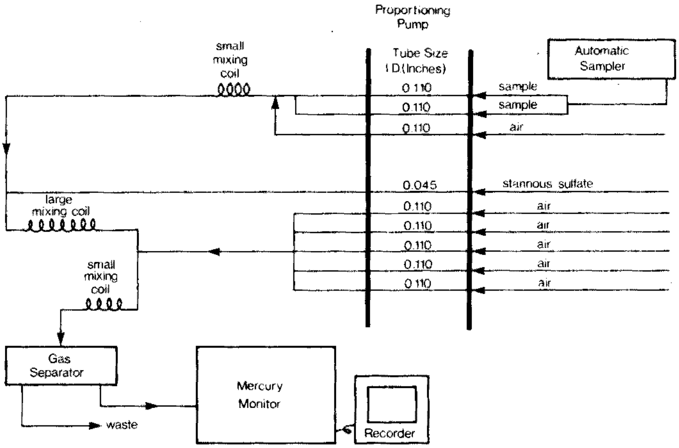

Fig. 1. Mercury manifold.

The system (Fig. 1) is similar to that used previously[2,3] except no heated digestion bath was employed, and only one reagent line was used, that for $SnSO_4$–H_2SO_4.

Reagents

High-purity certified reagents were used for all analyses.

Procedure

Determine the water content of a wet sediment by drying overnight to constant weight at 110°C.

Weigh out a representative wet sediment sample, equivalent to 1–2g of dry weight, into a 100-ml volumetric flask. Rinse the sediment down to the bottom of the flask with distilled–deionized water and add 15 ml of (2+1) 18 *M* sulfuric acid–12 *M* nitric acid slowly in an ice water bath. Place the volumetric flasks in a shaking water bath set for 50–60°C and digest for 2 h. Note: the volumes of the volumetric flasks were not affected when heated at 50–60°C.)

After digestion, allow the flasks to cool for 30 min. Carefully add 10 ml of 6% (w/v) potassium permanganate solution while cooling the flasks in an ice-water bath. If the color does not persist for 15 min, add more permanganate. After 30 min, add 5 ml of 5% (w/v) potassium persulfate solution with gentle stirring. Let stand overnight. If all the permanganate is reduced as witnessed by the absence of the purple color, add an additional amount until the color persists.

Add 10 ml of 6% (w/v) hydroxyammonium sulfate–6% (w/v) sodium chloride solution and stir gently until the solution clears and all the precipitated manganese dioxide has dissolved. Make up to volume. Centrifuge an aliquot of the solution at 2500 r.p.m. for 5 min. Transfer an aliquot of the clear supernate to glass sample cups and place in the automatic sampler for analysis. Use a cam designed for 20 samples an hour and a 1:5 sample-to-wash ratio. This corresponds to a 30-s sampling time and a 2.5-min wash time.

Treat all standards exactly like the above samples.

RESULTS AND DISCUSSION

Digestion

In choosing the proper reagents for sample digestion, one has to consider two factors: complete recovery of the metal of interest, and the ease of handling the reagents. Hydrochloric acid is undesirable for mercury analyses because of volatile mercury chlorides; and chloride ions react with manganese dioxide to give chlorine gas[19], which can cause violent frothing of the solution. Perchloric acid may be hazardous to use, in the presence of large amounts of organic matter, and is a strong oxidant only at high temperatures. Since relatively low temperatures must be used in open digestions of sediment samples to minimize possible volatilization losses, perchloric acid offers no advantages over acids such as sulfuric and nitric acid. Iskander *et al.*[17] have shown that higher recoveries of mercury are obtained from sediments when these two acids are used together, and that this procedure recovered many different forms of mercury satisfactorily.

It has been reported that considerable loss of some organomercurials occurs when sediment samples are dried. Iskander *et al.*[17] reported a loss of 16.8% when samples spiked with methylmercury(II) chloride were dried at 60°C. Jernelov *et al.*[20] found that rapid formation of mercury to volatile dimethylmercury occurred when mercury-contaminated wet organic sediments were exposed to air. The rate and amount of production increased with high pH values. Therefore, sediment samples were analysed wet.

To ensure complete oxidation of the organic matter and to provide an oxidizing environment, both permanganate and persulfate, which have been previously used, were found satisfactory. The oxidizing environment ensures complete retention of the mercury in solution as mercury(II). Shimomura and Kise[21] showed by radioactive tracers that mercury was lost from solution as a function of time and that oxidants such as hypochlorite and permanganate reduced the loss; reductants like tin(II) increased the rate of loss of mercury. Toribara *et al.*[22] stated that the only way of stabilizing mercury solutions by preventing volatilization, was to use an oxidant such as permanganate which has a higher oxidation potential than the Hg(II)–Hg(I) system. Jonasson *et al.*[13] have also used permanganate as a preservative for mercury in natural waters; permanganate decomposes to form MnO_2, the oxidized mercury (Hg^{2+}) coprecipitates with the MnO_2, and volatilization losses are thus overcome. When the sediment sample solutions are digested overnight as in the present study, the above effects ensure complete conservation of the mercury. Sample solutions left for one week showed no change in the mercury level.

Analysis

After acid extraction and overnight digestion in permanganate–persulfate, the digest contains large amounts of precipitated MnO_2. Mercury(II) adsorbs on the precipitate, and some of the metal appears in the solid phase mixed with the silicate residue of the sediment. Since the mercury detection apparatus is an automated flow system where homogeneous solutions must be aspirated, any solid residues must be removed, without removing any mercury. To show the association of mercury with MnO_2, several standard samples were pretreated differently. The highest results were achieved when the recommended mild reduction with hydroxyammonium sulfate was used before aspiration (Table I, column 5). If the precipitate is allowed to settle slowly, results are low (column 2) whereas most of the mercury is liberated if the solution is shaken vigorously just before aspiration into the system (column 3); in the latter case, however, the MnO_2 is partially adsorbed on the inner walls of the AutoAnalyzer tubing, reducing the signal height and contaminating subsequent analysis. In the presence of any undissolved silicate residue, this technique could not be used since insoluble material would clog the tubing and change the aspiration efficiency of the solution. Centrifugation allows a large percentage of the mercury to be recovered; in the highly acidic media, a large fraction of the mercury is desorbed back into solution. Lockwood and Chen[23] have shown that mercury may be adsorbed by manganese oxides over the pH range of 3–11, but below pH 3, adsorption decreases; however, the highly acidic medium in the solutions does not completely prevent adsorption.

Table I proves that complete dissolution is necessary in order to produce reliable results. The presence of MnO_2 (columns 2–4) caused less reproducible results than were obtained for reduced solutions. The relative standard deviations (10 analyses) for samples of 1000 ng g^{-1}, 600 ng g^{-1} and 100 ng g^{-1} were 2.5%, 4% and 10%, respectively, when the MnO_2 was reduced by the recommended method, and 4%, 7% and 20%, respectively, when the samples were simply centrifuged to remove the MnO_2. Also, lower recoveries of mercury were obtained depending on the amount of MnO_2 formed, when centrifugation was used.

The reducing agent used should be strong enough to reduce the excess of oxidant but not reduce the mercury, because this would cause volatilization losses

TABLE I

RECOVERY OF MERCURY FROM MnO_2 UNDER DIFFERENT CONDITIONS

Actual Hg concn. (ng ml^{-1})	*Scale reading*			
	Supernate	*MnO_2 reduced in automated system*[a]	*Centrifugation before aspiration*[b]	*Reduction before aspiration*[c]
1	3	5	4	7.5
5	3	30	30	34
10	5	54	51	58
20	40	70	71	75

[a] The MnO_2 and solution were shaken well before aspiration into the automated system.
[b] The MnO_2 was centrifuged down before the aspiration.
[c] The recommended prior reduction was used.

TABLE II

THE EFFECT OF REDUCING AGENTS ON THE INSTRUMENTAL SIGNAL

(1 ng Hg ml^{-1} solution containing the reagents outlined in the experimental section)

% (v/v) of 6% NH_2OH soln. in soln.	*Signal height*	*% (v/v) of 30% H_2O_2 in soln.*	*Signal height*	*% (v/v) of 5% oxalic acid in soln.*	*Signal height*	*% (v/v) of 50% Fe(II) soln. in soln.*	*Signal height*
3.5	22	1	20	20	16.5	7.5	20.5
8	21.5	4	20	30	14.5	10	20
15	21.5	9	20	40	13.5	15	20
20	21.5	15	19	50	13.5	20	19.5

before aspiration. Four reducing agents were studied: oxalic acid, acidic hydrogen peroxide, a solution of hydroxyammonium sulfate–sodium chloride, and iron(II) sulfate. Jonasson *et al.*[13] used oxalic acid to reduce the MnO_2 before analysis of natural water samples where it was used as a mercury preservative. Hydrogen peroxide in acidic media was used by Armstrong and Uthe[24] to dissolve the MnO_2 precipitate after digesting fish samples with acids and permanganate. Solutions of hydroxyammonium sulfate with sodium chloride were used by Hatch and Ott[11] and many later workers to reduce the excess of oxidant in the analysis of mercury solutions. Iron(II) has also been used to dissolve MnO_2 (ref. 19). Table II shows the effect on the mercury signal of adding different amounts of different reducing agents to a 1 p.p.b. solution of mercury containing excess of oxidant as given in the Experimental section. The first row in Table II is the condition where there exists just enough reducing agent to reduce the MnO_2 and excess of permanganate. The other rows show the effects of different excesses of reducing agents. Iron(II) sulfate and oxalic acid are obviously impractical for use. Hydrogen peroxide was impractical for routine use because its decomposition produced large amounts of oxygen which contributed to analytical difficulties and loss of mercury as evidenced by low recoveries in some cases. The solution of hydroxyammonium sulfate and sodium chloride gave rise to none of these problems. To test the behavior of this solution as a function of time, the solutions described in Table II were stored in the original volumetric flasks for 2 days; the mercury signals were unaffected.

Figure 2 shows calibration curves for sets of solutions containing the different oxidants and reductants used. An interesting effect can be seen from it. Curves D and E, where the solution is oxidizing, have a lower slope than curves A, B and C where the environment has been made reducing with hydroxylamine. The aspiration rate of the different solutions in Fig. 2 were all the same, so that the change in sensitivity cannot be attributed to this factor. The change in sensitivity can possibly be explained by considering the rate of reduction of mercury(II) by tin(II) in the system under different redox potentials. Magos[25] showed that organomercurials could actually be reduced by tin(II), but the rate of reduction was much slower than that of inorganic mercury. When an excess of tin(II) was used with a cadmium salt, the rate of reduction of the organomercurials became the same as that of inorganic mercury. In analogy to this, Fig. 2 indicates that the rate of reduction is slower in an oxidizing environment since there is a competition between mercury(II) and the excess of oxidants. Therefore, it was necessary to make all standards and samples with exactly the same amounts of reagents.

Figure 3 shows the calibration curve for the proposed method. The curve was prepared by spiking solutions containing sediment extracts with mercury(II) chloride. This showed that the sediment matrix had no effect on the mercury signal. The

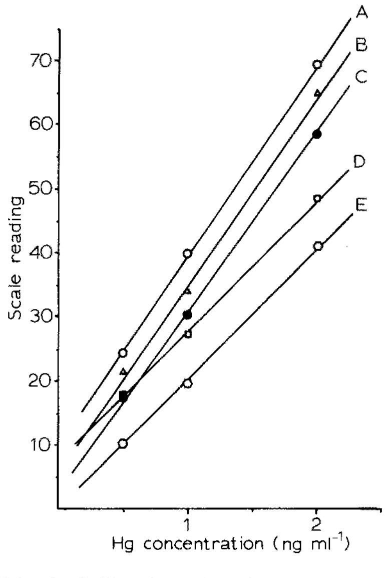

Fig. 2. Calibration plots for different conditions. (A) A solution of 15%(2+1)H_2SO_4–HNO_3 + 10% of 5% $KMnO_4$ + 10% of 5% $K_2S_2O_8$ + 10% of 6% hydroxyammonium sulfate–NaCl. (B) A solution of 15% (2+1)H_2SO_4–HNO_3 + 20% of 5% $KMnO_4$ + 10% of 6% hydroxyammonium sulfate–NaCl. (C) A solution of 15% (2+1)H_2SO_4–HNO_3 + 10% of 6% hydroxyammonium sulfate–NaCl. (D) A solution of 15% (2+1)H_2SO_4–HNO_3 + 10% of 5% $KMnO_4$ + 10% of 5% $K_2S_2O_8$. (E) A solution of 15% (2+1)H_2SO_4–HNO_3.

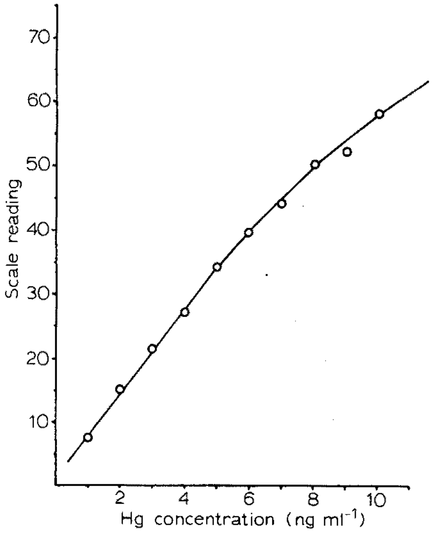

Fig. 3. Calibration curve for the recommended conditions.

curve is linear up to 6 ng ml^{-1}. The method has a detection limit of 0.1 ng ml^{-1} in solution and 10 $\mu g\ g^{-1}$ for a dry sediment based on a 1-g sample.

Initially, plastic cuvets were used in the automatic sampler. These gave rise to difficulties with respect to loss of mercury. It was found that glass cuvets—and other glassware—gave satisfactory results when they were precleaned with chromic acid.

SUMMARY

A manual method for the extraction of inorganic mercury and the oxidation of organomercurials has been modified and incorporated into an automated procedure for the determination of mercury in sediments. The method includes a digestion of the wet sediment with sulfuric and nitric acids followed by oxidation of the organomercurials with potassium permanganate and potassium persulfate. Errors caused by coprecipitation and adsorption of mercury on manganese dioxide are avoided by reduction of the dioxide with a solution of hydroxyammonium sulfate and sodium chloride. The mercury content in solution is determined by a cold vapor technique with tin(II) sulfate as a reductant in an automated system. This method can detect down to 10 p.p.b. of mercury in sediment (based on 1-g samples) and can handle automatically 20 samples per h after manual digestion.

REFERENCES

1 H. E. Hawkes and J. S. Webb, *Geochemistry in mineral exploration*, Harper and Row, New York, 1962, p. 369.
2 P. D. Goulden and B. K. Afghan, *Technicon International Congress, Vol. II, Nov. 2–4, 1970*, Futura Pub. Co., New York, 1970, p. 317.
3 P. D. Goulden and B. K. Afghan, *Inland Waters Branch, Department of Energy, Mines and Resources, Ottawa, Canada, Technical Bulletin No. 27*, 1970.
4 B. W. Bailey and F. C. Lo, *Anal. Chem.*, 11 (1971) 1525.
5 J. Vernet and R. Thomas, *Eclogae Geol. Helv.*, 65 (1972) 293.
6 I. R. Jonasson, *Geol. Surv. Can. Paper*, 70–57, 1970.
7 R. L. Thomas, *Can. J. Earth Sci.*, 9 (1972) 636.
8 J. Gavis and J. F. Ferguson, *Water Res.*, 6 (1972) 989.
9 J. E. Kennedy, R. R. Ruch and N. F. Shimp, *Geol. Surv. Environ. Geol.*, Note 44, 1971, p. 18.
10 N. F. Shimp, J. A. Schleicher, R. R. Ruch, D. B. Heck and H. V. Leland, *Geol. Surv. Environ. Geol.*, Note 41, 1971, p. 25.
11 W. R. Hatch and W. L. Ott, *Anal. Chem.*, 40 (1968) 2085.
12 R. E. Cranston and D. E. Buckley, *Environ. Sci. Technol.*, 6 (1972) 274.
13 I. R. Jonasson, J. J. Lynch and L. J. Trip, *Geol. Surv. Can. Paper*, 73-21, 1973.
14 D. H. Klein, *Environ. Sci. Technol.*, 6 (1972) 56.
15 P. C. Head and R. A. Nicholson, *Analyst. (London)*, 98 (1973) 53.
16 J. R. Melton, W. L. Hoover and P. A. Howard, *Soil. Sci. Soc. Amer., Proc.*, 35 (1971) 850.
17 I. K. Iskander, J. K. Syers, L. W. Jacobs, D. R. Keeney and J. T. Gilmour, *Analyst (London)*, 97 (1972) 388.
18 V. I. Muscat, T. J. Vickers and A. Andren, *Anal. Chem.*, 44 (1972) 218.
19 J. J. Lingane, *Analytical Chemistry of Selected Metallic Elements*, Reinhold, New York, 1966.
20 A. Jernelov, H. Lann and M. Lord, *Vatten*, 2-71 (1971) 234.
21 S. Shimomura and A. Kise, *Bunseki Kagaku*, 18 (1969) 1412.
22 T. Y. Toribara, C. P. Shields and L. Koval, *Talanta*, 17 (1970) 1025.
23 R. A. Lockwood and K. Y. Chen, *Environ. Sci. Technol.*, 7 (1973) 1028.
24 F. A. J. Armstrong and J. F. Uthe, *At. Absorption Newslett.*, 10 (1971) 101.
25 L. Magos, *Analyst (London)*, 96 (1971) 847.

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THE DETERMINATION OF GALLIUM BY ATOMIC ABSORPTION SPECTROMETRY IN PREMIXED INERT GAS(ENTRAINED AIR)–HYDROGEN FLAMES

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Relatively little attention has been given to the determination of gallium by atomic absorption spectrometry. Gatehouse and Willis[1], Allan[2] and Slavin[3] listed several lines for gallium and its sensitivities or its detection limits by conventional atomic absorption spectrometry; Fassel *et al.*[4] and McGee and Winefordner[5] reported values for a continuum as the spectral source. Mulford[6] reported a detection limit of 0.05 p.p.m. for gallium at 287.4 nm. Gupta *et al.*[7] obtained a sensitivity of 2.0 p.p.m. at 294.4 nm in an air–acetylene flame and described a procedure involving the extraction of gallium oxinate with a mixture of methyl isobutyl ketone and 1-pentanol. Popham and Schrenk[8] showed that gallium could be determined with a detection limit of 1.3 p.p.m. and a sensitivity of 4.0 p.p.m. at 287.4 nm and 294.4 nm in the air–acetylene flame, and with a detection limit of 0.3 p.p.m. and a sensitivity of 1.0 p.p.m. at 294.4 nm in the nitrous oxide–acetylene flame. Later, Pollock[9] and Lypka and Chow[10] reported on the determination of gallium in ores by solvent extraction–atomic absorption spectrometry.

Several authors have examined the so-called cool flames; these flames are usually entrained air–hydrogen flames in which the combustible gas (hydrogen) is diluted with an inert gas, such as argon or nitrogen. Such an inert gas(entrained air)–hydrogen flame has been used for atomic absorption[5,11–13], atomic fluorescence[14–18] and flame emission[19–22] spectrometry. The present authors have demonstrated that the premixed inert gas (entrained air)–hydrogen flames produced with a "multi-flame" burner[23] can be used as suitable atom reservoirs for the determination of tin[24], zinc[25], bismuth[26], arsenic[27] and selenium[27] by atomic absorption spectrometry.

This paper describes an investigation of the flame characteristics for gallium in the premixed argon(entrained air)– and nitrogen(entrained air)–hydrogen flames produced with the specially designed "multi-flame" burner[23], and of the various interferences with the gallium atomic absorption in these flames. Depressing interferences were observed over wide ranges of concentration of several acids and many diverse elements, but a large amount of magnesium eliminated the interferences of some of the elements examined. The method was successfully applied to the determination of gallium in some semi-conducting III-V compounds.

EXPERIMENTAL

Apparatus

A Nippon Jarrell-Ash Model AA-1 atomic absorption and flame emission spectrometer was used on a single-pass system to obtain all data. A specially designed long-path "multi-flame" burner[23] was used in conjunction with a Techtron standard nebulizer-chamber. The gallium atomic absorptions were measured in the premixed argon(entrained air)– and nitrogen(entrained air)–hydrogen flames. The height in the flame was taken as zero when the light beam from the hollow-cathode lamp just touched the top of the burner head. The analytical wavelength was 287.4 nm, sometimes 294.4 nm, and the light source was a gallium hollow-cathode lamp (Hamamatsu TV Co. Ltd., Type L233), operated at 4 mA. Gas flow rates were carefully regulated and monitored on calibrated flow meters.

Reagents

A stock solution of gallium (1000 p.p.m.) was prepared by gently heating 1.000 g of high-purity gallium metal (99.99%, Mitsuwa Chemicals Co. Ltd., Osaka) in 50 ml of 2 *M* hydrochloric acid and 10 ml of 6 *M* nitric acid until dissolved. This solution was diluted to 1 l with distilled water. Working solutions were prepared by appropriate dilution. All the other reagents were of either analytical-reagent grade or the purest grade available and used without further purification. Blanks were run on each solution for the interference study.

RESULTS AND DISCUSSION

Selection of wavelength

Table I shows the various spectral lines of gallium which, according to transition

TABLE I

LINE INTENSITIES AND SENSITIVITIES OF GALLIUM SPECTRAL LINES IN THE PREMIXED INERT GAS (ENTRAINED AIR)–HYDROGEN FLAMES

Gallium line (nm)	*Relative line intensity*[a]	*Sensitivity for 1% absorption (p.p.m.)*	
		$Ar(air)\text{–}H_2$	$N_2(air)\text{–}H_2$
229.4	0.001	30.8	20.9
237.1	0.002	36.5	33.2
245.0	0.040	2.57	1.88
250.0[b]	0.097	4.74	3.94
266.0	0.036	8.16	5.67
272.0	0.076	13.1	9.92
287.4	1.000	0.24	0.20
294.4[c]	2.097	0.45	0.42
403.3	3.022	0.89	0.72
417.2	5.196	1.15	1.15

[a] Arbitrary units; 10 mV f.s.d. for recorder.
[b] Doublet 250.017 nm and 250.070 nm.
[c] Doublet 294.364 nm and 294.418 nm.

probabilities[28], should be applicable for atomic absorption; the relative line intensities radiated from the lamp and the sensitivities for 1% absorption observed under identical flame conditions are listed for the two premixed flames. The gallium 287.4-nm resonance line was the most sensitive, and was therefore selected as the analytical line; the 294.4-nm doublet (294.364 nm and 294.418 nm), which could not be resolved with the monochromater used, gave higher line intensity but lower sensitivity than the 287.4-nm line.

Gallium sensitivities in different flames

The gallium sensitivities for 1% absorption in aqueous solutions were obtained in several different flames with the "multi-flame" burner[23] (Table II). The inert-gas(entrained air)–hydrogen flames gave much better sensitivity than the other hydrogen or acetylene flames, and the sensitivity at the 287.4-nm line was better than that at the 294.4-nm line. Thus such relatively volatile elements as arsenic, bismuth, gallium, selenium, tin and zinc are sufficiently atomized to provide good sensitivity even in low-temperature flames.

TABLE II

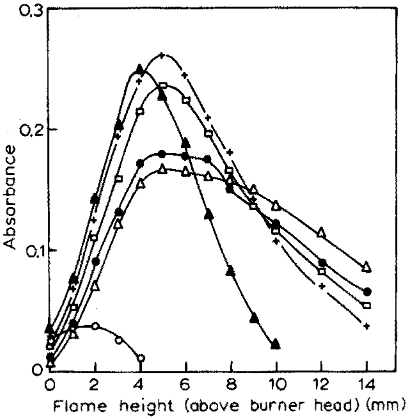
COMPARISON OF THE SENSITIVITIES OF GALLIUM IN DIFFERENT FLAMES WITH A "MULTI-FLAME" BURNER

Flame	*Sensitivity for 1% absorption (p.p.m.) at*	
	287.4 nm	*294.4 nm*
Air–H_2	0.75	0.97
N_2O–H_2	8.98	10.5
Air–C_2H_2	1.13	0.98
N_2O–C_2H_2	0.85	0.73
Ar(air)–H_2	0.24	0.45
N_2(air)–H_2	0.20	0.42

Effect of flame composition and flame height

At a fixed flow rate of the argon or nitrogen nebulizing gas, the hydrogen flow rates were varied from 3.6 to 12.6 l min^{-1} and the gallium atomic absorptions were measured for 20 p.p.m. of gallium at different flame heights in order to find the optimal flame composition and flame height. The results obtained in the nitrogen(entrained air)–hydrogen flame are shown in Fig. 1, which indicates that the results are remarkably dependent on both flame composition and flame height. Similar results were obtained for the argon(entrained air)–hydrogen flame. The optimal conditions were: either hydrogen, 7.2 l min^{-1}; argon, 4.5 l min^{-1} (1.5 kg cm^{-2}); height in the flame, 4 mm above the top of the burner head; or hydrogen, 7.2 l min^{-1}; nitrogen, 5.0 l min^{-1} (1.5 kg cm^{-2}); height in the flame, 5 mm above the top of the burner head.

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



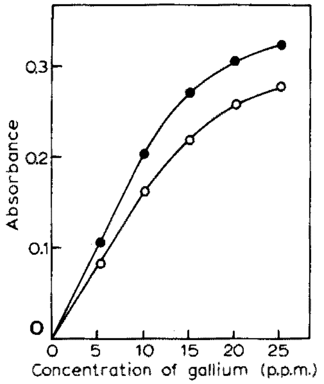


Fig. 1. Effect of flame composition and flame height in the nitrogen (entrained air)–hydrogen flame. Concentration of gallium: 20 p.p.m. Hydrogen flow rates: (○) 3.6 l min^{-1}; (▲) 5.4 l min^{-1}; (+) 7.2 l min^{-1}; (□) 9.0 l min^{-1}; (●) 10.8 l min^{-1}; (△) 12.6 l min^{-1}.

Fig. 2. Calibration graphs for gallium. (●) In the nitrogen (entrained air)–hydrogen flame; (○) in the argon (entrained air)–hydrogen flame.

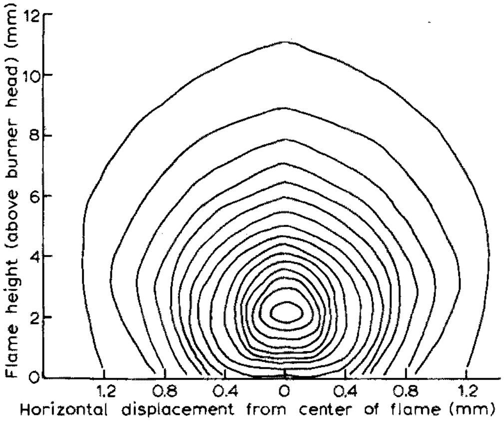
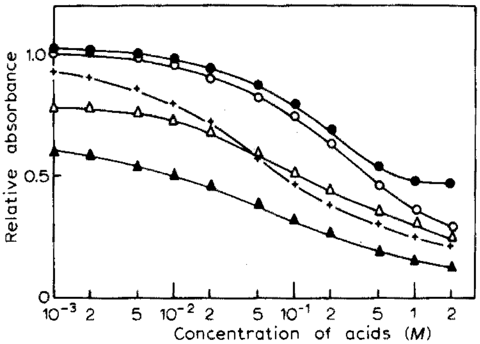


Fig. 3. Flame profile of gallium atoms in the flame by the pin-hole method. The maximum absorbance (0.80) is in the center of the flame and contours represent decreasing absorbance (the interval of absorbance contours is 0.05). Concentration of gallium: 20 p.p.m. Flame: argon (entrained air)–hydrogen.

Detection limits and calibration graphs for gallium

Under the above optimal conditions gallium could be determined with a detection limit (signal/noise = 2 : 1) of 0.08 p.p.m. and a sensitivity (for 1 % absorption) of 0.24 p.p.m. in the argon (entrained air)–hydrogen flame and with a detection limit of 0.07 p.p.m. and a sensitivity of 0.20 p.p.m. in the nitrogen (entrained air)–hydrogen flame.

The calibration graphs for gallium at 287.4 nm in both flames (Fig. 2) were linear for the concentration range 0–10 p.p.m. of gallium; at higher concentrations, the graphs curved towards the concentration axis. The graphs at 294.4 nm also showed curvature at higher concentrations of gallium. However, calibration graphs obtained in air– and nitrous oxide–acetylene flames with the same "multi-flame" burner were excellently linear between 0 and 25 p.p.m. of gallium. Therefore, the curvature of the calibration graphs above 10 p.p.m. in the cool flames must be associated with temperature phenomena. Further investigation showed that the curvature was caused by the extreme localization of gallium atoms in the premixed inert gas(entrained air)–hydrogen flames, as shown in Fig. 3; these data were obtained with a pin-hole of 1.0 mm in diameter as described by Rann and Hambly[29]. The gallium in various samples was, therefore, determined below 10 p.p.m. of gallium in the aspirating solutions.



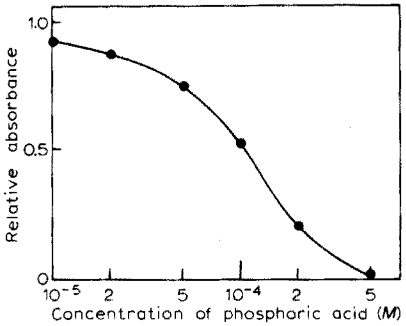


Fig. 4. Effect of acids on gallium atomic absorption. Concentration of gallium, 10 p.p.m.; Flame, argon(entrained air)–hydrogen. (●) Hydrofluoric acid; (○) hydrochloric acid; (+) sulfuric acid; (△) nitric acid; (▲) perchloric acid.

Fig. 5. Effect of phosphoric acid on gallium atomic absorption. Concentration of gallium: 10 p.p.m. Flame: argon(entrained air)–hydrogen.

Effect of acids

With air–acetylene and nitrous oxide–acetylene flames, Popham and Schrenk[8] studied the effects of hydrochloric, nitric, phosphoric and sulfuric acids on gallium atomic absorption; acid concentrations below 0.1 *M* did not seriously affect the results in the nitrous oxide flame which substantially reduced the acid interferences observed in the cooler air–acetylene flame. Lypka and Chow[10] reported a strong dependence of gallium absorbance on hydrochloric acid content in the aspirating solutions.

In the cool flames used here, the effects of common inorganic acids were examined for 10 p.p.m. of gallium over the concentration range 0.001–2.0 *M*. The results for hydrochloric, hydrofluoric, nitric, perchloric and sulfuric acids in the argon flame are shown in Fig. 4. Phosphoric acid in this concentration range gave zero absorbance for gallium, and its effects at lower concentrations ($1 \cdot 10^{-5}$–$5 \cdot 10^{-4}$ *M*) were therefore examined (Fig. 5). At zero relative absorbance, the ratio of gallium to phosphate is almost stoichiometric, hence the interference is probably due to the formation of GaP and/or $GaPO_4$ which is difficult to vaporize or dissociate in the low-temperature flames employed. The nitrogen(entrained air)–hydrogen flame produced the same results as the argon flame.

Effects of various other elements

Mulford[6] reported that only aluminum at a concentration 100 times that of

TABLE III

EFFECT OF OTHER ELEMENTS ON GALLIUM ATOMIC ABSORPTION

(10 p.p.m. Ga; 200 p.p.m. interfering element)

	Ar(air)-H_2	*N_2(air)-H_2*
No interference	Au[a], Ba[a], Bi[b], Ca[a], Ce[c], Co[a], Cs[a], Fe[a], Hg[a], In[a], K[a], La[a], Li[a], Mg[a], Na[a], Pd[a], Pt[a], Se[d], Sn[a], Sr[b], Ti[a], Tl[b], W[d]	Au[a], Ba[a], Bi[b], Ca[a], Ce[c], Co[a], Fe[a], In[a], K[a], La[a], Mg[a], Na[a], Pd[a], Pt[a], Sr[b], Ti[a], Tl[b], W[d]
Depression	Al[a], Ag[b], As[d], B[d], Be[c], Cd[b], Cr[a], Cu[c], Mn[b], Mo[c], Ni[c], Rb[a], Pb[b], Sb[a], Si[d], Te[d], Th[b], V[e], Y[b], Zn[b], Zr[b]	Al[a], Ag[b], As[d], B[d], Be[c], Cd[b], Cr[a], Cs[a], Cu[c], Hg[a], Li[a], Mn[b], Mo[c], Ni[c], Rb[a], Pb[b], Sb[a], Se[d], Si[d], Sn[a], Te[d], Th[b], V[e], Y[b], Zn[b], Zr[b]
Enhancement	None	None

[a] Added as chloride.

[b] Added as nitrate.

[c] Added as sulfate.

[d] Added as sodium salt.

[e] Added as ammonium salt.

gallium interfered significantly with gallium in an air–acetylene flame. Popham and Schrenk[8] reported that in the nitrous oxide–acetylene flame, only bismuth and nickel caused severe depression, while sodium and potassium caused some enhancement.

The effects of various elements on the gallium atomic absorption in both hydrogen flames were investigated at constant concentration levels of gallium and diverse ions. Many elements gave a depressing interference (Table III), the deviation of the absorbance for gallium being greater than 5%. Some elements such as calcium, lanthanum, magnesium *etc.* did not interfere, but no element enhanced the gallium atomic absorption. It has been observed that the temperature in the argon(entrained air)–hydrogen flame is higher at any position in the flame than that in the nitrogen-(entrained air)–hydrogen flame[25]. This probably explains the differences in the interference effects described in Table III.

Because flame composition and flame height are important parameters in the study of interference[30], the hydrogen flow rate and the flame height in the cool flames were varied to see if any effect would be produced on the depressing interference; it was found that the depressing interference was dependent on these parameters. Also the type of the compounds added had some effect on the magnitude of interferences.

In an attempt to eliminate these depressing interferences, the effect of the further addition of a non-interfering element was examined. Some elements were found to eliminate the depressing interferences, magnesium being the most effective (Table IV). When the standard and sample solutions were prepared so as to contain 1000 p.p.m. of magnesium (as chloride) as an interference-releasing agent, the depressing interferences were almost removed. This phenomenon would be applicable to the determination of gallium in practical samples.

Effect of organic solvents

The effect of organic solvents on the gallium atomic absorption was also examined. A series of primary alcohols was selected, and the concentration of the alcohols was from 10 to 50% by volume. The alcohols had a slightly depressing effect, and the gallium absorbance decreased with an increase in the alcohol concentration. A more detailed investigation was not made.

Application of the method to some semi-conducting compounds of Groups III–V

On the basis of the above observations, the following procedures were designed for the determination of gallium in some semi-conducting III–V compounds, *e.g.*, SbGa, GaP, $Ga_xIn_{1-x}P$, $Al_xGa_{1-x}P$.

TABLE IV

SUPPRESSION OF INTERFERENCES FROM OTHER ELEMENTS IN THE ARGON(ENTRAINED AIR)-HYDROGEN FLAME

(10 p.p.m. Ga; 200 p.p.m. interfering element; 1000 p.p.m. Fe, Ca, La or Mg. Results are expressed as the ratio of the absorbance for gallium in the presence of the interfering element to the absorbance in the absence of the interfering element)

Element	*Relative absorbance*				
	None	*Iron*	*Calcium*	*Lanthanum*	*Magnesium*
Al	0.17	0.74	0.86	0.80	0.99
As	0.32	0.90	1.00	0.97	0.98
Cd	0.48	1.00	1.03	1.01	1.01
Cr	0.27	0.86	0.89	1.01	1.02
Cu	0.56	0.97	0.90	0.97	0.98
Ni	0.89	0.90	0.95	0.92	1.03
Pb	0.88	0.88	0.90	0.97	0.97
Zn	0.35	1.02	0.96	0.98	0.97

TABLE V

DETERMINATION OF GALLIUM IN SOME SEMI-CONDUCTING COMPOUNDS

Sample	*Sample taken (mg)*	*Gallium content (weight %)*		
		Theoretical value	*Ar (air)–H_2*	*N_2 (air)–H_2*
SbGa(A)	33.4	36.4	36.8[a] 36.5[b]	35.9[a] 36.3[b]
SbGa(B)	21.3	36.4	36.7[a] 36.4[b]	36.6[a] 36.5[b]
GaP	29.8	69.2	69.0[a] 69.2[b]	69.1[a] 69.2[b]
$Ga_xIn_{1-x}P$	10.2	42.3	41.9[a] 42.4[b]	42.7[a] 42.5[b]
$Al_xGa_{1-x}P$	12.0	67.2	67.6[a] 67.3[b]	67.4[a] 67.2[b]

[a] Determined with the calibration graph method.

[b] Determined with the standard addition method.

The semi-conducting compound (10–30 mg) was weighed and dissolved with 5 ml of concentrated nitric acid and 5 ml of concentrated hydrofluoric acid in a polyethylene bottle on a water bath. After dissolution, the solution was diluted to 100 ml with distilled water. The gallium in the samples was determined three times by both the calibration graph and the standard addition methods. Aluminum, antimony, and hydrofluoric and nitric acids interfered, hence 1000 p.p.m. of magnesium (as chloride) was added to the sample and standard solutions in order to remove these interferences. The gallium was measured at 287.4 nm in the premixed argon(entrained air)– and nitrogen(entrained air)–hydrogen flames under the optimal conditions mentioned above. The results of the determinations (Table V) agreed closely with the theoretical values.

CONCLUSIONS

Gallium can be easily determined below 1 p.p.m. in aqueous solutions by atomic absorption spectrometry in cool flames such as the premixed inert gas (entrained air)–hydrogen flames with a "multi-flame" burner. The linear analytical range extends to *ca.* 10 p.p.m. The organic solvents tested did not produce an enhancement in the absorbance for gallium. Many other elements and some inorganic acids interfered; these depressing interferences could be eliminated by adding a large amount of magnesium chloride (1000 p.p.m. Mg) to the sample solutions.

The interest and encouragement of Professor Makoto Munemori in this work is gratefully acknowledged. The authors acknowledge the assistance given by Mr. Nobuo Horii in the experimental work.

SUMMARY

Gallium can be determined sensitively in premixed argon(entrained air)– and nitrogen(entrained air)–hydrogen flames at 287.4 nm; sensitivity (for 1 % absorption) is 0.20–0.24 p.p.m. and calibration graphs are linear up to 10 p.p.m. Many elements and acids interfere, but the addition of magnesium (1000 p.p.m.) as chloride is very effective in eliminating these interferences. This finding was satisfactorily applied to the determination of gallium in some semi-conducting III–V compounds.

REFERENCES

1 B. M. Gatehouse and J. B. Willis, *Spectrochim. Acta*, 17 (1961) 710.
2 J. E. Allan, *Spectrochim. Acta*, 18 (1962) 259.
3 W. Slavin, *Appl. Spectrosc.*, 20 (1966) 281.
4 V. A. Fassel, V. G. Mossotti, W. E. L. Grossman and R. N. Kniseley, *Spectrochim. Acta*, 22 (1966) 347.
5 W. W. McGee and J. D. Winefordner, *Anal. Chim. Acta*, 37 (1967) 429.
6 C. E. Mulford, *At. Absorption Newslett.*, 5 (1966) 28.
7 H. K. L. Gupta, F. J. Amore and D. F. Boltz, *At. Absorption Newslett.*, 7 (1968) 107.
8 R. E. Popham and W. G. Schrenk, *Spectrochim. Acta, Part B*, 24 (1969) 223.
9 E. N. Pollock, *At. Absorption Newslett.*, 10 (1971) 77.
10 G. N. Lypka and A. Chow, *Anal. Chim. Acta*, 60 (1972) 65.
11 H. L. Kahn and J. E. Schallis, *At. Absorption Newslett.*, 7 (1968) 5.
12 R. M. Dagnall, K. C. Thompson and T. S. West, *At. Absorption Newslett.*, 6 (1967) 117.

13 I. Rubeška and M. Mikšovský, *At. Absorption Newslett.*, 11 (1972) 57.
14 C. Veillon, J. M. Mansfield, M. L. Parsons and J. D. Winefoedner, *Anal. Chem.*, 38 (1966) 204.
15 D. W. Ellis and D. R. Demers, *Anal. Chem.*, 38 (1966) 1943.
16 H. P. Hooymayers and C. Th. J. Alkemade, *J. Quant. Spectrosc. Radiat. Trans.*, 6 (1966) 847.
17 R. Smith, C. M. Stafford and J. D. Winefordner, *Anal. Chem.*, 41 (1969) 946.
18 R. M. Dagnall, K. C. Thompson and T. S. West, *Talanta*, 14 (1967) 1467; 15 (1968) 677.
19 K. Zacha and J. D. Winefordner, *Anal. Chem.*, 38 (1966) 1537.
20 R. M. Dagnall, K. C. Thompson and T. S. West, *Analyst (London)*, 92 (1967) 506; 93 (1968) 72; 93 (1968) 518.
21 R. M. Dagnall, B. Fleet, T. H. Risby and D. R. Deans, *Talanta*, 18 (1971) 155.
22 R. Smith, C. M. Stafford and J. D. Winefordner, *Anal. Chim. Acta*, 42 (1968) 523.
23 T. Nakahara, H. Date, M. Munemori and S. Musha, *Bull. Chem. Soc. Jap.*, 46 (1973) 637.
24 T. Nakahara, M. Munemori and S. Musha, *Anal. Chim. Acta*, 62 (1972) 267.
25 T. Nakahara, M. Munemori and S. Musha, *Bull. Chem. Soc. Jap.*, 46 (1973) 639.
26 T. Nakahara, M. Munemori and S. Musha, *Bull. Chem. Soc. Jap.*, 46 (1973) 1166.
27 T. Nakahara, H. Nishino, M. Munemori and S. Musha, *Bull. Chem. Soc. Jap.*, 46 (1973) 1706.
28 C. H. Corliss and W. R. Bozman, *Experimental Transition Probabilities for Spectral Lines of Seventy Elements*, NBS Monograph No. 53, U.S. Department of Commerce, N.B.S., Washington, D.C., 1962, p. 111.
29 C. S. Rann and A. N. Hambly, *Anal. Chem.*, 37 (1965) 879.
30 J. A. Dean and T. C. Rains, *Flame Emission and Atomic Absorption Spectrometry*, Vol. 1, Marcel Dekker, New York, 1969.

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INFRAROTSPEKTROSKOPISCHE ANALYSE VON THIURAMDISULFIDFUNGIZIDEN

TEIL I. IDENTIFIZIERUNG UND BESTIMMUNG VON THIURAM*

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(Eingegangen den 2. Mai 1974)

Tetramethylthiuramdisulfid [bis-dimethyldithiocarbamonyldisulfid; $(CH_3)_2$-N–CS–S–S–CS–$N(CH_3)_2$, auch TMTD, Thiuram, Thiram] war schon lange vor dem Bekanntwerden seiner guten fungiziden Wirkung als Vulkanisationsbeschleuniger in Anwendung. Infolge seiner vielfältigen Anwendbarkeit gibt es zahlreiche Publikationen besonders auf dem analytischen Gebiet. Die Untersuchungen der Trennung und quantitativen Bestimmung wurden mit Hilfe Dünnschicht-[1–4] und Papierchromatographie[5–8] durchgeführt. In der Literatur findet man mehrere Veröffentlichungen über die spektrophotometrischen quantitativen Bestimmungen von Thiuram im p.p.m. Bereich sowohl in biologischen Stoffen[9–14] als auch in Gummimaterial[15] und in Luft[16]. Besondere Aufmerksamkeit verdienen die Arbeiten von Keppel[9], die die Thiuramrückstandanalyse von Getreide und Obst mit Hilfe der Kohlendisulfidevolutionsmethode[17–20] betreffen. Die obengenannte Methode und ihre Modifikationen wurden als schnelle Methode zur Marktkontrolle der D- und T-Fungiziden, jedoch ohne qualitative Differenzierung der einzelnen Wirkstoffe eingesetzt[21].

Im Gegensatz zu dieser Methode gibt die IR-Spektrophotometrie eine Möglichkeit der Identifizierung und der quantitativen Bestimmung der D- und T-Fungizide in den gemischten Präparaten[21–25]. Die vorliegende Arbeit ist eine Fortführung der Forschungen an den Dialkyldithiocarbamaten (D-Fungizide) und deren Oxydationsprodukten, den Thiuramdisulfiden (T-Fungizide)[24,25].

EXPERIMENTELLES

Chemikalien und Geräte

Tetramethylthiuramdisulfid (Thiram Vancide TM-95) umkristallisiert aus Chloroform–Äthanol p.a., von der Firma Vanderbilt N.Y. "Pomarsol-forte" (Thiuram-Präparat) von der Firma Bayer–Austria. "Rosenspritzmittel-K" (Thiuram + Schwefel + Füllstoffe) von der Firma Schering–Kwizda, Austria. "Tiuramosiarkol" (Thiuram + Schwefel + Füllstoffe) im Teststadium von dem Industriebetrieb "Azot" Polen. Kaliumbromid zur Spektroskopie von Merck, getrocknet und bei 110°C aufbewahrt. Aceton p.a.

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* Diese Arbeit wurde im Institut für Analytische Chemie und Mikrochemie der Technischen Hochschule Wien durchgeführt.

Perkin–Elmer-Gitterspektrophotometer 257 und 457. Pressform für 13 mm Dia. Presslinge, Presse, Vakuumpumpe, Achatmörser, Reagenzglas zur Vakuumfiltration, Glassintertrichter G-3, Vakuumexsikkator, Spektrographischer Analysator, Modell 26000-1.

Probenvorbereitung

Die Presslinge des Wirkstoffes und der Handelsprodukte. Die Einwaage des untersuchten Stoffes 1,0–0,2 mg TMTD und *ca.* 1,0 mg der Handelsprodukte wurde quantitativ in einen Achatmörser übergeführt und mit 200 mg KBr 10 Min lang verrieben. Dann wurde das Gemisch quantitativ in die Pressform eingesetzt, 5 Min evakuiert und schliesslich 1 Min unter 5 Tonnen und 4 Min unter 9 Tonnen Belastung zur üblichen Tablette verpresst.

Die Presslinge nach der Acetonextraktion der Handelsprodukte. Die Einwaage (1,0 mg) des Handelsproduktes wurde quantitativ auf den Glassintertrichter übergeführt, mit Aceton portionsweise gewaschen und unter Vakuum filtriert. Das Acetonfiltrat wurde im Vakuumexsikkator bis zur Trockne eingedampft. Der trockene Rückstand wurde mit 200 mg Kaliumbromid verrieben und nach dem obengenannten Verfahren zur Tablette verpresst.

AUFNAHME VON IR-SPEKTREN

Die Übersichtsspektren von Thiuram, Thiuramhandelsprodukten und ihren Acetonextrakten wurden mit dem Perkin–Elmer-Gitterspektrophotometer 457 (von 4000 bis 250 cm^{-1}) und mittlerer Vorschubgeschwindigkeit (*ca.* 280 cm^{-1} Min^{-1}) aufgenommen (Abb. 1–4). Die quantitativen Messungen wurden mit langsamer Vorschubgeschwindigkeit (*ca.* 70 cm^{-1} Min^{-1}) und mit dem Perkin–Elmer-Gitterspektrophotometer 257 durchgeführt. Die Auswertung der Intensitäten der characteristischen Banden erfolgte nach dem Grundlinienverfahren. Die Spektreneichung erfolgte mit Hilfe eines Polystyrolfilmes (Dicke 0.07 mm). Die Lage und Intensität der charakteristischen IR-Banden der Acetonextrakte wurden graphisch dargestellt und mit den Thiuram IR-Banden verglichen (Abb. 5).

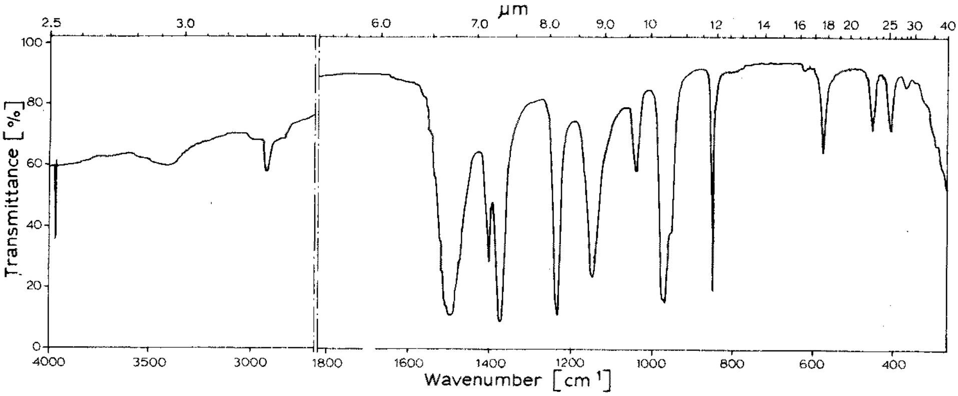

Abb. 1. IR-Spektrum von Thiuramdisulfid (in KBr); Messbanden: 1500, 975, 850.

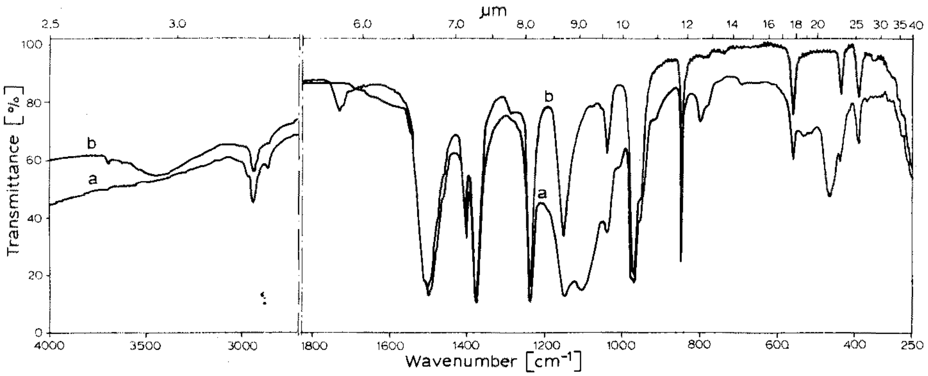

Abb. 2. IR-Spektren von: (a) Pomarsol-forte; (b) Acetonextrakt.

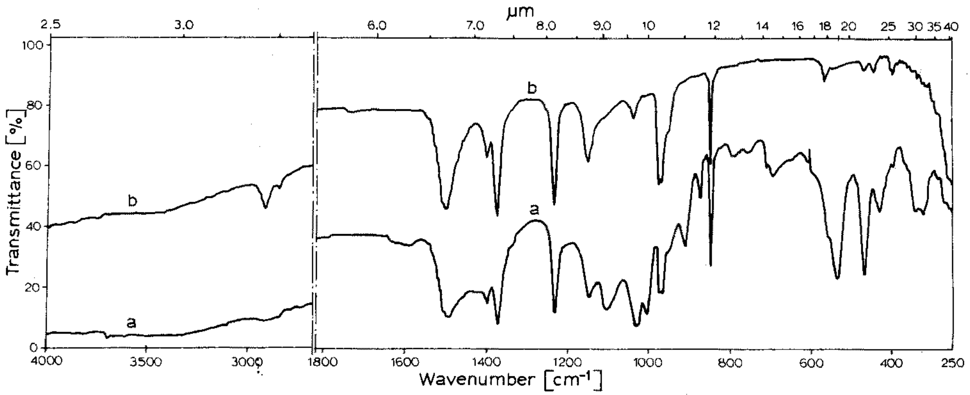

Abb. 3. IR-Spektren von: (a) Rosenspritzmittel-K; (b) Acetonextrakt.

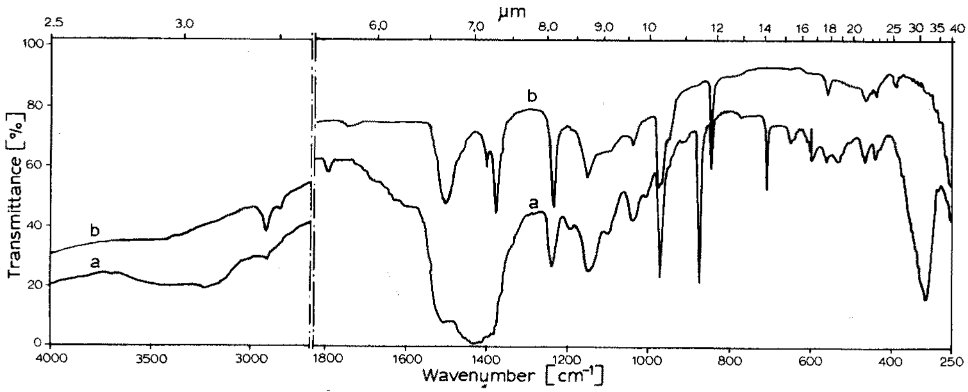

Abb. 4. IR-Spektren von: (a) Tiuramosiarkol; (b) Acetonextrakt.

Semiquantitative Funkenspektralanalyse

Es wurde ausserdem die semiquantitative Emissionsspektralanalyse des Thiurams und T-Fungiziden mit dem ARL Spektrographischen Analysator durchgeführt (Tab. I).

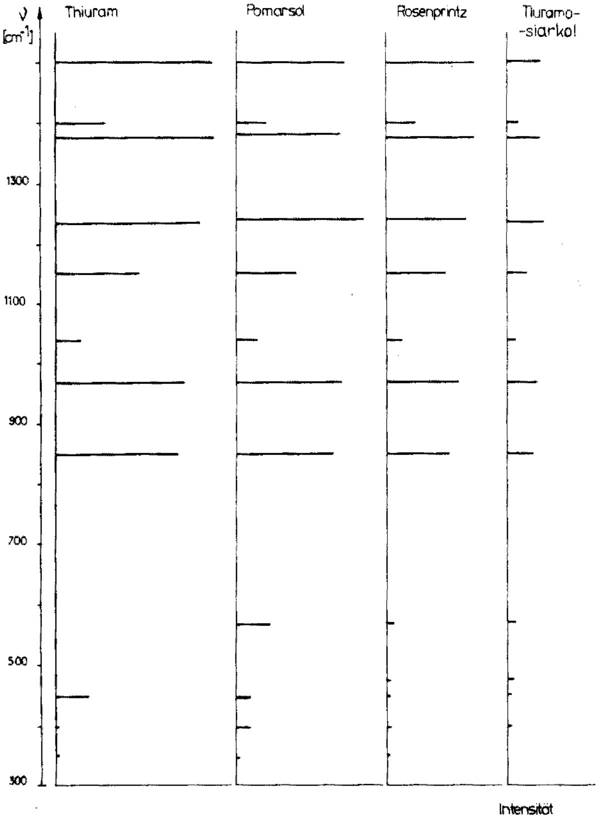

Abb. 5. Lage und Intensität der charakteristischen IR-Banden des Thiurams und der Acetonextrakten von Pomarsol, Rosenspritzmittel-K, Tiuramosiarkol.

Quantitative Untersuchungen

Es wurde gezeigt, dass das LBB-Gesetz für IR-Banden des Thiuramsspektrums (1500, 975, 850 cm^{-1}) bei der Anwendung der KBr-Präparationsmethode unter Voraussetzung der Konstanthaltung aller Parameter und innerhalb eines gewissen Konzentrationsbereiches gültig ist (Abb. 6, Tab. II).

Für jedes der untersuchten Handelsprodukte wurden nach der obengenannten Weise je 10 Testproben hergestellt und die Extinktionen der Absorptionsbande bei 850 cm^{-1} nach der Grundlinienmethode ermittelt. Die Ergebnisse dieser Messungen und die statistische Auswertung wurden in der Tabelle III zusammengestellt.

Auf Grund des Beerschen Gesetzes wurde der Gehalt dieses Wirkstoffes in 1 mg Einwaage der untersuchten Handelsprodukte ermittelt. Die Berechnungen des Zuverlässigkeitsintervalls wurden bei der Anwendung der Studentschen Verteilung nach der Beziehung: $x = \bar{x} \pm t(Pn)s$ durchgeführt. Das Zuverlässigkeitsintervall, in dem das wirkliche Ergebnis mit der Wahrscheinlichkeit $(1-\mu) = 0{,}95$ liegt, beträgt für: Pomarsol, $x = 0{,}732 \pm 0{,}022$ mg; Rosenspritz., $x = 0{,}243 \pm 0{,}016$ mg; Tiuramosiarkol, $x = 0{,}245 \pm 0{,}032$ mg.

TABELLE I

EMISSIONSSPEKTRALANALYSE DER T-FUNGIZIDEN

Elemente	*Probe*			
	Thiuram	*Pomarsol*	*Rosenspritzmittel-K*	*Tiuramosiarkol*
Zn	—	—	—	—
Na	—	0,3	—	—
As	—	—	—	—
Mn	0,01	0,01	0,03	0,004
Mg	—	—	0,6	—
Fe	—	0,03	0,02	0,02
Al	—	0,1	0,1	0,04
Cu	—	—	0,0005	0,002
Ca	—	—	0,6	0,07
Mo	—	—	—	—
Pb	—	—	—	—
Ti	—	0,006	0,02	—
Co	—	—	—	—
Hg	—	—	—	—
Ba	—	—	—	—

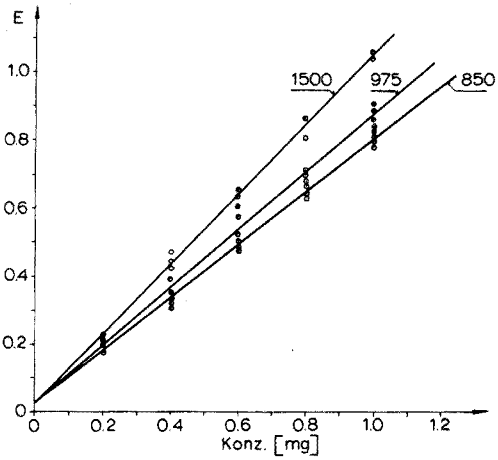

Abb. 6. Eichkurven von Thiuram (Substanzbedarf 1,0–0,2 mg); Messbanden: 1500, 850, 975.

TABELLE II

DIE ANGABEN DER REGRESSIVEN GERADEN DES THIURAMS ($y = a + bx$) BEI DER VERSCHIEDENEN MESSUNGSBANDEN

Lage der Messungsbande (cm^{-1})	*Koeffizient a*	*Koeffizient b*	*Korrelationskoeffizient (r)*
1500	0,0246	1,0194	0,9978
975	0,0333	0,8232	0,9796
850	0,0276	0,7620	0,9958

TABELLE III

DIE ERGEBNISSE DER QUANTITATIVEN BESTIMMUNGEN AUF 1 mg EINWAAGE BEZOGEN

Name	*Anzahl der Ergebnisse (n)*	*Mittlerer Wert der Extinktion* $(\bar{x})$	*Standardabweichung des arithmetischen* $(s_{\bar{x}})$	*Variations koeffizient* $(v\,\%)$
Pomarsol	10	0,588	0,0030	1,30
Rosenspritz.	10	0,195	0,0021	2,59
Tiuramosiarkol	10	0,197	0,0017	5,94

DISKUSSION

Nach Durchführung eines einfachen Extraktionsverfahrens zur Abtrennung von Füllstoffen konnte die KBr-Präparationsmethode zur Aufnahme von IR-Spektren des Wirkstoffes herangezogen werden. Diese bilden die Grundlage der Identifizierung und der quantitativen Bestimmung von Thiuram in Handelsprodukten im p.p.m. Bereich. Die bearbeitete Methode eignet sich gut zur Analyse von Thiuram in den Rohprodukten und Handelspräparaten.

Dem Österreichischen Bundesministerium für Wissenschaft und Forschung sei an dieser Stelle für das gewährte Stipendium herzlich gedankt. Herrn o. Prof.Dipl.Ing.Dr.techn. Hanns Malissa, Vorstand des Institutes für Analytische Chemie und Mikrochemie der TH Wien, möchte ich für das grosse Interesse am Fortgang dieser Arbeit und für die tatkräftige Unterstützung meinen aufrichtigen Dank ausdrücken. Herrn Dipl.Ing.Dr.techn. Robert Kellner danke ich herzlich für die stets erwiesene Hilfe bei der Lösung zahlreicher Probleme. Den Firmen Bayer-Austria, Schering-Kwizda und Vanderbilt N.Y. bin ich für die mir freundlicherweise übersandten Proben zu grossem Dank verpflichtet.

ZUSAMMENFASSUNG

Es wurde eine infrarotspektrophotometrische Methode zur Identifizierung und zur quantitativen Bestimmung des Thiurams in Rohprodukten und einigen handelsüblichen Formulierungen bearbeitet. Der Wirkstoff wurde mit Aceton extrahiert und nach der Verdampfung des Lösungsmittels im Vakuum mit Kaliumbromid verrieben und in eine Tablette verpresst. Die Extinktionswerte der ausgewählten Messbande (850 cm^{-1}) wurden nach der Grundlinienmethode ermittelt. Der gefundene Thiuramprozentgehalt beträgt in Pomarsol 73,2 ± 2,21%, in Rosenspritzmittel-K 24,3 ± 1,58%, in Tiuramosiarkol 24,5 ± 3,16%. Die Abschätzung der Genauigkeit der Analysenresultate charakterisieren die Variationskoeffizienten, die für: Pomarsol 1,30%, für Rosenspritzmittel-K 2,59% und für Tiuramosiarkol 5,94% betragen.

SUMMARY

Infrared methods have been developed for the detection and determination

of Thiuram in technical products and some commercial formulations. The biologically active component was extracted with acetone and after evaporation of the solvent *in vacuo*, KBr disks were prepared. Band absorbances were measured by the base-line method. The results for Thiuram were 73.2±2,21% in Pomarsol, 24.3±1.58% in Rosenspritzmittel-K, and 24,5±3.16% in Thiuramosiarkol; the relative standard deviations were 1.30%, 2.59% and 5.94%,respectively.

REFERENCES

1 C. A. Parker und J. M. Berriman, *Trans. Inst. Rubber Ind.*, 28 (1952) 279.
2 N. G. Porter, *J. Chromatogr.*, 28 (1967) 469.
3 J. Piechocka, *Rocz. Państw. Zakl. Hig.*, 19 (1968) 188.
4 L. Sluzewska, *Rocz. Państw. Zakl. Hig.*, 20 (1969) 177.
5 J. W. H. Zijp, *Rec. Trav. Chim. Pays-Bas*, 75 (1956) 1083.
6 W. P. McKinley und S. A. Magarvey, *J. Ass. Offic. Agr. Chem.*, 43 (1960) 717.
7 A. Popov, *C.R. Acad. Bulg. Sci.*, 15 (1962) 139.
8 J. Piechocka, *Rocz. Państw. Zakl. Hig.*, 17 (1966) 529.
9 G. E. Keppel, *J. Ass. Offic. Agr. Chem.*, 32 (1956) 709; 40 (1957) 270; 42 (1959) 545; 45 (1962) 410; 52 (1969) 162; 54 (1971) 528.
10 B. Mikolajczak-Bozilow, M. Bohoszewicz und Z. Dembiński, *Zesz. Nauk. Wyzsz. Szk. Roln. Wroclaw*, 2 (1967) 69.
11 J. J. Henriet, *Ind. Chim. Belge*, 32 (1967) 880.
12 G. Belluci und C. Leoni, *Ind. Conserve*, 45 (1970) 220.
13 J. R. Rangaswamy, P. Poornima und S. K. Majunder, *J. Ass. Offic. Anal. Chem.*, 53 (1970) 519.
14 M. Murata, *J. Agr. Chem. Soc. Japan*, 35 (1961) 977.
15 W. Scheele und Ch. Gensch, *Kaut. Gummi Kunstst.*, 6 (1953) WT 147.
16 D. Sprecher und M. Grigorowa, *Z. Ges. Hyg. Grenz.*, 13 (1967) 241.
17 D. G. Clarke, H. Baum, E. L. Stanley und W. F. Hester, *Anal. Chem.*, 23 (1951) 184.
18 W. K. Lowen, *Anal. Chem.*, 23 (1951) 1846.
19 H. L. Pease, *J. Ass. Offic. Agr. Chem.*, 40 (1957) 1133.
20 T. E. Cullen, *Anal. Chem.*, 36 (1964) 221.
21 J. Reinhard, *Mitt., Bl. Ges. Dtsch. Chem. Lebensmittel-gerichtl. Chem.*, 25 (1971) 1.
22 J. Mann, *Trans. Inst. Rubber. Ind.*, 27 (1951) 232.
23 D. Firestone und P. J. Vollmer, *J. Ass. Offic. Agr. Chem.*, 39 (1956) 866.
24 W. Sztark, H. Malissa und R. Kellner, *Anal. Chim. Acta*, 63 (1973) 285.
25 W. Sztark, *Chem. Anal. (Warsaw)*, im Druck.

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NAPHTHOQUINONEDIOXIME DERIVATIVES AS ANALYTICAL REAGENTS FOR THE SPECTROPHOTOMETRIC DETERMINATION OF NICKEL

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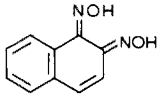
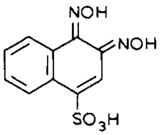
(Received 30th May 1974)

Many dioxime compounds have been synthesized since dimethylglyoxime was first prepared and applied to analytical studies in 1905[1]. Few naphthoquinonedioxime derivatives, however, have been examined. Recently[2,3], the authors synthesized several dioxime compounds, and found that of sixteen dioxime compounds examined, naphthoquinonedioxime-4-sulfonic acid had high sensitivity for nickel. In the work described here, several other new naphthoquinonedioxime derivatives were prepared and their sensitivities for some metal ions were examined. The composition ratio of the nickel–dioxime complexes and the effects of dioxane and zephiramine on enhancement of the sensitivity were studied, and the naphthoquinonedioximes were compared with the corresponding nitrosonaphthols.

The seven naphthoquinonedioximes used in this work are shown below; five of these reagents (asterisked) are new compounds.



I



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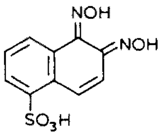
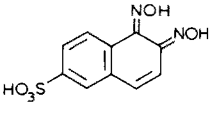


III*



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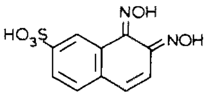

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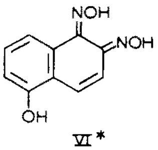

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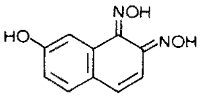

VII*

EXPERIMENTAL

Reagents

Naphthoquinonedioxime compounds. Each compound was prepared from the

TABLE I

ELEMENTAL ANALYSIS OF NAPHTHOQUINONEDIOXIME COMPOUNDS USED

Reagent		*% C*	*Found (calcd.)*	
			% H	*% N*
I	$C_{10}H_8N_2O_2$	63.5(63.8)	4.2(4.3)	14.8(14.9)
II	$C_{10}H_8N_2O_5S\cdot 2H_2O$	39.9(39.5)	4.5(4.0)	9.3(9.2)
III	$C_{10}H_8N_2O_5S\cdot 2H_2O$	39.4(39.5)	3.8(4.0)	9.5(9.2)
IV	$C_{10}H_8N_2O_5S\cdot 2H_2O$	40.6(39.5)	3.4(4.0)	8.9(9.2)
V	$C_{10}H_8N_2O_5S\cdot 3H_2O$	37.6(37.3)	4.2(4.4)	8.4(8.7)
VI	$C_{10}H_8N_2O_3$	60.2(58.8)	3.7(4.0)	13.3(13.7)
VII	$C_{10}H_8N_2O_3$	59.5(58.8)	4.5(4.0)	13.2(13.7)

following materials according to the method of Goldschmidt and Schmidt[4]: reagent [I] was prepared from 1-nitroso-2-naphthol, [II] from 2-nitroso-1-naphthol-4-sulfonic acid, [III] from 2-nitroso-1-naphthol-5-sulfonic acid, [IV] from 1-nitroso-2-naphthol-6-sulfonic acid, [V] from 1-nitroso-2-naphthol-7-sulfonic acid, [VI] from 2-nitroso-1,5-dihydroxynaphthalene and [VII] from 1-nitroso-2,7-dihydroxynaphthalene. Each dioxime was synthesized by reflux of the corresponding nitrosonaphthol[5,6] (1 mole) and hydroxyammonium chloride (1.2 mole), and the product was recrystallized. Each naphthoquinonedioxime sulfonic acid could also be prepared from the corresponding *o*-quinone sulfonic acid. Results of elemental analyses for the dioximes synthesized are shown in Table I.

Naphthoquinonedioxime compound solution. Naphthoquinonedioximes, I, VI and VII, were dissolved in ethanol and the other dioximes, II–V, in distilled water. Each solution was prepared to give 10^{-2} or 10^{-3} mole l^{-1}.

Buffer solution. The pH was adjusted with the following solutions; hydrochloric acid (pH 2–3), acetic acid–sodium acetate (pH 4–5), potassium dihydrogenphosphate–disodium hydrogenphosphate (pH 6–7), ammonium chloride–ammonia (pH 8–10), sodium carbonate–sodium hydrogencarbonate (pH 11) and potassium hydroxide (pH 12–14) solutions.

Metal ion solutions. Nickel sulfate hexahydrate, cobalt nitrate hexahydrate and Mohr's salt were used. Each metal solution was 10^{-3} or 10^{-4} mole l^{-1}. Hydroxyammonium chloride (1% w/w) was added to the iron(II) solution.

Zephiramine solution. Zephiramine (tetradecyldimethylbenzylammonium chloride; Dojindo Co. Ltd., Research Laboratories) was dissolved in distilled water to give a 10^{-2} mole l^{-1} solution.

Other reagents. Chloroform, nitrobenzene and benzyl alcohol were used as extracting solvents. Dioxane was used as the synergic reagent. All the reagents used were of analytical-reagent grade.

Apparatus

A Shimadzu model QV-50 spectrophotometer and a Hitachi model EPS-3T recording spectrophotometer were used for measuring the absorbance in 10-mm quarz cells. A Hitachi–Horiba model F-5 ss pH meter equipped with a combined electrode (6026-05T), and an Iwaki Model KM shaker were used.

Procedures

Determination of molar absorptivities of metal complexes. The molar absorptivities of the metal complexes of four naphthoquinonedioximes (II–V), which formed water-soluble chelate compounds, were measured in aqueous solution. Metal ion solution, dioxime solution and buffer solution (3 ml) of the optimal pH for coloration with metal ions were pipetted into a test tube in that order, and distilled water was finally added to give a total amount of 5 ml. After mixing thoroughly, the absorbance was measured.

For solvent extraction, the metal chelate of the naphthoquinonedioximes was extracted as a ternary complex (naphthoquinonedioxime–metal–zephiramine) into the solvent by addition of zephiramine. The metal chelate of reagent I was also extracted incompletely without zephiramine. Metal ion solution, naphthoquinonedioxime solution, buffer solution (3 ml) and 1 ml of zephiramine solution (10^{-2} mole l^{-1}) were pipetted into a stoppered 25-ml test tube, and distilled water was added to give a total amount of 6 ml. Finally, 5 ml of extracting solvent was pipetted into the tube. After shaking for 20 min, the mixture was allowed to stand for 30 min and the absorbance of the organic phase was measured. Chloroform, nitrobenzene and benzyl alcohol were examined as the extracting solvent.

Effect of dioxane in aqueous solution. Naphthoquinonedioximes II–V, which formed water-soluble chelates, were examined for the effect of dioxane. Nickel solution, naphthoquinonedioxime solution, buffer solution (3 ml) and dioxane (1 ml) were pipetted into a test tube, in that order, and distilled water was added to give a total volume of 5 ml. After mixing thoroughly, the absorbance of the solution was measured.

Effect of zephiramine in aqueous solution. When zephiramine solution was added to an aqueous solution of the nickel chelate of naphthoquinonedioxime sulfonic acids II–V, the absorbance increased. The procedure was the same as that for examining the effect of dioxane, but zephiramine solution (10^{-2} mole l^{-1}) was added instead of dioxane.

Determination of composition of the complex. The composition ratio of the nickel–reagent complex was determined by the mole ratio and the continuous variations methods. As the metal chelates of naphthoquinonedioximes were extracted into extracting solvent as a ternary complex with zephiramine, the compositions in extracting solvent were determined. The compositions of the water-soluble chelates of II–V were determined in aqueous solution. The composition on adding dioxane and zephiramine in aqueous solution was also examined.

RESULTS AND DISCUSSION

Molar absorptivities of metal chelate complexes

The optimal pH, the wavelengths of the absorption maxima and the molar absorptivities in aqueous solutions for the complexes with nickel, cobalt and iron(II) ions are shown in Table II. For comparison, the values of the corresponding nitrosonaphthols obtained by the same procedure as those of dioximes are also listed.

Of the extracting solvents examined, chloroform was found to have very

TABLE II

MOLAR ABSORPTIVITIES IN AQUEOUS SOLUTION[a]

Reagent	*Naphthoquinonedioximes*						*Nitrosonaphthols*[b]					
	Ni		*Co*		*Fe*		*Ni*		*Co*		*Fe*	
	λ_{max} *(nm)*	ε *(·10⁴)*	λ_{max} *(nm)*	ε *(·10⁴)*	λ_{max} *(nm)*	ε *(·10⁴)*	λ_{max} *(nm)*	ε *(·10⁴)*	λ_{max} *(nm)*	ε *(·10⁴)*	λ_{max} *(nm)*	ε *(·10⁴)*
I	(pH 8)		(pH 5)		(pH 8)		(pH 8)		(pH 7)		(pH 7)	
	307	0.95	305	2.98	314	2.01	401	1.11	424	3.1	732	1.60
	466	0.57	420	1.31	500	1.13	455	1.18				
II	(pH 6)		(pH 6)		(pH 4)		(pH 8)		(pH 7)		(pH 6)	
	301	2.06	307	4.80	294	2.87	352	1.03	368	3.3	720	2.12
	476	1.10	366	2.35	330	2.26	500	0.82				
			522	1.29	444	1.12						
					710	2.04						
III	(pH 5)		(pH 4)		(pH 6)		(pH 8)		(pH 7)		(pH 6)	
	305	2.24	311	3.64	304	3.44	349	1.29	368	3.8	728	2.02
	470	1.01	414	0.98	438	0.98	494	1.08				
					572	0.83						
					790	1.25						
IV	(pH 5)		(pH 4)		(pH 6)		(pH 8)		(pH 5)		(pH 6)	
	300	3.20	304	4.42	299	4.29	391	1.00	410	3.8	720	2.12
	466	1.18	412	1.09	436	0.97	461	1.00				
					574	1.00						
					800	1.29						
V	(pH 5)		(pH 4)		(pH 6)		(pH 8)		(pH 5)		(pH 6)	
	305	1.67	310	3.26	301	3.14	394	0.92	416	3.5	724	2.00
	466	0.91	416	0.94	440	0.98	461	0.98				
					578	0.87						
					800	1.07						
VI[c,d]	(pH 6)		(pH 6)		(pH 6)		(pH 6)		(pH 5)		(pH 6)	
	502	1.32	454	1.15	470	0.63	490	0.86	454	1.29	480	0.95

VII	(pH 6)		(pH 5)		(pH 6)		(pH 8)		(pH 7)		(pH 6)	
	309	1.71	302	4.06	312	3.43	411	1.71	450	3.5	712	1.69
	476	0.70	454	0.65	496	1.19						

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[a] These molar absorptivities were obtained from calibration curves; $[R]=2\cdot10^{-4}$ *M*.

[b] Nitrosonaphthols: I, 1-nitroso-2-naphthol; II, 2-nitroso-1-naphthol-4-sulfonic acid; III, 2-nitroso-1-naphthol-5-sulfonic acid; IV, 1-nitroso-2-naphthol-6-sulfonic acid; V, 1-nitroso-2-naphthol-7-sulfonic acid; VI, 2-nitroso-1,5-dihydroxynaphthalene; VII, 1-nitroso-2,7-dihydroxynaphthalene.

[c] Dioxane was added.

[d] As the complexes of this reagent were not stable, the amounts of the reagent added were three times more than those of other reagents.

TABLE III

MOLAR ABSORPTIVITIES IN CHLOROFORM

Reagent	*Naphthoquinonedioximes*						*Nitrosonaphthols*					
	Ni		*Co*		*Fe*		*Ni*		*Co*		*Fe*	
	λ_{max} (*nm*)	ε (· *10*^{4})	λ_{max} (*nm*)	ε (· *10*^{4})	λ_{max} (*nm*)	ε (· *10*^{4})	λ_{max} (*nm*)	ε (· *10*^{4})	λ_{max} (*nm*)	ε (· *10*^{4})	λ_{max} (*nm*)	ε (· *10*^{4})
I	(pH 8)		(pH 5)		(pH 5)		(pH 8)		(pH 7)		(pH 6)	
	310	3.13	307	3.70	304	2.61	382	0.65	414	3.4	730	1.80
	464	1.65	416	1.89	430	1.26	455	1.38				
II	(pH 8)		(pH 8)		(pH 8)		(pH 8)		(pH 7)		(pH 7)	
	307	5.12	312	6.21	297	4.20	480	2.11	368	4.0	716	2.12
	480	2.03	370	3.79	432	1.50						
			534	1.62	700	2.18						
III	(pH 5)		(pH 4)		(pH 6)		(pH 8)		(pH 6)		(pH 7)	
	322	3.58	321	3.80	315	3.22	486	1.65	368	3.9	724	1.97
	468	2.06	410	1.71	422	1.64						
					580	1.02						
IV	(pH 5)		(pH 4)		(pH 6)		(pH 6)		(pH 6)		(pH 7)	
	300	4.80	309	3.64	313	4.04	381	0.58	410	3.4	720	1.86
	468	2.19	412	1.98	424	1.56	458	1.48				
					578	1.00						
V	(pH 5)		(pH 4)		(pH 6)		(pH 8)		(pH 6)		(pH 7)	
	307	3.71	319	4.55	319	3.41	386	1.85	424	3.6	724	1.85
	468	2.04	422	1.69	438	1.79	454	1.58				
					588	1.11						
VI	(pH 6)		(pH 5)[a]		(pH 6)[a]		(pH 6)[a]		(pH 7)		(pH 6)	
	490	0.86	454	1.29	480	0.95	500	0.43	362	3.3	750	1.15
VII	(pH 5)[a]		(pH 6)[a]		(pH 6)[a]		(pH 8)		(pH 8)[b]		(pH 6)	
	468	1.33	456	1.73	486	1.05	408	1.73	456	3.1	708	1.65

[a] Extracting solvent nitrobenzene.

[b] Extracting solvent, benzyl alcohol.

good extractability. The extractions were therefore almost all carried out with chloroform. The optimal pH, the wavelengths of the absorption maxima and the molar absorptivities are shown in Table III. The molar absorptivities in Tables II and III were determined by preparing a calibration curve at each wavelength of maximal absorption; only reproducible values are shown in these Tables.

From Tables II and III, it can be seen that the molar absorptivities of the nickel chelates of naphthoquinonedioximes increase about twice on extraction into organic solvents as ternary complexes. Increases were usually also observed in the case of cobalt ions, but were only sometimes observed for the iron(II) ion. When nitrosonaphthols were used, such increases were observed only slightly for nickel chelates and hardly at all for cobalt and iron(II). In aqueous solutions, the molar absorptivities of the metal–naphthoquinonedioxime complex in the visible region were nearly equal for each metal ion and were about $1 \cdot 10^4$. On extracting the metal complex into organic solvent, however, the selectivity and sensitivity for the nickel complex increased; for example, with reagent II, the ratio of the molar absorptivities in aqueous solution for the Ni:Co:Fe complexes was 1.10:1.29:1.12 = 1:1.2:1, while the ratio in organic solvent was 2.03:1.62:1.50 = 1:0.8:0.7. From Fig. 1, it is seen that the absorption spectrum of the nickel complex of reagent II is different from that of the others (III–V); reagents III–V show large absorption of the complex and small absorption of the reagent itself at the maximal absorption wavelength of the complex in the visible region, while the absorption spectrum of reagent II is similar to that of nitrosonaphthols. This is due to the following reason. Reagent II is more aromatic than reagents III–V because of the electrons being fixed in the ring containing the two oxime groups by the electrophilic effect of the sulfonic group at the 4-position; reagents III–V appear more aliphatic than aromatic because of electrons being attracted to the other ring by the sulfonic group at the 5-, 6- or 7-position. Therefore, the absorption maxima of reagents III–V shift to short wavelength, and reagents III–V are more akin to the aliphatic dioximes, such as benzildioximes; they show higher selectivity for nickel than reagent II.

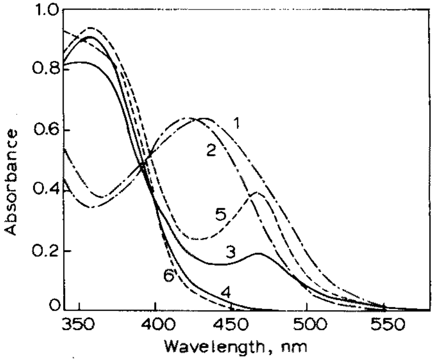


Fig. 1. Absorption spectra of nickel chelates of naphthoquinonedioxime sulfonic acid; $[R]=2\cdot 10^{-4}$ *M*; $[Ni^{2+}]=2\cdot 10^{-5}$ *M*. Curve 1; reagent II (reference, distilled water); curve 2; reagent blank of curve 1; curve 3: reagents III–V (reference, distilled water); curve 4: reagent blank of curve 3; curve 5: reagents III–V, extraction with chloroform (reference, chloroform); curve 6: reagent blank of curve 5.

The absorption spectra of the nickel chelates of the naphthoquinonedioxime sulfonic acids II–V are shown in Fig. 1. From Tables II and III and Fig. 1, the molar absorptivity of the nickel chelate increases about twice on extraction as a ternary complex.

Effect of dioxane in aqueous solution

The effects of adding dioxane to aqueous solutions of the nickel chelates of reagents II–V and the corresponding nitrosonaphthols on the absorption maxima in the visible region and the molar absorptivities are shown in Table IV. It can be seen that the molar absorptivities of the complexes with II–V increase 1.4–1.7 times on adding dioxane, while those of the corresponding nitrosonaphthols increase about 1.2 times. The stability of nickel chelates on adding dioxane was examined; Fig. 2 shows that the nickel chelates were not very stable except for the chelate of reagent II.

Effect of zephiramine in aqueous solution

The effect of added zephiramine (10^{-2} mole l^{-1}) on reagent III is shown in

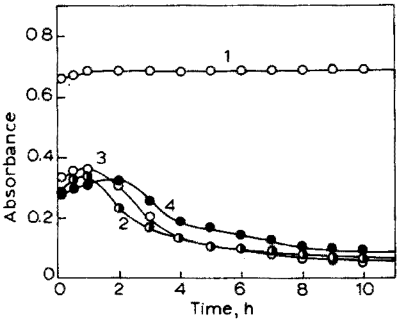


Fig. 2. Stability of nickel chelate on adding dioxane. $[R]=2\cdot10^{-4}$ *M*; $[Ni^{2+}]=2\cdot10^{-5}$ *M*; dioxane, 1 ml; reference: distilled water. Curve 1: reagent II; curve 2: reagent III; curve 3: reagent IV; curve 4: reagent V.

TABLE IV

MOLAR ABSORPTIVITIES ON ADDING DIOXANE

Reagent	*Naphthoquinonedioxime*				*Nitrosonaphthol*			
	No dioxane		*Dioxane added*[a]		*No dioxane*		*Dioxane added*[a]	
	λ_{max} (nm)	ε $(\cdot10^4)$	λ_{max} (nm)	ε $(\cdot10^4)$	λ_{max} (nm)	ε $(\cdot10^4)$	λ_{max} (nm)	ε $(\cdot10^4)$
II	476	1.10	476	1.56	500	0.82	500	0.95
III	470	1.01	470	1.61	494	1.08	494	1.26
IV	466	1.18	468	1.67	461	1.00	461	1.16
V	466	0.91	466	1.54	461	0.98	[b]	[b]

[a] One ml of dioxane per 5 ml of solution was added.

[b] Reproducible values could not be obtained.

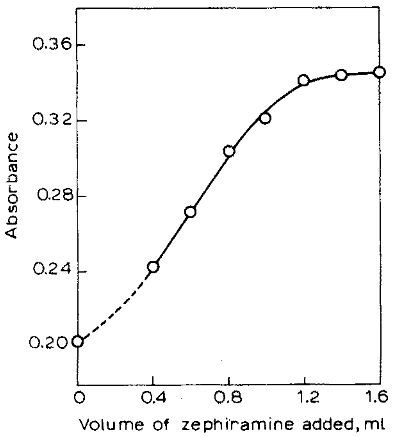


Fig. 3. Effect of zephiramine. Reagent III, $2 \cdot 10^{-4}$ M; [Ni], $2 \cdot 10^{-5}$ M; reference, distilled water; wavelength, 470 nm. The total amount of aqueous solution was 5 ml.

TABLE V

MOLAR ABSORPTIVITIES ON ADDING ZEPHIRAMINE

(1.4 ml of zephiramine (10^{-2} M) was added. The total volume of the solution was 5 ml.)

Reagent	*No zephiramine*		*Zephiramine added*	
	λ_{max} *(nm)*	ε $(\cdot 10^4)$	λ_{max} *(nm)*	ε $(\cdot 10^4)$
II	476	1.10	484	1.51
III	470	1.01	466	1.77
IV	466	1.18	468	1.60
V	466	0.91	466	1.40

Fig. 3; about 1.4 ml of zephiramine solution sufficed to give maximal effect.

The molar absorptivities of the nickel chelates of four naphthoquinonedioximes II–V at the absorption maxima, on adding 1.4 ml of zephiramine solution, are shown in Table V.

The stability of nickel chelates on adding zephiramine was also examined for reagent III. The zephiramine produced a remarkable improvement in stability; as in Fig. 2, the absorbance increased up to 1 h, but then remained stable for at least 10 h.

The results showed that, on adding a 140-fold amount of zephiramine compared to nickel ion, a stable complex was formed and the molar absorptivity increased 1.4–1.7 times. In the case of the corresponding nitrosonaphthols, the nickel chelate precipitated.

The composition of nickel–naphthoquinonedioxime complexes

The ratios of nickel to naphthoquinonedioxime were determined by the mole ratio and the continuous variations methods in aqueous solution and in the

TABLE VI

COMPOSITION RATIO OF NICKEL AND NAPHTHOQUINONEDIOXIME

Reagent[a]	*Mole ratio method*	*Continuous variations method*
	Ni:R	*Ni:R*
[I]CF	1:3.0	1:3.2
[I]Do	1:4.1	1:3.8
[II]CF	1:3.1	1:3.2
[II]Aq	1:3.0	1:3.0
[II]Do	1:4.0	1:3.8
[III]CF	1:3.0	1:3.1
[III]Aq	1:3.3	1:3.1
[III]Do	1:4.0	1:4.0
[III]Zep	1:3.0	1:3.2
[IV]CF	1:3.1	1:3.2
[IV]Aq	1:3.1	1:2.9
[IV]Do	1:4.1	1:4.3
[IV]Zep	1:3.0	1:2.9
[V]CF	1:3.1	1:3.1
[V]Aq	1:3.0	1:3.0
[V]Do	1:4.1	1:4.0
[V]Zep	1:3.0	1:3.1
[VI]	[b] [b]	[b] [b]
[VII]NB	1:3.1	1:2.8
[VII]Do	1:4.1	1:4.2

[a] Aq, aqueous solution; CF, chloroform; NB, nitrobenzene; Do, aqueous solution on adding 1 ml of dioxane; Zep, aqueous solution on adding zephiramine. The ratios in extracting solvent were obtained by adding zephiramine, and the ratios on adding dioxane were determined within 30 min of addition of dioxane.

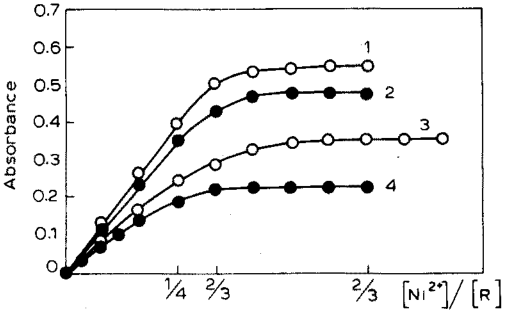
[b] Reproducible values could not be obtained.

extracting solvent. The results are shown in Table VI. The composition ratio changed from 1:3 to 1:4 on adding dioxane. This phenomenon also occurred in the case of the nitrosonaphthols.

As examples of the determination of the composition, results for reagent III in aqueous solution (1:3), in chloroform (1:3), in aqueous solution containing dioxane (1:4) and zephiramine (1:3) by the mole ratio and the continuous variations methods are shown in Figs. 4 and 5. These results show that the composition of the nickel chelates of naphthoquinonedioxime sulfonic acid increased from 1:3 to 1:4 on adding dioxane. The (1:4) complex, however, was not very stable. From the point of view of the coordination of the reagent to nickel ion, the series of naphthoquinonedioximes seem to be more akin to the nitrosonaphthols than to typical dioximes.

CONCLUSIONS

A summary of all the results is shown in Table VII. It can be seen that the molar absorptivity increases about twice when the ternary complex is extracted from the aqueous phase. Though the molar absorptivity of the aqueous solution



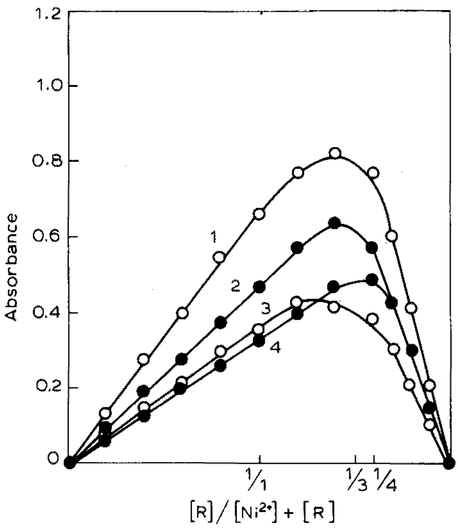


Fig. 4. Mole ratio method. Curve 1: $[\mathrm{III}]_{\mathrm{CF}}$, $[\mathrm{III}] = 10^{-4}$ *M* (468 nm). Curve 2: $[\mathrm{III}]_{\mathrm{zep}}$, $[\mathrm{III}] = 10^{-4}$ *M* (468 nm). Curve 3: $[\mathrm{III}]_{\mathrm{aq}}$, $[\mathrm{III}] = 10^{-4}$ *M* (470 nm). Curve 4: $[\mathrm{III}]_{\mathrm{Do}}$, $[\mathrm{III}] = 5 \cdot 10^{-5}$ *M* (470 nm).

Fig. 5. Continuous variations method. Curve 1: $[\mathrm{III}]_{\mathrm{CF}}$, $[\mathrm{Ni}^{2+}] + [\mathrm{III}] = 2 \cdot 10^{-4}$ *M* (468 nm); curve 2: $[\mathrm{III}]_{\mathrm{zep}}$, $[\mathrm{Ni}^{2+}] + [\mathrm{III}] = 2 \cdot 10^{-4}$ *M* (466 nm); curve 3: $[\mathrm{III}]_{\mathrm{aq}}$, $[\mathrm{Ni}^{2+}] + [\mathrm{III}] = 2 \cdot 10^{-4}$ *M* (470 nm); curve 4: $[\mathrm{III}]_{\mathrm{Do}}$, $[\mathrm{Ni}^{2+}] + [\mathrm{III}] = 2 \cdot 10^{-4}$ *M* (474 nm).

increases 1.4–1.7 times on adding dioxane or zephiramine, the cause of each increase is different. The increase of the molar absorptivity on adding dioxane depends on the increase in number of the coordinating ligand, and in the case of zephiramine, the increase depends on forming the ion pair.

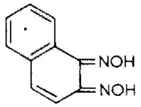
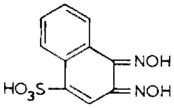
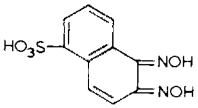
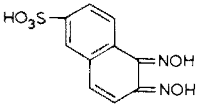
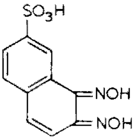
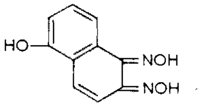
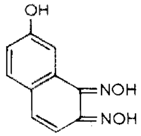
Though the series of naphthoquinonedioximes has the disadvantage of lack of selectivity for nickel, the molar absorptivity in the extracting solvent of the ternary complex (Ni^{2+}–reagent–zephiramine) is about $2 \cdot 10^4$ in the visible region, and the sensitivity is the highest of all well-known dioximes. Furthermore, as previously reported[3], the excess of reagent in extracting solvent can be removed by washing with chloride ion solution, so that the absorbance of the reagent blank in the visible region becomes very small. In the series of naphthoquinonedioxime sulfonic acids (II–V), the new reagent IV, *i.e.*, naphthoquinonedioxime-6-sulfonic acid, appears to be very useful for the solvent extraction–spectrophotometric determination of nickel, having the following advantages: large sensitivity for nickel, little absorbance of the reagent itself at the absorption maximum of the nickel complex, solubility of the reagent and the complex in aqueous solution, and stability of the reagent and the complex.

The authors are very grateful to Mr. Takashi Korenaga of Okayama University for valuable discussions and assistance in the experimental work.

SUMMARY

Seven naphthoquinonedioxime compounds, including five new compounds, were synthesized and their reactions with nickel, cobalt and iron(II) ions were examined. The metal chelates of these dioximes absorb in the visible region, and the molar absorptivities of the complexes are about $1 \cdot 10^4$ l mole^{-1} cm^{-1} in

TABLE VII
EFFECTS OF DIOXANE AND ZEPHIRAMINE

Reagent	*aq. soln.*		*dioxane*		*zephiramine*		*org. soln.*	
	λ_{max} *(nm)*	ε *(·10⁴)*	λ_{max} *(nm)*	ε *(·10⁴)*	λ_{max} *(nm)*	ε *(·10⁴)*	λ_{max} *(nm)*	ε *(·10⁴)*
	p.p.t.		466	0.57	p.p.t.		464 CF	1.65
	476	1.10	476	1.56	484	1.51	480 CF	2.03
	470	1.01	470	1.61	466	1.77	468 CF	2.06
	466	1.18	468	1.67	468	1.60	468 CF	2.19
	466	0.91	466	1.54	466	1.40	468 CF	2.04
	p.p.t.		502	1.32	p.p.t.		490 CF	0.86
	p.p.t.		476	0.70	p.p.t.		468 NB	1.33
Composition ratio (Ni^{2+} : R)	1:3		1:4		1:3		1:3	

aqueous solution. The chelates can be extracted into chloroform with zephiramine, and the molar absorptivities of the nickel chelates are about $2 \cdot 10^4$ l mole^{-1} cm^{-1}. Of the dioximes examined, 1,2-naphthoquinonedioxime-6-sulfonic acid shows the highest sensitivity for nickel; the molar absorptivity of the nickel complex extracted into chloroform with zephiramine is $2.19 \cdot 10^4$ l mole^{-1} cm^{-1} at 468 nm.

REFERENCES

1 L. A. Tschugaeff, *Z. Anorg. Allg. Chem.*, 46 (1905) 144.
2 S. Kuse, S. Motomizu and K. Tôei, *Nippon Kagaku Kaishi*, (1973) 1611.
3 S. Kuse, S. Motomizu and K. Tôei, *Anal. Chim. Acta*, 70 (1974) 65.
4 H. Goldschmidt and H. Schmidt, *Ber. Bunsenges. Phys. Chem.*, 17 (1884) 2066.
5 K. Tôei, S. Motomizu, *Nippon Kagaku Zasshi*, 92 (1971) 92.
6 T. Korenaga, S. Motomizu and K. Tôei, *Nippon Kagaku Kaishi*, (1972) 2445.

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THE 4-PHENYL-3-THIOSEMICARBAZONE OF BIACETYLMONOXIME AS AN ANALYTICAL REAGENT. SPECTROPHOTOMETRIC DETERMINATION OF MANGANESE

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Phenylthiosemicarbazones have been little used as analytical reagents. Niederschulte and Ballschmiter[1] have reported methods for the determination of some metal ions with phenylthiosemicarbazones of biacetyl and glyoxal. A gravimetric procedure for the determination of palladium with the phenylthiosemicarbazone of furfural has been established recently[2].

The thiosemicarbazone of biacetylmonoxime ($BTOH_2$) has been used as a spectrophotometric reagent in determinations of manganese[3], cobalt[4], nickel[5], iron[6], copper and bismuth[7]. Complexes of manganese(II) and (III) have been investigated polarographically[8]. Some complexes have been isolated and studied[9].

In this paper, the properties and analytical possibilities of a new compound, the 4-phenyl-3-thiosemicarbazone of biacetylmonoxime ($PBTOH_2$) are described; the preparation is briefly outlined.

Incorporation of the benzene ring into the structure of $BTOH_2$ to give the reagent $PBTOH_2$ is very advantageous. The spectrophotometric reactions with Co(II), Ni(II), Fe(II), Cu(II) and Mn(III) become more sensitive, and there is a bathochromic effect. These reactions, and a new spectrophotometric method for the selective determination of manganese with $PBTOH_2$ are described in this paper.

A great number of possible alkyl, aryl and acid group modifications, with single and multiple substitutions, might be investigated. Their systematic study is a complicated problem.

EXPERIMENTAL

Apparatus

Unicam SP800, Unicam SP-600-s.2, and Beckman DU spectrophotometers with 1.0-cm glass or quartz cells were used, as well as a digital pH meter (Philips, PW 9408) with glass–calomel electrodes.

Reagents

The 4-phenyl-3-thiosemicarbazone of biacetylmonoxime. The following solutions were prepared: 0.1% (w/v) in dimethylformamide, 0.1 and 0.05% in amyl alcohol, and 0.05 and 0.025% in chloroform. All solutions were nearly colourless.

Standardized solutions of manganese(II), nickel(II), cobalt(II), copper(II) and iron(II) and (III), acetic acid–acetate buffer solutions, pH 4.8, and ammonia–ammonium chloride buffer solutions, pH 10.0, were also prepared.

All the solvents and reagents used were of analytical-reagent quality.

Synthesis of $PBTOH_2$

$PBTOH_2$ was prepared by refluxing equimolecular amounts of biacetylmonoxime (Merck) and 4-phenyl-3-thiosemicarbazide (Aldrich), in acetic acid–acetate medium. The product was recrystallized from ethanol (m.p. 210–212°C). Elemental analysis confirmed the synthesis (found: 52.9% C, 5.6% H, 22.1% N, 13.0% S; calculated: 52.8% C, 5.6% H, 22.4% N, 12.8% S).

The infrared spectrum was obtained in KBr discs, and the bands were assigned (cm^{-1}) to the stretching vibrations of –NH– (3260 m and 3200 m) –CN (1595 s and 1545 s) and C=S (1175 m, 1130 s, 1030 w and 1018 m).

SPECTROPHOTOMETRIC STUDY OF REACTIONS WITH CATIONS

The influence of pH on the absorption spectra in aqueous medium is shown in Fig. 1. Acid dissociation constants of the free ligand were measured by Phillips and Merritt's method[10]; absorbance, at 320 nm, was plotted *versus* pH, and the values of pK_a were calculated. Results are shown in Table I, and compared with the values for some related compounds.

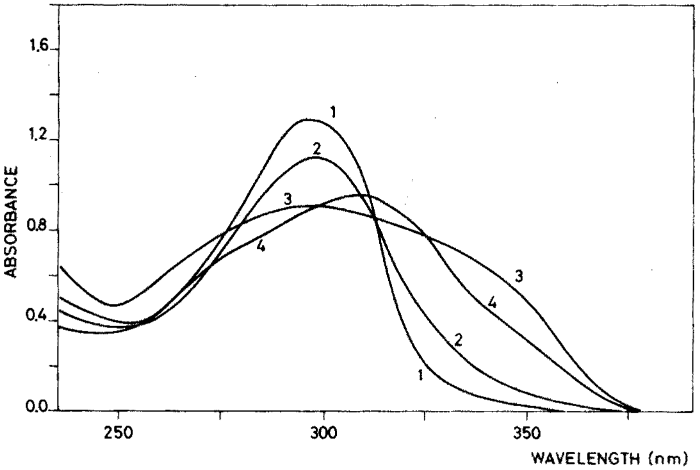


Fig. 1. Absorption spectra of $PBTOH_2$ in aqueous solutions at various pH values ($4 \cdot 10^{-5}$ *M*): (1) pH 8.50; (2) 10.15; (3) 11.70; (4) 11.20.

TABLE I

pK_a VALUES OF DIVERSE THIOSEMICARBAZONES

Compound	pK_1	pK_2	*Ref.*
Biacetylmonoxime phenylthios.	10.40	11.50	—
Biacetylmonoxime thios.	10.10	11.50	12
Picolinaldehyde phenylthios.	3.66	10.47	13
Picolinaldehyde thios.	4.60	9.75	11
Benzaldehyde phenylthios.	—	11.50	13
Benzaldehyde thios.	—	11.30	11

Reducing agents in moderate concentrations did not alter the absorption spectra of $PBTOH_2$, but oxidizing substances did. Oxidation of $PBTOH_2$ gave the same final form, with maximal absorption at 272 nm.

The reactions of 36 ions with $PBTOH_2$ were tested at various pH values. As(III) or (V), Sn(II) or (IV), Al(III), Cr(III), Be, UO_2(II), Th, La, Ce(III), W(VI), Mo(VI), alkali and alkaline earth metal ions did not react. The most sensitive reactions were shown for Co(II), Ni(II), Fe(II) and (III), and manganese as Mn(III); these metal ions formed intensely coloured complexes, that are eminently suitable for spectrophotometric determinations.

The absorption spectra of these metal-$PBTOH_2$ complexes were recorded in the most favourable conditions of pH (Fig. 2). Maximal absorption bands appeared between 345 and 375 nm (yellow colour), except for the manganese(III) (red colour, $\lambda_{max} = 550$ nm). The absorption spectrum of iron(II) complex coincided with that of iron(III); the reagent caused the reduction of iron(III).

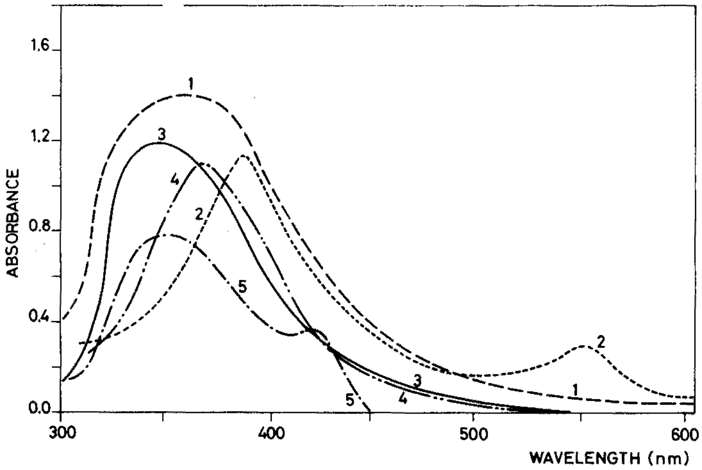


Fig. 2. Absorption spectra of the complexes of $PBTOH_2$ with different metal ions at concentrations of 4 p.p.m., in the most favourable conditions for each case: (1) Fe(II); (2) Mn(III); (3) Co(II); (4) Ni(II); (5) Cu(II).

The red manganese(III)–$PBTOH_2$ complex was formed quickly, owing to aerial oxidation of manganese(II) above pH 9; the presence of oxidizing agents was not necessary for the development of the colour. When an inert atmosphere was used, the yellow colour of a manganese(II) complex appeared, and the red complex was not formed. Reducing agents, such as ascorbic acid, caused reduction of the manganese(III) complex to a yellow complex with maximal absorption at 385 nm.

Effect of pH. Beer's law

The optimal pH range for the formation of the complexes, and other variables of analytical interest were studied (Table II). Absorbance remained unaltered during 24 h, at least, in all cases. Beer's law was obeyed over a wide range of concentrations, and molar absorptivities were calculated. The copper(II)

TABLE II

CHARACTERISTICS OF $PBTOH_2$ AND $BTOH_2$ COMPLEXES IN SOLUTION

Cation	*Biacetylmonoxime phenylthiosemicarbazone*			*Biacetylmonoxime thiosemicarbazone*			
	Optimal pH	*λ (nm)*	*ε (l mol^{-1} cm^{-1})*	*Optimal pH*	*λ (nm)*	*ε (l mol^{-1} cm^{-1})*	*Ref.*
Co(II)	3.0–8.0	345	17,700	5.0	325	9,400	4
Ni(II)	5.2–10.0	375	17,100	9.5	356	8,800	5
Fe(II)	4.0–9.3	350	17,600	5.0	335	14,490	6
Cu(II)	8.5–9.7	360	12,700	8.5–9.5	345	10,600	7
Mn(III)	9.0–12.0	550	3,600	9.2–10.3	545	2,700	—

complex precipitated at below pH 8. The most important results are compared with those of $BTOH_2$.

Composition of the complexes

The combining ratios of metal ions to $PBTOH_2$ were investigated by Job's method (Fig. 3). The nickel(II) complex showed a composition variable with the

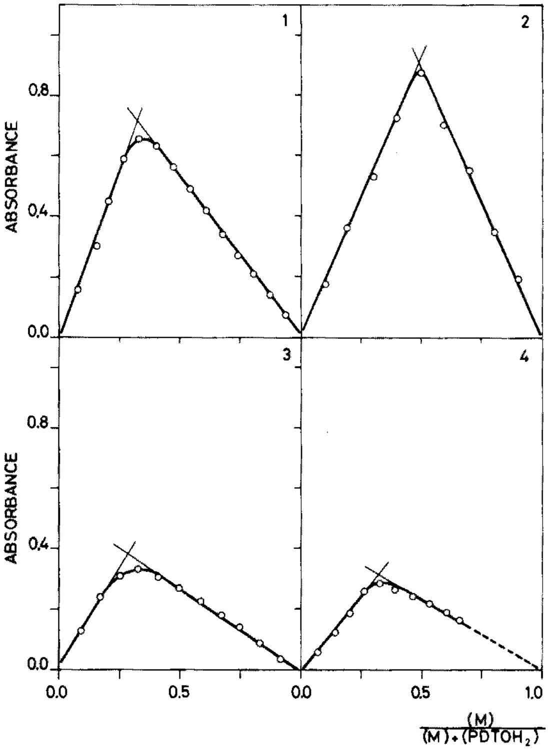


Fig. 3. Composition of the $PBTOH_2$ complexes by the continuous variations method: (1) Co(II), $3.4 \cdot 10^{-4}$ *M* (345 nm); (2) Cu(II), $6.6 \cdot 10^{-4}$ *M* (360 nm); (3) Fe(II), $3.6 \cdot 10^{-4}$ *M* (355 nm); and (4) Mn(III), $9 \cdot 10^{-4}$ *M* (550 nm).

concentration. Results were 1:2 for Co(II), Fe(II) and Mn(III), and 1:1 for Cu(II). The yellow Mn(II) complex showed a 1:2 stoichiometric ratio.

The formation constants of some complexes were calculated from the absorbance measurements shown in Fig. 3. The results were: $5.8 \cdot 10^{11}$ (Co), $1.4 \cdot 10^{10}$ (Fe) and $1.5 \cdot 10^{10}$ (Mn).

Extraction

Extraction of the complexes was tested into several organic solvents. The most favourable solvents were chloroform and amyl alcohol. The effect of pH on the equilibrium phenylthiosemicarbazone concentration in chloroform was studied (initial concentration: $2.14 \cdot 10^{-3}$ *M*) (Fig. 4). At pH 0–10, the equilibrium concentration of the phenylthiosemicarbazone in the organic phase was practically equal to the initial concentration. When the pH value was higher, the equilibrium concentration of the phenylthiosemicarbazone in the organic phase was decreased by dissociation of the molecule.

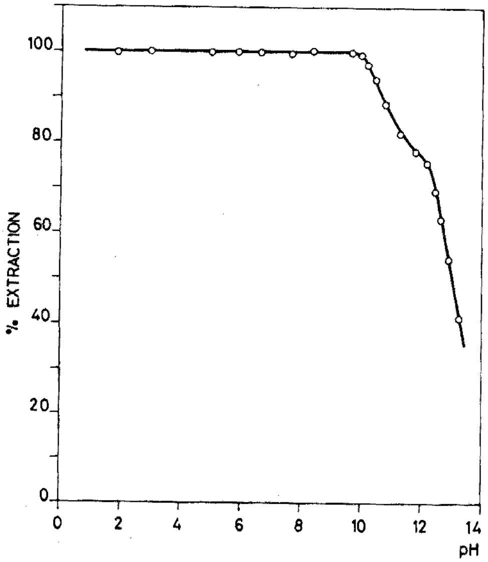
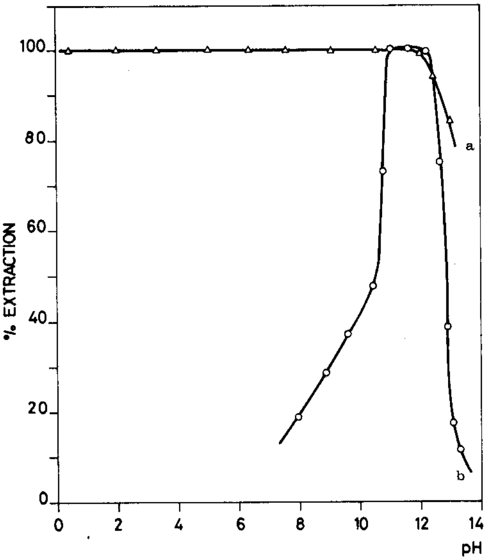


Fig. 4. Effect of pH on the equilibrium $PBTOH_2$ concentration in chloroform. Initial concentration of $PBTOH_2$ $2.14 \cdot 10^{-3}$ *M*. Absorbances were measured at 370 nm.

Extraction of the metal complexes into chloroform and amyl alcohol, and the effects of the pH and other variables, were studied. The reagent was dissolved in the organic phase (0.025% in chloroform, 0.05% in amyl alcohol). To 20 μg of the metal ions (100 μg in the case of manganese) in 10 ml of aqueous solution (ionic strength = 0.1, with 2 ml of 0.5 *M* $KClO_4$), 10 ml of the reagent in the organic solvent were added; after shaking for 5 min in all cases, the two phases were separated, and the concentrations of the metal ion in the aqueous phase and/or organic phase were determined spectrophotometrically. The percentage of metal extracted was then calculated from the known total concentration of metal, and from the equilibrium concentration of metal ion in the aqueous or in the



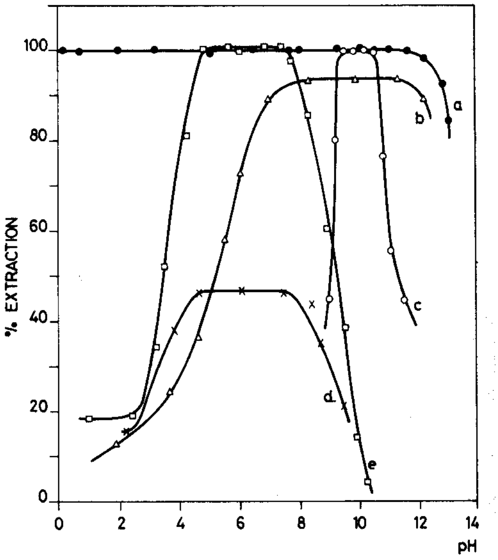


Fig. 5. Effect of pH on the extraction into chloroform of the $PBTOH_2$ complexes. (a) Cu(II) (400 nm); (b) Ni(II) (375 nm).

Fig. 6. Effect of pH on the extraction into amyl alcohol of the $PBTOH_2$ complexes. (a) Cu(II) (400 nm); (b) Ni(II) (450 nm); (c) Mn(III) (550 nm); (d) Fe(II) (345 nm); (e) Co(II) (385 nm).

organic phase. All distribution experiments were carried out at 20°C. Results are plotted *versus* pH values in Figs. 5 and 6. Extraction of the Co(II), Ni(II) and Mn(III) complexes was unsuccesful in chloroform; in amyl alcohol, the complexes of Cu(II), Mn(III) and Co(II) were extracted completely at certain pH values; extraction was complete for Ni(II) and Fe(III); when iron(III) was used, the percentage extraction decreased.

SPECTROPHOTOMETRIC DETERMINATION OF MANGANESE

The reaction of manganese with $PBTOH_2$ provides a favourable analytical method for the spectrophotometric determination of this metal ion in solution. All variables were studied.

Recommended procedure for direct spectrophotometry

To the manganese solution containing 100–600 μg of Mn(II) in a 50 ml-volumetric flask, add 10 ml of 0.1% (w/v) $PBTOH_2$ solution in dimethylformamide, and 10 ml of buffer solution pH 10.0. Dilute to volume with water. Measure the absorbance at 550 nm, against distilled water.

Absorbance was stable for 24 h at least. Beer's law was obeyed between 2 and 12 p.p.m. The relative error of the method ($P=0.05$) was $\pm 0.22\%$. The foreign ions tolerated in the determination of 10 p.p.m. of manganese were: Hg(II), Zn(II), Cd(II), V(V), Mo(VI), As(III) and (V), Ag(I), Ca(II), Mg(II), Sr(II), Ba(II), SCN^-, PO_4^{3-}, citrate, tartrate, oxalate and chloride when they were present in concentrations 100 times greater (by weight) than that of manganese. Co(II), Ni(II), Fe(II) and (III), and Cu(II) caused serious interference above 1 p.p.m.

Recommended procedure for extraction spectrophotometry

When the manganese(III) complex was extracted, interferences were less.

To the aqueous manganese solution (20–120 μg Mn) in a separating funnel, add 5 ml of buffer solution pH 10.0, 2 ml of 0.5 M KNO_3 or $KClO_4$, and 10 ml of 0.1% (w/v) reagent solution in amyl alcohol. Shake vigorously for 4–5 min, allow the phases to separate, and transfer the organic phase to a flask containing anhydrous sodium sulphate. Measure the absorbance of this solution at 550 nm, against distilled water.

The final absorbance remained constant for 3 h. Beer's law was obeyed between 2 and 12 p.p.m. The relative error of the method ($P=0.05$) was ±0.45%. Interferences were less important: Co(II), Cu(II), Fe(II) and (III) interfered at concentrations greater than 10 p.p.m., and Ni(II) above 8 p.p.m.

TABLE III

DETERMINATION OF MANGANESE IN THE PRESENCE OF IRON

(10 p.p.m. Mn taken; 0.25 g of sodium tartrate added to each sample)

Fe taken (p.p.m.)	30.0	50.0	75.0	100.0	120.0
Mn found (p.p.m.)	10.0	9.9	10.0	10.0	10.3

Interference of iron(III) could be eliminated by adding 0.25 g of sodium tartrate to the aqueous phase before extraction. It was possible to determine 2–12 p.p.m. of manganese in the presence of up to 100 p.p.m. of iron(II). Results obtained in this determination are shown in Table III. Quantities of sodium tartrate above 0.35 g are inconvenient, owing to an appreciable decrease in the absorbance.

DISCUSSION

The results given in Table I show that the presence of the electron-donating phenyl group in the molecule decreases the acid strength of the oxime group (K_1) of biacetylmonoxime phenylthiosemicarbazone, and that of the –SH group (K_2) of the picolinaldehyde and benzaldehyde analogues. This effect can be attributed to the inductive and mesomeric action of the phenyl group. The first ionization constant (K_1) of picolinaldehyde thiosemicarbazone and phenylthiosemicarbazone is due to protonation of the nitrogen atom in the pyridine ring[11].

The phenyl group produces an auxochromic effect on the complexes formed. Molar absorptivities are greater in all cases, and the absorption spectra show bathochromic shifts (Table II); analytical possibilities are, therefore, also greater.

The complexes of $PBTOH_2$ are similar to those of $BTOH_2$. Apparently, both substances act as terdentate chelating agents, and form octahedral complexes, as picolinaldehyde thiosemicarbazone[11] and phenylthiosemicarbazone[12].

The red complex of manganese(III) is formed only in the presence of oxygen above pH 9 (ammonium buffer). Its formation is fast (3–5 min), but proceeds much more slowly in borate or phosphate buffers; with increasing pH, the reaction rate increases. Its absorption maximum at 550 nm provides evidence for the presence of manganese(III), by analogy with other octahedral manganese-(III) complexes (bis-oxalate, bis-malonate, and bis-acetylacetonate complexes), which exhibit an absorption band[14] in the region 500–550 nm. The red complex is anionic; evidence was obtained from its retention on an anionic ion-exchanger. The reduction rate of the manganese(III) complex increases with the amount of reducing agent employed. The behaviour of the Mn(III)–$PBTOH_2$ complex is analogous to that of the $BTOH_2$ in homogeneous medium.

The extraction study of the metal complexes shows that the solvent extraction of metal ions by $PBTOH_2$ is easier in amyl alcohol; the charged complexes cannot be extracted into chloroform, because of their very low dielectric constant. The copper(II) complex is very easily extracted into both solvents over the pH range 0–12; this fact offers possibilities for the selective determination of copper(II). However, the spectrophotometric determination of manganese with the most suitable extraction procedure in amyl alcohol is possible only with $PBTOH_2$; when $BTOH_2$ is used, the manganese(III) complex is not extracted.

SUMMARY

The analytical possibilities of the 4-phenyl-3-thiosemicarbazone of biacetylmonoxime were examined, and compared with those of the thiosemicarbazone of biacetylmonoxime. Extraction of metal complexes into amyl alcohol and chloroform was studied in relation to pH. The manganese(III) complex is proposed for the selective spectrophotometric determination of manganese, by means of extraction in amyl alcohol, at pH 10. Beer's law is obeyed between 2 and 12 p.p.m. of manganese (550 nm), the molar absorptivity being 3600 $l\ mol^{-1}\ cm^{-1}$. Cobalt, copper and iron interfere, but interference of iron(III) may be eliminated by masking with tartrate.

REFERENCES

1 U. Niederschulte and K. Ballschmiter, *Z. Anal. Chem.*, 261 (1972) 191.
2 J. M. Cano Pavón and F. Pino, *Anal. Lett.*, 7 (1974) 159.
3 T. Naito, S. Una and S. Suguira, *Nagoya Shiritsu Daigaku Yakugakubu Kiyo*, 5 (1957) 57.
4 D. P. Bendito and F. Pino, *Inform. Quim. Anal.*, 21 (1967) 31.
5 D. P. Bendito and F. Pino, *Inform. Quim. Anal.*, 22 (1968) 1.
6 D. P. Bendito and F. Pino, *Inform. Quim. Anal.*, 22 (1968) 277.
7 M. Valcarcel and D. P. Bendito, *Inform. Quim. Anal.*, 24 (1970) 49.
8 M. Valentova and L. Sucha, *Collect. Czech. Chem. Commun.*, 27 (1972) 22.
9 A. V. Ablov and N. I. Belichuk, *Zh. Neorg. Khim.*, 8 (1963) 1142.
10 J. P. Phillips and L. L. Merritt, *J. Amer. Chem. Soc.*, 70 (1943) 410.
11 J. M. Cano Pavón and F. Pino, *Talanta*, 19 (1972) 1659.
12 P. Martínez, Thesis, Anales Univ. Hisp., Seville, 1973.
13 J. L. Gómez Ariza and J. M. Cano Pavón, Unpublished work.
14 R. Dingle, *Acta Chem. Scand.*, 20 (1966) 33.

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NOUVELLE MÉTHODE DE DOSAGE PHOTOMÉTRIQUE AUTOMATIQUE DES PROTÉINES DANS LE LAIT ENTIER

PARTIE III. APPLICATION À L'ANALYSE EN FLUX CONTINU

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Les bases théoriques ainsi qu'un essai d'application manuelle (optimisation, étude de la linéarité, de la sélectivité et de la spécificité) de la méthode ont fait l'objet des deux publications précédentes[1,2]. Cette troisième partie présente les résultats obtenus lors de l'application de la méthode à l'analyse dite en flux continu.

PARTIE EXPERIMENTALE

Diagramme des flux et appareillage

La Figure 1 montre le diagramme des flux et le matériel utilisé pour réaliser le "manifold". Le lait, dilué 10 fois avec de l'eau (*cf.* paragraphe "Linéarité"), est ajouté au mélange bullé des réactifs (*cf.* paragraphe suivant). La bobine de mélange (Technicon 114-0209-01 ou 114-0209-02) est thermostatisée à 70°C pour accélérer la dissolution des caséines et surtout de la matière grasse. Le développement de la coloration s'effectue ensuite à température ambiante dans une spirale de réaction en verre* (40 pieds de longueur: 1,6 mm de diamètre intérieur) immergée dans un bac d'eau à température ambiante. Après débullage**, le flux est mesuré à 540 nm dans une microcellule à flux continu de 50 mm de longueur (Hellma type OS/178). Au lieu de les jeter à l'évier, les solutions mesurées sont stockées, puis distillées pour récupérer la n-butylamine (économie et lutte contre la pollution).

L'appareillage utilisé, choisi en fonction des disponibilités du laboratoire, comprend: un passeur d'échantillon (distributor SD3 de Carlo Erba), une pompe péristaltique (mp 25 GJ-4 d'Ismatec à Zürich), un bain-marie à circulation (K2-D de Lauda), un spectrophotomètre à double faisceau (124 de Perkin-Elmer), et un enregistreur analogique linéaire (165 de Perkin-Elmer).

Les tuyaux de pompe sont en tygon (ou PVC), à l'exception de ceux qui

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* Des essais ont été effectués avec une spirale de réaction en téflon[3].

** Le débulleur C3 est directement connecté à l'entrée de la cuvette de mesure au moyen d'un manchon en caoutchouc au silicone. Ultérieurement, on désignera ce matériau par "silicone".

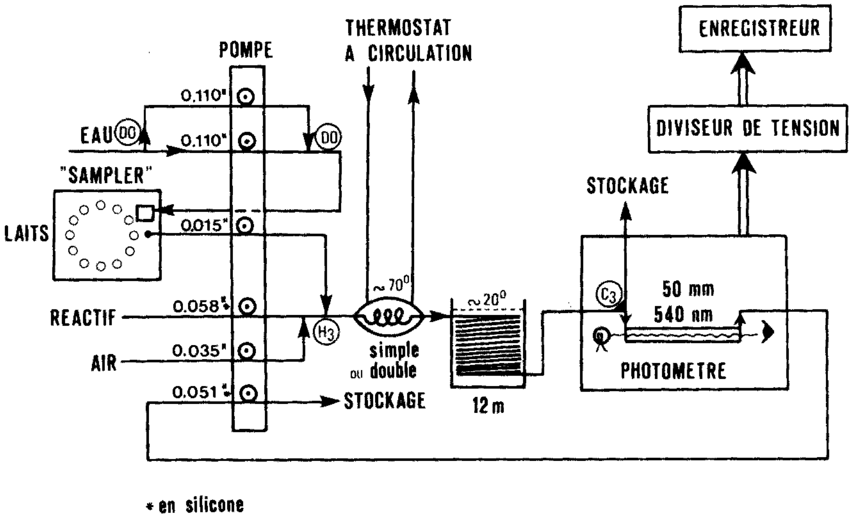

Fig. 1. Diagramme des flux.

entrent en contact avec la n-butylamine (BTA). Ces derniers sont en "silicone", matériau qui, faute de mieux, a été retenu sur la base d'une étude préliminaire[4]. Selon le code de Technicon, il s'agit des types suivants:

— clair/clair (2,65 ml min^{-1}—débit effectivement mesuré avec la pompe utilisée sur le rapport 10), en silicone, pour le réactif;

— orange/vert (1,15 ml min^{-1}), en tygon, pour les laits dilués;

— rouge/rouge (2,00 ml min^{-1}), en tygon, pour l'air (bulles);

— gris/gris (2,00 ml min^{-1}), en silicone, pour le "push-pull";

— violet/blanc (2·9,75 ml min^{-1}), en tygon, pour l'eau de rinçage.

Remarques. (1) Afin d'obtenir l'écoulement le plus rapide possible pour le rinçage de l'installation (accroissement de la cadence des analyses) et le plus régulier possible (amélioration de la précision des résultats), la pompe Ismatec est utilisée à sa vitesse maximale (rapport 10), ce qui multiplie par un facteur 2.5 les débits indiqués par Technicon pour les tuyaux précités.

(2) Ne possédant qu'une seule cellule de mesure en flux continu de 50 mm*, on a équipé le faisceau de référence du photomètre d'un atténuateur d'énergie (diaphragme) pour compenser approximativement l'extinction de la cuvette de mesure remplie avec le blanc (réglage grossier de la ligne de base). Le réglage fin s'opère avec le potentiomètre "zéro. abs." du spectrophotomètre.

(3) Pour faciliter l'évacuation des bulles éventuelles qui peuvent traverser la cuvette de mesure, il est recommandé d'incliner légèrement le spectrophotomètre.

(4) La plus grande sensibilité de lecture est atteinte lorsque les pics enregistrés occupent la plus vaste plage d'enregistrement; on l'obtient en combinant l'expansion d'échelle que permet l'enregistreur (réglage grossier) avec l'adaptation du signal de sortie que permet le petit potentiomètre (diviseur de tension) monté en

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* Les volumes pompés étant très supérieurs à celui de la cellule ($<0{,}2$ ml), on peut utiliser une cuvette de 50 mm qui permet de limiter l'expansion d'échelle.

série. Les divers essais rapportés dans cette étude n'ont pas toujours été réalisés avec le même réglage de ce potentiomètre.)

(5) Les essais effectués à 342 nm (épaule dans l'u.v.) montrent que les extinctions obtenus sont trop élevées, ce qui se traduit par un signal peu stable (photomultiplicateur trop sollicité) et une mauvaise linéarité; il faut en effet tenir compte de la forte extinction produite par la cuvette elle-même ($E \simeq 0{,}85$, en valeur absolue).

Composition du réactif

La stabilité mécanique et chimique des tuyaux de pompe en silicone augmente lorsque la teneur en amine diminue[4]. On en déduit qu'il est préférable de mélanger tous les réactifs—eau, soude, complexonate de cuivre(II) (Siegfried) et n-butylamine (Fluka puriss, ou purum)—avant le pompage.

L'expérience indique d'autre part que la qualité du mélange lait/réactif, tant pour la dissolution des caséines et des graisses que pour le développement de la coloration, est meilleure lorsque les échantillons de lait sont préalablement dilués. En réalisant cette dilution avec de l'eau dans un rapport 1:10, on diminue notablement le risque d'un dépôt de lait à la sortie du cactus d'injection (H 3) et sur les premières spires de la bobine de mélange. On compense l'effet de cette dilution en montant un tuyau d'aspiration (des échantillons) de débit approximativement 10 fois plus élevé et en augmentant la concentration des réactifs du biuret de manière à conserver approximativement le rapport des concentrations en protéines, cuivre(II) et soude préconisé pour l'analyse manuelle; pour NaOH, on est limité par les produits de solubilité (démixtion du mélange eau/amine).

Ces quelques remarques ont amené à utiliser, dans le montage définitif, les tuyaux de pompe indiqués sur le diagramme des flux. Sur la base de l'optimisation des paramètres effectuée manuellement[1], on en déduit alors la composition suivante pour le réactif: 1 vol. de NaOH 0,6 M, 1 vol. d'une sol. (aqueuse) de $Cu.EDTA.Na_2.\text{-}2H_2O$ (40 g l^{-1}) (*ca.* 0,1 M) et 3 vol. de n-butylamine.

Remarque. Une fois le lait dilué introduit, seule la concentration en n-butylamine se trouve être notablement diminuée (environ de moitié). Les essais effectués ont cependant démontré qu'en maintenant la bobine de mélange à 70°C, une telle concentration de n-butylamine était encore suffisante pour assurer une dissolution complète.

RÉSULTATS EXPÉRIMENTAUX

Pour juger de la méthode, les critères suivants ont été retenus: linéarité en présence de quantités variables de lactose; reproductibilité (pour estimer la précision); sensibilité; concordance (coefficient de corrélation) avec la méthode de Kjeldahl admise habituellement comme référence (azote protéique: $PN = TN - NPN$)[5,7].

La limite de détection n'a pas d'intérêt pratique puisqu'il y a toujours assez de réactant (ponts peptidiques). L'exactitude dépend de la précision et de la qualité de la corrélation, puisque la méthode est relative (solutions étalons).

Etant donné qu'il s'agit d'une méthode d'analyse automatique, une brève étude est encore consacrée à la cadence de travail de l'appareil, ainsi qu'aux divers temps de séjour ou de réaction des échantillons dans l'analyseur.

Les résultats sortent de l'analyseur sous la forme de pics enregistrés (*cf.*

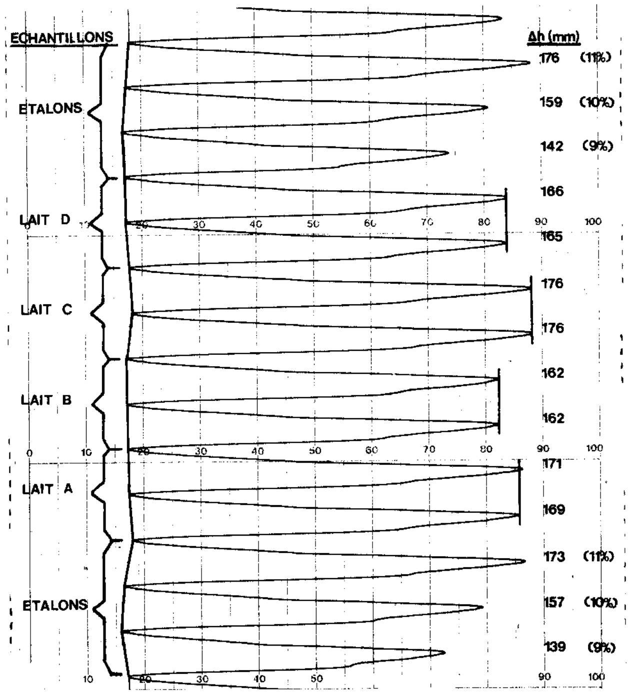

Fig. 2. Allure des pics enregistrés (lait étalon à 3 dilutions différentes et laits inconnus analysés à double).

Fig. 2). Vu la dérive de la ligne de base (*cf.* paragraphe "reproductibilité"), la lecture s'effectue de la manière suivante: on relie les deux minima consécutifs définissant le début et la fin du pic par un segment de droite (= base du pic). La distance géométrique du milieu de ce segment au sommet du pic est la mesure de la hauteur Δh de ce pic. Le lieu géométrique des diverses bases des pics correspond à la ligne de base vraie si le rinçage est complet. De même, le sommet des pics correspond au plateau ("steady state") si le temps d'aspiration des échantillons est suffisamment long (*cf.* paragraphe "cadence des analyses").

Linéarité et influence du lactose

La proportionnalité existant entre l'absorbance à 540 nm et la teneur en protéines est théoriquement dépendante, dans un certain domaine, de la teneur en lactose du lait, puisqu'il peut y avoir compétition entre ces deux chélateurs du cuivre(II). La validité de la loi de Beer–Lambert a donc été vérifiée (dans les conditions indiquées précédemment) en mesurant les absorbances obtenues avec un même lait à des dilutions respectivement inférieure (1 : 6,6), égale (1 : 10) et supérieure (1 : 20) à celle recommandée en routine, sans et avec adjonctions de lactose pur (à savoir 0,0%, 0,5% et 1,0% absolus). Le lait contenant naturellement *ca.* 5% absolus de lactose, cela correspond en fait à des laits contenant respectivement 5,0%, 5,5% et 6,0% absolus de lactose. Les résultats sont présentés par le Tableau I. Il ressort de cette étude que la loi de Lambert–Beer est, pour la pratique, suffisamment bien vérifiée pour permettre, une fois l'appareil calibré, le calcul de la teneur en pro-

TABLEAU I

HAUTEUR MOYENNE DES PICS ($\overline{\Delta h}$) ENREGISTRÉS POUR DIFFÉRENTES ADJONCTIONS DE LACTOSE (% ABSOLUS) À UN LAIT À DIVERSES DILUTIONS (100% RELATIFS = LAIT NON DILUÉ)

Dilution du lait avec H_2O	*Conc. du lait (% relatifs)*	*$\overline{\Delta h}$ (cm) mesurée pour 3 laits de teneur (absolue) en lactose égale à*		
		5,0%	*5,5%*	*6,0%*
1/∞	0	0,00	0,00	0,00
1/20	5	6,10	6,17	6,23
1/10	10	11,83	11,83	11,90
1/6,6	15	17,20	17,40	17,37

téines de n'importe quel lait par simple interpolation linéaire; la calibration de l'analyseur est décrite dans la remarque du paragraphe intitulé "concordance avec la méthode de Kjeldahl". Le domaine de variations des teneurs en protéines, même pour des laits individuels, est en effet suffisamment restreint pour permettre d'assimiler la "courbe correspondante" à un segment de droite.

Le Tableau I indique d'autre part que les variations naturelles de la concentration en lactose ne modifient pas sensiblement les valeurs d'extinction obtenues. Comme le prévoyait l'étude manuelle[2], on peut donc considérer la teneur et l'influence de ce composant du lait comme constante pour ce type d'analyse, ce qui facilite grandement l'interprétation des résultats.

Reproductibilité

L'essai de reproductibilité rapporté dans le Tableau II a été réalisé avec un lait pasteurisé et homogénisé du commerce (pour éviter une séparation de la matière grasse en cours d'expérience), dilué 10 fois avec de l'eau. Les temps d'aspiration et de rinçage sont chacun de 3 min. A première vue, la reproductibilité semble

TABLEAU II

ESSAI DE REPRODUCTIBILITÉ (50 MESURES) AVEC UN MÊME LAIT

(Δh en cm)

1ère heure	*2ème heure*	*3ème heure*	*4ème heure*	*5ème heure*
22,60	23,10	23,25	23,70	23,90
22,70	23,20	23,30	23,70	23,90
22,85	23,25	23,30	23,55	23,90
23,10	23,20	23,35	23,60	23,80
22,80	23,20	23,60	23,70	23,55
22,90	23,25	23,50	23,75	23,40
23,00	23,30	23,50	23,65	23,20
23,00	23,25	23,55	23,80	23,30
23,00	23,35	23,40	23,80	23,30
23,10	23,25	23,70	23,80	23,30

satisfaisante. Néanmoins, on constate non seulement une dérive des pics sur le papier de l'enregistreur, (ce qui ne ressort pas du Tableau II puisqu'il ne donne qùe les Δh), mais encore une augmentation lente, mais systématique, de la hauteur Δh du pic au cours du temps: 22,60 au début; 23,10 après 1 h; 23,25 après 2 h; 23,70 après 3 h et 23,90 après 4 h. En supprimant les 3 premières mesures qui correspondent à la période de démarrage, de même que les 4 dernières qui ont été obtenues après une correction importante de ligne de base, on peut établir une corrélation relativement bonne entre la position n de l'échantillon dans la série et la hauteur Δh (en cm) du pic correspondant:

$$\Delta h = 22{,}95 + 0{,}021_6\ n$$

avec un coéfficient de corrélation égal à 0,911. La valeur 22,95 est la hauteur du pic extrapolée à l'origine de l'abscisse.

La cause de cette dérive, très gênante pour l'analyse, doit être recherchée dans la variation relativement régulière du débit du tuyau aspirant le réactif. Ce tuyau accuse en effet une plus forte diminution de débit, sous l'influence du solvant organique, que le tuyau de tygon, sous l'influence du lait dilué[4]: cela se traduit par un changement dans le rapport réactif/réactant. Il en résulte que l'exactitude des mesures sera d'autant meilleure que la fréquence des étalonnages sera plus grande (compensation de l'augmentation des Δh). Le Tableau III donne pour ces 43 mêmes déterminations la hauteur moyenne des pics $\overline{\Delta h}$, l'écart-type s et le coefficient de variation v, calculés heure par heure d'abord*, puis pour tout l'essai d'un bloc.

TABLEAU III

DÉTERMINATION DE $\overline{\Delta h}$ (cm), s ET v

Grandeur	*1ère heure*	*2ème heure*	*3ème heure*	*4ème heure*	*En bloc*
$\overline{\Delta h}$	23,05	23,27	23,56	23,78	23,42
s	0,1343	0,0474	0,1235	0,1059	0,2971
v	0,0058	0,0020	0,0052	0,0045	0,0127

Seul un étalonnage répété chaque heure peut donc permettre une détermination reproductible à ±1% relatif. Cette condition, nécessaire mais non suffisante—à cause des brusques modifications de débit des tuyaux de pompe—diminue la cadence d'analyses de l'automate.

Sensibilité

La sensibilité est définie comme le rapport $\Delta(\overline{\Delta h})/\Delta c$, où $\Delta(\overline{\Delta h})$ est l'accroissement de la hauteur moyenne du pic $\overline{\Delta h}$, rapportée à la variation de la concentration en protéines correspondante Δc. L'expérience montre que la sensibilité dépend sensiblement des conditions de travail, notamment de l'âge des tuyaux, surtout de ceux en silicone, de la propreté des conduits, de la qualité des jonctions lors du

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* Les 3 premières mesures étant omises, il s'agit des mesures 4–13 pour la première heure, 14–23 pour la deuxième et ainsi de suite.

TABLEAU IV

DÉTERMINATION DE LA SENSIBILITÉ DE LA MÉTHODE

Concentration du lait (% relatifs)	*Hauteur Δh du pic enregistré (cm)*				*$\Delta(\overline{\Delta h})$ Différence (cm)*
	1ère mesure	*2ème mesure*	*3ème mesure*	*Moyenne*	
90	18,3	18,3	—	18,3	0,4
92	18,7	18,8	18,6	18,7	0,4
94	19,0	19,1	19,1	19,1	0,5
96	19,5	19,6	19,7	19,6	0,4
98	19,9	20,0	—	20,0	0,4
100	20,4	20,4	20,3	20,4	

montage et de la propreté des cuvettes*. Pour une installation très soignée, on parvient à abaisser le seuil de sensibilité jusqu'à 1% relatif, comme le montre le Tableau IV, ce qui est indispensable en pratique pour différencier des laits. (On a signalé, au paragraphe "linéarité", la relativement faible variabilité de la teneur en protéines des laits normaux. Ce qui était précédemment un avantage devient ici un handicap.) Pour cet essai, les temps d'aspiration et de rinçage sont de 2 min chacun. La sensibilité atteinte $\Delta(\Delta h)/\Delta c$ est donc de 2 mm par 1% relatif de protéines (lait entier = 100% relatifs en protéines). On devrait pouvoir l'augmenter encore en digitalisant la lecture photométrique.

Concordance avec la méthode de Kjeldahl

Pour déterminer dans quelle mesure la méthode proposée concorde avec la méthode de référence, celle de Kjeldahl[5,7], 65 échantillons de laits individuels et 39 échantillons de laits de mélange (provenant de 10 vaches au moins) ont été analysés successivement par l'une et l'autre méthode (*cf.* Fig. 3). Les coefficients de corrélation obtenus sont respectivement $r_{\blacktriangle} = 0{,}950$ et $r_{\bullet} = 0{,}938$. La méthode semble donc applicable aussi bien aux laits de mélange qu'aux laits individuels. Pour l'ensemble des 104 échantillons de laits, sans distinction d'origine, on obtient $r = 0{,}948$ (droite de regression: g% $\mathrm{PN}_{\mathrm{biuret}} = 0{,}895$ g% $\mathrm{PN}_{\mathrm{Kjeldahl}} + 0{,}058$). La concordance obtenue est donc meilleure que celle indiquée par Renner et Ömeroglŭ[6] pour la méthode du biuret. En supprimant 2 valeurs aberrantes, on obtient la répartition statistique suivante: 35% des valeurs obtenues avec la méthode du biuret s'écartent de $\leqslant \pm 1\%$ des valeurs correspondantes obtenues avec la méthode de Kjeldahl, 58% de $\leqslant \pm 2\%$, 76% de $\leqslant \pm 3\%$ et 91% de $\leqslant \pm 4\%$.

Remarque concernant l'étalonnage de l'analyseur. La méthode du biuret étant une méthode relative, elle nécessite l'emploi de solutions étalons. Vu l'influence (constante mais effective) des autres constituants du lait sur ce type d'analyse, il est important d'utiliser un lait comme "standard", dont on détermine la teneur en protéines par la méthode de Kjeldahl[5,7]. Dans ce but, un lait pasteurisé/homogénéisé frais du commerce est particulièrement recommandé: il provient d'une population statistique considérable, correspondant donc à un mélange moyen idéal des diverses protéines; du fait de son homogénéisation, sa matière grasse n'écrème

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* Il est recommandé de rincer chaque soir l'installation avec un détergent.

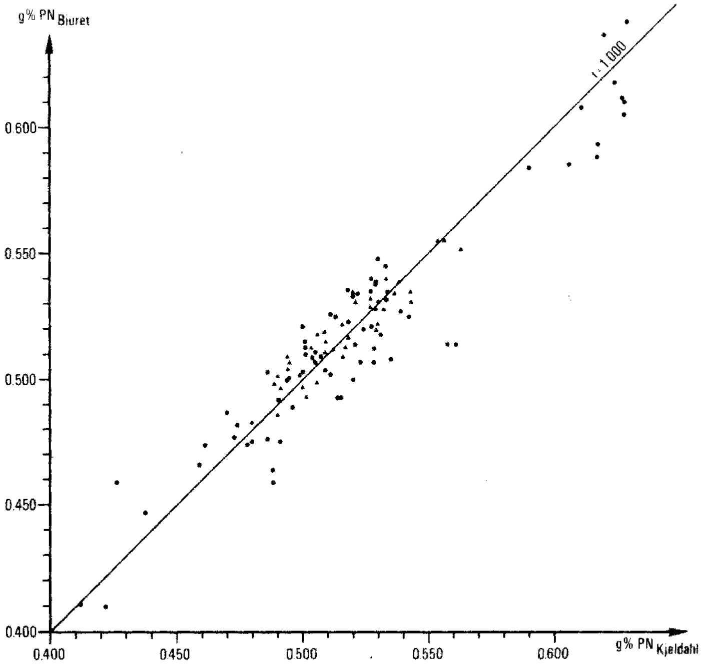

Fig. 3. Concordance entre les méthodes dites du biuret et de Kjeldahl. (●) Lait de mélange; (▲) lait individuel.

pas pendant les mesures et sa conservation est améliorée par la pasteurisation. Pour ne pas avoir à refaire un dosage selon Kjeldahl lors de chaque calibration, le solde de ce lait étalon ("standard") a été surgelé dans l'azote liquide en petites portions et conservé au congélateur. A chaque fois, il a été placé à 3 dilutions différentes (concentrations correspondant à 9%, 10% et 11% relatifs) dans le carousel, de manière à passer au moins une fois par heure.

Temps de séjour et de réaction

Les temps de séjour mesurés sont les suivants (pour un rapport de vitesse de pompage = 10 (Ismatec)): *ca.* 1 min pour la spirale de mélange/chauffage simple (14 spires); *ca.* 9 min pour la spirale de réaction.

Si l'on tient compte encore des diverses connections, on dispose au total de plus de 13 min, ce qui est donc suffisant pour atteindre l'équilibre: l'étude manuelle indiquait un temps de réaction de *ca.* 15 min.

Un bref essai consistant à remplacer la bobine de réaction (*ca.* 12 m) par une spirale de mélange double, à 28 petites spires (*ca.* 2 m), a permis d'enregistrer des pics de hauteurs Δh (cm) égales respectivement à 8,4 (au lieu de 9,3 pour 5% de lait), à 16,7 (au lieu de 17,4 pour 10%) et à 23,1 (au lieu de 24,2 pour 15%), ce qui correspond assez bien au type de cinétique observé lors de l'étude manuelle. Par ailleurs, cet essai a mis en évidence un autre fait, paradoxal à première vue: que l'on emploie la bobine de réaction de 12 m ou celle de 2 m, le temps nécessaire pour atteindre "le palier" ("steady state")—aussi bien lors de l'aspiration de l'échantillon que lors du rinçage—reste pratiquement le même. De plus, les pics enregistrés ont la même allure. On peut en déduire que la spirale de réaction, en dépit de sa très grande surface de contact avec le liquide, n'est pas à l'origine de la diffusion principale (contamination entre segments liquides), qui provoque l'élargissement et le chevauchement partiel des pics enregistrés. La cause la plus plausible de cette contamination est à rechercher dans la lenteur du mélange lait/dissolvant à la sortie du cactus d'injection H3. On remarque en effet que les deux flux adjacents se déplacent relativement longtemps à vitesses inégales, vu leur différence de densité. En outre, chaque connection verre/verre ou verre/nipple au moyen d'un manchon est une source de contamination supplémentaire. La seule solution vraiment parfaite consisterait à tout souder, ce qui est impensable pour un appareil de recherche. Finalement, l'écoulement du fluide non segmenté depuis le débulleur jusqu'au faisceau optique est également un facteur de contamination, d'autant plus important que les diamètres intérieurs de la branche sortie du débulleur et de l'entrée dans l'ultramicrocuvette sont différents. C'est au niveau de ces divers éléments que l'on pourrait intervenir pour augmenter la cadence des analyses sans perdre en résolution des pics, comme le montre le paragraphe suivant.

Cadences des analyses

Le Tableau V donne la hauteur des pics obtenus $\overline{\Delta h}$ en fonction de la cadence des analyses (t_a = temps d'aspiration de l'échantillon; t_r = temps de rinçage à l'eau). L'échantillon est un lait dilué 10 fois. La qualité de l'analyse—d'autant meilleure que le prélèvement d'échantillon et le rinçage sont quantitatifs—va donc à l'encontre de la quantité d'analyses effectuées par heure. Les valeurs $t_a = t_r = 3$ min (= 10 analyses/h) représente un bon compromis. On pourrait admettre à la rigueur $t_a = t_r = 2$ min avec 83% du pic intégral (= 15 analyses/h).

TABLEAU V

INFLUENCE DE LA CADENCE DES ANALYSES

t_a *(min)*	t_r *(min)*	$\overline{\Delta h}$ *(cm)*	$\overline{\Delta h}/h_{max}$ *(%)*	*Nbr. anal./h*
0,5	0,5	1,5	8	60
1,0	1,0	5,5	31	30
1,5	1,5	11,5	64	20
2,0	2,0	14,9	83	15
3,0	3,0	17,2	96	10
4,5	4,5	18,0[a]	100	$6\frac{2}{3}$
6,0	6,0	18,0[a]	100	5

[a] Plateau atteint ("steady state"): h_{max} = 18,0 cm.

DISCUSSION ET CONCLUSION

La méthode proposée dans ce travail, comme n'importe quelle autre, présente des qualités et des défauts.

Au compte de ses avantages, on peut citer sa simplicité, sa sensibilité, sa spécificité, l'influence du lactose et de la matière grasse s'avèrant suffisamment constante. La méthode ne nécessite qu'un nombre minimum de modules (passeur d'échantillons/pompe/bobines de mélange et de réaction/colorimètre/enregistreur), évitant l'emploi délicat du dialyseur nécessité par les méthodes au "dye-binding"[8] ou du minéraliseur requis pour la méthode de Kjeldahl[9,10]. Elle n'exige aucun traitement préliminaire, si ce n'est une dilution d'un facteur 10 avec de l'eau, opération que l'on pourrait également automatiser en flux continu.

Au compte des points critiques, il faut signaler surtout la résistance par trop variable des tuyaux de pompe en silicone. L'expérience a montré que pour un même lot de tuyaux (paquet de 6 pièces) les uns lâchent très vite (de quelques minutes à quelques heures), alors que d'autres peuvent résister une à deux semaines sans interruption. Ces tuyaux se déforment plus ou moins vite, ce qui se traduit par une dérive gênante tant de la ligne de base que de la hauteur des pics enregistrés pour une concentration donnée. La reproductibilité et par conséquent la fiabilité de la méthode peuvent être mises en cause. Il s'agit en fait d'un problème de technologie des plastiques et non de méthodologie. L'avenir de cette méthode dépend dans une grande mesure des possibilités de substitution des tuyaux en silicone, notamment de celui qui injecte le réactif, par des tuyaux moins sensibles au vieillissement mécanique et chimique ou par un autre dispositif de pompage équivalent. Un essai a été tenté en ce sens, consistant à injecter le réactif par une pompe à deux pistons à "débits compensés" (pompe Ismatec pmp-10, CH-Zürich), mais le flux obtenu ne s'est pas avéré suffisamment constant pour donner satisfaction.

L'analyse en discontinu automatique est peut-être une autre solution à ce problème puisqu'elle ne requiert que des pompes à piston inattaquables (verre et téflon en général). De plus, la cadence d'analyses de tels automates est beaucoup plus élevée, ce qui est dû au fait que la diffusion (la "contamination") entre échantillons est presqu'inexistante.

Les grandes variations du coefficient de corrélation biuret/Kjeldahl, calculé pour les diverses séries* de lait, qui passe de 0,90 (médiocre) à 0,98 (très bon), s'explique vraisemblablement en partie par cette instabilité du système de pompage. Dans la situation actuelle, une multiplication des tests de corrélation ne se justifie donc pas.

Quelles que soient les améliorations que l'on puisse apporter au dispositif expérimental, le coefficient de corrélation ne vaudra pourtant jamais exactement 1,000 en raison des différences des coefficients d'extinction des différentes protéines[2].

Cette dernière réflexion amène à repenser la définition de la "teneur en protéines totale". Ce terme recouvre en effet un vaste ensemble d'éléments variés, impossible à caractériser par un poids moléculaire ou une formule brute. Il ne s'agit pas d'une entité précise, univoquement définie: l'extension et la compréhension de ce concept est fonction du critère analytique choisi. Et ces critères sont nombreux: teneur en liaisons peptidiques (biuret ou absorption à *ca.* 210 nm), teneur en azote (TN ou PN selon Kjeldahl ou selon Dumas), capacité de fixer un colorant en donnant un complexe insoluble (méthode au "dye-binding"), pouvoir absorbant des fonctions amides à *ca.* 1530–1548 cm^{-1} (dosage dans l'infra-rouge), insolubilité dans certains milieux (précipitation dans CCl_3COOH à 12% ou avec des sels de métaux lourds), absorption à *ca.* 280 nm due aux acides aminés aromatiques (dosage dans l'ultra-

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* Pour des raisons pratiques, les 104 laits ont été analysés en 7 séries consécutives.

violet) ou à tel ou tel acide aminé donnant une réaction colorée, teneur en acides aminés totale après hydrolyse (dosage à la ninhydrine), "titrabilité" de certaines fonctions (dosage à la formaldehyde), réponse immunologique, etc. Le problème a déjà été soulevé lors de l'étude de la spécificité et de la sélectivité de cette méthode[2].

RÉSUMÉ

Les auteurs présentent les résultats de l'application de la méthode dite du biuret à l'analyse automatique en flux continu. La méthode est d'une grande simplicité. La spécifité de la réaction est acceptable: l'influence du lactose et des lipides est en effet suffisamment constante pour être compensée par un étalonnage de l'analyseur au moyen d'un lait "standard" à teneur en azote protéique connu. La loi de Lambert–Beer est vérifiée. La sensibilité permet de différentier des laits à teneur en protéines différant de moins de 2% relatifs. La reproductibilité d'analyses à double ou à triple consécutives est satisfaisante (*ca.* ±1%). Par contre, la stabilité du flux du réactif pose encore certains problèmes technologiques. Les tuyaux de pompe, même en silicone, sont en effet trop peu résistants au vieillissement chimique et mécanique qu'occasionne la forte concentration en *n*-butylamine requise pour dissoudre intégralement le lait. Une série de tests est ensuite consacrée à l'étude de la concordance avec la méthode de Kjeldahl; le coefficient de corrélation obtenu pour 104 déterminations à double est $r=0{,}950$. Les temps de réaction et l'influence de la cadence des analyses font encore l'objet de quelques essais complémentaires ($\leqslant$ 15 analyses/h).

SUMMARY

Results obtained from the application of the so-called biuret method to an automatic continuous flow analyzer are presented. The method is of great simplicity. The "specificity" of the reaction is acceptable: the influence of lactose and lipids is constant enough to be compensated by a calibration of the automatic analyzer by means of a "standard" milk of known protein nitrogen content. Beer's law is valid: the sensitivity is sufficient to differentiate between milks differing relatively in protein concentration by at least 2%. The repeatability of consecutive double or triple analyses is usually satisfactory (*ca.* ±1%). The stability of the reagent flow poses some technological problems however: the pump tubings, even in silicone, are not very resistant to chemical and mechanical wear, owing to the high concentration of n-butylamine necessary completely to dissolve the milk. The correlation with the Kjelahl method was studied, the correlation coefficient being $r=0.95$ ($N=104$ duplicate determinations of individual and pooled milks). The reaction time and the influence of the rate of analyses were also studied ($\leqslant$ 15 analyses per h).

BIBLIOGRAPHIE

1 J. Bosset, B. Blanc et E. Plattner, *Anal. Chim. Acta*, 70 (1974) 327.
2 J. Bosset, B. Blanc et E. Plattner, *Anal. Chim. Acta*, 71 (1974) 97.
3 J. Bosset, B. Blanc et E. Plattner, *Anal. Chim. Acta*, 75 (1975) 474.
4 J. Bosset, B. Blanc et E. Plattner, *Anal. Chim. Acta*, 68 (1974) 331.

5 *Schweiz. Lebensmittelbuch*, Bd. II, *5. Aufl.*, Eidg. Drucksachen und Materialzentrale, Berne 1969 Kap. I. Methode 21, pp. 22–33.
6 E. Renner et S. Ömeroglů, *Z. Lebensm. Unters.-Forsch.*, 149 (1972) 335.
7 J. Bosset et G. Steiger, *Mitt.-Gebiete Lebensm. Hyg.*, 65 (1974) 470.
8 A. Conetta, L. Stookey et H. Zehnder, *Technicon International Congres 1970, Advances in Automated Analysis, Vol. II*, Median Incorporated, New York, 1971, pp. 81–85.
9 W. Schulz, *Technicon Symp. 1966, Automation in Analytical Chemistry, Vol. II*, Median Incorporated, New York, 1967, pp. 63–65.
10 G. J. Brisson, *Technicon Symp. 1965, Automation in Analytical Chemistry*, Median Incorporated, New York, 1966, p. 54–56.

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THE SEPARATION AND DETERMINATION OF GLYCOLIC AND MALIC ACIDS BY ION-EXCHANGE CHROMATOGRAPHY

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The separation and subsequent determination of low-molecular-weight organic acids is hard to accomplish by most modern analytical techniques. In the past few decades, separations of various organic acids have been reported by paper chromatography, thin-layer chromatography (t.l.c.) and liquid chromatography. Hartley and Lawson[1,2] studied the separation of some 128 organic acids in several different solvent systems by paper chromatography. They listed R_F values for these numerous acids for each solvent system. Stern *et al.*[3], also used this technique to study the separation of the urinary organic acids. Bleiweis *et al.*[4] studied the separation of some acids by t.l.c. while Chafetz and Penner[5] studied the detection of the carboxylic acids on t.l.c. by their reaction with iodide–iodate and amylase. Bulen *et al.*[6] separated organic acids from plant tissue on a silica gel, sulfuric acid-impregnated column. Several investigators have studied the separation of the acids with anion-exchange resins. Harlow and Morman[7] used water to elute some 50 acids from an anion-exchange column with no pretreatment. Samuelson and Thede[8] used an acetate form of resin with a sodium acetate eluant for their study. Three additional studies[9–11] were made with the acetate resin form, the first two employing magnesium acetate as eluant and the latter, zinc acetate. Davies *et al.*[12] studied 94 organic acids, using an anion-exchange resin in its formate form. They eluted each of these acids with from zero to 25 *M* formic acid as the eluants.

The aforementioned studies, in some cases, had a twofold purpose: one, separation; the other, detection. The paper-chromatographic and t.l.c. methods generally incorporate some acid–base indicator into the solvent system. Some of the indicators used for detection were bromophenol blue[1,3,4], thymol blue[1], and chlorophenol red[3]. In some cases the indicator can be sprayed onto the chromatogram.

In the liquid column methods, various methods of detection were employed. Bulen *et al.*[6] ran the acids individually, collecting small fractions and titrating each cut with standard base and an acid–base indicator. Harlow and Morman[7] used standard base titration but employed an automatic syringe and glass electrodes for the determination. A number of the determinatons were made by a simultaneous carbazole and chromic acid method[8–11]. Another method of detection was that of Shimomura and Walton[13], who used a differential refractometer to monitor the effluents of organic acids from an anion-exchange column. This was one of the first attempts to determine directly the acid concentration in a system.

The present work describes the application of the various methods for the separation and detection of glycolic and malic acids.

EXPERIMENTAL

Paper chromatography

Paper chromatography was used to monitor qualitatively effluent fractions from liquid chromatographic columns. The paper used was Whatman No. 1 and was developed in the following solvent system: ethyl formate:98% aqueous formic acid:H_2O (2:1:1, v/v/v) containing 0.15% (w/v) bromophenol blue and 0.05% (w/v) sodium formate. The chromatogram can also be developed with this solvent system excluding the indicator. The indicator can then be sprayed onto the plate in an ethanolic solution after drying of the chromatograms.

Procedure. 1–10 μl of sample was spotted on the paper; the solvent was allowed to evaporate (occasionally the paper was heated slightly to remove traces of formic acid and water) and then placed into a developing tank. The chromatogram was removed and allowed to air-dry. The appearance of acid spots required 15–60 min.

Thin-layer chromatography

Miniature thin-layer plates were used. T.l.c. was investigated from two points of view, as a separation technique and as an identification technique. The 6-cm × 6-cm plates were coated with silica gel G for t.l.c. according to Stahl (E. Merck). The plates were spread to a thickness of 1 mm and activated in a vacuum oven for 4 h at 120°C. The various developing solvent systems and visual identification techniques used were: (1) 20% butanol in chloroform sprayed with bromophenol blue; (2) 10% butanol in chloroform sprayed with bromophenol blue; (3) ethanol:chloroform: aqueous 28% ammonia solution:water (53:30.3:15.2:1.5, v/v/v/v) with identification by spraying with bromocresol green, bromothymol blue, and 2,7-dichlorofluorescein, as well as charring (each identification was done separately); (4) aqueous 28% ammonia solution sprayed with bromocresol green; (5) aqueous 28% ammonia solution:ethanol (1:1, v/v) sprayed with bromocresol green; (6) aqueous 28% ammonia solution:ethanol (1:2, v/v) sprayed with bromocresol green; (7) ethyl formate:98% formic acid:water (2:1:1, v/v/v) containing 0.015% (w/v) sodium formate.

Procedure. 1–10 μl of acid sample in 2 *M* formic acid was placed on the plate; the plate was dried at 70°C for 30 min and developed. After development the plate was again dried and visualized by either spraying or charring. The only exception to this procedure was a triple development (develop, dry, develop, etc.) with solvent system (3). The retention values for the migration of malic and glycolic acids in the various solvent systems are given in Table I.

Liquid column chromatography

Column A. This was an 8-cm long by 0.5-cm i.d. microcolumn packed with 1.5 g of 100–200 mesh silica gel (Davidson Chemical, Baltimore, Md.). Packing was accomplished by addition of the adsorbent with gentle tapping. The bed was supported by a glass wool plug, and the acid sample was placed at the top of the dry bed. The sample was eluted with solvent system (3) (see t.l.c. developing solvents). Small cuts were taken and qualitative analysis of the cuts was undertaken by t.l.c. (with solvent system (3)).

Column B. This was a 0.7-cm i.d. by 50-cm long glass column equipped with

TABLE I

MIGRATION VALUES FOR MALIC AND GLYCOLIC ACIDS ON SILICA GEL T.L.C. PLATES

Solvent system	*Acid*	R_F[a]	R_l[b]	R_t[c]	*Indicator*
(1)	Glycolic	35	70	0	BPB[d]
	Malic	20	40	0	
(2)	Glycolic	30	60	0	BPB
	Malic	15	30	0	
(3)	Glycolic[e]	10	—	—	BCG[f], BTB[g], DFC[h] and charring
	Malic[e]	3	—	—	
	Glycolic[i]	60	—	—	
	Malic[i]	10	—	—	
(4)	Glycolic	100	—	—	BCG
	Malic	100	—		
(5)	Glycolic	100	—		BDG
	Malic	100	—	—	
(6)	Glycolic	58	75	40	BCG
	Malic	40	55	25	
(7)	Glycolic	100	—	—	BPB
	Malic	100	—	—	

[a] $R_F = \frac{\text{Distance of spot center from spot point}}{\text{Distance of solvent front from spot point}} \times 100.$

[b] $R_l = \frac{\text{Distance of leading edge of spot from spot point}}{\text{Distance of solvent front from spot point}} \times 100.$

[c] $R_t = \frac{\text{Distance of trailing edge of spot from spot point}}{\text{Distance of solvent front from spot point}} \times 100.$

[d] Bromophenol blue.

[e] Single development.

[f] Bromocresol green.

[g] Bromothymol blue.

[h] 2,7-Dichlorofluorescein.

[i] Triple development.

a Teflon stopcock and a 100-ml solvent reservoir. The column was packed with 50–100 mesh Dowex 1-X8 anion-exchange resin (a quaternary ammonium salt). The column was packed by filling first with water and then adding a mixture of resin and water to the reservoir. The stopcock was opened and the resin was allowed to settle in the column. A glass wool plug was used to support the resin bed. The resin was put into its formate form by passage of 200 ml of 2 *M* sodium formate over the bed, followed by 10 ml of 25 *M* formic acid. The column was then washed with 200 ml of water and put into final form by elution with formic acid at the concentration to be used in the separation. Malic and glycolic acid samples were placed on the column, and the column was eluted with 200 ml of 0.2 *M* formic acid. Forty 5-ml cuts were taken and analyzed qualitatively by paper chromatography. The results indicated acid components in cuts 3–11 and cuts 21–26. The column was washed thoroughly with water and a similar sample which also included tetramethylammonium bromide was placed on the column. This mixture was eluted with 50 ml of water, followed by 100 ml of 0.2 *M* formic acid, and finally by 2.0 *M* formic acid.

Cuts were again taken (5-ml) and analyzed by paper chromatography. Spots appeared in cuts 1 and 2 (tetramethylammonium bromide), 15–23 (glycolic acid) and 34–37 (malic acid).

Column C. This was a 0.95-cm o.d. by 2.8-mm i.d. by 122-cm long, heavy-wall, glass column packed with 50–100 mesh, Dowex 1-X8 as described above except that stainless steel fittings were used at either end for bed support. The fittings were filled with glass beads to eliminate dead volume and back-mixing. The column was placed in a closed system, as shown in Fig. 1. Samples were injected directly on the column, and the stream effluent was monitored directly by an R-401 differential refractometer (Waters Associates, Framingham, Mass.). A typical trace for glycolic and malic acids is given in Fig. 2.

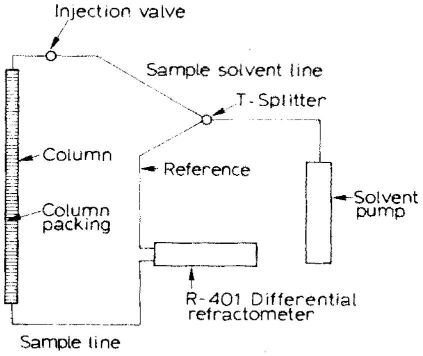

Fig. 1. Liquid chromatographic system.

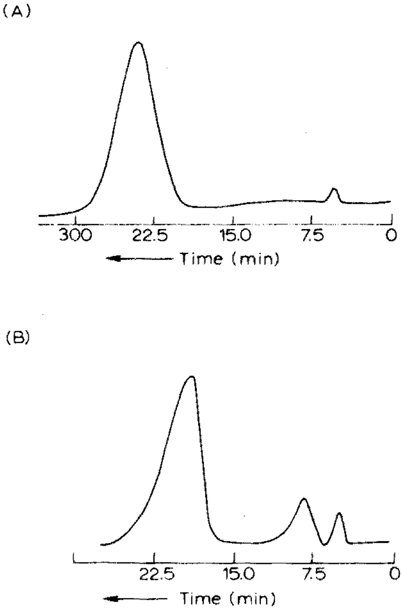

Fig. 2. Liquid chromatograms on Dowex 1-X8 anion exchange resin in 0.2 *M* formic acid (column C). (A) Malic acid: 50 μl of 5% sample solution at 0.62 ml min^{-1}; peak maximum at 15 ml. (B) Glycolic acid: 0.5 μl of 10% sample solution at 0.70 ml min^{-1}; peak maximum at 13 ml.

Column D. This was a 2.8-mm i.d. by 122-cm long, heavy-wall, glass column packed with 100–200 mesh, Amberlite CG-400 anion-exchange resin (a quaternary ammonium salt, Rohm and Haas Co.). The resin was put into its formate form in a manner similar to that used for the Dowex resin. The column was placed in the chromatographic system. A typical chromatogram for the separation of glycolic and malic acids is given in Fig. 3. The glycolic and malic acids had elution volumes of 8.74 and 23.85 ml, respectively. Reproducibility studies on the peak area responses (in.^{2} ml^{-1} of eluant) for various glycolic acid concentrations were also run. The results of this study are given in Table II. Triplicate runs of the malic acid at

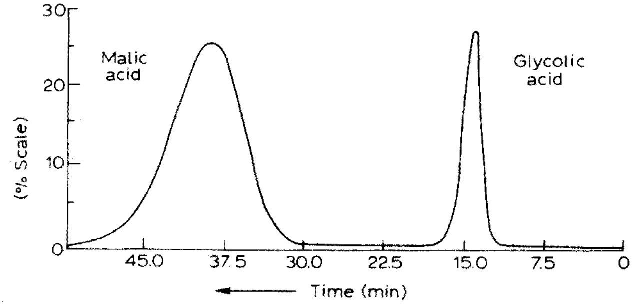

Fig. 3. Separation of glycolic and malic acids on Amberlite anion exchange columns (column D). 50 μl of sample passed at 0.67 ml min^{-1}; formic acid as eluant; attenuation × 64.

TABLE II

REPRODUCIBILITY OF PEAK AREAS FOR VARIOUS CONCENTRATIONS OF GLYCOLIC ACID IN 2 *M* FORMIC ACID

Glycolic acid (%)	*Peak area (in.^{2} ml^{-1} of eluant · 10^2)*				
	Run 1	*Run 2*	*Run 3*	*Value at 50% conf. level*	*Percent relative error*[a]
1	182.4	178.4	184.7	181.8 ± 1.5	8.68
2.5	471.0	477.9	483.3	477.4 ± 2.9	1.74
5.0	945.0	931.0	939.0	938.3 ± 3.3	2.05
10.0	1808.7	1780.5	1841.1	1810.1 ± 14.3	0.54

[a] $\frac{\text{Known peak area} - \text{experimental peak area}}{\text{Known peak area}} \times 100.$

TABLE III

PEAK AREAS FOR VARIOUS CONCENTRATIONS OF MALIC ACID IN 2 *M* FORMIC ACID

Percent malic acid (uncorrected)	*Peak area*[a] *(in.^{2} ml^{-1} of eluant) · 10^2*	*Percent relative error*
0.85	51.8 ± 0.4	1.85
1.95	117.8 ± 2.7	2.72
3.75	239.2 ± 0.8	1.37
7.35	464.8 ± 1.9	0.19

[a] Average of three runs at 50% confidence level.

various concentrations were obtained and these data are summarized in Table III. The data given in Tables II and III showed rectilinear calibration plots over the ranges given.

Electron microprobe

An ARL-EMX electron microprobe was used to investigate the structural

Fig. 4. Scanning probe electron microscope of 50/100 mesh Dowex 1-X8 and 100/200 mesh Amberlite CG-400 (scale: 100 μm cm^{-1}). Left: Dowex 1-X8. Right: Amberlite CG-400.

differences in the Dowex and Amberlite resins. The results of a 100-μm cm^{-1} scan are given in Fig. 4. A closer examination of an individual resin particle of each resin at 1000-μm cm^{-1} and 2000-μm cm^{-1} scans is given in Fig. 5.

RESULTS AND DISCUSSION

The results of the paper chromatographic method were inconclusive. Glycolic and malic as well as hydrochloric acids had R_F values of 100. This method seems sufficient for a spot test when only one known acid is present in a given system.

The t.l.c. methods merit more consideration. These methods are fair qualitative tests. In general, t.l.c. methods which do not use some strong base or acid either in the developing solvent or impregnated into the gel result in serious tailing. The problem associated with impregnation of the gel is that of identification. An acid–base spray indicator is generally used for identification of the spots. One can readily see that acid impregnation would eliminate this method of detection.

The various developing solvent systems are given in Table I and in the Experimental part. The systems containing 50% or more (by volume) of ammonia solution (solvent systems (4) and (5)) or 25% (by volume) formic acid (solvent system (7)) resulted in R_F values of 100 for malic as well as glycolic acid. When the ammonia concentration was decreased by the addition of more ethanol (solvent system (6)), a slight separation was observed but there was overlapping. The spot migration for solvent system (6) resulted in an elongated spot with a trailing edge (R_t) of 25 and a leading edge (R_l) of 55 for malic and corresponding values of 40 and 75 for glycolic (see Table I). When both acid and base were removed from the developing solvent (solvent systems (1) and (2)), tailing from the spot point upward was observed. The spot for the malic acid had an R_t value of zero and an R_l value of 40. The glycolic ranged from zero to 70 for the R_t and R_l values.

The only system showing promise for separation by t.l.c. was solvent system (3) (53% ethanol:30.3% chloroform:15.2%, 28% aqueous ammonia solution:1.5%

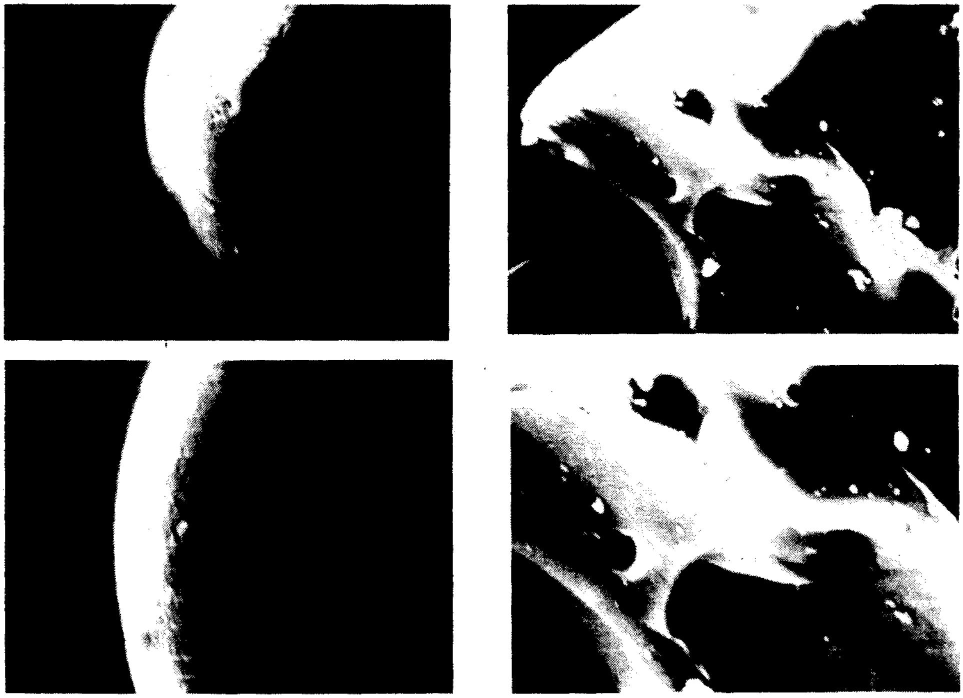

Fig. 5. Scanning probe electron microscope of the various anion exchange resins at the given magnifications. Photographs: Upper left, Dowex 1000 μm cm^{-1}; upper right, Amberlite 1000 μm cm^{-1}; lower left, Dowex 2000 μm cm^{-1}; lower right, Amberlite 2000 μm cm^{-1}.

water, v/v/v/v) which is a combination of some of the other systems discussed. A single development with this solvent showed a slight separation, but a triple development resulted in R_F values of 10 for malic and 60 for glycolic acid. In both cases, there was no evidence of tailing.

The indicators used were bromocresol green, bromophenol blue, and dichlorofluorescein. The bromocresol green seemed to be the best indicator and the dichlorofluorescein the poorest, since the acids showed no pronounced fluorescence. Charring also proved to be insufficient, particularly for the glycolic acid. Therefore, t.l.c. separation seems to be sufficient, but determination appears to be unlikely.

The ion-exchange chromatographic columns seem to offer the best possibility for complete separation and determination. The column system C described under Experimental (packed with Dowex 1-X8) was evaluated first. This column yielded peak maxima elution volumes of 13.39 ml and 14.97 ml (Table IV) for glycolic and malic acids. Another anion-exchange resin selected for evaluation was Amberlite CG-400. This column D (see Experimental) gave elution volumes of 8.74 and 23.85 ml for glycolic and malic acids (Table IV).

To compare the separating power of each column, there are two factors that can be calculated: the theoretical plate count (N) of the column and the resolution factor (R_s) of the two peaks eluted from the column[14–16].

The theoretical plate count is calculated from:

TABLE IV

ELUTION VOLUMES AND THEORETICAL PLATE COUNT FOR GLYCOLIC AND MALIC ACIDS ON COLUMNS PACKED WITH DOWEX AND AMBERLITE ANION-EXCHANGE RESINS

Acid	*Column*	E_v[a] (ml)	B_w[b] (ml)	N[c]
Glycolic	Dowex	13.39	4.83	123
Malic	Dowex	14.97	4.56	172
Glycolic	Amberlite	8.74	2.31	229
Malic	Amberlite	23.85	8.42	128

[a] E_v = peak maximum elution volume (ml).
[b] B_w = peak base width (ml).
[c] N (theoretical plates) = $16(E_v/B_w)$.

$$N = 16\left(\frac{E_v}{B_w}\right)^2, \tag{1}$$

where E_v is the peak maximum elution volume for a chromatographic peak and B_w is the band width (in ml) determined by the intersection with the baseline of the tangents of the inflection points of the peak. The plate counts calculated for glycolic and malic acids on the Dowex column were 123 and 172. The corresponding theoretical plate (N) counts resulting from the Amberlite column were 229 and 128 (Table IV). The resolution factor (R_s) can be given by the equation:

$$R_s = \frac{2(E_{v_2} - E_{v_1})}{(B_{w_1} + B_{w_2})}, \tag{2}$$

where E_{v_1} and E_{v_2} are the peak maxima values for the first and second eluted peaks, and B_{w_1} and B_{w_2} are the band widths determined by the intersection of the tangents of the inflection points of the peaks with the baseline. For rapid separation, an R_s value of one is taken as a satisfactory separation, while R_s values of less than 0.8 usually indicate unsatisfactory separation. The R_s value for the Dowex column was 0.34 and the Amberlite gave a value of 2.82.

From these results it can be seen that both columns give approximately the same theoretical column plate count (N) but significantly different resolution factors (R_s). The plate count is a measure of the efficiency of the column for a single component[16] while R_s is a measure of ability of the column to separate two components[17]. Practically, the good separation is important; therefore, the Amberlite column is much more suitable for separation of these two acids.

The Amberlite column was evaluated for its reproducibility at various concentrations of glycolic acid. From Table II it can be seen that the reproducibility of the peak areas at the 50% confidence level ranges from ± 1.5 at low concentrations, up to 14% at higher concentrations. The average relative error obtained from the analysis of both acids was 2.39% with a maximum error of 8.68%. (Individual relative errors were determined by dividing the difference in concentration weighed and concentration found by the concentration weighed.) A least-squares plot of these data showed a linear relationship to exist between the peak area and percent glycolic acid. Malic acid was also run. The data are given in Table III; a least-squares plot of the data again showed the linear relationship. From these facts it can be concluded that malic and glycolic acids can be determined in the 1–10% range simultaneously.

The Amberlite resin is capable of completely resolving the glycolic and malic acids. The Dowex resin seemed to differ from the Amberlite resin only in particle size; both are quaternary ammonium salts. Therefore, it might be supposed that the increased resolution of the acids must be due to the particle size of the resin. Actually, there are several factors that could bring about greater resolution of the two acids. A few of these factors are: column length, resin particle size, and resin structure. All these factors can play a significant role.

Column length would probably be the most likely step to improve resolution. Theoretically, resolution and column length can be related by an equation[15] which shows that the resolution factor increases by the square root of the column length when all other factors are held constant. Therefore, to double resolution the column length must be increased by a factor of 4. In addition, there is an important limiting factor, that of pressure. Viscosities of liquids are approximately 100 times greater than those of gases. Therefore, the pressure drop in liquid chromatography will be 100 times greater than in g.l.c. It can be shown theoretically[16] that, as the column length is increased, the pressure required to maintain constant mobile-phase velocity must be increased. An increase in pressure will also result in a corresponding decrease in the height equivalent to a theoretical plate, *H*. In the present systems, a maximum of 2000 p.s.i. pressure could be obtained with a stainless steel column and 600 p.s.i. in the glass system used. Therefore, the column length could be increased only until a maximum pressure drop of 600 p.s.i. (or 2000 p.s.i. for stainless steel) was required, to maintain a reasonable analysis time.

The particle size (d_p) is also significant in the separation of liquid chromatographic systems. The square of the particle size is approximately equal to *H* for g.l.c., thus[16]:

$$H \sim d_p^2 \tag{3}$$

For liquid chromatography, spherical packings follow the relationship[16]:

$$H \sim d_p^{1.6} \tag{4}$$

while nonspherical packings have been found to have the relationship[17]:

$$H \sim d_p^{0.8} \tag{5}$$

For a first approximation, relationship (3) can be used. Thus, the efficiency, measured as *H*, increases as the particle size decreases. In fact, experimental data have shown that in g.l.c. systems, going from 20–30 mesh to 100–150 mesh support results in a fourfold increase in efficiency while going from 50–60 mesh to 100–150 mesh shows a twofold increase[18]. In the present study the particle size was decreased from 50–100 mesh to 100–200 mesh. From previously cited data[18], there should be approximately a twofold increase in R_s. The values for the Dowex and Amberlite columns were 0.34 and 2.82, respectively. Therefore, the R_s value was increased almost tenfold.

The other parameter that might be used to explain the large increase in R_s is that of resin structure. There are three types of structural resins: (1) microreticular,

(2) macroreticular, and (3) pellicular resins[14]. The microreticular resin is a spherical resin with micropores through the bead. The macroreticular resins have micropores as well as macropores. The macropores are large enough to allow solute molecules to pass through the resin bed; therefore, the macroreticular resins have a much greater surface area for exchange of ions than the microreticular resins since they have internal as well as external active sites. The pellicular resins are solid-core beads coated with ion-exchange resins. They are used for analytical rather than preparative work, owing to their low loading capabilities.

The results of the electron microprobe (Fig. 4) show that the Dowex resin is a spherical-type particle while the Amberlite resin consists of cubic particles. A closer examination of an individual resin particle of each resin at the 1000-μm cm^{-1} and 2000-μm cm^{-1} scans (Fig. 5) shows an even greater difference in the surface structures. In the Dowex resin, the surface is rather smooth with no visible pores through the molecules. The Amberlite, however, shows numerous pores and channels penetrating the resin molecule. Therefore, the Amberlite appears to be a macroreticular resin with a large surface area, internal as well as external, while the Dowex is either a pellicular resin with no interior surface activity or a microreticular resin with pores too small to allow solute molecules to pass through. This structural difference would easily account for the higher resolution factor for the glycolic and malic acids on Amberlite compared to Dowex resin.

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SUMMARY

An ion-exchange chromatographic method for the separation of glycolic and malic acids was developed. It was found that the resin structure plays an important role in the resolution of the two acids. The best system for separating the acids was a 2.8-mm i.d., 122-cm long Amberlite CG-400 anion-exchange column. The acids in concentrations of 1–10% in 2 *M* formic acid gave linear peak area responses.

REFERENCES

1 R. D. Hartley and G. J. Lawson, *J. Chromatogr.*, 4 (1960) 410.
2 R. D. Hartley and G. J. Lawson, *J. Chromatogr.*, 1 (1962) 69.
3 F. Stern, G. Grumet, F. Trabal, A. Mennis and H. Zinsser, *J. Chromatogr.*, 19 (1965) 130.
4 A. S. Bleiweis, H. C. Reeves and S. J. Ajl, *Anal. Biochem.*, 20 (1967) 335.
5 L. Chafetz and M. H. Penner, *J. Chromatogr.*, 49 (1970) 340.
6 W. A. Bulen, J. E. Vorner and R. C. Burrell, *Anal. Chem.*, 24 (1952) 187.
7 G. A. Harlow and D. H. Morman, *Anal. Chem.*, 36 (1964) 2438.
8 O. Samuelson and L. Thede, *J. Chromatogr.*, 30 (1967) 556.
9 L. Bengtsson and O. Samuelson, *Anal. Chim. Acta*, 44 (1969) 217.
10 K. S. Lee and O. Samuelson, *Anal. Chim. Acta*, 37 (1967) 357.
11 U-B. Larsson, T. Isaksson and O. Samuelson, *Acta Chem. Scand.*, 20 (1966) 1965.
12 L. Davies, R. D. Hartley and G. L. Lawson, *J. Chromatogr.*, 18 (1965) 47.
13 K. Shimomura and H. F. Walton, *Anal. Chem.*, 37 (1965) 1012.
14 C. D. Scott in J. J. Kirkland (Ed.), *Modern Practices of Liquid Chromatography*, Wiley-Interscience,

New York, 1971, p. 292.
15 J. C. Giddings, *Dynamics of Chromatography*, Marcel Dekker, New York, 1965, p. 269.
16 B. L. Karger in J. J. Kirkland (Ed.), *Modern Practices of Liquid Chromatography*, Wiley-Interscience, New York, 1971, Ch. 1, p. 3.
17 L. R. Snyder, *J. Chromatogr. Sci.*, 1 (1969) 352.
18 J. Bohemen and J. H. Purnell in D. H. Desty (Ed.), *Gas Chromatography 1958*, Butterworths, London, p. 8.

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SYNERGIC EXTRACTION AND PHOTOMETRIC DETERMINATION OF VANADIUM(V) WITH 8-QUINOLINOL IN THE PRESENCE OF PHENOLS

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Synergic extraction of metal chelates has been mostly explained in terms of the formation of complex addition compounds, *i.e.* replacement reactions of water molecules bound to the central metal ion by basic neutral organic molecules (TBP, TOPO, pyridine, etc.), or the formation of simple addition compounds, *i.e.* with no replacement reaction. Recently, some novel examples of synergic extraction have been explained either as esterification of the complex in the presence of alcohols[1–4], or as the formation of binuclear complexes in the presence of a second metal ion[5–9].

The V–OH group in vanadium 8-quinolinolate (oxo-bis(8-quinolinolate)-vanadic acid) is acidic and is subject to esterification in the presence of alcohols[1–4,10], giving rise to a hypsochromic effect. On the basis of these phenomena, methods for the photometric determination of alcohols have been proposed by many workers. The V=O group in the same complex is basic and reacts with various acids including phenols[11–13], producing a bathochromic effect. Thus the vanadium complexes of iodo-derivatives of 8-quinolinol have been proposed as reagents for the photometric detection of phenols[14].

The present paper deals with the synergic extraction of vanadium 8-quinolinolate in the presence of *p*-phenylphenol. A sensitive method for the extraction–photometric determination of vanadium has been developed. The method has been applied successfully to the determination of vanadium in silicate rocks.

RESULTS AND DISCUSSION

Absorption spectra of the adducts of vanadium 8-quinolinolate with phenols

As shown in Fig. 1, when phenols are added to benzene solutions of vanadium 8-quinolinolate, $VOOx_2OH$, the wavelength of maximum absorption shifts to longer wavelength and the absorbance increases with increasing concentration of phenols. For *ca.* 10^{-2} M concentrations of phenols, the wavelength of maximum absorption is different for different sorts of phenols (Table I). At phenol concentrations higher than 0.1 M, absorbance at the maximum wavelength remains almost constant, and only the wavelength of maximum absorption shifts to a longer

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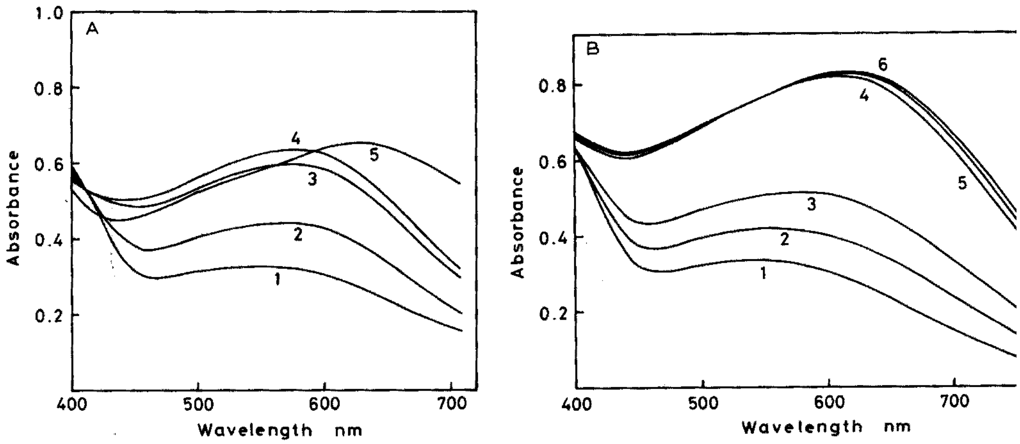

Fig. 1. Absorption specta of vanadium 8-quinolinolate in the presence of phenols. (A) *p*-Chlorophenol. (1) None; (2) $2.50 \cdot 10^{-4}$ *M*; (3) $1.00 \cdot 10^{-3}$ *M*; (4) $1.00 \cdot 10^{-2}$ *M*; (5) 1.00 *M*. (B) *p*-Phenylphenol. (1) None; (2) $4.00 \cdot 10^{-4}$ *M*; (3) $1.00 \cdot 10^{-3}$ *M*; (4) $1.00 \cdot 10^{-2}$ *M*; (5) $3.00 \cdot 10^{-2}$ *M*; (6) $5.00 \cdot 10^{-2}$ *M*. $c_V = 1.07 \cdot 10^{-4}$ *M*; $c_{HOx} = 1.00 \cdot 10^{-2}$ *M*.

TABLE I

THE MAXIMUM WAVELENGTHS OF THE COMPLEXES FORMED IN THE PRESENCE OF VARIOUS PHENOLS

Phenol	*[Phenol]* *(M)*	λ_{max} *(nm)*
Phenol	$1.5 \cdot 10^{-2}$	570
p-Methoxyphenol	$1.0 \cdot 10^{-2}$	650
p-Chlorophenol	$1.0 \cdot 10^{-2}$	580
o-Phenylphenol	$1.0 \cdot 10^{-2}$	590
p-Phenylphenol	$1.0 \cdot 10^{-2}$	610
o-Methylphenol	$1.5 \cdot 10^{-2}$	590
p-Methylphenol	$1.0 \cdot 10^{-2}$	600
p-Nitrophenol	$1.5 \cdot 10^{-2}$	575

wavelength with increasing concentration of phenols. Similar reactions were also observed for the other phenols listed in Table I.

To determine the composition of the adduct of vanadium 8-quinolinolate with phenols, the absorbance at 650 nm was plotted against the concentration of phenols. As is evident from Fig. 2, two adducts are formed: one is a 1:1 complex and the other a 1:2 complex. The circles in Fig. 2 are the experimental data and the line is the theoretical curve calculated from the value obtained by means of the least-squares method. Calculated values are in good accord with experimental values. The formation constant of the 1:1 complex is about $10^{3.2-3.5}$ irrespective of the phenols previously mentioned, while the molar absorptivity of the 1:1 complex is larger for phenols having a high resonance system. In the following experiments, *p*-phenylphenol is used as the phenol because of its large distribution coefficient and the high absorptivity of the resulting adduct.

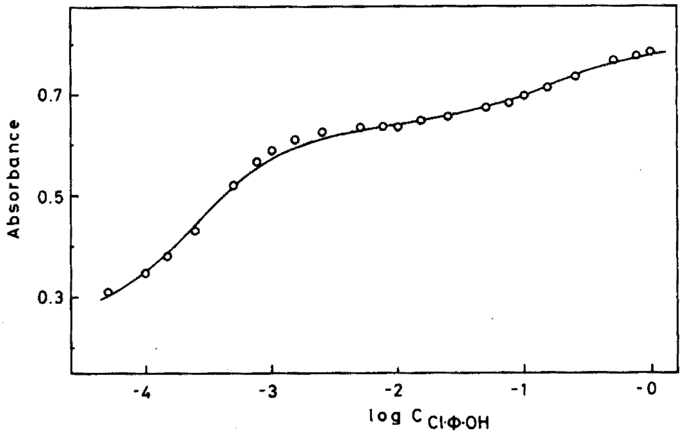

Fig. 2. Formation function of the adduct of vanadium 8-quinolinolate with *p*-phenylphenol. $c_V = 1.07\cdot10^{-4}$ *M*; $c_{HOx} = 1.00\cdot10^{-2}$ *M*; $\log K_1 = 3.75$; $\log K_2 = 0.86$; $\varepsilon_{VOOx_2OH} = 2.36\cdot10^3$; $\varepsilon_{VOOx_2OH\cdot ArOH} = 6.36\cdot10^3$; $\varepsilon_{VOOx_2OH\cdot(ArOH)_2} = 7.96\cdot10^3$.

Extraction equilibrium of vanadium 8-quinolinolate in the absence and presence of phenols

The partition of vanadium 8-quinolinolate between water and benzene is expressed as follows[3,15];

$$VO_2^+ + 2\,HOx_{org} \overset{K_{ex}}{\rightleftharpoons} VOOx_2OH_{org} + H^+ \tag{1}$$

$$K_{ex} = \frac{[VOOx_2OH]_{org}[H^+]}{[VO_2^+][HOx]_{org}^2} \tag{2}$$

$$VOOx_2OH_{org} + HOx_{org} \overset{K_{f(Ox)}}{\rightleftharpoons} VOOx_2OH\cdot HOx_{org} \tag{3}$$

$$K_{f(Ox)} = \frac{[VOOx_2OH\cdot HOx]_{org}}{[VOOx_2OH]_{org}[HOx]_{org}} \tag{4}$$

Then the distribution ratio is given by:

$$D = K_{ex}[HOx]_{org}^2(1 + K_{f(Ox)}[HOx]_{org})[H^+]^{-1} \tag{5}$$

At 8-quinolinol concentrations lower than 10^{-2} *M* in the organic phase, reaction (3) is not appreciable. In the presence of phenol, the distribution ratio *D* is a function of the concentration of phenol in the organic phase. However, it is difficult to determine the composition of the adduct by the log–log plot of partition, because of the slow attainment of the extraction equilibrium and possible decomposition of the complex in acidic media (see Fig. 4). The 1:1 adduct is responsible for the extraction of vanadium 8-quinolinolate in the presence of phenol (0.01–0.1 *M*) (see Fig. 2); at higher concentrations of phenol, the formation of the 1:2 adduct is evident.

The 1:1 adduct being assumed in the presence of phenol, the distribution ratio of vanadium is given by eqn. (6):

$$D = K_{ex}[HOx]^2_{org}(1+K_{f(ph)}[ArOH]_{org})[H^+]^{-1} \qquad (6)^\star$$

where

$$VOOx_2OH_{org} + ArOH_{org} \overset{K_{f(ph)}}{\rightleftharpoons} VOOx_2OH\cdot ArOH_{org} \qquad (7)$$

$$K_{f(ph)} = \frac{[VOOx_2OH\cdot ArOH]_{org}}{[VOOx_2OH]_{org}[ArOH]_{org}} \qquad (8)$$

Extraction of vanadium in the absence and presence of p-phenylphenol

The percentage extraction of vanadium 8-quinolinolate in the absence and presence of *p*-phenylphenol is given in Fig. 3. Vanadium is completely extracted into benzene at pH 2.4–5.0 irrespective of the absence or presence of *p*-phenylphenol, whereas, above pH 5.0, the percentage extraction of vanadium decreases with increasing pH. It should be noted that extraction in the presence of *p*-phenylphenol occurs at a lower pH than that in the absence of phenol, *i.e.* synergic extraction of vanadium 8-quinolinolate is observed in the presence of *p*-phenylphenol. A similar reaction was also observed for the other phenols, and the synergic extraction can be explained by the formation of the 1:1 adduct.

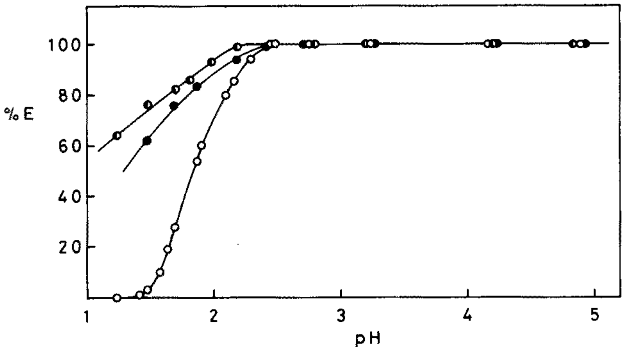

Fig. 3. Extraction curves of vanadium with 8-quinolinol in the absence and presence of *p*-phenylphenol. $c_{HOx} = 1.00\cdot10^{-2}$ *M*; $c_V = 1.07\cdot10^{-4}$ *M*; c_{ArOH}, (◐) 0.050 *M*, (●) 0.010 *M*, (○) none.

Effect of the shaking time on the extraction of vanadium

The extraction rate of vanadium 8-quinolinolate in the presence of *p*-phenylphenol is slow especially in acidic medium. As is evident from Fig. 4, the percentage extraction of vanadium increases with increased shaking time and maximum extraction is obtained within 30 min under the present experimental conditions. The extraction rate depends on the concentration of *p*-phenylphenol, 8-quinolinol, and hydrogen ion. At pH 2.4–5.0, shaking for 10 min is sufficient for complete extraction in the presence of 0.05 *M* *p*-phenylphenol. No effect of prolonged extraction was observed, and the extract is stable for at least several hours on standing. At lower pH, the partition equilibrium is reached slowly and the percentage extraction sometimes decreases in the course of prolonged extraction.

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* Taking reaction (3) into account, we have

$$D = K_{ex}[HOx]^2_{org}(1+K_{f(Ox)}[HOx]_{org}+K_{f(ph)}[ArOH]_{org})[H^+]^{-1}$$

Under the present experimental conditions, the second term in the parentheses may be neglected.

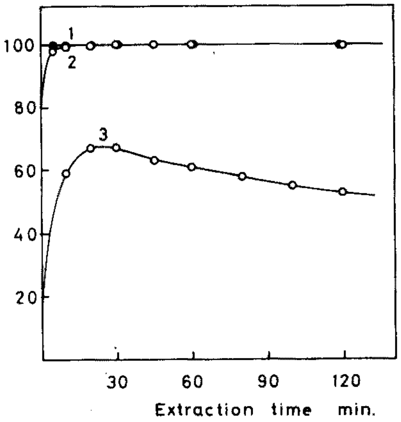
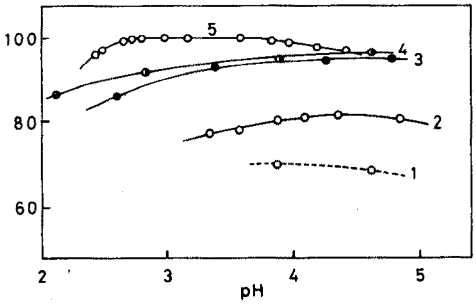


Fig. 4. Effect of shaking time on extraction of vanadium. $c_v = 1.07 \cdot 10^{-4}$ *M*; $c_{HOx} = 1.00 \cdot 10^{-2}$ *M*; pH (1), 4.17; (2) 2.40; (3) 1.23.

Effect of DCyTA in the extraction of vanadium

Under the present experimental conditions, many metal ions are extracted. Of these, iron(III) interferes in the extraction–photometric determination of vanadium. It has been reported that 1,2-cyclohexanediamine,N,N,N′,N′-tetraacetic acid (DCyTA) has only a very small effect on the color reactions of vanadium with xylenol orange[16] or thiazolylazoresorcinol[17] in aqueous solution. Based on these results, DCyTA was used as a masking agent for iron(III) in the present study. As is evident from Fig. 5, extraction of vanadium 8-quinolinolate in the presence of *p*-phenylphenol is considerably affected by the concentration of DCyTA. This undesirable depression of extraction can be completely overcome by the use of the Zn–DCyTA ligand buffer solution[18], though the pH range of complete extraction becomes narrower than in the absence of the ligand buffer. In addition,



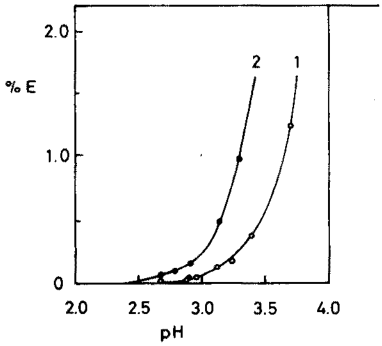


Fig. 5. Effect of masking agents on extraction of vanadium in the presence of 0.050 *M* *p*-phenylphenol. $c_V = 1.07 \cdot 10^{-4}$ *M*; $c_{HOx} = 1.00 \cdot 10^{-2}$ *M*. (1) $c_{EDTA} = 1.00 \cdot 10^{-3}$ *M*; (2) $c_{DCyTA} = 1.00 \cdot 10^{-2}$ *M*; (3) $c_{DCyTA} = 1.00 \cdot 10^{-3}$ *M*; (4) $c_{DCyTA} = 1.00 \cdot 10^{-4}$ *M*; (5) $c_{Zn} = 2.00 \cdot 10^{-3}$ *M* + $c_{DCyTA} = 1.00 \cdot 10^{-3}$ *M*.

Fig. 6. Effect of shaking time on extraction of iron(III) from ligand buffer solution in the presence of 0.050 *M* *p*-phenylphenol. $c_{Fe} = 8.00 \cdot 10^{-4}$ *M*; $c_{Zn} = 2.00 \cdot 10^{-3}$ *M*; $c_{DCyTA} = 1.00 \cdot 10^{-3}$ *M*; $c_{HOx} = 1.00 \cdot 10^{-2}$ *M*. Extraction time (1) 20 min; (2) 45 min.

the time necessary for complete extraction of vanadium from the ligand buffer solution becomes longer than that from the solution containing no masking agent. A shaking time of 45 min suffices for almost complete extraction of vanadium and the pH range for complete extraction is 2.7–3.6. The back-washing of the extract with the Zn–DCyTA solution of pH 2.8–3.5 causes no variation of the absorbance of the extract.

Below pH 3.2, only a small amount of iron(III) (< 0.5%) is extracted into benzene from the Zn–DCyTA solution in the presence of *p*-phenylphenol. The extraction of iron increases with increasing shaking time (Fig. 6).

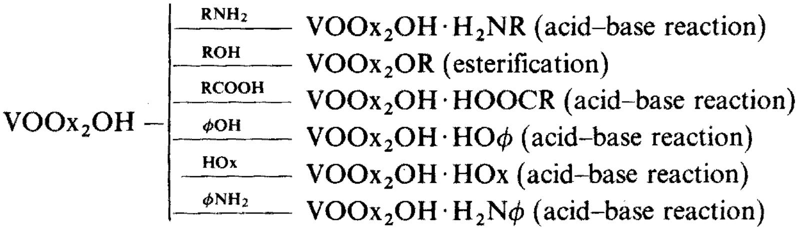
The same results for the extraction and back-washing of vanadium and iron complexes were obtained with dichloroethane instead of benzene as solvent.

Calibration curves for vanadium

The calibration curve for vanadium obtained by the present method is given in Fig. 7. Calibration curves of other methods with 8-quinolinol are given for comparison. As is evident from Fig. 7, the present method is the most sensitive one with 8-quinolinol.

Reaction of vanadium 8-quinolinolate with various neutral organic substances

As mentioned by Buscarons *et al.*[11] and by Blair *et al.*[10,12], vanadium 8-quinolinolate reacts with many neutral organic substances to form the corresponding adduct or ester in the organic solvents. These reactions are given schematically as follows:



$$\mathrm{VOOx_2OH} - \left| \begin{array}{l} \xrightarrow{\mathrm{RNH_2}} \mathrm{VOOx_2OH \cdot H_2NR} \text{ (acid–base reaction)} \\ \xrightarrow{\mathrm{ROH}} \mathrm{VOOx_2OR} \text{ (esterification)} \\ \xrightarrow{\mathrm{RCOOH}} \mathrm{VOOx_2OH \cdot HOOCR} \text{ (acid–base reaction)} \\ \xrightarrow{\phi\mathrm{OH}} \mathrm{VOOx_2OH \cdot HO\phi} \text{ (acid–base reaction)} \\ \xrightarrow{\mathrm{HOx}} \mathrm{VOOx_2OH \cdot HOx} \text{ (acid–base reaction)} \\ \xrightarrow{\phi\mathrm{NH_2}} \mathrm{VOOx_2OH \cdot H_2N\phi} \text{ (acid–base reaction)} \end{array} \right.$$

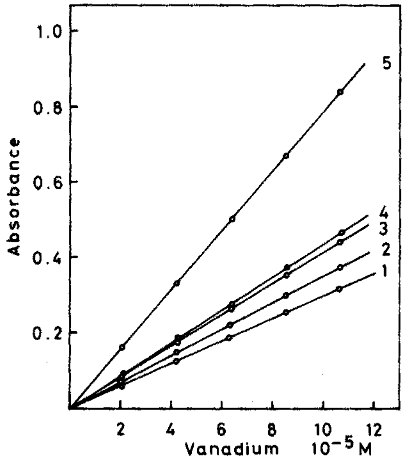


Fig. 7. Calibration curves. (1) $1.00 \cdot 10^{-2}$ *M* HOx at 550 nm; (2) $1.00 \cdot 10^{-2}$ *M* HOx+2.0 *M* capric acid at 550 nm; (3) $1.00 \cdot 10^{-2}$ *M* HOx+0.10 *M* octanol at 470 nm; (4) 0.51 *M* HOx at 550 nm; (5) $1.00 \cdot 10^{-2}$ *M* HOx+0.050 *M* *p*-phenylphenol at 620 nm.

Acidic organic substances react with the V=O group in the vanadium 8-quinolinolate to form the corresponding adduct, giving rise to a bathochromic effect, whereas amines react with the V–OH group in the same complex to form an adduct, producing a hypsochromic effect.

For the vanadium complexes of the other reagents, *e.g.* β-isopropyltropolone, benzoylphenylhydroxylamine (BPHA), maltol, etc., similar phenomena were observed. These phenomena will be reported elsewhere[19].

Recovery of vanadium in the presence of iron

Many metal ions are extracted under the present experimental conditions, but only the interference of iron(III) was examined. The analytical results of vanadium in synthetic composite samples, in which the concentration of iron was varied to about 100 times as high as that of vanadium, are shown in Table II. As can be seen, satisfactory, reliable, and reproducible results for the recovery of vanadium were obtained.

Application to analysis of silicates

The analytical results for vanadium in standard silicate rock samples, *i.e.* USGS-BCR-1 (Split 56), USGS-W-1, USGS-PCC-1 (Split 1), USGS-G-2 (Split 75), GSJ-JB-1 (Split 2), GSJ-JB-1 (Split 1) are shown in Table III. These values are in reasonably good agreement with those obtained by Donaldson[20], Flanagan[21], Akaiwa *et al.*[22], and Ando *et al.*[23].

EXPERIMENTAL

Reagents

All the reagents used were of G.R. grade. Benzene, dichloroethane, *p*-

TABLE II

RECOVERY OF VANADIUM IN THE PRESENCE OF IRON(III)

Vanadium taken (μg)	*Iron present (mg)*	*Vanadium found (μg)*
Benzene as solvent		
54.5	0	54.5
	2.24	54.7, 54.3
	4.49	54.3, 54.8
	6.73	55.5
136.3	0	136.3
	2.24	136.1, 136.0
	4.49	135.7, 136.0
Dichloroethane as solvent		
54.5	0	54.5
	4.49	54.8
	6.73	54.2
136.3	0	136.3
	4.49	136.1
	6.73	135.8

TABLE III

ANALYTICAL RESULTS OF VANADIUM IN STANDARD SILICATE ROCKS

Sample	*Vanadium (p.p.m.)*				
	Donaldson[20]	*Flanagan*[21]	*Akaiwa et al*[22]	*Ando et al.*[23]	*Present method*
USGS-BCR-1	420, 424	399			419
USGS-W-1	272, 274	264			274
USGS-PCC-1	22, 23	30			31
USGS-G-2	35.5, 35.5	35.4			34
GSJ-JB-1			178 ±7.4	200, 300	224, 227[a]
GSJ-JG-1			23.3±1.1	25, 21	29

[a] Obtained by the standard addition method.

phenylphenol, ammonium metavanadate, perchloric acid, sodium acetate, DCyTA, and anhydrous sodium carbonate were obtained from Wako Pure Chemical Co., Osaka, Japan. Benzene was first shaken with concentrated sulfuric acid and then successively with water, dilute sodium hydroxide solution, water, dilute hydrochloric acid solution, and finally with water 5 times and stored without dehydration. Dichloroethane was similarly treated and stored without dehydration. *p*-Phenylphenol and 8-quinolinol were recrystallized from aqueous ethanol. Sodium acetate was recrystallized from water and stored over silica gel. Zinc–DCyTA ligand buffer solution was prepared by mixing equal volumes of zinc ($4.00 \cdot 10^{-2}$ *M*) and DCyTA ($2.00 \cdot 10^{-2}$ *M*) solutions. Standard vanadium solution ($5.335 \cdot 10^{-4}$ *M*) was prepared by diluting a stock solution standardized gravimetrically and titrimetrically. Iron solution ($1.00 \cdot 10^{-2}$ *M*) was prepared by dissolving 401.2 mg of Fe_2O_3 (SpecPure) in 500 ml of dilute hydrochloric acid solution and was standardized against standard EDTA solution with the CuY–TAR indicator system[24]. Benzene solutions of *p*-phenylphenol (0.05 *M*) and 8-quinolinol (0.01 *M*) were used.

General procedures

All experiments were carried out in a room thermostated at 25±1°C. The initial volume of the aqueous and organic phases was always 25 ml except for the extraction–photometric determination of vanadium in the presence of iron and in silicate rocks (aq.: org. = 50:25). The initial concentration of vanadium in the system was below $1.5 \cdot 10^{-4}$ *M* and the ionic strength of the aqueous phase was kept constant at 0.1 *M* $(Na,H)ClO_4$ except for the extraction–photometric determination of vanadium. The aqueous and organic phases were contacted in a separatory funnel, a reciprocating shaker (200–250 strokes per min) being used. After the equilibration, the pH of the aqueous solution was measured with a Radiometer type PHM 22 pH meter. Vanadium in the organic phase was measured photometrically with a Beckman DU or Shimadzu QV 50 spectrophotometer in 10-mm silica cells. The absorbance was read at 620 nm against benzene. The amounts of vanadium were evaluated by consulting the calibration curve previously constructed.

Determination of vanadium in standard rock samples

Fuse 1 g of standard rock sample with 5–8 g of anhydrous sodium carbonate in a platinum crucible in the usual way. After complete decomposition, allow to cool, add hot water, and crush and grind the cake with a flattened glass rod. Reduce manganate by adding 2 drops of ethanol, filter through a medium-texture paper, and finally wash the residue well with hot 1% (w/v) sodium carbonate solution. Dilute the filtrate with water to 100 ml in a volumetric flask. Pipet 10 ml of the solution thus prepared into a 100-ml separatory funnel, add 10 ml of Zn–DCyTA solution and 10 ml of 0.05 *M* sodium acetate solution. After adjusting the pH to 2.8–3.1 with 1 *M* perchloric acid solution, follow the recommended procedure below.

Recommended procedure

Place 50 ml of test solution containing less than 150 μg of vanadium and no more than 8 mg of iron in a separatory funnel. Add 15 ml of a diluted Zn–DCyTA solution containing $2.00 \cdot 10^{-3}$ *M* zinc and $1.00 \cdot 10^{-3}$ *M* DCyTA, and adjust the pH of the solution to 2.8–3.2 with sodium acetate. Extract for 45 min with 25 ml of a 0.01 *M* benzene solution of 8-quinolinol containing 0.05 *M* *p*-phenylphenol. After dehydration of the organic phase with purified anhydrous sodium sulfate, read the absorbance at 620 nm against benzene. Establish the vanadium concentration from a calibration curve previously constructed.

In the absence of iron the addition of the ligand buffer may be omitted and the extraction is quantitative over a wider pH range, *i.e.* 3.0–4.5.

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SUMMARY

Vanadium(V) 8-quinolinolate reacts with phenols to form a 1:1 addition compound in organic solvents. Enhanced extraction of vanadium 8-quinolinolate in the presence of phenols can be accounted for in terms of the following reaction; $\mathrm{VOOx_2OH_{org}} + \mathrm{ArOH_{org}} \rightleftharpoons \mathrm{VOOx_2OH \cdot ArOH_{org}}$. On the basis of the bathochromic effect of phenols and the high molar absorptivity of the complex formed, a sensitive method for the extraction–photometric determination of vanadium has been developed. The analytical results for vanadium in the standard silicate rocks, USGS-BCR-1, USGS-W-1, USGS-PCC-1, USGS-G-2, GSJ-JB-1, and GSJ-JG-1, agreed well with the data reported previously.

REFERENCES

1 H. E. Jungnickel and W. Klinger, *Z. Anal. Chem.*, 203 (1964) 257; 206 (1964) 275.
2 N. Kurmaiah, D. Satyanarayana and V. Pandu Ranga Rao, *Talanta*, 14 (1967) 495; and papers cited therein.
3 M. Tanaka and I. Kojima, *J. Inorg. Nucl. Chem.*, 29 (1967) 1769.
4 H. Kawamoto and H. Akaiwa, *Nippon Kagaku Zasshi*, 94 (1973) 90.
5 N. V. Shakhova, I. P. Alimarin and Yu. A. Zolotov, *Dokl. Akad. Nauk SSSR*, 152 (1963) 884.

6 T. V. Healy, *Solvent Extraction Chemistry*, North-Holland, Amsterdam, 1967, p. 119.
7 R. A. Alekperov and N. N. Makov, *Zh. Anal. Khim.*, 23 (1968) 460.
8 Yu. A. Zolotov, *Dokl. Akad. Nauk SSSR*, 180 (1968) 1367.
9 N. Nakasuka, Y. Mitsuoka and M. Tanaka, *J. Inorg. Nucl. Chem.*, 36 (1974) 431; N. Nakasuka, T. Ito and M. Tanaka, *Chem. Lett.*, (1973) 553.
10 A. J. Blair, D. A. Pantony and G. I. Minkoff, *J. Inorg. Nucl. Chem.*, 5 (1958) 316.
11 F. Buscarons, J. L. Marin and J. Claver, *Anal. Chim. Acta*, 3 (1958) 310.
12 A. J. Blair and D. A. Pantony, *Anal. Chim. Acta*, 13 (1955) 1.
13 A. J. Blair and E. Bayer, *Justus Liebigs Ann. Chem.*, 684 (1953) 96.
14 I. M. Korenman, V. G. Ganina, G. R. Baranchikova and V. I. Zyuzina, *Tr. Khim. Tekhnol.*, (1969) 124; *Chem. Abst.*, 74 (1971) 9418c.
15 M. Tanaka and I. Kojima, *Anal. Chim. Acta.*, 36 (1966) 522.
16 O. Budevsky and R. Pribil, *Talanta*, 11 (1964) 1313.
17 O. Budevsky and L. Johnova, *Talanta*, 12 (1965) 291.
18 M. Tanaka and N. Awata, *Anal. Chim. Acta*, 39 (1967) 485.
19 I. Kojima, to be published.
20 E. M. Donaldson, *Talanta*, 17 (1970) 583.
21 F. J. Flanagan, *Geochim. Cosmochim. Acta*, 37 (1973) 1189.
22 H. Akaiwa, H. Kawamoto and H. Kondo, *Bunseki Kagaku*, 23 (1973) 402.
23 A. Ando, H. Kurasawa, T. Ohmori and E. Takeda, *Geochem. J.*, 5 (1971) 151.
24 H. Yamada, T. Maeda and I. Kojima, *Anal. Chim. Acta*, 72 (1974) 426.

Analytica Chimica Acta, 75 (1975) 377–384

THE EXTRACTION OF THULIUM(III), DYSPROSIUM(III) AND SAMARIUM(III) BY DIOCTYLARSINIC ACID IN CHLOROFORM

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Dioctylarsinic acid has recently been found to extract heavy lanthanide ions much better than the lighter ions[1]. Representative extraction coefficients determined for the systems containing 10^{-3} *M* lanthanide trichloride in aqueous sodium acetate–acetic acid buffer of pH 6 and 0.1 *M* dioctylarsinic acid are $6 \cdot 10^{-4}$, $2.5 \cdot 10^{-2}$, 3.5 and 4.5 for cerium(III), europium(III), holmium(III) and ytterbium(III), respectively. Reagent dependence and pH dependence studies suggested that the extracted complexes contained two dioctylarsinic acid anions and three neutral dioctylarsinic acid molecules. Because the extraction coefficients were sufficiently different to make an extractive separation of lanthanide ions with dioctylarsinic acid possible, the extractive behavior of the three additional lanthanide ions thulium(III), dysprosium(III) and samarium(III) has now been studied in detail. In addition, the influence of ionic strength and the effect of various anions on the extractibility of these three cations has been investigated. The results obtained in this study are the subject of this paper.

EXPERIMENTAL

Reagents

The γ-emitter ^{170}Tm($t_{\frac{1}{2}} = 134$ days) was obtained from International Chemical Nuclear Corporation as the trivalent chloride. The 99.9% pure $TmCl_3 \cdot 6\,H_2O$ (Apache Chemicals), 99.9% pure $DyCl_3$ and $SmCl_3$ (Research Organic/Inorganic Chemicals Corp.) were irradiated with neutrons at the Nuclear Science Center Reactor, Texas A and M University. The γ-emitting nuclides 144-day ^{159}Dy and 47-h ^{153}Sm were obtained.

Dioctylarsinic acid (HDOAA) was prepared as described in the literature[2].

The HDOAA solutions in chloroform were prepared in the usual way; the chloroform was ethanol-free and pre-equilibrated with water, being purified as described earlier[3].

Procedures

The pH of the aqueous solutions was measured with a Corning glass combination electrode and a Corning, Model 101, Digital pH meter. The pH was

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adjusted with acetate buffers, perchloric acid or nitric acid.

For some experiments, solutions free of chloride were required; this was done by heating 0.5 ml of 0.1 *M* $TmCl_3$ and 1 ml of tracer solution (10^{-2} *M* Tm) with 2 ml of 8 *M* perchloric acid or 2 ml of glacial acetic acid.

In the preparation of the final radioactive metal chloride solutions, the required amounts of NaCl, $NaClO_4$, $NaNO_3$ and Na_2SO_4 were added to give chloride, perchlorate and nitrate ion concentrations equal to 1 *M* and 4 *M* and a sulfate ion concentration equal to 1 *M*. The volumetric flasks were then filled to the mark with the appropriate buffer prepared from 1 *M* acetic acid and 1 *M* sodium acetate or with appropriately acidified distilled water.

In the pH dependence experiments, equal volumes (5 ml) of aqueous 10^{-3} *M* metal ion solutions, at different pH, with their ionic strengths adjusted with the appropriate salts were shaken for 30 min at room temperature with 0.1 *M* solutions of HDOAA in chloroform.

In the reagent dependence experiments, equal volumes (5 ml) of aqueous 10^{-3} *M* metal ion solutions, adjusted to the required pH, were shaken with HDOAA in chloroform for 30 min at room temperature. The concentrations of the HDOAA solutions varied from about 0.01 *M* to 0.1 *M*. In the experiments in which perchloric or nitric acid was used to adjust the pH, it was necessary to add some drops of 0.1 *M* sodium hydroxide solution to keep the pH constant.

Raman spectra were recorded on a Cary Model 82 Raman Spectrometer using the 514.5-nm line of an argon ion laser.

The calculations were carried out as reported earlier[1].

The monomer–dimer equilibrium ($K=10^3$) of HDOAA was taken into account. Computer programs were used to calculate least-squares slopes for the pH- and reagent-dependence curves. The extraction coefficient, E_a^0, was calculated from the γ-activities in the aqueous and organic phases at equilibrium and is defined as, *e.g.*, $[Tm(III)]_a/[Tm(III)]_a$, irrespective of the nature of the complexes formed by the metal ions.

RESULTS AND DISCUSSION

Thulium(III), dysprosium(III) and samarium(III) are easily extracted into chloroform by HDOAA from acidic aqueous solutions, the ionic strength of which has been adjusted with NaCl, $NaClO_4$, $NaNO_3$ or Na_2SO_4.

It can be seen from the dependence of the extraction coefficients for Tm(III), Dy(III) and Sm(III) on the aqueous equilibrium pH (Figs. 1–3) that the pH ranges in which these lanthanide ions are extracted shift to lower pH values with increasing atomic mass of the ion. Thulium, dysprosium and samarium were extracted in the pH ranges 1–6.5, 2–7 and 4–8, respectively, with extraction coefficients of approximately 0.1 for the lowest and 10 for the highest pH.

The extractability of the lanthanide ions increased with increasing ionic strength for each ion in all systems, and decreased in most cases in the order $ClO_4^- >$ $NO_3^- > Cl^- > SO_4^{2-} >$ acetate, for solutions of the same molarity, Table I lists the extraction coefficients at three different pH values as a function of ionic strength and the nature of the anion. The increase of the extraction coefficient with increasing ionic strength can be attributed to a salting-out effect. From experiments made in the

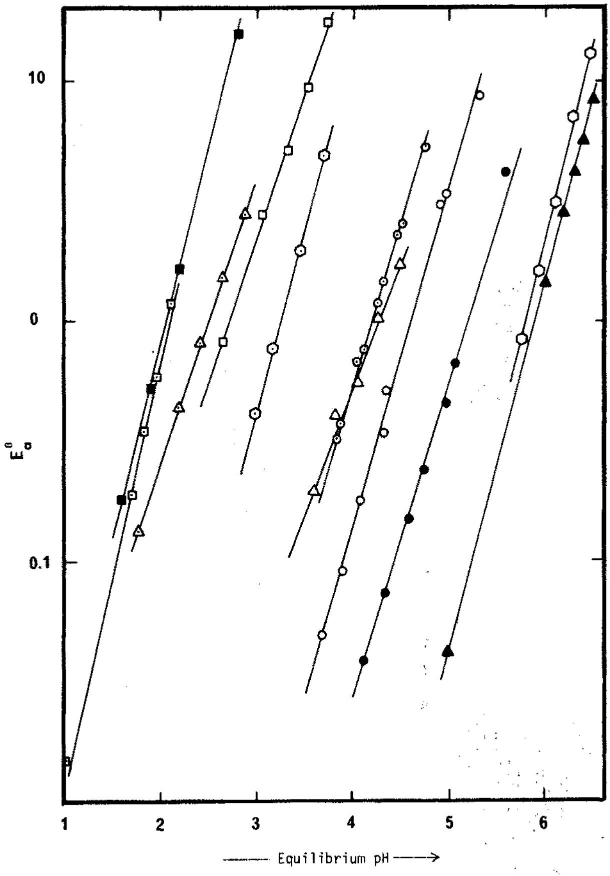
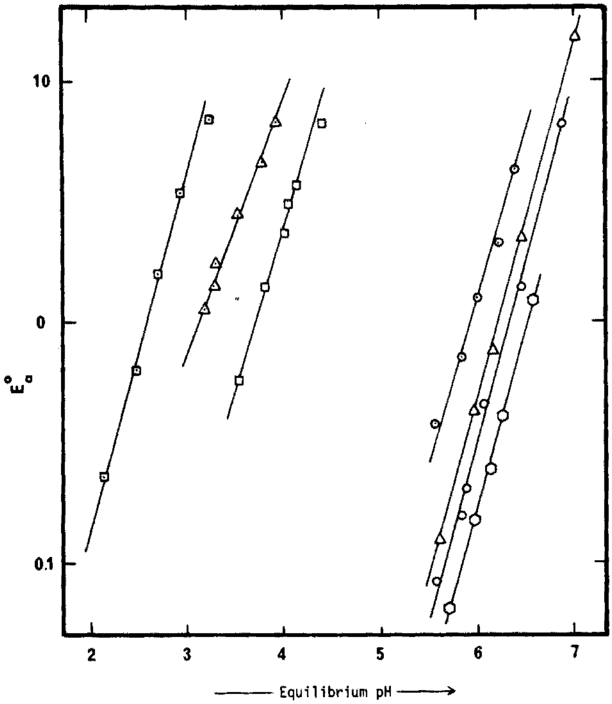


Fig. 1. pH Profile of the extraction of thulium(III) by dioctylarsinic acid in chloroform: HDOAA 0.1 *M*, 5 ml; phase ratio 1:1; extn. time 30 min.; $[Tm^{3+}]_{init.}$ $1.00 \cdot 10^{-3}$ *M*; (●) 10^{-3} *M* Cl^-; (▲) 1 *M* acetate (no Cl^-); (○) 1 *M* Cl^-; (⊙) 4 *M* Cl^-; (⬡) 0.5 *M* ClO_4^-/0.5 *M* Cl^-; (□) 1 *M* ClO_4^-; (⊡) 4 *M* ClO_4^-; (■) 4 *M* ClO_4^-(no Cl^-); (△) 1 *M* NO_3^-; (◬) 4 *M* NO_3^-; (⬡) 1 *M* SO_4^{2-}.

thulium–4 *M* perchlorate system it was noticed that chloride ions did not affect the slope of the hydrogen ion- or reagent-dependence curves, but slightly decreased the extractability. From the pH profiles (Figs. 1–3) those experimental conditions were selected for the pH- and reagent-dependence studies, which produced similar γ-activities in both phases. The results of these studies are summarized in Table II. The slopes of the pH-dependence curves (plotting E_a^0 *versus* the aqueous equilibrium pH at constant [HDOAA] and $[M^{3+}]$) vary from 1.05 to 1.87 with most of them having values close to 1.5. Such a slope can be reasonably explained by the assumption of the presence in the chloroform solution of approximately equimolar amounts of two complexes with one and two DOAA anions as ligands, respectively. The formation of a binuclear species, which could cause such a pH dependence, seems to be unlikely at metal ion concentrations of 10^{-3} *M*. With a few systems (Table II) slopes close to 2 were obtained, indicating the predominant presence of a complex in the organic phase containing two DOAA anions. Such species have been



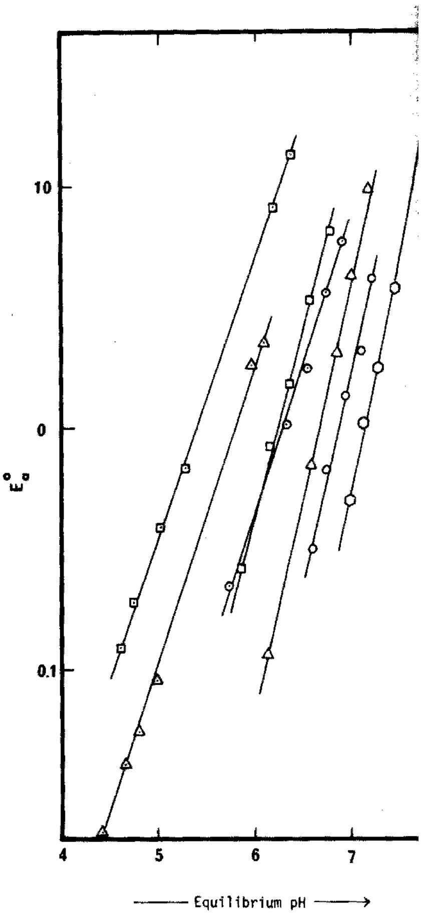


Fig. 2. pH Profile of the extraction of dysprosium(III) by dioctylarsinic acid in chloroform: HDOAA 0.1 *M*, 5 ml, phase ratio 1:1; extn. time 30 min; $[Dy^{3+}]_{init.}$ $1.17 \cdot 10^{-3}$ *M*; (○) 1 *M* Cl^-; (⊙) 4 *M* Cl^-; (□) 1 *M* ClO_4^-; (⊡) 4 *M* ClO_4^-; (△) 1 *M* NO_3^-; (◬) 4 *M* NO_3^-; (⬡) 1 *M* SO_4^{2-}.

Fig. 3. pH Profile of the extraction of samarium(III) by dioctylarsinic acid in chloroform: HDOAA 0.1 *M*, 5 ml; phase ratio 1:1; extn. time 30 min., $[Sm^{3+}]_{init.}$ $0.895 \cdot 10^{-3}$ *M*; (○) 1 *M* Cl^-; (⊙) 4 *M* Cl; (□) 1 *M* ClO_4^-; (⊡) 4 *M* ClO_4^-; (△) 1 *M* NO_3^-; (◬) 4 *M* NO_3^-; (⬡) 1 *M* SO_4^{2-}.

observed in the extraction[1] of Ce(III), Ho(III), Eu(III) and Yb(III). Slopes close to 1 have been obtained with nitrate systems. The results add credibility to the above proposed presence of two different complexes in systems, which gave slopes of approximately 1.5. The data in Table II seem to indicate, that the slopes decrease with increasing ionic strength. It is likely that with an increasing concentration of salt, with which the ionic strength is adjusted, the anion (Cl^-, NO_3^-, SO_4^{2-} or ClO_4^-) replaces a DOAA anion in the complex. Nitrate seems to be most effective in this respect (Table II). The reagent-dependence curves (plotting E_a^0 *versus* the equilibrium concentration of uncomplexed HDOAA at constant pH and $[M^{3+}]$) had slopes ranging from 4.0 to 5.3 with a few at 3.7. Most of these results can again be explained by assuming the presence of complexes with four and five di-

TABLE I

THE DEPENDENCE OF THE EXTRACTION COEFFICIENTS FOR Tm(III), Dy(III) AND Sm(III) UPON IONIC STRENGTH, pH and NATURE OF ANION

pH	*Anion*	E_a^0; $\mu=1$ *M*			E_a^0; $\mu=4$ *M*		
		Tm(III)	*Dy(III)*	*Sm(III)*	*Tm(III)*	*Dy(III)*	*Sm(III)*
2	ClO_4^-	$1.0\cdot10^{-1}$	$4.0\cdot10^{-3}$	$4.9\cdot10^{-7}$	$5.8\cdot10^{-1}$	$1.2\cdot10^{-1}$	$1.2\cdot10^{-4}$
	NO_3^-	$3.5\cdot10^{-3}$	$6.0\cdot10^{-7}$	$7.2\cdot10^{-9}$	$2.5\cdot10^{-1}$	$6.5\cdot10^{-2}$	$2.2\cdot10^{-5}$
	Cl^-	$1.7\cdot10^{-4}$	$3.3\cdot10^{-7}$	$4.5\cdot10^{-9}$	$1.2\cdot10^{-3}$	$3.6\cdot10^{-6}$	$4.5\cdot10^{-6}$
	SO_4^{2-}	$7.0\cdot10^{-7}$	$1.5\cdot10^{-7}$	$9.0\cdot10^{-10}$	—	—	—
	Acetate	$1.7\cdot10^{-6}$	—	—	—	—	—
4	ClO_4^-	$3.5\cdot10^{-1}$	2.5	$4.8\cdot10^{-4}$	$1\cdot10^{3}$	$1.4\cdot10^{2}$	$2.5\cdot10^{-2}$
	NO_3^-	$5.4\cdot10^{-1}$	$5.4\cdot10^{-4}$	$2.2\cdot10^{-5}$	$9.0\cdot10^{2}$	8.0	$6.4\cdot10^{-3}$
	Cl^-	$1.4\cdot10^{-1}$	$3.0\cdot10^{-4}$	$1.1\cdot10^{-5}$	$5.4\cdot10^{-1}$	$2.0\cdot10^{-3}$	$1.7\cdot10^{-3}$
	SO_4^{2-}	$6.0\cdot10^{-4}$	$2.0\cdot10^{-4}$	$1.3\cdot10^{-6}$	—	—	—
	Acetate	$1.3\cdot10^{-3}$	—	—	—	—	—
6	ClO_4^-	$1.2\cdot10^{4}$	$1.2\cdot10^{3}$	$4.2\cdot10^{-1}$	$1.4\cdot10^{6}$	$9.0\cdot10^{4}$	4.6
	NO_3^-	$7.6\cdot10^{1}$	$4.5\cdot10^{-1}$	$5.8\cdot10^{-2}$	$1.3\cdot10^{4}$	$1.0\cdot10^{3}$	1.7
	Cl^-	$1.0\cdot10^{4}$	$3.0\cdot10^{-1}$	$3.5\cdot10^{-2}$	$2.3\cdot10^{2}$	1.2	$4.2\cdot10^{-1}$
	SO_4^{2-}	2.0	$1.7\cdot10^{-1}$	$8.4\cdot10^{-3}$	—	—	—
	Acetate	1.7	—	—	—	—	—

TABLE II

SUMMARY OF THE RESULTS OF THE pH AND REAGENT DEPENDENCE STUDIES

Ln(III)	*Ionic strength*	*Acetate*[a]		*Chloride*		*Perchlorate*[a]		*Nitrate*[a]		*Sulfate*[a]	
		H$^+$	*R*	*H*$^+$	*R*	*H*$^+$	*R*	*H*$^+$	*R*	*H*$^+$	*R*
Tm	$1 \cdot 10^{-3}$	—	—	−1.42[b]	5.13[b]	—	—	—	—	—	—
	1	−1.53[b]	5.07[b]	−1.34[b]	4.82[b]	−1.40	5.30	−1.05[b]	4.54[b]	−1.85[b]	5.30[b]
	4	—	—	−1.52[b]	5.30[b]	−1.67	4.98	−1.16	5.45	—	—
Dy	1	—	—	−1.41[b]	4.75[b]	−1.35[b]	5.10[b]	−1.46[b]	4.00[b]	−1.45[b]	4.80[b]
	4	—	—	−1.31[b]	5.12[b]	−1.50	4.50	−1.05	4.12[b]	—	—
Sm	1	—	—	−1.66[b]	3.60[b]	−1.60[b]	4.80[b]	−1.80[b]	3.70[b]	−1.87	4.20[b]
	4	—	—	−1.20[b]	3.70[b]	−1.10[b]	4.50[b]	−1.24[b]	4.30[b]	—	—

[a] All these solutions are approximately $3 \cdot 10^{-3}$ *M* with respect to chloride ions.

[b] Acetate buffered system.

octylarsinic acid units (DOAA anions plus HDOAA) mixed in the appropriate proportion.

The following equilibria are in agreement with the experimental facts:

$$M^{3+}_{(a)} + 2\,X^{-}_{(a)} + 5\ \mathrm{HDOAA} \rightarrow [MX_2(\mathrm{DOAA})(\mathrm{HDOAA})_4]_{(o)} + H^{+}_{(a)}$$
$$M^{3+}_{(a)} + X^{-}_{(a)} + 4\ \mathrm{HDOAA} \rightarrow [MX(\mathrm{DOAA})_2(\mathrm{HDOAA})_2]_{(o)} + 2\,H^{+}_{(a)}$$
$$M^{3+}_{(a)} + 2\,X^{-}_{(a)} + 4\ \mathrm{HDOAA} \rightarrow [MX_2(\mathrm{DOAA})(\mathrm{HDOAA})_3]_{o} + H^{+}_{(a)}$$
$$M^{3+}_{(a)} + X^{-}_{(a)} + 5\ \mathrm{HDOAA} \rightarrow [MX(\mathrm{DOAA})_2(\mathrm{HDOAA})_3]_{o} + 2H^{+}_{(a)}$$

$(M = Sm, Dy, Tm;\ X = OH, Cl, NO_3, ClO_4, SO_4/2)$

Since the pH-dependence studies showed that at most two DOAA anions were bound to one lanthanide ion, other anions, X^-, must be present in the organic phase to produce neutral complexes. All attempts to determine these additional anions gave only qualitatively reliable results. Laser Raman spectroscopy was employed in an attempt to learn more about the environment of the metal ions in the organic phase. Unfortunately, the absorptions of chloroform, the only common solvent in which HDOAA is reasonably soluble at room temperature, are too strong in the region of interest.

Very little of a definite nature is known about the structure of lanthanide complexes in dilute systems. However, the possibility that complexes with coordination numbers larger than 6 exist, is generally accepted[5]. Such a higher coordination number can be easily achieved by the lanthanide ions in the chloroform phase by using water molecules as additional ligands. The extracted species are therefore tentatively formulated as $[MX_n(\mathrm{DOAA})_m(\mathrm{HDOAA})_p\ (H_2O)_q]$ $(n+m=3;$ $m+p=4$ or $5;\ q \geqslant 0)$. Chloroform equilibrated with water contains 0.088 moles of water per liter (ref. 3). Although the lanthanide ions coextract only negligible amounts of water[1], there is enough of it present in the chloroform to coordinate to the metal ions and complete the coordination sphere.

All the structures for extracted complexes of lanthanide ions with phosphorus or arsenic compounds which have been suggested in the literature, are solely based on pH- and reagent-dependence studies. It has, for instance, been reported, that dialkylphosphoric acids (HA) in toluene[6–8] form complexes, whose composition has been given as $LnA_3 \cdot 3\ HA$. Dioctylphosphinic acid[9] in benzene supposedly extracted lanthanide ions as $LnA_3 \cdot 2\ HA$. It seems, therefore, that dioctylarsinic acid can form a larger variety of complexes than similar phosphorus compounds.

In order to evaluate the suitability of HDOAA for an extractive separation of Sm(III), Dy(III) and Tm(III), the log E^0_a *vs.* pH curves were extended towards smaller pH values on the assumption that the slopes of these curves remain constant. The separation of samarium from dysprosium and thulium should present no problems. The 10^{-3} *M* chloride–4*M* perchlorate system is the most favorable. In this system at an equilibrium pH of 3.7, the E^0_a values are $1.1 \cdot 10^{-2}$, 45 and 340, respectively, for Sm, Dy and Tm. The separation coefficients $E^0_{aM}/E^0_{aM'}$ are therefore 4090 (Dy/Sm), 30909 (Tm/Sm) and 7.5 (Tm/Dy).

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SUMMARY

Dioctylarsinic acid, HDOAA, in chloroform (0.1 *M*) extracts thulium(III), dysprosium(III) and samarium(III) from their aqueous solutions in the pH ranges 1–6.5, 2–7 and 4–8, respectively, with extraction coefficients of approximately 0.1 for the lowest and 10 for the highest pH. The extractability increased with increasing ionic strength for each ion and decreased in the order $ClO_4^- > NO_3^- > Cl^- > SO_4^{2-} >$ acetate for solutions of the same molarity. pH-Dependence curves had slopes ranging from 1.05 to 1.87. The reagent-dependence studies gave curves with slopes between 3.60 and 5.30. The general formula $[MX_n(DOAA)_m(HDOAA)_p(H_2O)_q]$ ($X=Cl^-$, NO_3^-, $SO_4^{2-}/2$, ClO_4^-, acetate, OH^-; $n+m=3$, $m+p=4$ or 5, $q \geqslant 0$) is suggested for the extracted species.

REFERENCES

1 A. M. Olivares and K. J. Irgolic, *Mikrochim. Acta.*, (1974) 369.
2 K. J. Irgolic, R. A. Zingaro and M. R. Smith, *J. Organometal. Chem.*, 6 (1966) 17.
3 A. M. Olivares and K. J. Irgolic, *J. Inorg. Nucl. Chem.*, 34 (1972) 1399.
4 S. Lewey, G. W. Mason and D. F. Peppard, *J. Inorg. Nucl. Chem.*, 33 (1971) 2531.
5 T. Moeller in H. T. Emeleus (Ed.), *M and P International Review of Science, Lanthanides and Actinides, Inorganic Chemistry, Series One, Vol. 7*, University Park Press, 1972, p. 275.
6 D. F. Peppard, S. W. Molline and G. W. Mason, *J. Inorg. Nucl. Chem.*, 4 (1957) 344.
7 D. F. Peppard, G. W. Mason, W. J. Driscoll and R. J. Sironen, *J. Inorg. Nucl. Chem.*, 7 (1958) 276.
8 Z. Kolarik and H. Paukova, *J. Inorg. Nucl. Chem.*, 28 (1966) 2325.
9 D. F. Peppard, G. W. Mason and S. Lewey, *J. Inorg. Nucl. Chem.*, 27 (1965) 2065.

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UNTERSUCHUNGEN ÜBER DIE EXTRAHIERBARKEIT VON METALLIONEN MIT HILFE ALIPHATISCHER n-ARSONSÄUREN

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Es ist seit längerer Zeit bekannt, dass mit Hilfe organischer Lösungsmittel Carbonsäureverbindungen verschiedener Metallionen aus wässeriger Lösung extrahiert werden können[1–4]. Dabei wurden sowohl aliphatische wie auch aromatische Grundgerüste verwendet. Eine ausführliche Bearbeitung der Extraktionsfähigkeiten aliphatischer n-Carbonsäuren[5] zeigte, dass sich diese sehr gut zu Extraktionen eignen und auch eindeutige Zusammenhänge zwischen dem Ausmass der Extraktion und der Struktur bestehen. Einen praktischen Niederschlag erhielt diese Untersuchung durch die Bestimmungsmöglichkeit von Thorium mit Buttersäure[6].

Unter Verwendung einer anderen primäraktiven Säuregruppe, der Arensäuregruppe, wurden bei doppelter Substitution in den Arinsäuren ebenfalls Verbindungen erhalten, die die Eigenschaft haben, mit Metallionen Verbindungen zu geben, die extrahierbar sind[7–9]. Auch hier wieder ergeben sich praktische Anwendungsmöglichkeiten in der Extraktion von Zink[10], Wismut[11], Uran[12] und anderen.

Es lag daher nahe, die aliphatische Reihe der Arsonsäuren auf ihre Extraktionsfähigkeit hin zu untersuchen. Um eine Vergleichbarkeit der Ergebnisse im grösseren Rahmen zu ermöglichen und Schlüsse daraus ziehen zu können, wurde die Arbeitsweise weitgehend jener bei der Bearbeitung der Carbonsäuren angeglichen[5].

EXPERIMENTELLER TEIL

Die Untersuchungen wurden auf die Metallionen Be^{2+}, Mg^{2+}, Ca^{2+}, Ba^{2+}, Ce^{4+}, Ti^{4+}, Zr^{4+}, Th^{4+}, Cr^{3+}, UO_2^{2+}, Mn^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Al^{3+}, Pb^{2+} und Bi^{3+} erstreckt. An Arsonsäuren wurden die n-Butylarsonsäure, n-Amylarsonsäure, n-Hexylarsonsäure, n-Heptylarsonsäure, n-Octylarsonsäure und n-Nonylarsonsäure bearbeitet. Diese Säuren wurden durch Umsetzung von Alkaliarsenit mit Alkylbromiden in der Hitze hergestellt[13]. Nach sorgfältiger Umkristallisation entsprachen die bei Analysen erhaltenen Arsengehalte der Theorie.

Bei sämtlichen Extraktionsversuchen wurde gleicherweise verfahren. Von den Metallionen wurden 0,4 Milligrammatom in 80 ml wässeriger Lösung eingesetzt und mit 2,0 Millimol der betreffenden Säure in 20 ml Chloroform durch kräftiges Schütteln in einem Schütteltrichter extrahiert. Die Einstellung und Kontrolle des Extraktions-pH-Wertes erfolgte in der wässerigen Lösung mit einem normalen p_H-Meter. Die unten befindliche Chloroformphase wurde nach genügender Schichtentrennung dennoch prinzipiell durch Blaubandfilter (Schleicher u. Schüll) filtriet, um Verschleppungen gänzlich auszuschalten. Nach Verdampfen des Chloroforms wurde der Rückstand in geeigneter Weise quantitativ bestimmt.

Aus Gründen der Übersichtlichkeit und Einfachheit werden die Extraktionsergebnisse, die mit den einzelnen Arsonsäuren bei durchwegs einmaliger Extraktion erziehlt wurden, in den Abb. 1–5 graphisch dargestellt. Der Abstand zwischen zwei Metallionen auf der Ordinate bedeutet jeweils 100% Extraktion. Nicht extrahierte Metallionen wurden ausgelassen. Auf interessante Details wird im Folgenden eingegangen.

Bei n-Butylarsonsäure werden nur Ti^{4+}, UO_2^{2+} und Zr^{4+} in geringem Ausmass in schwach saurem Gebiet extrahiert.

Bei n-Amylarsonsäure werden schon etwas mehr Metallionen, nämlich Be^{2+}, Ti^{4+}, Cr^{3+}, UO_2^{2+} und Ni^{2+} extrahiert. Die Extraktionsverhältnisse gibt die Abb. 1 wieder.

Eine sprunghafte Ausweitung der Extrahierbarkeiten sowohl im Ausmass wie auch in der Zahl der erfassten Metallionen beobachtet man bei n-Hexylarsonsäure. Wie die Abb. 2 zeigt, werden die Ionen Be^{2+}, Ti^{4+}, Zr^{4+}, Cr^{3+}, UO_2^{2+}, Co^{2+}, Cd^{2+} und Pb^{2+} zu teilweise schon hohem Ausmass extrahiert. Cu^{2+} und Mn^{2+} werden in Spuren extrahiert.

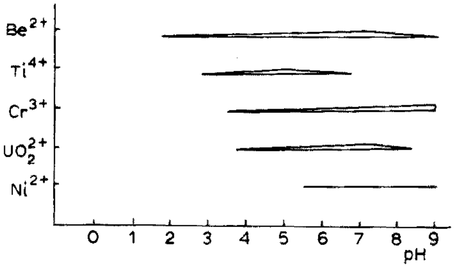

Abb. 1. Extraktionen mit n-Amylarsonsäure.

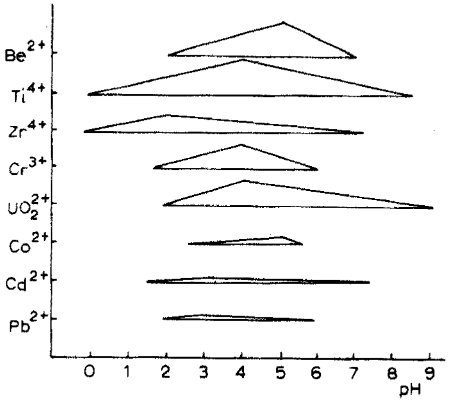

Abb. 2. Extraktionen mit n-Hexylarsonsäure.

Bei n-Heptylarsonsäure geht die Ausweitung des Extraktionsumfanges weiter. Bei den Ionen Be^{2+}, Ti^{4+} und Zr^{4+} tritt bei der einmaligen Extraktion unter den angegebenen Bedingungen bereits 100%ige Extraktion ein. Bei den Ionen Cr^{3+}, UO_2^{2+}, Mn^{2+}, Co^{2+} und Ni^{2+} ist sie ebenfalls sehr beträchtlich. Ba^{2+}, Ce^{4+}, Th^{4+} und Zn^{2+} sind in Spuren extrahiert worden. Die Abb. 3 zeigt die Verhältnisse.

Die Entwicklung zu höheren Extrahierbarkeiten geht bei der n-Octylarsonsäure weiter (Abb. 4). Zu 100% sind Ti^{4+} und Zr^{4+} extrahierbar. Zu rund 75% die Ionen Be^{2+}, Cr^{3+}, UO_2^{2+}, Mn^{2+}, Co^{2+} und Ni^{2+}, in geringem Ausmass auch Mg^{2+}, Ba^{2+} und Cd^{2+}. Sehr wenig bis in Spuren werden Ca^{2+}, Ce^{4+}, Th^{4+}, Cu^{2+}, Zn^{2+} und Pb^{2+} extrahiert. Überhaupt keine Extraktion zeigte Bi^{3+}.

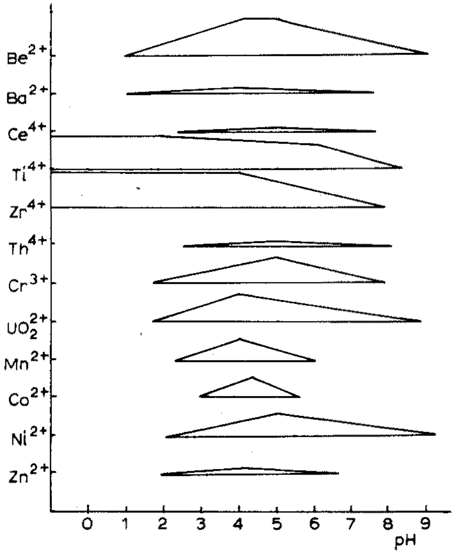

Fig. 3. Extraktionen mit n-Heptylarsonsäure.

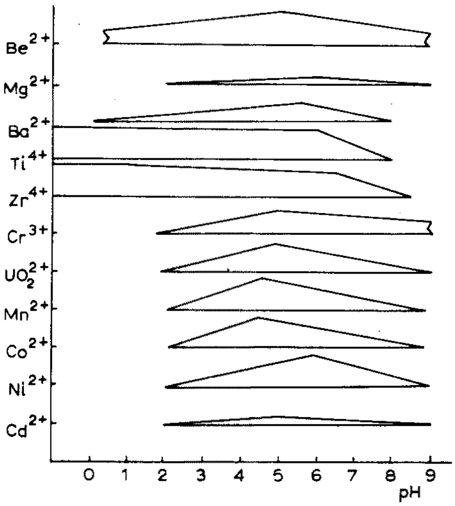

Abb. 4. Extraktionen mit n-Octylarsonsäure.

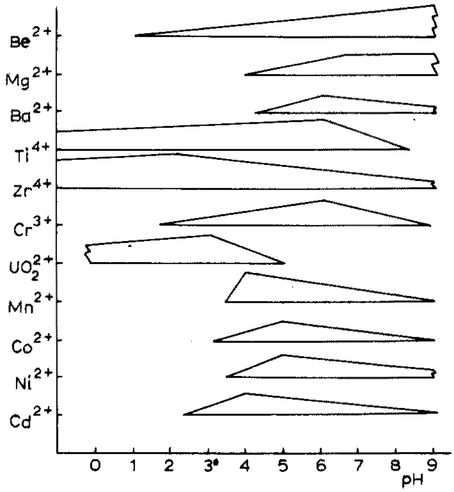

Abb. 5. Extraktionen mit n-Nonylarsonsäure.

Wie aus dem Vorhergehenden nicht anders zu erwarten, zeigt hinsichtlich der Zahl der extrahierbaren Metallionen die n-Nonylarsonsäure den grössten Umfang (Abb. 5). Das Ausmass der Extraktion sinkt hingegen verschiedentlich etwas ab. Eine starke Extraktion bei der einmaligen Ausschüttelung ergibt sich bei den Ionen Be^{2+}, Ti^{4+}, Zr^{4+}, Cr^{3+}, UO_2^{2+}, Mn^{2+}, Ni^{2+} und Cd^{2+}, wobei allerdings nur mit Zr^{4+} eine quantitative Extraktion erreicht wird. Mittlere Extraktionsausmasse erhält man bei Mg^{2+}, Co^{2+} und Ba^{2+}, während Ca^{2+}, Ce^{4+}, Th^{4+}, Fe^{3+}, Cu^{2+}, Zn^{2+}, Al^{3+}, Pb^{2+} und Bi^{3+} nur in sehr geringem Ausmass extrahiert werden.

Dissoziationskonstanten

Um das extraktive Verhalten mit der Basizität der Anionen vergleichen zu können wurden die Dissoziationskonstanten der bearbeiteten Arsonsäuren einerseits untereinander, aber auch mit jenen der Carbonsäuren verglichen. Da von den Arsonsäuren nur von den niedrigen Gliedern Angaben in der Literatur zu finden sind[14], wurden nach der Methode von Auerbach und Smolczyk[15] die Dissoziationskonstanten der ganzen Reihe der bearbeiteten Arsonsäuren bestimmt. Zu den erhaltenen Werten soll bemerkt werden, dass sie nur Vergleichswerte von nicht zu hoher absoluter Genauigkeit darstellen. Dies gilt insbesondere für die sehr wenig in Wasser löslichen höheren Glieder der Reihe. Die Methode gilt streng genommen nur für einbasige Säuren. Da sich die Dissoziationskonstanten der beiden Protonen von Arsonsäuren aber um rund fünf Zehnerpotenzen unterscheiden, ist eine wesentliche Beeinflussung der ersten Dissoziation durch die zweite nicht zu erwarten. Der über den Punkt der Halbneutralisation erhaltene Wert ist somit K_1 zuzuordnen.

Bei den niederen Gliedern der Reihe wurden die Werte sowohl durch direkte Titration wie auch durch Rücktitration ermittelt. Bei den höheren Säuren konnte wegen der geringen Wasserlöslichkeit nur durch Rücktitration gearbeitet werden. Die Ergebnisse bei den n-Arsonsäuren zeigt Tab. I.

Die Vergleichswerte der n-Carbonsäuren konnten zum grössten Teil aus der Literatur entnommen werden. Lediglich die Caprinsäure wurde wie vorher beschrieben durch Rücktitration vermessen. Für den erhaltenen Wert gelten die angegebenen Einschränkungen. Die Werte sind zum Vergleich auch in Tab. I zusammengefasst.

In beiden Säurereihen zeigt sich mit zunehmender Kohlenstoffkettenlänge eine Abnahme der Dissoziation, was einer Zunahme der Basizität des betreffenden Anions bedeutet.

TABELLE I

DISSOZIATIONSKONSTANTEN DER REIHEN DER n-ARSONSÄUREN UND n-CARBONSÄUREN

Säure		*Konstante* $(\cdot 10^{-5})$	*Säure*		*Konstante* $(\cdot 10^{-5})$	*Lit.*
Butylarsonsäure	C_4–AsO_3H_2	5,7	Buttersäure	C_3–COOH	1,45	16
Amylarsonsäure	C_5–AsO_3H_2	5,6	Valeriansäure	C_4–COOH	1,52	17
Hexylarsonsäure	C_6–AsO_3H_2	5,2	Capronsäure	C_5–COOH	1,44	18
Heptylarsonsäure	C_7–AsO_3H_2	5,0	Oenantsäure	C_6–COOH	1,42	19
Octylarsonsäure	C_8–AsO_3H_2	4,5	Pelargonsäure	C_8–COOH	1,12	20
Nonylarsonsäure	C_9–AsO_3H_2	~1,0	Caprinsäure	C_9–COOH	~0,4	—

VERSUCHE ZUR AUFKLÄRUNG DER NATUR DER EXTRAHIERTEN METALLVERBINDUNGEN

Zu diesem Zweck wurde versucht durch Fällung Präparate herzustellen, die den extrahierten Verbindungen weitgehend nahe kommen. Die Untersuchungen konzentrierten sich besonders auf die stark bearbeiteten Ionen Ti^{4+} und Zr^{4+} mit n-Heptylarsonsäure. Es wurden hierbei die verschiedensten Verhältnisse von Metall zu Säure und verschiedene Fällungsdurchführungen angewendet. Alle erhaltenen

Zirkonpräparate waren in Chloroform unlöslich, die Titanpräparate kurz nach der Fällung in Chloroform löslich, später ebenfalls unlöslich. Die angestellten Analysen ergaben schwankende Werte, was eine uneinheitliche Zusammensetzung zeigt. Die Zirkonverbindungen hatten in Durchschnitt ein Verhältnis von 2 Zr:5 Säure, die Titanverbindungen eines von 1 Ti:2 Säure. Dies stimmt in etwa mit den quantitativen Extraktionsbedingungen dieser Metalle überein[21].

Präparativ völlig unter den Extraktionsbedingungen hergestellte Extraktionspräparate zeigten, dass für die Zirkonverbindung ein Verhältnis von rund 2 Zr:7 Säure vorliegt. Weiters war zu beobachten, dass das Zirkonextrakt stark hydrolysiert, wobei wieder eine Fällung der Zusammensetzung 2 Zr:5 Säure ausfällt. Die Titanverbindung hingegen hydrolysiert nicht.

Infrarotspektroskopische und thermogravimetrische Untersuchungen an den verschiedenen Präparaten ergaben, dass es sich mit grösster Wahrscheinlichkeit nicht um echte Verbindungen handelt. Die IR-Banden der Säure sind zwar etwas verschoben, jedoch nicht derart, dass von einer echten Verbindungsbildung zu sprechen ist. Der Gewichtsverlust beim Erhitzen erfolgt stetig und ohne wesentliche Stufen.

AUSWERTUNG DER ERGEBNISSE

Wie erwartet zeigte sich die Tatsache, dass mit entsprechend langen Kohlenstoffketten aufgebaute n-Arsonsäuren ebenso wie die analogen n-Carbonsäuren Metallverbindungen liefern, die in Chloroform extrahiert werden können. Die Extrahierbarkeit setzt um eine Kohlenstoffkette von 6 Gliedern schlagartig ein, um sich bei Verlängerung nur mehr wenig zu verbessern. Dem geht formal parallel eine Verkleinerung der Dissoziationskonstanten der Säure, die allerdings die plötzliche Veränderung der Extrahierbarkeit nicht zu erklären vermag. Ähnliche diskontinuierliche Eigenschaftsveränderungen traten schon öfters, etwa bei n-Carbonsäuren[5], Arsinsäuren[7] und Acyloinoximen[22] auf. Nach den Dissoziationskonstanten sind die Arsonsäuren etwas stärker dissoziiert als die Carbonsäuren. Demzufolge sind die entsprechenden Anionen schwächere Basen, was die beobachtete Gesamttatsache, dass die Arsonsäuren etwas weniger gut extrahieren als die Carbonsäuren, erklärlich macht. Durch die Ähnlichkeit der die primäraktiven Gruppen tragenden Kohlenstoffgrundgerüste sind solche Vergleiche mit entsprechendem Vorbehalt zulässig[23]. Analoges zeigt sich auch deutlich darin, dass etwa die mit Carbonsäuren hergestellten Fällungspräparate in Chloroform löslich sind, die analogen Arsonsäurepräparate jedoch nicht[24].

Auffallend ist auch die Tatsache der möglichen Extraktion von Ti^{4+} und Zr^{4+} aus stark saurer Lösung, wie auch eine gewisse Extrahierbarkeit der Erdalkalien.

ZUSAMMENFASSUNG

Es wird über die Möglichkeit der Extraktion von Metallionen mit Hilfe von aliphatischen n-Arsonsäuren in Chloroform berichtet. Die Reihe der homologen Säuren von C_4 bis C_9 wird in ihrem Verhalten gegen 20 ausgewählte Metallionen bearbeitet. Die Ergebnisse werden mit den Dissoziationskonstanten der Arsonsäuren

und jenen der analogen n-Carbonsäuren verglichen und diskutiert. Es ist anzunehmen dass es sich bei den Verbindungen der Metallionen mit den Arsonsäuren nicht um echte Verbindungen handelt. Dennoch eröffnen die vorliegenden Extraktionsunterschiede eine Reihe guter Trennungsmöglichkeiten.

SUMMARY

The extraction of metal ions with a series of aliphatic n-arsonic acids in chloroform is described. Homologous (C_4 to C_9) arsonic acids were examined for 20 metal ions. Results are discussed in relation to acid dissociation constants and are compared with results for analogous carboxylic acids. No true compounds are formed between the metal ions and the arsonic acids. Various separations of metal ions are possible.

LITERATUR

1 E. B. Sandell, *Colorimetric Determination of Traces of Metals*, Interscience, New York, 2nd edn., 1950, p. 537.
2 P. W. West, F. C. Lyons und J. K. Carlton, *Anal. Chim. Acta*, 6 (1952) 400.
3 M. Tanaka und T. Niinomi, *J. Inorg. Nucl. Chem.*, 27 (1965) 431.
4 M. Tanaka, N. Nakasuka und S. Goto, in D. Dyrssen, J. O. Liljenzin und R. Rydberg (Herausgebern), *Solvent Extraction Chemistry*, North Holland, Amsterdam, 1967, p. 754.
5 R. Pietsch und H. Sinic, *Anal. Chim. Acta*, 49 (1970) 51.
6 R. Pietsch und H. Sinic, *Mikrochim. Acta*, (1968) 1287.
7 R. Pietsch und P. Ludwig, *Mikrochim. Acta*, (1964) 1082.
8 R. Pietsch, *Mikrochim. Acta*, (1963) 111.
9 R. Pietsch und E. Pichler, *Mikrochim. Acta*, (1961) 860.
10 R. Pietsch und G. Nagl, *Z. Anal. Chem.*, 203 (1964) 253.
11 R. Pietsch und E. Pichler, *Mikrochim. Acta*, (1962) 954.
12 R. Pietsch und E. Pichler, *Z. Anal. Chem.*, 190 (1962) 319.
13 R. Pietsch, *Monatsh. Chem.*, 96 (1965) 138.
14 H. J. Backer und C. C. Bolt, *Rec. Trav. Chim. Pays-Bas*, 54 (1935) 186.
15 F. Auerbach und E. Smolczyk, *Z. Phys. Chem. Stoechiom. Verwandschaftslehre*, 110 (1924) 65.
16 E. Bauer, *Z. Phys. Chem. Stoechiom. Verwandschaftslehre*, 56 (1906) 215.
17 E. Klein, *Lotus*, 71 (1923) 287.
18 I. M. Kolthoff und W. Bosch, *Rec. Trav. Chim. Pays-Bas*, 47, 875
19 E. Larsson and B. Adell, *Z. Phys. Chem. A*, 156 (1931) 390.
20 E. Franke, *Z. Phys. Chem. Stoechiom. Verwandschaftslehre*, 16 (1895) 477.
21 R. Pietsch und P. T. Gilani, *Anal. Chim. Acta*, 64 (1973) 345.
22 F. Feigl, *Chemistry of Specific, Selective and Sensitive Reactions*, Academic Press, New York, 1949, p. 267.
23 A. Ringbom, *Complexation in Analytical Chemistry*, Interscience, New York, 1963, p. 13.
24 R. Pietsch, *Anal. Chim. Acta*, 53 (1971) 287.

Analytica Chimica Acta, 75 (1975) 391–400

ANALYTICAL APPLICATIONS OF THIO, SELENO AND TELLUROETHERS

PART IV. COMPARATIVE BEHAVIOR OF SOME THIOGLYCOLIC ACID DERIVATIVES IN AQUEOUS SOLUTIONS

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In previous papers[1–3] of this series, the analytical applications of thio, seleno and telluroethers were reported; solvent extraction techniques were used because of the solubility characteristics of the reagents and their complexes. It was decided to extend these studies to the analytical potentialities of similar water-soluble compounds. As is well known, the introduction of carboxylic, sulfonic or amine groups into organic molecules[4] increases the water solubility of the compound. The compounds classified by Reid[5] as "sulfide acids" were selected for initial study.

The complexing ability of organic ligands containing nitrogen atoms as donors and carboxylic acid groups is widely known, even apart from the investigations carried out by Schwarzenbach *et al.* But from an analytical point of view, nothing has been systematically studied on compounds that have sulfur, selenium or tellurium instead of the nitrogen atom[6].

The introduction of the carboxylic acid group into thioether molecules should endow water solubility, but the selectivity will be diminished as the compounds will probably act as hybrid ligands with a soft donor atom (sulfur) and a hard one (oxygen). However, in these "sulfide acids", the complexing ability of the carboxylic group will be pH-dependent, thus in acidic medium, this reaction could be blocked, and complexation could again be possible only by the soft donor atom, so that the same selectivity[1–3] would be achieved.

The comparative study was initiated with four "sulfide acids": ethylthioglycolic acid (I, C_2H_5–S–CH_2–COOH), thiodiglycolic acid (II, HOOC–CH_2–S–CH_2–COOH), β-ethylthioethylenethioglycolic acid (III, C_2H_5–S–$(CH_2)_2$–S–CH_2–COOH), and ethylene-bis(thioglycolic)acid (IV, HOOC–CH_2–S–$(CH_2)_2$–S–CH_2–COOH).

EXPERIMENTAL

Apparatus

A Zeiss Spectrophotometer model PMQ II with 1-cm silica cells was used for absorbance measurements. Absorbance spectra were obtained with a Cary spectrophotometer model 14.

For pH measurements, a Metrohm potentiometer E 322 was used. Conductance measurements were obtained with a conductivity bridge I.I. Inc. model RC 16 B2 and 1-cm^2 platinized platinum electrodes (at 25.0±0.1°C).

For n.m.r. spectra, a Varian spectrometer model T60 (radio frequency of 60 MHz) was used.

Reagents

Ethylthioglycolic acid (I). The compound was prepared by the method of Larsson[7] (b.p., 117.0°C, 10 mm Hg; lit. b.p., 117.3°C, 10 mm Hg[7]). The sodium salt was obtained by adding 20% NaOH solution to give pH 6.5 and then adding excess of acetone.

Thiodiglycolic acid (II). The acid was prepared by the Loven procedure[8] (m.p. 129–130°C after recrystallization; lit. m.p. 129°C). The method described above was used to obtain the sodium salt.

β-Ethylthioethylenethioglycolic acid (III). The ω-bromodiethyl sulfide was prepared as described by Steinkopf *et al.*[9].

The required acid was obtained by the following procedure. To 200 ml of cooled absolute ethanol, 2.5 g of sodium was added and after the sodium ethylate had formed, 14.3 g of ethyl thioglycolate was carefully added dropwise to avoid temperature rise. Finally, 20 g of ω-bromodiethyl sulfide was added with the same caution. Four hours later, the mixture was warmed in a water bath (not boiling) until the solution showed a pH around 7. The excess of ethanol was eliminated in a boiling water bath, under low pressure. The reaction product was poured into ice and extracted with diethyl ether. The product, after elimination of ether, distilled (b.p. 112–113°C, 2 mm Hg; yield 80%).

P.m.r. data (60 MHz, CCl_4, τ): 5.85 (q, 2H, $J=7.3$ Hz); 6.85 (s, 2H); 7.25 (s, 4H); 7.44 (q, 2H, $J=7.3$ Hz); 8.72 (t, 3H, $J=7.3$ Hz).

A suspension of the ether (0.54 mole) and sodium hydroxide (0.75 mole, 290 ml of 10%) was stirred, with cooling until homogenization was complete. Thereafter, enough concentrated hydrochloric acid was added to give pH 2. The acid was extracted with diethyl ether, and the normal procedure was used to eliminate the ether. The acid was distilled (b.p. 144–146°C, 1 mm Hg; yield 60%).

P.m.r. data (60 MHz, CCl_4, τ): 6.76 (s, 2H); 7.20 (s, 4H); 7.44 (q, 2H, $J=7.3$ Hz); 8.75 (t, 3H, $J=7.3$ Hz); -1.5 (s, 1H).

The sodium salt was obtained in the same way as before.

Ethylene-bis (thioglycolic) acid (IV). The acid was prepared by the method of Ramberg and Tiberg[10]; the yield was 70% (m.p. 107–108°C; lit. 108–109°C (ref. 10)). The sodium salt was prepared by the usual method.

Standard palladium solution. This was prepared from palladium chloride to contain *ca.* 1.14 mg Pd ml^{-1} in 0.1 *M* hydrochloric acid. It was standardized gravimetrically with dimethylglyoxime.

Solutions of diverse ions. Stock solution of platinum group metals containing *ca.* 5.0 mg ml^{-1}, were prepared from their chlorides in 0.1 *M* hydrochloric acid; other ions were used from solutions containing *ca.* 25 mg ml^{-1}.

Sodium perchlorate solutions were standardized by passing through a resin column in the acid form (Merck-I) and titrating with standard sodium hydroxide solution.

All inorganic chemicals used were of analytical grade.

PRELIMINARY STUDIES

Visual changes

In preliminary tests, visual changes were observed in acidic solutions (0.1 *M*) of "soft" Lewis acids such as Pd(II), Ag(I), Hg(II), Au(III) and Cd(II); some "borderline" acids such as Cu(II), Zn(II), Pb(II), Rh(III), Pt(IV), Ir(IV), Os(IV), Ru(III), Co(II) and Ni(II); and some "hard" Lewis acids such as Fe(III), Cr(III) and Mn(II). Series of experiments were run with one drop of those solutions (500 μg per drop) and several drops of an aqueous $2\cdot10^{-3}$ *M* solution of the sodium salt of reagents I–IV. The acidity dependence of the visual changes was observed by adding one drop of 70% perchloric acid, before the addition of the ligand solution.

TABLE I

VISUAL CHANGES WITH LIGANDS I–IV[a]

Metallic ion		*Sulfide acid*			
		I	*II*	*III*	*IV*
Fe(III)		0	0	0	+ +
	(H$^+$)	0	0	0	0
Cu(II)		0	0	+	0
	(H$^+$)	0	0	+	0
Ag(I)		0	0	0	+ + +
	(H$^+$)	0	0	0	0
Hg(II)		+ +	+ +	+ +	+ + +
	(H$^+$)	+ +	+ +	+ +	0
Au(III)		0	0	+ + +	+ + +
	(H$^+$)	0	0	+ + +	+ + +
Pd(II)		+	+	+	+
	(H$^+$)	+	+	+	+

[a] (H$^+$) Acidity increased; (0) no change; (+) color change; (+ +) precipitation; (+ + +) precipitate dissolves in excess of ligand.

Table I shows the positive reactions obtained. No reaction was observed with any of the reagents with Co(II), Ni(II), Zn(II), Cd(II), Cr(III), Mn(II), Pb(II), Pt(IV), Rh(III), Ir(IV), Os(IV) or Ru(III) in neutral or acidic media. Visual changes with all four ligands were observed with Hg(II) and Pd(II) (typical "soft" Lewis acids); some selectivity for palladium(II) appeared with ligands I, II and IV in strongly acidic media.

In view of the above results and because, as is well known, ring formation would increase the stability of the complexes (in acidic medium, ring formation would be accomplished through the sulfur atoms), it was decided to collect more information about the behavior of reagent IV towards the above ions, through conductometric titrations. Reagent III did not present the same preliminary selectivity characteristics, but a parallel study was made, because it is a new compound and probably also acts as a bidentate ligand in acidic medium too, on reacting with "soft" Lewis acids.

Table II shows the molar ratios obtained by conductimetric titrations for the reactions of some metals with reagents III and IV. Although "electrical-conductance measurements in themselves merely indicate interactions or production of ions in chemical reactions"[17], Table II shows that the same molar ratios of ligand IV to metal were obtained as by other methods. It is interesting that for Co(II), Ni(II), Zn(II) and Cd(II), the molar ratios of ligand III to metal were different from the values for ligand IV. However for Pb(II), Ag(I) and Cu(II), the molar ratios were the same.

TABLE II

LIGAND–METAL MOLAR RATIOS OBTAINED FROM CONDUCTIMETRIC TITRATIONS IN NEUTRAL AND ACIDIC MEDIA

Metal ion	*Ligand III*		*Ligand IV*		
	Neutral	*[H] = 4.0·10⁻² M*	*Neutral*	*[H] = 4.0·10⁻² M*	*Lit. value*
Co(II)	2:1	2:1	1:1		1:1 (ref. 11)
Ni(II)	2:1		1:1		1:1
			2:1		2:1 (ref. 11)
Cu(II)	1:1	1:1	1:1	1:1	1:1
	2:1	2:1	2:1		2:1 (refs. 11, 12)
Zn(II)	2:1	1:1	1:1	1:1	1:1 (refs. 12, 13)
Cd(II)	2:1		1:1	1:1	1:1 (refs. 12, 13)
Pb(II)	1:1		1:1	1:1	1:1 (ref. 13)
Ag(I)	1:1	1:1	1:1	1:1	1:1
	2:1		2:1	2:1	2:1 (ref. 14)
Hg(II)		1:1		1:1	1:1
		2:1		2:1	2:1 (refs. 15, 16)
Au(III)		1:1		1:1	
		2:1		2:1	
Pt(IV)		1:1		1:1	
		2:1		2:1	
Ir(IV)		1:1		1:1	
		2:1		2:1	
Rh(III)		1:1		1:1	
		2:1		2:1	
Ru(III)		1:1		1:1	
		2:1		2:1	

In order to obtain more information about selectivity, within the acidity limits set by the technique, the conductimetric titrations were repeated in acidic solutions ($[H^+] = 4.0 \cdot 10^{-2}$). For mercury(II), gold(III) and the platinum metals group, no variation in molar ratios was observed with change in ligand. For the other ions, the increased acidity changed the molar ratios in the Zn(II) or Ag(I) complexes of ligand III and in the copper(II) complex of ligand IV, but had no effect on the Co(II) or Cu(II) complexes of ligand III or on the Zn(II), Cd(II), Pd(II) or Ag(I) complexes of ligand IV. Finally, the increased acidity prevented interactions between Ni(II), Cd(II), Pb(II) and ligand III, as well as between Co(II) or Ni(II) and ligand IV.

Because of the promising selectivity for palladium(II) of ligands III and IV, and because of the lack of information in the literature about interactions of noble metals with ligands I and II, the nature of the reactions in aqueous solutions containing $[PdCl_4]^{2-}_{aq}$ and ligands I–IV was studied.

REACTIONS OF $[PdCl_4]^{2-}_{aq}$ WITH THE FOUR LIGANDS

Reaction of palladium (II) with sodium ethylthioglycolate (I)

Conductimetric titrations of $5.5 \cdot 10^{-4}$ *M* palladium solution ($5.0 \cdot 10^{-2}$ *M* in H^+) with $1.0 \cdot 10^{-2}$ *M* reagent I (sodium salt) showed that only one species with the molar ratio 1:1 was present.

To observe changes in the $[PdCl_4]^{2-}_{(aq)}$ absorption spectrum, suitable amounts of ligand were added so that the molar ratio of ligand to palladium varied from 0 to 4. Figure 1 shows that at molar ratios of 2, 3 and 4, the characteristic $[PdCl_4]^{2-}_{(aq)}$ maximum (278 nm) disappeared, and the absorbance value at 400 nm increased, but no definite maxima were observed in the measured region.

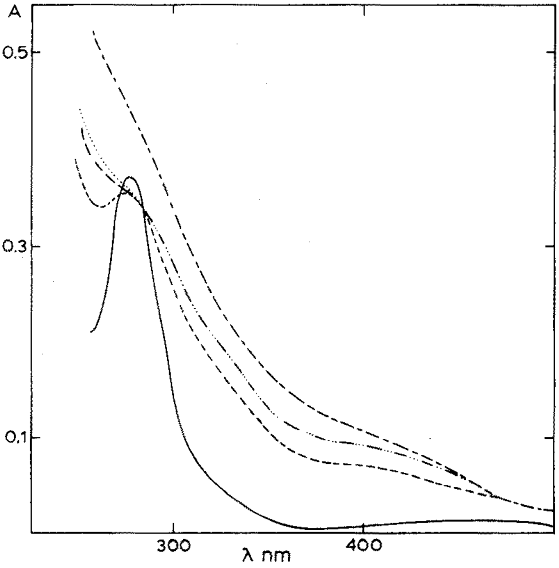

Fig. 1. Absorption spectra. In all cases, $5.8 \cdot 10^{-5}$ *M* $PdCl_2$ was present. A (——) No ligand; B (- - -) $5.8 \cdot 10^{-5}$ *M* I; C (— — —) $11.6 \cdot 10^{-5}$ *M* I; D (···) $17.4 \cdot 10^{-5}$ *M* I; E (— - — -) $23.4 \cdot 10^{-5}$ *M* I. $\mu = 0.5$; $pH = 1.5 \pm 0.1$. Measurements against reagent blank.

Reaction of palladium (II) with sodium thiodiglycolate (II)

Only the 2:1 species (ligand–palladium) was found when $4.0 \cdot 10^{-4}$ *M* palladium solution ($4.0 \cdot 10^{-2}$ *M* in H^+) was conductimetrically titrated with $5.0 \cdot 10^{-3}$ *M* reagent II (sodium salt).

The same molar ratio variations as above were followed to examine any spectral changes in acidic $[PdCl_4]^{2-}_{aq}$ solutions (Fig. 2). With increasing molar ratio, the absorption maximum of $[PdCl_4]^{2-}_{(aq)}$ was eliminated, but the new species did not present a well defined maximum, although at 400 nm the absorbance value again increased.

Reaction of palladium (II) with sodium β-ethylthioethylenethioglycolate (III)

Conductimetric titration of $5.5 \cdot 10^{-4}$ *M* palladium solution ($5.5 \cdot 10^{-2}$ *M* in H^+) with $9.0 \cdot 10^{-3}$ *M* reagent III (sodium salt) showed that two complexes were

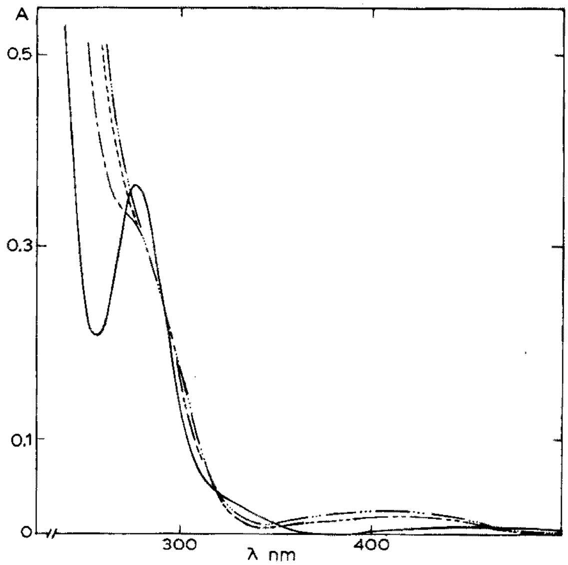

Fig. 2. Absorption spectra. In all cases, $5.8 \cdot 10^{-5}$ *M* $PdCl_2$ was present. A (——) No ligand: B (— — —) $5.8 \cdot 10^{-5}$ *M* II; C (---) $11.6 \cdot 10^{-5}$ *M* II; D (···) $17.4 \cdot 10^{-5}$ *M* II; E (— —) $23.4 \cdot 10^{-5}$ *M* II. $\mu = 0.5$; $pH = 1.5 \pm 0.1$. Measurements against reagent blank.

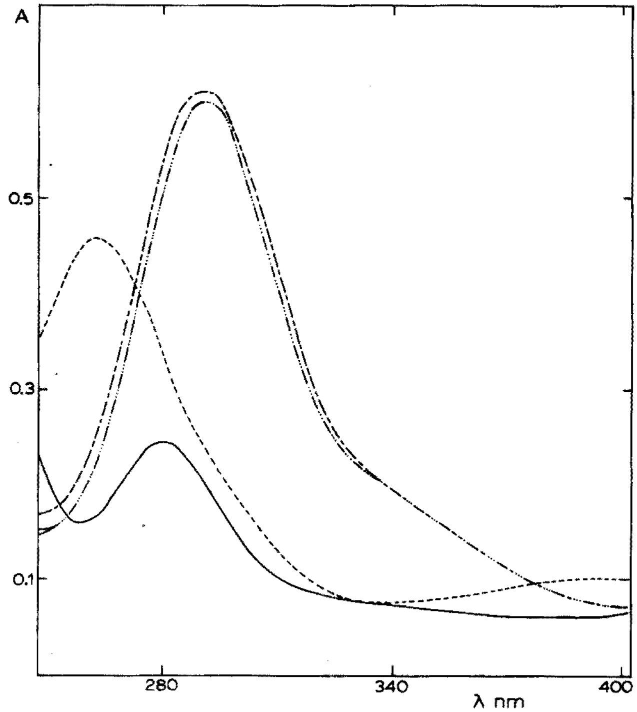

Fig. 3. Absorption spectra. In all cases, $3.0 \cdot 10^{-5}$ *M* $PdCl_2$ was present. A (——) No ligand; B (---) $3.0 \cdot 10^{-5}$ *M* III; C (— — —) $6.0 \cdot 10^{-5}$ *M* III; D (···) $9.0 \cdot 10^{-5}$ *M* III; E (— — — -) $1.2 \cdot 10^{-4}$ *M* III. $\mu = 0.5$; $pH = 1.5 \pm 0.1$. Measurements against reagent blank.

formed; the molar ratios were 1:1 and 2:1.

The $[PdCl_4]^{2-}_{(aq)}$ spectrum changes were studied for the same molar ratio variations as above. Figure 3 shows that when equimolar amounts of palladium(II) and reagent III were present, a well defined maximum appeared at 260 nm and the absorbance at 400 nm increased. For molar ratios greater than 1 (2, 3, 4), the maximum was shifted to 290 nm, and the absorbance values remained almost constant. To confirm these compositions, the Job and molar ratio methods were used. The Job method, as modified by Vosburgh and Cooper[18], was applied at different wavelengths (300, 270, 290, 288 nm); the compositions 1:1 and 2:1 (pH = 1.5 ± 0.1 and ionic strength = 0.5) were confirmed. Finally, the molar ratio method under the same conditions provided further evidence for the 1:1 and 2:1 compositions of the two complexes.

Reaction of palladium (II) with sodium ethylene-bis (thioglycolate) (IV)

Complex compositions 1:1 and 2:1 were found when $5.5 \cdot 10^{-4}$ *M* palladium solution ($5.0 \cdot 10^{-2}$ *M* in H^+) was conductimetrically titrated with $1.0 \cdot 10^{-2}$ *M* reagent IV (sodium salt).

Figure 4 shows the spectral changes for different molar ratios. With equimolar amounts of palladium(II) and reagent, two maxima, at 255 nm and 400 nm, appeared. With increasing ratio of ligand to metal, the 400-nm band was eliminated and the 255-nm maximum was shifted to higher wavelengths until it stabilized at 290 nm.

These compositions were confirmed by the Job method at 270 and 275 nm, and by the molar ratio method at 255, 270, 283 and 290 nm. In both, absorbances were measured at pH 1.5 ± 0.1 and ionic strength 0.5.

DISCUSSION

Many papers have been published on the behavior of these "sulfide acids" with some metallic ions[10-16, 19-25]. These papers have reported data on complex compositions and their constants; considerations on the chelating properties (acting as mono-, bi-, tri- and tetradentate, depending on pH); and some scattered considerations about "hard and soft" characteristics of ligands and interacting ions. But no comparative study with respect to analytical applications has as yet been made.

Although the ligands have a certain resemblance to the compounds studied by Schwarzenbach, the basic idea is quite different: whereas the "sulfide acids" have been studied in searches for selective reagents through "soft" donor-atoms, Schwarzenbach was looking for "universal" reagents.

It was considered that if aqueous solutions are to be used, any comparative study should be designed to obtain information that could be applied for spectrophotometric and titrimetric purposes. Although visual changes in the chemical systems gave only qualitative data (omitting verification of interactions in the u.v. region), selectivity seemed to be obtained only for mercury(II) and palladium(II) in the preliminary studies.

Although conductimetric measurements merely indicate complex formation and do not demonstrate chelating phenomena[17] the results obtained with reagent IV agreed with Podlaha's[11] assumptions on the tetradentate capacity of this ligand. On a similar basis, the anion of reagent III could be assumed to act as a tridentate ligand.

If $pK_1 = 3.17$ and $pK_2 = 3.89$ are taken for the ligand IV constants[11], calculation

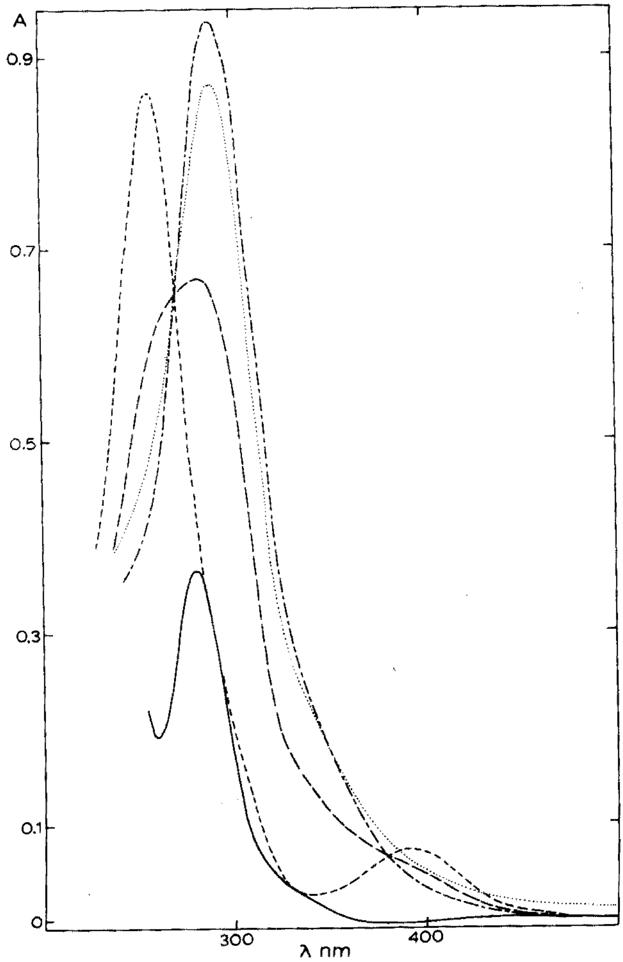

Fig. 4. Absorption spectra. In all cases, $5.8 \cdot 10^{-5}$ *M* $PdCl_2$ was present. A (——) No ligand; B (- - -) $5.8 \cdot 10^{-5}$ *M* IV; C (— — —) $11.6 \cdot 10^{-5}$ *M* IV; D (···) $17.4 \cdot 10^{-5}$ *M* IV; E (— — —) $23.4 \cdot 10^{-5}$ *M* IV. $\mu = 0.5$; pH = 1.5 ± 0.1. Measurements against reagent blank.

of α_0, α_1 and α_2 and plotting the relative amounts of the species at various pH, indicates that at pH 2, 93.5% of the ligand is present as H_2L and 0.6% as HL^-; at pH 3, 49.1% is present as H_2L, 40.2% as HL^- and 0.7% as L^{2-}. If it is assumed that during titrations in an acidic medium, the pH could vary within this range, the ligand species present in the higher percentage is always H_2L.

The trend of the stability constants of the 1 : 1 complexes of ligand IV with the metals of the first transition row, was consistent with the Irving–Williams series[20]; in an acidic medium, the less stable complexes, Co(II) and Ni(II), were not detectable through conductimetric measurements, but the strongest—copper(II)—was detectable. The complexes with Zn(II), Cd(II) and Pb(II), which are weaker than the Cu(II) complex[13] were detectable; undoubtedly more data should be obtained to try to explain these phenomena.

The new ligand III—β-ethylthioethylenethioglycolic acid—showed quite different behavior in acidic medium. Studies on the pK values and complex stability constants of this ligand are in progress. Another interesting fact that requires further investigation is that ligands III and IV behave similarly with regard to acidic solutions of Hg(II), Au(III) (typical "soft" acids), Pt(IV), Ir(IV), Rh(III) and Ru(III).

Diagrams for ethylthioglycolic acid (I) showed that HL is present to the extent of 99–91% within the pH range 2–3, therefore the interaction with palladium(II) should be through the sulfur atom. Livingstone *et al.*[26] obtained palladium(II) complexes with *o*-methylmercaptobenzoic acid ($PdCl_2 \cdot 2L$) in acidic medium, where the carboxylic group remained intact. But the conductimetric results with ligand I could be interpreted as involving formation of the binuclear complex $Pd_2Cl_4L_2$, although Ramberg and Tiberg[10] obtained with the same ligand a platinum(II) complex with the molar ratio 2:1.

In the pH range 2–3, thiodiglycolic acid (II), which has pK values roughly equal to those of ligand IV[23], would probably have a similar HL^-–H_2L distribution to ligand IV; on this basis, the conductimetric results indicate that the ligand behaves similarly to all thioethers with regard to palladium(II) complexes, *i.e.* the $PdCl_2 \cdot 2L$ complex is formed.

From the conductimetric data, ligands III and IV are probably bidentate with respect to Pd(II), forming five-membered rings through both sulfur atoms.

Wyatt[27] pointed out that in the pH range 1–3, the square planar palladium(II) monomer is surrounded by an average of 2.7 chloride ligands, so that probably the following equilibrium exists:

$$[PdCl_3H_2O]^- \rightleftharpoons [PdCl_2(H_2O)_2] \rightleftharpoons [PdCl_2H_2OOH]^-$$

Wyatt found that the absorption spectra in this pH range did not change, presenting one band at 23000 cm^{-1}, which was attributed to the $[PdCl_2(H_2O)_2]$ species.

All the four absorption spectra obtained in the present work for 1:1 molar ratios presented one band at 25000 cm^{-1}. Preliminary considerations indicate that this band probably should be attributed to a *d–d* transition, which would be allowed owing to the lower symmetry in the $PdCl_2$–III and $PdCl_2$–IV species. Such considerations agree with the opinions of Fabretti *et al.*[28] about *d–d* transitions in $[PdX_2L]$ complexes. This band at 25000 cm^{-1} disappears, when the ratio of ligand to palladium(II) increases, on reaching the species $[PdL_2]^{2+}$; this is probably due to the D_{2h} symmetry. Studies on the assignments for all the spectra obtained are in progress. The band around 35000 cm^{-1} probably should be considered as due to charge transfer.

From the results obtained, ligands III and IV show promise for determinations of palladium(II) by spectrophotometric or titrimetric methods. Copper(II), mercury(II) and silver(I) can probably also be determined with one of the studied ligands, and investigations on such methods are in progress.

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SUMMARY

Comparative studies on the behaviour of ethylthioglycolic(I), thiodiglycolic-(II), β-ethylthioethylenethioglycolic(III) and ethylene-bis(thioglycolic)(IV) acids towards metallic ions in aqueous solutions are described. Complexes are formed with Pd(II), Cu(II), Hg(II) and Ag(I) ("soft" Lewis acids). The stoichiometry of complex formation was studied by conductimetric titrations. Spectrophotometric data on the palladium(II) complexes with the four ligands are presented. Ligands III and IV offer promising analytical applications.

REFERENCES

1 Luiz R. M. Pitombo, *Anal. Chim. Acta*, 46 (1969) 158.
2 Luiz R. M. Pitombo, *Anal. Chim. Acta*, 62 (1972) 103.
3 Luiz R. M., Pitombo and Elisabeth Q. Cartaxo, *Talanta*, 21 (1974) 965.
4 F. Feigl, *Specific, Selective and Sensitive Reactions*, Academic Press, New York, 1949, p. 173.
5 E. E. Reid, *Organic Chemistry of Bivalent Sulfur, Vol. III*, Chemical Publishing Company, New York, 1960, p. 181.
6 I. M. Kolthoff and P. J. Elving, in A. Ringbom (Ed.), *Treatise on Analytical Chemistry, Vol. I, Pt. I*, Interscience, New York, 1959, p. 549.
7 E. Larsson, *Ber. Deut. Chem. Ges.*, 63 (1930) 1347.
8 J. M. Loven, *Ber. Deut. Chem. Ges.*, 17 (1884) 2818.
9 W. Steinkopf, J. Herold and J. Stohr, *Ber. Deut. Chem. Ges.*, 58 (1920) 1010.
10 L. Ramberg and A. Tiberg, *Ber. Deut. Chem. Ges.*, 47 (1914) 730.
11 J. Podlaha and J. Podlahová, *Inorg. Chim. Acta*, 5 (1971) 413.
12 G. Saini, G. Ostacoli, E. Campi and N. Cibrario, *Gazz. Chim. Ital.*, 91 (1961) 242.
13 K. Suzuki and K. Yamasaki, *J. Inorg. Nucl. Chem.*, 24 (1962) 1093.
14 L. J. J. Jansen and J. G. Hoogland, *J. Electroanal. Chem. Interfacial Electrochem.*, 37 (1972) 413.
15 J. Kotek, H. Klierová, J. Dolezal and M. Kopanica, *J. Electroanal. Chem. Interfacial Electrochem.*, 31 (1971) 451.
16 D. Veselinovic, L. Rajkovic and D. Suznejevic, *J. Electroanal. Chem. Interfacial Electrochem.*, 28 (1970) 375.
17 A. E. Martell and M. Calvin, *Chemistry of Metal Chelate Compounds*, Prentice-Hall, Englewood Cliff, N.J., 1952, p. 39.
18 W. C. Vosburgh and G. R. Cooper, *J. Amer. Chem. Soc.*, 63 (1941) 437.
19 A. Tiberg, Thesis, Lund, Sweden, 1924.
20 H. M. Irving and R. J. P. Williams, *Nature (London)*, 162 (1948) 764.
21 G. Saini and G. Ostacoli, *Atti. Accad. Sci. Torino*, 92 (1957–8) 483.
22 K. Suzuki and K. Yamasaki, *J. Inorg. Nucl. Chem.*, 28 (1966) 473.
23 J. Podlaha and J. Podlahová, *Inorg. Chim. Acta*, 4 (1970) 521, 549; 5 (1971) 413.
24 A. Sandell, Inaugural Dissertation, Division of Inorganic Chemistry, Chemical Center, University of Lund, Sweden, 1971.
25 M. Aplincourt, D. Noizet and R. Hugel, *Bull. Soc. Chim. Fr.*, (1972) 26.
26 S. E. Livingstone, R. A. Plowman and J. Sorensen, *J. Proc. Roy. Soc. N.S.W.*, LXXXIV (1951) 28.
27 I. R. Wyatt, *Chem. Weekbl.*, 62 (1966) 310.
28 A. C. Fabretti, G. C. Pellacani and G. Peyronel, *Gazz. Chim. Ital.*, 103 (1973) 397.

Analytica Chimica Acta, 75 (1975) 401–407

ANALYTICAL APPLICATIONS OF THIO, SELENO AND TELLUROETHERS

PART V. TITRIMETRIC DETERMINATION OF PALLADIUM WITH SODIUM ETHYLENE-BIS-(THIOGLYCOLATE)

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Many papers on titrimetric methods for various noble metals have been published; most of these are based on electrometric techniques, and the titrants are usually electrogenerated[1]. Beamish[1] has pointed out that the development of the more classical titrimetric techniques remains important, particularly for the analyst who must work with a minimum of equipment.

On the basis of results obtained in a previous paper[2], a new method for the determination of palladium has been developed based on visual and spectrophotometric titrations with disodium ethylene-bis(thioglycolate) ($NaOOC.CH_2.S.C_2H_4.S.CH_2.COONa$). The selectivity ideas outlined in previous papers[2–5] were followed, and again confirmed.

Preliminary studies

The initial step was a search for an indicator that would complex palladium in a strong acid medium, to form a stable coloured compound. The first attempt was made with xylenol orange, because a reasonable selectivity towards palladium in perchloric, sulphuric or nitric acids medium has been claimed[8]. Palladium solutions containing concentrated perchloric acid were warmed (±60°C) until a red colour appeared. However, no sharp end-points were observed, even when an auxiliary indicator was used, and no satisfactory reproducibility could be achieved.

Nitroso-R salt has also been reported[9a] as a reasonably selective reagent for colorimetric palladium determination. Recently, this reagent was used in acidic or alkaline medium[10], for palladium determinations. In the present work, a sharp change from red to greenish yellow was obtained when drops of Na_2EBTG solution were added to an acidic solution of the palladium–nitroso-R salt complex; good reproducibility was also obtained, within the limitations of these semi-quantitative experiments. Further tests showed that direct tiration of tetrachloropalladate with Na_2EBTG was possible when nitroso-R salt served as the indicator.

EXPERIMENTAL

Apparatus

A Beckman spectrophotometer model B and a specially designed 7.0-cm cell[6] were used for spectrophotometric titrations.

A calibrated 10.00-ml semimicro-burette was used for visual and spectrophotometric titrations.

Infrared spectra were taken in KBr disks or Nujol mulls on a Perkin-Elmer spectrophotometer model 333. Raman spectra were obtained from the solid substance (pastille), with a Jarrell-Ash spectrophotometer model 25.

Reagents

Standard palladium solution. Gravimetric standardization with dimethylglyoxime was used for the palladium chloride solution (0.1 *M* in hydrochloric acid), which contained 1.142 mg Pd ml^{-1}.

Solutions of diverse ions. Stock solutions containing 40 mg Pt(IV) ml^{-1} and platinum group metal solutions (25.0 mg Me ml^{-1}) were prepared from their chlorides in 0.1 *M* hydrochloric acid. The other cations were used as solutions of their nitrates containing *ca.* 25 mg ml^{-1} in 0.1 *M* nitric acid. For solutions of anions, sodium salts were prepared in the same concentrations.

Standard Na_2EBTG solution. Sodium ethylene-bis(thioglycolate)(Na_2EBTG) was obtained as previously reported[2]. Drying at 130°C for 24 h produced no change in mass, and the Karl Fisher method showed that no water of crystallization was present. After exposure for 14 h to 70% relative humidity, the sample did not increase in mass. The purity was determined by passing the sodium salt through a cation-exchange resin (Merck I) and titrating the free acid with standard sodium hydroxide solution. A purity above 99.7% was found. On the basis of these results Na_2EBTG was considered to be a primary standard. A suitable amount was weighed and the molarity was checked by the method used for testing the purity.

Nitroso-R Salt. An aqueous 0.02 *M* solution was prepared.

Isolation of palladium complex. Sodium ethylene-bis(thioglycolate) (5.59 g; 22 mmole) was dissolved in 240 ml of water; to this solution were added 15 ml of 70% perchloric acid and, with continuous stirring, 250 ml of hydrochloric acid solution containing 1.77 g of $PdCl_2$ (10 mmole). After 24 h, the yellow crystals formed were filtered off (yield 6.30 g, 90%; m.p. 177–183°C (decomp.).

Analytical results: calculated for $(HOOC.CH_2.S.C_2H_4.S.CH_2COOH)_2Pd(ClO_4)Cl.2H_2O$ (m.w. = 697.90), 20.65% C, 3.5% H, 18.4% S, 5.15% H_2O; found 20.4% C, 3.3% H, 18.1% S, 4.85% H_2O (Karl Fischer method).

The absorption spectra of the compound isolated and of that obtained in a previous investigation[2] were identical, showing a maximum at 290 nm.

Table I presents some selected i.r. and Raman bands.

TABLE I

SELECTED I.R. AND RAMAN BANDS (cm^{-1})

Compound	$\nu_{(C-S)}$	$\nu_{s(COO)}$	$\nu_{a(COO)}$	δ_{H_2O}	$(\nu_1, \nu_2, \nu_3, \nu_4) ClO_4$ *ionic*
$[(EBTGA)_2Pd]ClO_4Cl.2H_2O$	I.r. $637_{(m)}$	$1370_{(m)}$	$1700_{(s)}$	$1610_{(w)}$	$1080–1090_{(m)}$; $624_{(m)}$
	R $325_{(s)}$	$1430_{(m)}$			$933_{(s)}$; $458_{(m)}$; $1080–1090_{(m)}$; 62
EBTGA	I.r. $726_{(s)}$	$1390_{(m)}$	$1675_{(s)}$		
		$1430_{(m)}$	$1715_{(s)}$		
Na_2EBTG	I.r. $722_{(s)}$	1400	$1575_{(s)}$		
		1420	$1570_{(sh)}$		

Recommended procedure for visual titrations

To 10.00 ml of sample solution (which should be 0.1 *M* in hydrochloric acid) containing 5.70–31.0 mg of Pd(II), add 3.0 ml of 70% perchloric acid. After adding 10 drops of 0.02 *M* nitroso-R salt, stir and wait for 1 min until a clear red colour appears. Titrate slowly with $5 \cdot 10^{-2}$ *M* Na_2EBTG solution until the red colour changes to yellow-greenish.

In the presence of tungstate, enough solid citric acid should be added to clear any precipitate. If iridium(IV) is present, enough solid ascorbic acid should be added.

Recommended procedure for spectrophotometric titrations

Transfer 25.00 ml of the sample solution containing 2.50–10.05 mg of palladium (II) (which should be 0.1 *M* in hydrochloric acid) to a titration vessel. After adding 14.0 ml of 70% perchloric acid and 10 ml of water (final volume 60 ml), stir and adjust the wavelength[7] to 510 nm. With the sensitivity and slit knobs, adjust the transmittance value to 63%. With the addition of 10 drops of 0.02 *M* nitroso-R salt solution, the transmittance value drops, and after a few minutes remains constant. Titrate with 0.01 *M* Na_2EBTG solution adding 0.25-ml portions. The transmittance values increase and, after a certain volume has been added, become constant. During the titration the sensitivity should be suitably changed. If iridium (IV) is present, add 4.0 ml of an aqueous 1% solution of ascorbic acid and 17.0 ml of water. Establish the end-point by plotting transmittance *versus* volume.

RESULTS

Visual titrations

Effect of acidity. For the study of the effects of acidity and of the nitroso-R salt concentration, an arbitrary concentration of palladium, 10.0 mg ml^{-1}, was selected. Attempts to adapt the acidity used by Shamir and Schwartz[7]—pH *ca.* 2 with acetic or hydrochloric acid—failed, because of indistinct end-points. With increase of acidity (perchloric acid), the colour change became sharp; the best final acid concentration was found to be 2.5 *M*. Replacement of perchloric acid by sulphuric or nitric acid at the same concentration did not give a clear colour change, as some turbidity appeared when Na_2EBTG was added.

Effect of nitroso-R salt concentration. Titrations were run with 1–15 drops of aqueous 0.02 *M* nitroso-R salt solutions. The best results, with regard to clear and reproducible end-points, were obtained with 10 drops, when the titrant addition rate was 1 drop per 3 s. With more than 10 drops of indicator, sharp and reproducible end-points were obtained, provided that the titrant addition rate was decreased.

Effect of chloride concentration. Special attention was given to this effect because palladium is normally present as $[PdCl_4]^{2-}$ in aqueous solutions. Palladium chloride solutions containing *ca.* 5.0 mg of palladium per 10.00 ml and variable chloride concentrations at 2.5 *M* acidity were titrated. Chloride concentrations higher than $8.0 \cdot 10^{-2}$ *M* gave low results.

Optimal range of palladium. Samples containing 5.0–31 mg of palladium in a constant volume, at fixed acidity and with controlled chloride concentrations were analysed by the recommended procedure. The results are shown in Table II; the average recovery was 100·1% and the standard deviation was 0.31%.

TABLE II

VISUAL TITRATIONS OF PALLADIUM(II)

Pd(II) present (mg)	*Pd(II) found[a] (mg)*	*Recovery (%)*
5.71	5.72	100.2
9.98	10.02	100.4
18.71	18.72	100.2
30.93	30.85	99.8

[a] Average of 3 titrations.

Study of interferences. Besides platinum(IV), special attention was given to the so-called "associated metals" and some anions such as nitrate, sulphate, molybdate, tungstate and phosphate, as potential interfering ions.

Silver(I) and lead(II) are incompatible because the method starts from hydrochloric acid solution. Gold(III) interferes as was pointed out previously[2]. Separations of those ions has been already reported[9b,11] when they are present in platinum metal samples, and the main interest of the present paper is not to check out separation methods, but to determine palladium in the presence of diverse ions.

Ionic interferences such as bromide, iodide, azide, thiocyanate, oxalate,

TABLE III

DETERMINATION OF PALLADIUM IN THE PRESENCE OF DIVERSE IONS[a]

(9.98 mg Pd(II) was taken in all cases for visual titrations. 2.36 mg Pd(II) was taken for spectrophotometric titrations.)

Diverse ion	*Amount added (mg)*	*Visual method*		*Spectrophotometric method*	
		Pd(II) found[b] (mg)	*Recovery (%)*	*Pd(II) found[c] (mg)*	*Recovery (%)*
Pt(IV)	10	10.02	100.4	2.36[d]	100.0[d]
Ir(IV)	25	10.075	100.95	2.355	99.8
Co(II)	25	9.96	99.8	2.36	100.0
Cu(II)	25	10.02	100.4	2.36	100.0
Ni(II)	25	10.02	100.4	2.36	100.0
Cr(III)	25	—	—	2.315	98.1
Fe(III)	25	10.03	100.5	2.35	99.6
Hg(II)	25	9.965	99.85	2.36	100.0
SO_4^{2-}	25	10.02	100.4	2.36	100.0
NO_3^-	25	10.055	100.75	2.36	100.0
MoO_4^{2-}	25	10.04	100.6	2.35	99.6
WO_4^{2-}	25	10.04	100.6	2.35	99.6
HPO_4^{2-}	25	10.04	100.6	2.35	99.6
$HAsO_4^{2-}$	25	10.04	100.6	2.345	99.2

[a] Some determinations were run by different operators, to check the feasibility of the method.
[b] Average of 2 determinations; in no case did the difference between duplicates exceed 0.03 mg Pd.
[c] Average of 2 determinations; in no case did the difference between duplicates exceed 0.02 mg Pd.
[d] 23 mg of Pt(IV) was added.

sulphide, sulphite, thiosulphate and nitrite can easily be eliminated with aqua regia, which is used in the commonest procedures for dissolution of alloys and minerals.

In this study, limitations were caused by the colour intensities of some ions. For Rh(III), Ru(IV), Os(IV) and Cr(III), titrations were impossible, but the interference of Ir(IV) was avoided by reduction with ascorbic acid. In the case of Ni(II), Cu(II), Co(II) and Fe(III), the determination was feasible when the Pd:Me ratio was 1:25. It was possible to determine palladium(II) in the presence of platinum(IV) only when the ratio was below 1:1.

Table III gives the results for the determination of palladium in the presence of diverse ions.

Spectrophotometric titrations

In an attempt to increase the tolerance for diverse ions based on the opinions of Goddu and Hume[12] about the advantages offered by spectrophotometric titrations, experiments were run with varying palladium and titrant concentrations, but at the same acidity. These tests resulted in the development of the procedure given in the Experimental part.

TABLE IV

SPECTROPHOTOMETRIC TITRATIONS OF PALLADIUM(II)

Pd(II) present (mg)	*Pd(II) found*[a] *(mg)*	*Recovery (%)*
2.36	2.36 ± 0.0	100.0
5.30	5.31 ± 0.02	100.2
7.41	7.41 ± 0.01	100.0
10.05	10.05 ± 0.02	100.0

[a] Average of 3 titrations.

Table IV presents the results obtained by the recommended procedure. The average recovery obtained over the range 2.4–10 mg of palladium was 100%, and the standard deviation was 0.18%.

Table III gives the results for the spectrophotometric titration of palladium in the presence of diverse ions.

DISCUSSION

Although many titrimetric methods for the determination of palladium have been reported, Beamish[9c] has pointed out the scarcity of acceptable methods. Many are based on turbidimetric and heterometric titrations[13,14] precision data being ignored; in these methods, rigorous control of experimental details is essential, and the results are extremely dependent on the skill of the operator.

Two methods based on EDTA back-titrations are satisfactory with regard to precision data[15,16], but both are greatly limited by interferences. Titrations with iodide are available[17–20], as are direct titrations with diethyldithiocarbamate[21] or nitroso-R salt[10] solutions, but these procedures are very tedious.

The proposed visual and spectrophotometric titrations are quite easily done, and their tolerance for "associated ions" (mainly Pt(IV)) is good. The reproducibility is comparable to that of EDTA methods and the concentration range of *ca.* 40–160 μg Pd(II) ml^{-1} is fairly suitable[9d].

Classical reasoning for the choice of indicator was impossible because the constants for the palladium(II) complexes with the indicator and EBTG ligand are unknown. However, the choice was not completely empirical. The structural formula for the [nitroso-R salt–Pd(II)] complex has not been elucidated, but the molar ratio is known. Palladium(II) should be bound by the $\mathrm{O{\leftarrow}\underset{|}{N}{-}OH}$ and $>$C=O groups ("hard" groups). Na_2EBTG in a strongly acidic medium will have the carboxylic acid groups blocked, and should therefore act as a bidentate ligand forming a strong 5-membered ring with the two sulphur atoms ("soft" groups). In several tests, in which the Pd(nitroso-R $salt)_2$ was taken as a parameter, it was verified that under the same acid conditions, ethylthioglycolic acid and thiodiglycolic acid (one sulphur atom) did not decolorize the red complex, whereas β-ethylthioethylenethioglycolic acid and ethylene-bis(thioglycolic) acid did. The hypothesis, that complexes containing a ring with two sulphur atoms should be stronger than the others, was thus partially proved. Determinations of the formal constants for palladium(II) and the four mentioned ligand systems are in progress.

The absorption spectrum of the isolated complex demonstrated that the molar ratio L:Me is 2:1. From the i.r. and Raman spectra (Table I), one may conclude that the observed four fundamental perchlorate bands, with tetrahedral symmetry, agree with earlier results[22] on the ionic nature of that ion. Moreover, the fact that all frequencies are active in Raman spectroscopy and only the ν_3 and ν_4 frequencies in i.r. spectroscopy confirms the interpretation. The C–S, symmetric and asymmetric COO stretching frequencies in Na_2EBTG and in the acid agree with earlier results[23]. The palladium–sulphur coordination in the isolated complex was evidenced by the fact that the C–S stretching frequency is shifted to lower wavenumbers, compared with the free acid and its sodium salt[23]. Another fact that seems to confirm this assumption is the intense band at 325 cm^{-1} in the Raman spectrum. In ($PdCl_2.2R.S.C_2H_4.S.R$) complexes[24,25], the Pd–S stretching frequency was also observed in the range 310–340 cm^{-1}. A comparison of the ν_s and ν_a COO frequencies obtained for the isolated complex, Na_2EBTG and the free acid indicates that the carboxylic groups are intact in the palladium complex. Another point in favour of this, is the intense and wide absorption in the range 2300–3600 cm^{-1} with various maxima. This is characteristic for the COOH group involved in hydrogen bond association[26].

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SUMMARY

Palladium solutions can be titrated visually and spectrophotometrically with *sodium ethylene-bis(thioglycolate). Titrations were done in 2.5 M perchloric acid with nitroso-R salt as indicator. Palladium was determined in the range 5.0–30 mg*

(visual titration) and 2.0–10 mg (spectrophotometric titration); the tolerance for diverse ions is good, particularly with the spectrophotometric end-point. The probable structure of the isolated complex is given.

REFERENCES

1 F. E. Beamish, *Talanta*, 13 (1966) 1053.
2 L. R. M. Pitombo and G. Oliveira Neto, *Anal. Chim. Acta*, 75 (1975) 391.
3 L. R. M. Pitombo, *Anal. Chim. Acta*, 46 (1969) 158.
4 L. R. M. Pitombo, *Anal. Chim. Acta*, 62 (1972) 103.
5 L. R. M. Pitombo and E. Q. Cartaxo, *Talanta*, 21 (1974) 965.
6 P. B. Sweetser and G. E. Bricker, *Anal. Chem.*, 25 (1953) 253.
7 J. Shamir and A. Shwartz, *Talanta*, 8 (1961) 330.
8 M. Otomo, *Bull. Chem. Soc. Jap.*, 36 (1963) 889.
9 F. E. Beamish, *The Analytical Chemistry of the Noble Metals*, Pergamon, Oxford, 1966, (a) p. 441; (b) pp. 68, 109, 130; (c) pp. 324, 334; (d) p. 341.
10 O. W. Rollins and M. M. Oldham, *Anal. Chem.*, 43 (1971) 262.
11 F. E. Beamish, *Talanta*, 14 (1971) 991.
12 R. F. Goddu and D. N. Hume, *Anal. Chem.*, 26 (1954) 1740.
13 M. Bobtelsky and B. Mayer, *Anal. Chim. Acta*, 15 (1956) 164.
14 M. Bobtelsky and J. Ersenstadter, *Anal. Chim. Acta*, 16 (1957) 479.
15 W. N. MacNevin and H. O. Kriege, *Anal. Chem.*, 27 (1955) 535.
16 T. A. Kiss, F. F. Gaol and T. M. Suranyc, *Glas. Hem. Drus. Beograd*, 34 (1969) 423; *Chem. Abst.*, 74 (1971) 9323.
17 R. Kersting, *Ann. Chem. Pharm.*, 87 (1953) 25.
18 R. H. Atkinson, *Analyst (London)*, 79 (1954) 368.
19 R. H. Atkinson, R. N. Rhoda and R. G. Lomell, *Analyst (London)*, 80 (1955) 838.
20 R. H. Atkinson and R. N. Rhoda, *Anal. Chem.*, 28 (1956) 535.
21 W. B. Pollard, *Analyst (London)*, 67 (1942) 184.
22 B. J. Hathaway and A. E. Underhill, *J. Chem. Soc., London*, (1961) 3091.
23 J. Podlaha and J. Podlahová, *Inorg. Chim. Acta*, 5 (1971) 413.
24 G. E. Coates and C. Parkin, *J. Chem. Soc., London*, (1963) 421.
25 J. Pluščec and A. D. Westland, *J. Chem. Soc., London*, (1965) 5371.
26 L. J. Bellamy, *Advances in Infrared Group Frequency*, Methuen, London, 1968, p. 270.

Analytica Chimica Acta, 75 (1975) 409–420

SIMULTANEOUS DETERMINATION OF CADMIUM, COPPER, LEAD AND ZINC IN LEAD AND ZINC CONCENTRATES BY A.C. POLAROGRAPHIC METHODS

COMPARISON WITH ATOMIC ABSORPTION SPECTROMETRY

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Atomic absorption spectrometry (a.a.s.) enjoys considerable popularity in geochemical analysis because of the ease and convenience with which it can be applied to a large number of samples[1–4]. In many cases, several elements can be determined sequentially from a solution derived directly from a single fusion and completely without separation procedures. Polarographic methods, whilst being applicable in principle to most of the Periodic Table[3–5], have not been extensively used for routine geochemical analysis because of their lack of selectivity. Where polarographic methods have been used[3], extensive separation procedures have generally been included in the overall analysis scheme, and polarography predominantly has had only restricted or specialized use rather than general routine use for direct determinations of a number of elements in complex mixtures of the kind commonly encountered in geochemical analysis.

Whilst there is no doubt that d.c. polarography is rarely likely to be competitive with a.a.s. in routine analysis, modern polarographic techniques[6] such as pulse, a.c. and linear-sweep polarography offer considerable improvement in resolution, speed of analysis, sensitivity and ease of automation. Indeed, it has been pointed out that such methods meet many of the requirements for at least simple element determinations in extremely complex mixtures[7–10]. However, there is a general paucity of real analytical data to evaluate the actual capabilities of modern polarographic methods for multi-element determination under practical operating conditions. For example, little is known about the possible need for matrix corrections of the kind generally needed with other instrumental methods of analysis when applied to complex mixtures of widely varying composition.

In the present paper, the direct simultaneous determination of cadmium, copper, lead and zinc in lead and zinc concentrates by a variety of a.c. polarographic methods is reported: the lead and zinc concentrates are subjected to only a simple dissolution, and the determination of the four elements is carried out directly and simultaneously. These samples provide instrumentally difficult conditions covering the range of major to minor trace analysis for both zinc and lead, the determination of trace zinc in the presence of a large excess of the more positively reduced lead[11] and considerable matrix variation for the determination of each of the four elements.

Most of the work was undertaken on an inexpensive commercially available instrument by conventional a.c. polarography. The use of more sophisticated a.c. methods, such as phase-selective second harmonic a.c. polarography and linear-sweep a.c. polarography are briefly described in order to show further advantages which can be obtained with more expensive and complex instrumentation. The a.c. polarograph used for most of the work is considered to be a conservatively designed instrument by modern standards as would the instrumentation used for a.a.s. Hence, in both polarography and a.a.s., no endeavour was made to use ultra-modern instrumentation and techniques in the initial investigations, and a generally conservative comparative basis has been adopted.

EXPERIMENTAL

Chemicals

All chemicals used were of reagent-grade purity.

Polarography

Dissolution techniques. Approximately 0.50 g of powdered sample was accurately weighed and placed in a polythene beaker. To each sample, 10 ml of 48% hydrofluoric acid and 5 ml of concentrated nitric acid were added and the solution was evaporated to dryness[12]. The residue remaining after evaporation was dissolved in 2 *M* hydrochloric acid and in most instances was quantitatively transferred to a 100-ml standard flask with 2 *M* hydrochloric acid for washing purposes. For samples containing very high concentrations of lead and zinc, 100 ml of 2 *M* hydrochloric acid was insufficient to dissolve these elements as their chlorides, and either larger volumes (250-, 500- or 1000-ml standard flasks) were used, or the dissolution procedure was repeated with a smaller sample weight down to 0.10 g.

Standards. Metallic Cu, Pb, Zn, and Cd were dissolved in 10 ml of (1:5) nitric acid and the solution was evaporated to dryness. A standard solution containing $2.0 \cdot 10^{-3}$ *M* of each of the elements was then prepared. From this stock solution standards containing all four elements covering the range 10^{-5}–$2.0 \cdot 10^{-3}$ *M* in 2 *M* hydrochloric acid were prepared.

Instrumentation. Conventional a.c. polarographic curves were recorded with a Metrohm System combining Polarocord E 261, AC Modulator E 393 and IR Compensator E 446. The simple conversion to a three-electrode system has been described elsewhere[13]. Controlled drop-times of 0.20 s were obtained with a Metrohm Polarographie Stand E 354. A frequency of 50 Hz at 10 mV, r.m.s., was used with this instrumentation.

Phase-selective fundamental and second-harmonic a.c. voltammograms were obtained, by synchronizing the drop-time and scan rate circuitry with Linear Sweep Accessory Model 174/51 and by using a PAR (Princeton Applied Research Corporation, Princeton, N.J.) Electrochemistry System Model 170. Modifications to obtain the second-harmonic and a.c. linear-sweep variations have been described[14,15]. Phase-selective a.c. polarography was also achieved with this instrumentation. The reference electrode was Ag/AgCl (1 *M* NaCl) and the auxiliary electrode platinum foil. No thermostating was used and results were obtained usually at the ambient temperature of (22±0.5)°C. All solutions run on the Metrohm Instrumentation (low frequency) were degassed with argon. With high-frequency a.c. work on the PAR Instrumentation, removal of oxygen was not required (see later).

Atomic absorption spectrometry

The determinations of copper and cadmium were done with a Techtron AA4 Atomic Absorption Spectrophotometer and a nitrous oxide–acetylene flame; the same solutions and standards as prepared for polarography were used. The 324.7-nm and 228.8-nm lines were used respectively for copper and cadmium.

The zinc and lead atomic absorption determinations were performed by the Zinc Corporation Ltd. Dissolution was achieved by the general acetate method. The sample (1 g) was weighed into a 250-ml beaker and 20 ml of concentrated hydrochloric acid were added. The sample was simmered for 20 min; about 7 ml of concentrated nitric acid was then added and the solution was gently allowed to evaporate to dryness. If much manganese was present, a further evaporation with 10 ml of concentrated hydrochloric acid was carried out. Finally 5 ml of (1:1) hydrochloric acid was added to complete the dissolution and 95 ml of acetate solution (1 vol. 0.880 ammonia:1 vol. water:1 vol. glacial acetic acid) was added to bring the total volume to 100 ml. For lead, the 283.4-nm, 261.3-nm and 364.0-nm lines were used with an air–acetylene flame. For zinc, the 213.8 nm and 307.6 nm lines were used, again with an air–acetylene flame. The actual line used for the determination depended on the concentration. The a.a.s. method is generally reported to have ±4% relative error.

One of the samples (ZPS 526) was analysed for zinc by a combined alkaline hexacyanoferrate(II)–a.a.s. method. Samples containing high lead concentration were also determined by titration with EDTA. Both these determinations were performed by the Zinc Corporation and are reported to have relative errors of less than ±1%.

x-Ray fluorescence. Samples on which copper and cadmium were determined were qualitatively examined by x-ray fluorescence spectrometry. Pressed discs were made from 0.50 g of sample and the examinations were carried out on a Siemens Sequential x-Ray Spectrometer SRS1.

RESULTS AND DISCUSSION

In 2 *M* hydrochloric acid, copper, cadmium and lead are reversibly reduced and give rise to extremely well defined a.c. and d.c. polarographic waves. However, zinc gives rise to a quasireversible electrode process. Under d.c. polarographic conditions, the zinc electrode process is masked by the hydrogen ion reduction, but the wave is well defined under a.c. conditions[16] because a.c. polarography discriminates considerably against the irreversibly reduced hydrogen ion reduction[17,18]. The shape of the a.c. wave for zinc is asymmetric and very dependent on drop-time. The electrode processes and their a.c. peak potentials, E_p, are as follows:

$\mathrm{Cu(I)} \overset{e}{\rightleftarrows} \mathrm{Cu}$ (amalgam), $E_p = -0.314$ V *vs.* Ag/AgCl;

$\mathrm{Pb(II)} \overset{2e}{\rightleftarrows} \mathrm{Pb}$ (amalgam), $E_p = -0.514$ V *vs.* Ag/AgCl;

$\mathrm{Cd(II)} \overset{2e}{\rightleftarrows} \mathrm{Cd}$ (amalgam), $E_p = -0.728$ V *vs.* Ag/AgCl;

$\mathrm{Zn(II)} \overset{2e}{\rightleftarrows} \mathrm{Zn}$ (amalgam), $E_p = -1.05$ V *vs.* Ag/AgCl.

The d.c. half-wave potentials are very similar to the E_p values.

Typical a.c. polarograms of a standard solution and of one of the samples used in this work are shown respectively in Figs. 1 and 2. Figure 3 shows calibration curves for all the four elements. Completely linear plots were obtained over the entire concentration range examined. For Cu, Pb and Cd, the short controlled drop-times of 0.20s—so-called rapid a.c. polarography—permitted the use of fast scan rates and short analysis time. However, because of the quasi-reversible nature of the zinc(II) electrode process, the sensitivity decreases markedly at very short drop-times. Figure 3 shows that calibration curves for zinc with rapid drop-times give far lower current per unit concentration than the other elements. Further, the shape of the curve and certain other aspects of the zinc electrode process make the conventional natural drop time method the generally preferred method for determining zinc[19]. Thus, the initial potential was set at around −0.10 V *vs.* Ag/AgCl and scanned rapidly (1 V min^{-1}) until a potential of −0.95 V *vs.* Ag/AgCl was reached. At this time the mechanical control of the drop time was removed and slow scan rates (1 V/6 min) were used, with the natural drop-time of about 3 s for recording the zinc wave.

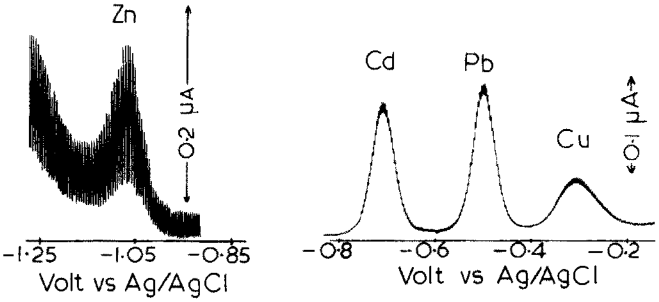

Fig. 1. A.c. polarogram of $2 \cdot 10^{-4}$ *M* Cd, Cu, Pb and Zn in 2 *M* hydrochloric acid. Cd, Pb and Cu recorded under rapid polarographic conditions; Zn with natural drop-time. Total alternating current recorded. Amplitude = 10 mV, r.m.s. at 50 Hz.

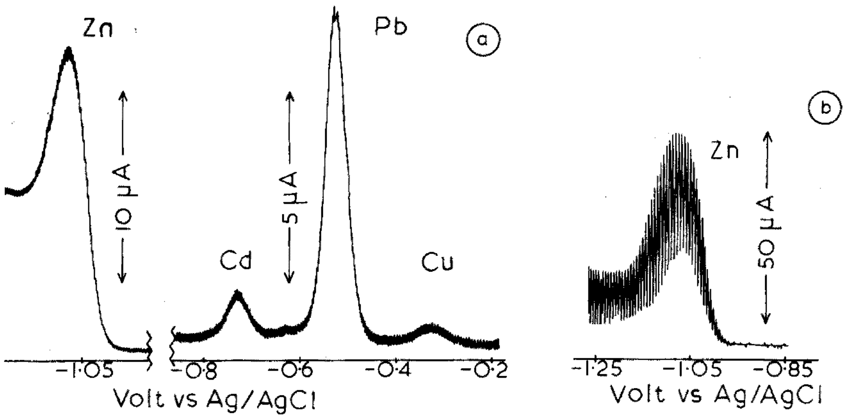

Fig. 2. A.c. polarogram of Sample EL 424. Same instrumental conditions as Fig. 1 except for Zn which is shown with both rapid (2a) and natural (2b) drop-times.

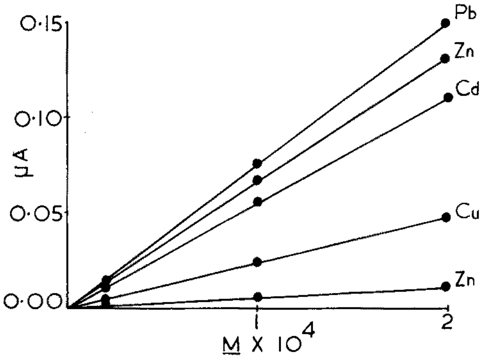

Fig. 3. Calibration curves for Cd, Cu, Pb and Zn in 2 *M* hydrochloric acid. Rapid drop-time of 0.20 s used except for upper zinc curve which refers to natural drop-times. Same instrumental conditions as in Fig. 1.

Results of the polarographic determinations are presented in Table I, along with those obtained by a.a.s. For zinc concentrates, the lower sensitivity does not preclude the use of the rapid method and for these samples all four elements can be determined from the one rapid polarogram. From the Table, it can be seen that generally good agreement is obtained between the two techniques. This suggests that matrix correction problems are not particularly significant in a.c. polarography at least when a high concentration of supporting electrolyte such as 2 *M* hydrochloric acid is used, and that a.c. polarography does have the required selectivity and sensitivity for multielement analysis in samples of considerably variable composition. A comparison with a.a.s. in several important areas is given below.

Calibration curves

Provided that a three-electrode system was used, linear calibration curves were always obtained in a.c. polarography. This was not the case with atomic absorption where curvature was usually noted at the higher concentration levels. Furthermore, once a calibration curve has been obtained by a.c. polarography it can be used for lengthy periods of time, provided that the capillary and mercury column height are not altered. Calibration curves have to be frequently checked in a.a.s.

Speed and ease of obtaining data

Polarography enables all four elements to be determined simultaneously from one experiment, *i.e.* one polarographic curve. The atomic absorption method requires sequential experiments involving change of lamps for each element and even the use of different lines depending on the concentration ranges of the element being determined. A.c. polarographic data are obtained from measurement of a peak height, whereas atomic absorption uses direct readout of absorption. Whilst the a.c. polarographic measurements did not present any difficulties on the samples examined, generally the readout in a.a.s. by its very nature is simpler and is not expected to create any of the difficulties potentially present in a.c. polarography. Whilst the time taken in a.c. polarography for individual element determination is undoubtedly longer than in atomic absorption, the possibility of simultaneous, rather than sequential, multi-

TABLE I

DETERMINATION OF Cd, Cu, Pb AND Zn IN LEAD AND ZINC CONCENTRATES BY A.C. POLAROGRAPHY AND ATOMIC ABSORPTION SPECTROMETRY

Sample no.[a]	% Pb			% Zn		% Cu		% Cd	
	A.c.p.[b]	A.a.s.[c]	EDTA[c]	A.c.p.[b]	A.a.s.[c]	A.c.p.[b]	A.a.s.[b]	A.c.p.[b]	A.a.s.[b]
EL 410	33.3	33.6	34.6	18.1	19.6				
EL 411	10.5	10.8	10.8	24.2	24.6				
EL 412	0.39	0.46		52.0	50.8				
EL 413	1.60	1.60		12.7	12.0				
EL 414	0.23	0.17		0.14	0.18				
EL 415	70.2	67.6	69.6	5.07	4.8				
EL 417	0.38	0.32		53.6	54.5				
EL 418	1.05	1.16		41.6	42.2	0.12	0.11	0.09	0.10
EL 420	0.24	0.27		0.52	0.6				
EL 421	52.0	50.0	51.3	7.77	8.0				
EL 422	60.3	60.2	61.0	6.36	6.5				
EL 424	1.84	1.76		35.2	35.2	0.13	0.13	0.14	0.14
EL 426	0.54	0.45		1.68	1.76				
EL 431	2.34	3.04		6.15	4.7	0.22	0.25	0.04	0.04
EL 432	0.47	0.57		0.51	0.49				
EL 437	6.84	6.5		33.2	32.8	0.12	0.15	0.08	0.10
EL 442	6.59	7.7		39.0	41.0				
NPS 440	0.35	0.35		0.81	1.11				
NPS 448	0.52	0.59		13.3	14.0	0.08	0.06	0.05	0.05
ZPS 521	72.6	—	74.9	3.06	3.55				
ZPS 526	0.84	1.00		52.0	52.26[d]				

[a] Samples provided by the Zinc Corporation.
[b] Results obtained in these laboratories.
[c] Results obtained by the Zinc Corporation.
[d] Determined by the hexacyanoferrate–a.a.s. method.

element determinations means that in the present experiments the a.c. polarographic method taken overall is faster.

Checks on interference

In a.c. polarography, interference is usually easily recognized by a change in wave shape or peak potential compared with standards. Peak potentials were never found to vary more than ±15 mV from the standards. The wave shape is readily characterized by measuring the width at half the peak height. For reversible electrode processes, such as for lead, cadmium and copper, the half-width is close to the theoretical value of $(90/n)$ mV (where n is the number of electrons involved in the charge-transfer step, *i.e.* $n=1$ for Cu and $n=2$ for Cd and Pb). For the quasi-reversible zinc ($n=2$) electrode process, the half-width depends on drop-time, but is around 85 mV at normal drop-times. Importantly, half-widths should not differ from standards by more than ±2 mV, otherwise interference can be suspected. In a.a.s., direct checks on interference are not so easily undertaken, particularly when absorbance or transmission data are the only parameters read in each experiment.

Interference in a.c. polarography, when it occurs, is therefore much more likely to be detected than in a.a.s. The possibility of having another element giving a wave overlapping with Cu, Cd, Pb and Zn is of course much higher in a.c. polarography than the equivalent kind of spectral interference in atomic absorption.

Reproducibility

Reproducibility in a.c. polarography was found to be better than 1% and almost independent of the concentration and element being determined. In a.a.s., the reproducibility was very much dependent on the concentration, the line being used, and the element. An average reproducibility of about 2% was found in this technique. However, variations arising from sampling, dissolution and other sources were greater than the reproducibility of measurement, and, based on triplicate determination, an overall reproducibility of approximately 3% was found in both methods.

Sensitivity

Comparison of sensitivity between two techniques always presents a difficult task because so many factors need to be taken into account.

The limit of detection with a.a.s. was found to be better than that of the a.c. polarographic method described above. For all elements, *ca.* 10^{-5} M was found to be the lower usable limit in a.c. polarography. However, the use of other polarographic techniques, described below, increases this limit by one or two orders of magnitude into the 10^{-6}–10^{-7} M range; this compares favourably with a.a.s.

For a really detailed comparison of the relative sensitivity of the two techniques, other variables need to be taken into account such as cost of instrumentation and degree of operator skill required to attain the sensitivity reported in each technique. However, in summary, the present findings are that for the four elements under consideration, a.a.s. is more sensitive than fundamental-harmonic total current a.c. polarography; but in making comparisons within pulse polarography, second-harmonic a.c. polarography and phase-selective fundamental-harmonic a.c. polarography there is little to choose. For the more sophisticated techniques, the limits of detection specified by Florence for pulse polarography and compared to a.a.s.[20] were qualitatively confirmed in the present work. Other areas where comparisons may be made between the two techniques have been considered by Rooney[21].

Figures 4(a) and (b) show high-frequency phase-selective polarographic waves of copper, cadmium and lead. This method avoids the need for the elimination of oxygen[9,17]. However, because the zinc electrode process is quasi-reversible, the sensitivity for this element decreases even further at high frequencies and best results are obtained for copper, cadmium and lead. The short controlled drop-time method is readily used in conjunction with this technique. Figure 4(c) shows that current-sampled a.c. techniques improved the readout considerably.

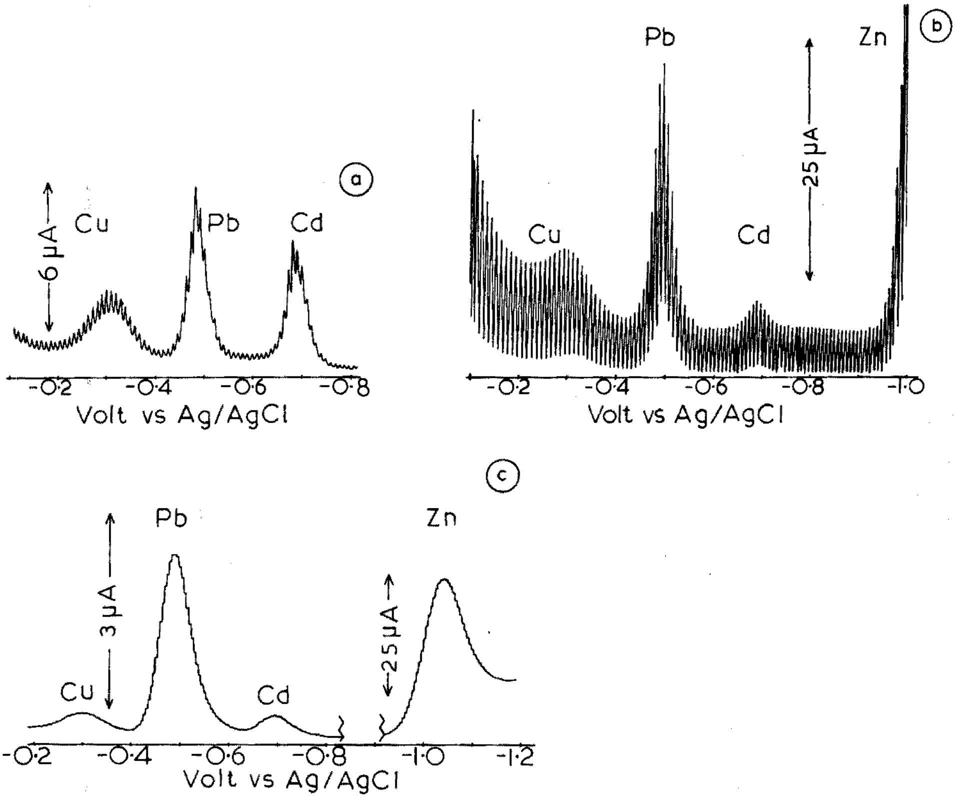

Fig. 4. (a) Rapid high-frequency phase-selective a.c. polarogram of $2 \cdot 10^{-4}$ *M* Cu, Cd and Pb in 2 *M* hydrochloric acid. Amplitude = 10 mV, p–p, at 500 Hz. No removal of oxygen required. (b) Sample NPS 448. Natural drop-time phase-selective a.c. polarogram. Same instrumental conditions as Fig. 4(a). (c) Sample EL 424. Controlled drop-time (0.5 s), current-sampled phase-selective a.c. polarogram. Amplitude = 10 mV, p–p, at 400 Hz.

Figure 5(a) shows a second-harmonic polarographic curve of a standard solution and Fig. 5(b) that for a sample. The elimination of oxygen is again unnecessary and a considerably lower limit of detection of around 10^{-7} *M* is obtained for each element, except for zinc where *ca.* $5 \cdot 10^{-6}$ *M* is the lower limit. Because of the smaller current associated with the second-harmonic method, particularly at short

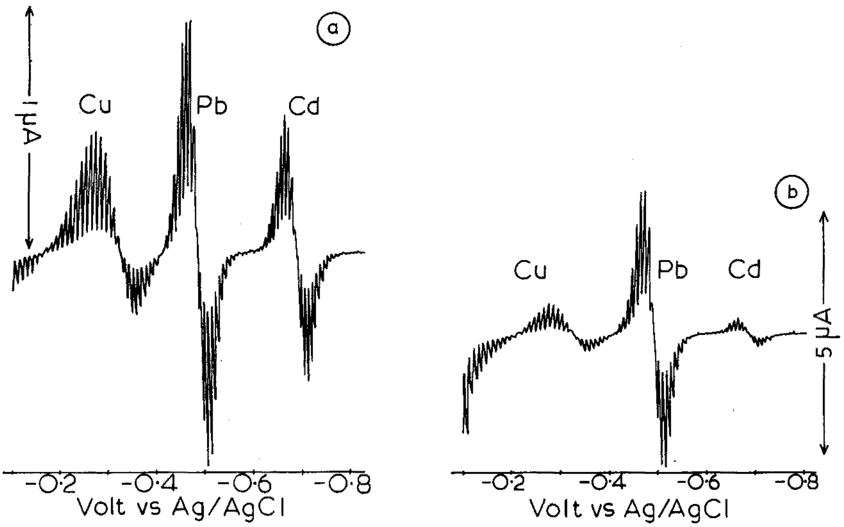

Fig. 5. (a) Second-harmonic phase-selective a.c. polarogram of $2 \cdot 10^{-4}$ *M* Cd, Cu and Pb in 2 *M* hydrochloric acid. Amplitude = 10 mV, p–p, at 500 Hz. (b) Sample NPS 448. Same instrumental conditions as Fig. 5(a).

drop-times, natural drop-times were required for the determination of extremely low concentrations by this technique.

Phase-selective fundamental- and second-harmonic linear sweep a.c. voltammograms for the simultaneous determination of the four elements were also recorded (Fig. 6). These were obtained by synchronizing the sweep rate with the dropping mercury electrode[15,22,23]. Smooth, easily read curves were obtained which were ideal for analytical work. Fast scan rates and therefore, very short analysis time, the unnecessary elimination of oxygen and the high sensitivity make this method very competitive with a.a.s. in every respect. All four elements can be determined simultaneously by this method and the recording of a voltammogram takes less than 20 s.

Finally, Fig. 7 shows a differential pulse polarogram. Because of the inability of pulse polarography to discriminate against the irreversible reduction of hydrogen ion, to the same extent as in the a.c. experiments, the zinc ion wave is masked in 2 *M* hydrochloric acid. However, for the determination of copper, cadmium and lead, pulse polarography is most suitable. It should be noted that with this method, oxygen needs to be eliminated from the solution and slower scan rates must be used than can be used in rapid or linear-sweep a.c. techniques.

Conclusions

For the simultaneous determination of Cu, Cd, Pb and Zn, in lead and zinc concentrates, a.c. polarographic methods are shown to be highly competitive with a.a.s. Linear calibration curves over wide concentration ranges allow these elements to be determined when present as either major or minor constituents. Ready checks on interference are also available and the four elements can be determined rapidly from the one polarographic curve.

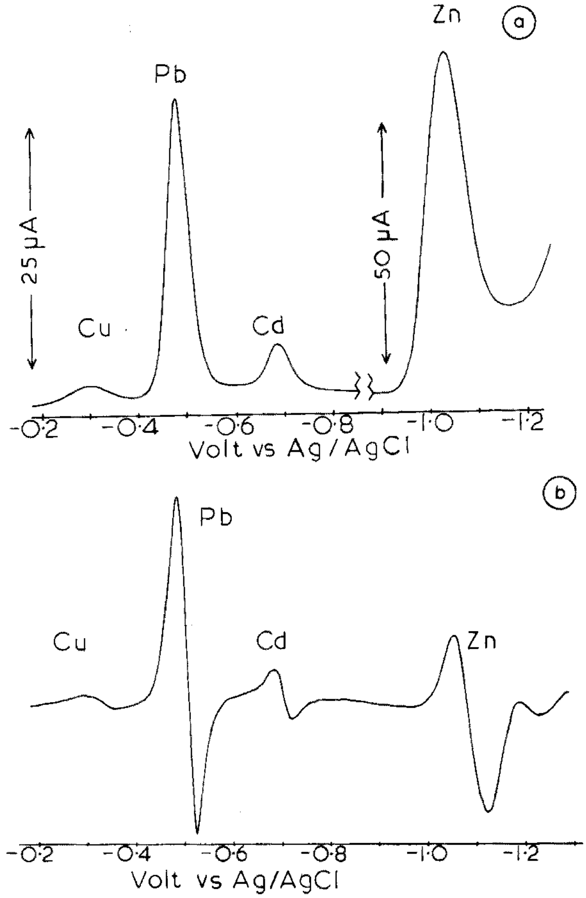

Fig. 6. (a) Phase-selective fundamental-harmonic linear-sweep a.c. voltammogram of sample EL 424. Amplitude = 10 mV, p–p, at 400 Hz. Sweep rate of 100 mV s^{-1} commenced 1 s after drop begins to grow. (b) Phase-selective second-harmonic linear-sweep a.c. voltammogram of sample EL 424. Same instrumental conditions as Fig. 6(a).

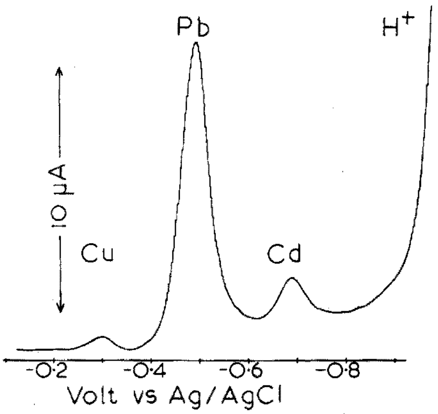

Fig. 7. Differential pulse polarogram of sample EL 424. Amplitude = 25 mV, drop-time = 1 s.

The authors gratefully acknowledge the assistance of the Zinc Corporation Limited in providing the samples used and for permission to publish the data. Collaboration with the Geology Department of this University at various stages of this work was also invaluable, and we have much pleasure in acknowledging their contribution.

SUMMARY

The simultaneous determination of Cd, Cu, Pb and Zn in lead and zinc concentrates by fundamental, second-harmonic and linear-sweep a.c. and pulse polarographic methods is described. Calibration curves are linear over wide concentration ranges, so that both major and minor trace constituents can be determined in the same experiment; thus the polarographic method is highly competitive with atomic absorption spectrometry (a.a.s.). Conventional a.c. polarography and a.a.s. were compared in the first instance with conservative instrumentation. More sophisticated polarographic methods were then utilized; with the phase-selective linear sweep a.c. (fundamental- and second-harmonic) methods the four elements were determined simultaneously from voltammograms obtained in less than 20 s down to the 10^{-6}–10^{-7} M concentration range.

REFERENCES

1 J. Ramirez-Munoz, *Atomic-Absorption Spectroscopy*, Elsevier, Amsterdam, 1968.
2 E. E. Angino and G. K. Billings, *Atomic Absorption Spectrometry in Geology*, Elsevier, Amsterdam, 1967.
3 M. Pinta, *Detection and Determination of Trace Elements*, (English Translation, Israel Program for Scientific Translations, Jerusalem, 1966) Dunod, Paris, 1962.
4 G. H. Morrison (Ed.), *Trace Analysis, Physical Methods*, Interscience, New York, 1965.
5 I. M. Kolthoff and J. J. Lingane, *Polarography*, Interscience, New York, 2nd edn., 1952.
6 H. Schmidt and M. von Stackelberg, *Modern Polarographic Methods*, Academic Press, New York, 1963.
7 E. J. Maienthal, *Anal. Chem.*, 45 (1973) 644.
8 E. J. Maienthal, *Amer. Lab.*, June 1973, pp. 25–33.
9 A. M. Bond, *Anal. Chem.*, 45 (1973) 2026.
10 A. M. Bond, V. Biskupski and D. A. Wark, *Anal. Chem.*, 46 (1974) 1551.
11 A. M. Bond and J. H. Canterford, *Anal. Chem.*, 43 (1971) 1658.
12 F. J. Langmyhr and P. E. Paus, *Anal. Chim. Acta*, 43 (1968) 397.
13 A. M. Bond and J. R. Thackeray, *Chem. Instrumen.*, 4 (1972) 299.
14 H. Blutstein, A. M. Bond and A. Norris, *Anal. Chem.*, 46 (1974) 1754.
15 H. Blutstein and A. M. Bond, *Anal. Chem.*, 46 (1974) 1934.
16 T. Ishii and S. Musha, *Bunseki Kagaku*, 19 (1970) 938.
17 A. M. Bond, *Talanta*, 20 (1973) 1139.
18 A. M. Bond and J. H. Canterford, *Anal. Chem.*, 43 (1971) 228.
19 A. M. Bond, *Anal. Chem.*, 44 (1972) 315.
20 T. M. Florence, *Proc. Roy. Aust. Chem. Inst.*, 39 (1972) 211.
21 R. C. Rooney, *Polarography or Atomic Absorption*, Electronic Equipment News, May 1967.
22 R. D. Jee, *Z. Anal. Chem.*, 264 (1973) 143.
23 B. Fleet, R. D. Jee and C. J. Little, *J. Electroanal. Chem. Interfacial Electrochem.*, 43 (1973) 349.

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PULSED ANODIC STRIPPING VOLTAMMETRY OF ZINC, CADMIUM AND LEAD WITH A MERCURY-COATED WAX-IMPREGNATED GRAPHITE ELECTRODE

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Anodic stripping voltammetry (a.s.v.) is an electroanalytical technique which has been widely used for trace analysis of metal ions that can be electrochemically reduced to a metal or metal amalgam. Differential pulse anodic stripping voltammetry (d.p.a.s.) has been suggested as a means to enhance the sensitivity of a.s.v.[1–3]. Instrumentation is available commercially for performing analysis by d.p.a.s., and conditions for application of this instrumentation have been described[4]. With d.p.a.s., a metal is electrolytically reduced onto an electrode in a manner which allows preconcentration in a reproducible manner. The metal is then stripped from the electrode with a positive-going linear voltage ramp with voltage pulses of up to 100 mV superimposed on the ramp at regular intervals. The differential current is obtained by subtracting the current measured before the application of the voltage pulse from the current measured after the pulse is applied. The current is sampled near the end of the pulse in order to minimize contributions from the capacitive current[5,6].

Several different types of electrodes have been used in a.s.v. for the preconcentration-stripping process. Most of these electrodes are potentially applicable to d.p.a.s. The hanging mercury drop electrode (HMDE) probably has been most widely used[7,8]. Several features of the HMDE make it a desirable electrode for a.s.v. and d.p.a.s. Reproducible electrode areas can be obtained, the electrode is easily renewed, and the relatively large volume of the mercury drop makes the analysis relatively insensitive to intermetallic compound formation. The large mercury volume makes the HMDE less sensitive than thin-film electrodes which have high area-to-volume ratios[9].

The most widely used thin-film electrodes are carbon, graphite, or wax-impregnated graphite rods coated on the exposed, planar surface with a film of mercury. Florence[10,11] applied a mercury coated glassy carbon electrode to the a.s.v. of iron and lead. Gilbert and Hume[12] determined bismuth and antimony with a mercury-coated, waxed graphite electrode developed by Matson *et al.*[13]. Copeland *et al.*[14] have described a method for determining cadmium and lead by d.p.a.s. at a mercury-coated vitreous carbon electrode. An electrode, called a wax-impregnated

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* Operated by Union Carbide Corporation for the U.S. Atomic Energy Commission.

graphite electrode (WIGE), similar to the one developed by Matson *et al.*, is available from Princeton Applied Research (PAR). This electrode, when plated with a thin mercury film, has several features which make it attractive for a.s.v. or d.p.a.s. of metals reduced at a mercury electrode. The large area-to-volume ratio, characteristic of this electrode, makes it applicable for high sensitivity analysis. The WIGE is inexpensive and easy to clean and use. The electrode is not subject to memory effects such as the trapping of electrolyte solution in fractures or mounting hardware. A potentially undesirable feature of the WIGE is its susceptibility to intermetallic compound formation owing to the small volume of mercury in the film.

Application of the electrode to d.p.a.s. was investigated for the determination of lead, cadmium and zinc at the ng ml^{-1} level. Methods of highly sensitive analysis for these metals are needed for pollution abatement and ecological studies. Instrumental parameters were optimized for the PAR Model 174 Polarographic Analyzer and simultaneous analysis of the above elements in natural waters was performed. Detection limits were established for each of the metals under practical conditions. Since sensitivity is dependent on the thickness of the mercury film, the optimization of this parameter is described. A detailed investigation of the serious interference of copper with the determination of zinc was made by both electrochemical and radiochemical techniques.

EXPERIMENTAL

Apparatus

All experiments were performed with a PAR Model 174 Polarographic Analyzer. The 25-ml sample cell was constructed from a 60-ml capacity wide-mouth bottle, fitted with a threaded teflon cap. The cap held a Beckman Model 39178 saturated calomel electrode (SCE), a platinum wire counter electrode, WIGE (Model 9319 Electrode, PAR), and two gas-dispersing tubes. Mercury was plated onto the 0.25 in. polished end (area 0.2 cm^2) of the WIGE from a quiescent mercury-(II) solution at -0.4 V for 5 min.

Argon was used to remove oxygen from the cell. The electrolytic cell was placed in a lucite glove box (open ports) to reduce the blank level caused by dustfall from laboratory air. A well-type sodium iodide γ-ray scintillation counter was used to determine the amount of ^{65}Zn present in the intermetallic compound studies.

Reagents

All solutions were prepared from triply distilled water. A stock electrolyte solution of 0.5 *M* sodium acetate and 0.06 *M* hydrochloric acid (pH 5.7) was prepared from Merck's Suprapur reagents, except where noted. Stock solutions of analyte were prepared by dissolving the reagent-grade metal in 6 *M* nitric acid, heating to drive off excess of acid, and diluting with the electrolyte solution to reach 3000 μg ml^{-1} levels of metal ions ($> 10^{-2}$ *M*). Successive dilutions were made to reach ng ml^{-1} levels of metal ion concentration. These dilutions were prepared once a week to avoid storage problems. Mercury plating of the WIGE was carried out in a solution of $6.5 \cdot 10^{-3}$ *M* mercury(II) made slightly acidic by nitric acid.

Intermetallic compound formation studies between copper and zinc were performed using a ^{65}Zn tracer prepared by neutron irradiation of zinc metal to a specific activity of $6.0 \cdot 10^6$ disintegrations min^{-1} mg^{-1}.

Procedure

A sodium acetate–hydrochloric acid (0.1 *M*–0.012 *M*) supporting electrolyte buffer (pH 5.7) was used in all studies. After the sample to be analyzed and the sodium acetate–hydrochloric acid buffer were introduced into the cell, oxygen was removed by passing argon saturated with water vapor through the solution. The argon was then diverted to purge the cell space above the solution. The initial plating potential was set at −1.2 V *versus* SCE. A magnetic stirrer was used to effect agitation of the solution during plating. After the plating period, usually 1–5 min, the stirring was stopped. After a 15-s delay, the metals were stripped from the electrode. Two scan rate (pulse amplitude) combinations were commonly used: 20 mV s^{-1} (10 mV) or 5 mV s^{-1} (5 mV). A 0.5-s pulse repetition rate, the maximum rate available, was used routinely.

Two sets of experiments were performed to study the intermetallic compound formation of copper and zinc. The first set of experiments was designed to determine if copper hindered the plating of zinc onto the electrode. A buffer solution containing 50 ng Zn ml^{-1} was placed into the cell, degassed, and the zinc plated on the mercury-coated WIGE at −1.2 V. The electrode was then rinsed, placed into a clean sodium acetate electrolyte solution, stripped to −0.7 V, and lifted from the solution. The mercury film was dissolved in 8 *M* nitric acid. The original electrolyte, the stripping electrolyte, including rinse water from the electrode, and the mercury film solution were then counted. The experiment was then repeated with equimolar amounts of zinc and copper. Other experiments included stripping the electrode to +0.1 V.

The second set of experiments was designed to determine at what potential, if any, the copper–zinc compound stripped from the electrode. The experimental design was the same, except for the stripping process. The electrode was stripped to −0.7 V, −0.3 V, +0.1 V, and +0.29 V. Aliquots of electrolyte were taken at each potential and 30 min were allowed to elapse between each aliquot. Each aliquot was then counted.

RESULTS AND DISCUSSION

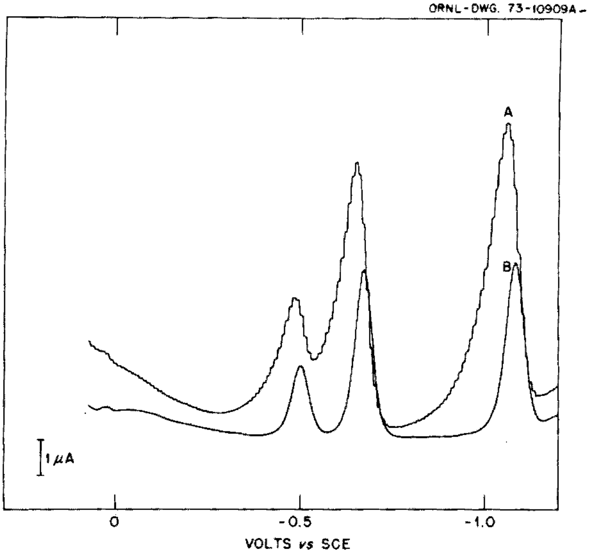
Choice of supporting electrolyte

The determination of zinc(II) in an acid solution is not feasible because the reduction of zinc(II) at a mercury electrode is more negative than, or is equal to, the potential of the reduction of hydrogen ions. A buffered supporting electrolyte is desirable for analysis of natural water samples since the pH of these samples may vary. Šinko and Doležal[15] have successfully utilized an acetate buffer in determining Cu, Pb, Cd and Zn by a.s.v. at a HMDE. The applicability of this buffer, pH 5.7, was extended to the simultaneous determination of lead, cadmium and zinc with a WIGE. However, copper seriously interferes with the zinc determination, and the copper peak is broad and of dubious analytical utility.

Optimization of instrumental parameters

Copeland *et al.*[14] have presented optimal conditions for utilization of a modified PAR Model 174 Polarographic Analyzer for the determination of lead and cadmium. Instrumental modifications suggested by Christie *et al.*[4] to allow larger pulse amplitudes without distortion of peaks were used in this modified instrument. Even though there are practical and instrumental limitations, the unmodified instrument is acceptable for analytical applications. Because the current measuring time constant is so long in the unmodified instrument, there is an upper limit of scan rates and pulse amplitudes that can be used. When the limit is exceeded, skewed peaks result. Separation of lead and cadmium peaks when lead is less concentrated than cadmium is possible only when the pulse amplitude is small; *e.g.*, 5 mV (Fig. 1). Very slow scan rates are desirable in order to improve resolution; but a scan rate of 1 mV s^{-1} requires 20 min to scan from -1.2 V to 0.0 V, thereby limiting its practical usefulness. Only four minutes are required for a scan rate of 5 mV s^{-1} for the same potential region, effecting adequate separation of peaks and yielding sensitivity acceptable for most analysis purposes.

Plating times for deposition of metals into the mercury film is another im-



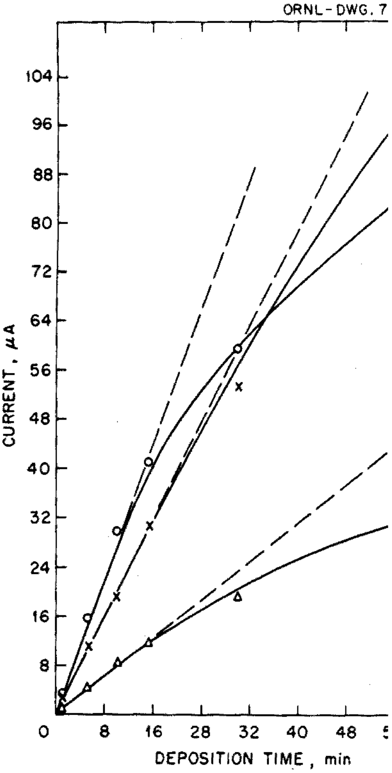


Fig. 1. Differential pulse stripping curves in 0.1 *M* $NaC_2H_3O_2$ and 0.01 *M* HCl for 9.9 ng Pb ml^{-1}, 19 ng Cd ml^{-1}, and 20 ng Zn ml^{-1}. 1-min deposition time at -1.2 V. Curve A, 20 mV s^{-1} scan rate with 10 mV pulse amplitude; B, 5 mV s^{-1} scan rate with 5-mV pulse amplitude.

Fig. 2. Differential pulse stripping peak current *vs.* deposition time of lead, cadmium and zinc: (△) 9.9 ng Pb ml^{-1}; (×) 19 ng Cd ml^{-1}; (○) 20 ng Zn ml^{-1}. -1.2 V deposition potential; 5 mV s^{-1} scan rate with 5-mV pulse amplitude.

portant parameter related to sensitivity. A peak current *vs.* plating time curve is shown in Fig. 2. Response is linear up to a plating time of 15 min. Longer times result in curvature towards the *x*-axis; *i.e.*, less metal plated per unit time. Zinc shows this effect most strongly since a four-fold increase in time resulted in only a two-fold increase in sensitivity.

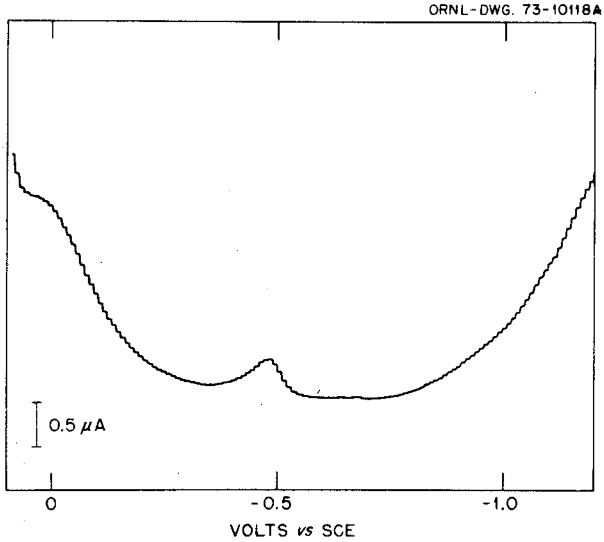


Fig. 3. Differential pulse stripping curves for reagent-grade sodium acetate electrolyte (0.1 *M* sodium acetate, 0.01 *M* hydrochloric acid, quartz-distilled water); 20 mV s^{-1} scan rate with 10-mV pulse amplitude; 1-min deposition time.

Impurities in the buffer limit the practical detection limit. As can be seen in Fig. 3, these impurities in a buffer prepared from reagent grade sodium acetate can be discerned at deposition times as short as 1 min. Lead, usually in the range of 1–2 ng ml^{-1}, is present in the blank solution and sometimes cadmium exists as high as 0.5 ng ml^{-1}. The sporadic occurrence of zinc in the blank indicates that it usually results from fallout from laboratory air and not from reagent impurities.

Optimization of the electrode surface

Barendrecht[9] states that high area-to-volume ratios of mercury film thicknesses yield greater sensitivities. Under the conditions recommended by PAR[16] for mercury plating, $1.75 \cdot 10^{-7}$ mole mercury per cm^2 of electrode area was plated. Table I lists peak currents for lead, cadmium and zinc for various amounts of mercury plated on the electrode; mercury plated approximately 20 times heavier than PAR instructions yields the optimum sensitivity. These levels of mercury were calculated based on the assumptions that the current efficiencies in plating were 100% and that the electrode area was 0.2 cm^2. Heavier mercury plating results in decreased sensitivity in agreement with Barendrecht's observations. The decreased sensitivities at the lower levels of mercury are probably due to incomplete coating of the graphite surface. Microscopic examination of the electrode surface by Matson[17] indicated that mercury formed droplets averaging 0.15 μm in diameter, rather than forming a flat film of mercury. If no flattening of the spheres is assumed, approximately 30% and 40% of the electrode surface is covered by these droplets for $1.75\cdot10^{-7}$ and $2.75\cdot10^{-7}$ mole mercury cm^{-2}, respectively. At the optimal level of mercury, $4.5\cdot10^{-6}$ mole mercury cm^{-2}, and greater, the electrode is completely covered by mercury.

TABLE I

DEPENDENCE OF PEAK CURRENT ON VARIATIONS IN MERCURY LEVELS ON THE WIGE AT CONSTANT Pb(II), Cd(II) AND Zn(II) CONCENTRATIONS[a]

Amount of mercury on the WIGE[b] *(mole Hg cm^{-2})*	*Peak current (μA)*[c]			$i_{p,Zn}/i_{p,Cd}$	*Peak at −0.1 V present*
	Pb	*Cd*	*Zn*		
Metals deposited for 1 min at −1.2 V					
No Hg plated	1.88	1.96	0.36	0.18	Yes
[d]$1.75\cdot10^{-7}$	4.58	6.98	11.0	1.6	Yes
$2.75\cdot10^{-7}$	4.90	8.10	16.0	2.0	Yes
$4.5\cdot10^{-6}$	7.75	14.0	32.6	2.3	No
$2.7\cdot10^{-5}$	6.95	13.5	29.8	2.2	No
Metals deposited for 5 min at −1.2 V					
No Hg plated	11.6	15.1	1.60	0.11	Yes
$1.75\cdot10^{-7}$	14.6	21.9	17.6	0.8	Yes
$2.75\cdot10^{-7}$	16.9	29.1	39.8	1.4	Yes
$4.5\cdot10^{-6}$	29.2	55.6	129.6	2.3	No
$2.7\cdot10^{-5}$	27.2	52.0	123.6	2.4	No

[a] Scan rate; 0.5 mV s^{-1}; pulse amplitude, 5 mV; pulse repetion time, 0.5 s.
[b] Deposited at −0.4 V *vs.* SCE.
[c] 29 ng Pb ml^{-1}, 38 ng Cd ml^{-1}, 49 ng Zn ml^{-1}.
[d] Reference 17.

Zinc, owing to its very negative reduction potential, is the most sensitive to the mercury film thickness of the metals studied; the peak current increases by almost 200% from the smallest amount of mercury to the optimal film thickness at 1-min deposition times. By comparing the peak currents of zinc and cadmium at each mercury film thickness, it is seen from Table I that a constant ratio of zinc and cadmium peak currents is obtained at the optimal film thickness and greater. One reason for this result is that zinc is not plated as efficiently as other metals onto an electrode that is only incompletely coated by mercury. Graphite has a much lower hydrogen overpotential than mercury does, thereby generating small amounts of hydrogen at exposed graphite sites.

The determination of zinc is affected more by impurities in the solution than most other metals[18]. As seen in Table I, the peak that appeared at the potential of copper oxidation disappeared as the film thickness approached the optimum for sensitivity. Consequently interferences for zinc should be fewer at a thickness that yields maximum sensitivity for lead, cadmium and zinc.

Intermetallic compound studies

Intermetallic compounds of zinc and copper under polarographic conditions have been reported[19,20]. Shuman and Woodward[21] have reported interference by copper on zinc determinations in human tissues by a.s.v. using a thin mercury film

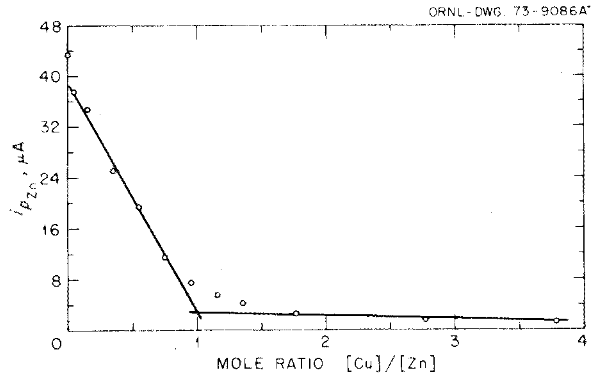


Fig. 4. Differential pulse stripping current for zinc *vs.* the molar concentration ratio of copper to zinc.

glassy carbon electrode. Similar results were found in our system using d.p.a.s. and a WIGE. A plot of i_p for zinc *versus* mole-ratio of Cu:Zn (Fig. 4) indicates that a 1:1 compound is formed. Previous reports confirm that this compound is indeed the one most likely to be formed[19,21].

When zinc and copper were present together, the zinc peak height decreased significantly. Tracer studies were made with ^{65}Zn to determine if copper hindered the plating of zinc into the mercury film. Additional studies were made to determine at what potential, if at all, the copper–zinc intermetallic compound was stripped from the electrode.

The total counts from the stripping solution and the dissolved mercury film were the same whether copper was present or not in the electrolyte solution. The percentage of zinc present in the stripping electrolyte solution is 90% when copper is absent and 30% when equimolar amounts of copper are added. This indicates that zinc is not hindered by copper from being plated. Also, zinc is not oxidized from the electrode with the same efficiency as when copper is absent.

To determine what happens to the zinc once it has been plated onto the electrode, aliquots of electrolyte solution were taken at various potentials and counted to determine the amount of zinc stripped from the electrode. In the absence of copper, at least 90% of the zinc was stripped at −0.7 V. However in the presence of equimolar amounts of copper and zinc, approximately 80% of the zinc was recoverable in the electrolyte solution when allowed to electrolyze for 30 min. Only 30% was found in aliquots taken at the same potential after only 3 min. The remainder of ^{65}Zn was recovered when the electrode was slowly stripped to +0.1 V after a total elapsed time of 1.5 h. When the copper:zinc mole ratio was increased to 10:1, the stripping of zinc was hindered still further. The differential pulse peak height of zinc was severely reduced and the amount of ^{65}Zn in the electrolyte solution was only 80% when the potential reached +0.1 V, again after an elapsed time of 90 min. Recovery approached 100% at the end of 2 h. The results of these experiments indicate that perhaps the $(ZnCu)_x$ exists in equilibrium with Zn(O) as suggested by Stromberg and Gorodovykh[19] and Kozlovsky and Zebreva[20]. If the equilibrium process

$$(\mathrm{ZnCu})_x \overset{\text{Rate 1}}{\rightleftharpoons} x\mathrm{Zn(O)} + x\mathrm{Cu(O)}$$

is assumed to exist, the suppression of the

$$\mathrm{Zn(O)} \xrightarrow{\text{Rate 2}} \mathrm{Zn(II)}$$

stripping wave is explained if rate 1 is less than rate 2 and the rate of direct oxidation of zinc from the compound is very slow or non-existent.

Other intermetallic compound formations have been described in the literature, specifically the possible formation of intermetallic compounds between copper and cadmium[22]. A series of experiments was performed with approximately 50 ng ml^{-1} each for Pb(II), Cd(II) and Zn(II). As much as 1.1 μg ml^{-1} of the other metals listed was added to these solutions to determine if, under the experimental conditions for sample analysis, any intermetallic compound formation interference existed. Table II lists these results. There is no significant change in the determination of each element with the exception of zinc when copper is present, as discussed before.

TABLE II

THE EFFECT OF INTERMETALLIC COMPOUND FORMATION ON METAL ION CONCENTRATION FOUND

Concentration of possible interferences (μg ml^{-1})	*Concentration of analyte found (ng ml^{-1})*		
	Pb	*Cd*	*Zn*
0	46.7	47.0	46.4
Copper			
0.233		49.4	
0.579	48.8		
0.808		46.4	
1.15	50.3		
Lead			
0.578			48.5
1.14		45.9	52.7
Cadmium			
0.234	46.1		
0.582			53.5
0.811	43.2		
1.15			47.9
Zinc			
0.231		47.5	
0.574	47.4		
0.800		45.1	
1.14	49.1	42.3	

Calibration

In the absence of copper, the linear least squares regression equations for peak current as a function of concentration of Pb(II), Cd(II) and Zn(II) showed a sensitivity of 0.17, 0.23, and 0.31 μA ng^{-1} ml, respectively. Concentrations ranged between 2 and 200 ng ml^{-1} for Pb, 0.1 and 100 ng ml^{-1} for Cd, and 10 and 100 ng ml^{-1} for Zn. The F-statistics for linear fit were 18,108 for lead, 6198 for cadmium, and 660 for zinc. These are all significant to the F_{99} level. There was no bias for lead determination in this concentration range, but there was a bias of +0.5

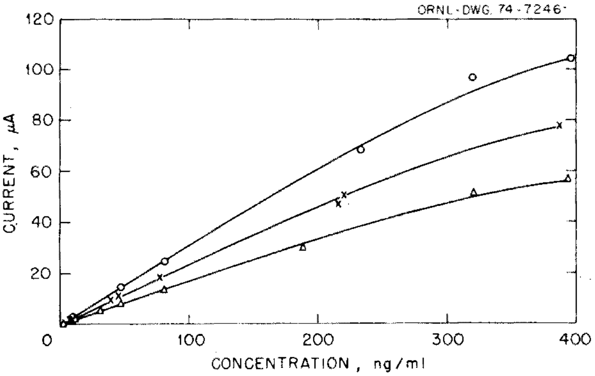


Fig. 5. Calibration curves for lead(II) (△), cadmium(II) (×), and zinc(II) (○).

ng ml^{-1} for cadmium and −2.5 ng ml^{-1} for zinc. These are explained by possible cadmium contamination in the cell and the susceptibility of Zn to any impurities present such as oxygen, organic material, or trace amounts of copper[9]. Calibration curves for lead, cadmium and zinc are shown in Fig. 5. For concentrations greater than 100 ng ml^{-1} for zinc and cadmium and 200 ng ml^{-1} for lead, there is a decrease in sensitivity.

Analyses

Table III lists the analytical results for soil extractions by 0.1 *M* calcium nitrate and water samples from an area surrounding a steam plant. These analyses were performed by standard addition. Zinc was determined successfully in samples that were apparently copper-free. With one exception the results of the flame and flameless atomic absorption methods were assumed to be accurate. The high levels of zinc found by these methods were probably due to dustfall contamination, a major problem in any low-level determination. Another serious problem was encountered

E III

ARY OF ANALYTICAL RESULTS

type	Sample	D.p.a.s.[a] (ng ml^{-1})			Known conc. (ng ml^{-1})			A.a.s.
		Pb	Cd	Zn	Pb	Cd	Zn	
urrounding a plant	Creek water	1.5	0.11	8.9	2.5	<0.1	10	a.a.s.[b]
	Spring water	0.6	0.4	<1	<1	<0.1	19	a.a.s.
	Dryfall	1170	9.7	241	1180	29	250	a.a.s.
mples extrac- Ca(NO_3)$_2$	1	6.9	29	3.8	<100	16	<5	f.a.a.s.[c]
	2	472	2500	2120	680	2300	2490	f.a.a.s.
	3	13	62	2.4	<100	20	<5	f.a.a.s.
	4	214	1410	1450	300	1230	1660	f.a.a.s.
	5	18	213	97	<100	212	226	f.a.a.s.
	6	464	746	409	830	762	689	f.a.a.s.

ential pulse anodic stripping.
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in the determination of all metals at concentrations higher than 100 ng ml^{-1}. This method is so sensitive that sample dilutions up to a factor of 25 were required. Small uncertainties in the amount of analyte within the cell result in large uncertainties for the undiluted sample. Successive dilutions could have been made to eliminate small aliquot additions to the buffer, but each added step increases the chances for contamination of the sample. Therefore this method is most applicable to the direct analysis of samples which contain an inherently low concentration of analyte such as natural water samples. Additionally, the absence of copper is a prerequisite for the accurate determination of zinc.

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SUMMARY

The use of a thin mercury-film wax-impregnated graphite electrode for the simultaneous determination of cadmium, lead and zinc in an acetate buffer by differential pulse anodic stripping voltammetry is described. Optimal instrumental parameters for maximum resolution and sensitivity for simultaneous analysis of these three elements in natural waters are discussed. The interference of copper with the determination of zinc is investigated in detail. An optimal mercury film thickness for this electrode is suggested.

REFERENCES

1 G. D. Christian, *J. Electroanal. Chem. Interfacial Electrochem.*, 23 (1969) 1.
2 J. B. Flato, *Anal. Chem.*, 44 (1972) 75A.
3 H. Siegerman and G. O'Dom, *Amer. Lab.*, 4 (1972) 59.
4 J. H. Christie, J. Osteryoung and R. A. Osteryoung, *Anal. Chem.*, 45 (1973) 210.
5 G. Barker and A. W. Gardner, *Z. Anal. Chem.*, 173 (1960) 79.
6 E. P. Parry and R. A. Osteryoung, *Anal. Chem.*, 37 (1965) 1634.
7 R. Naumann and W. Schmidt, *Z. Anal. Chem.*, 257 (1971) 337.
8 L. Duic, S. Szechter and S. Srinivasan, *J. Electroanal. Chem. Interfacial Electrochem.*, 41 (1973) 89.
9 E. Barendrecht in Allen J. Bard (Ed.), *Electroanal. Chem., Vol. 2*, Dekker, New York, 1967, pp. 53–109.
10 T. M. Florence, *J. Electroanal. Chem. Interfacial Electrochem.*, 26 (1970) 293.
11 T. M. Florence, *J. Electroanal. Chem. Interfacial Electrochem.*, 27 (1970) 273.
12 T. R. Gilbert and D. N. Hume, *Anal. Chim. Acta*, 65 (1973) 451.
13 W. R. Matson, D. K. Roe and D. E. Carritt, *Anal. Chem.*, 37 (1965) 1594.
14 T. R. Copeland, J. H. Christie, R. A. Osteryoung and R. K. Skogerboe, *Anal. Chem.*, 45 (1973) 2171.
15 I. Šinko and J. Doležel, *J. Electroanal. Chem. Interfacial Electrochem.*, 25 (1970) 299.
16 *PAR Instructions for Use, PAR Model 9319 Wax-Impregnated Graphite Electrode*, Princeton Applied Research, Inc., Princeton, N.J.
17 W. R. Matson, Ph.D. Dissertation, Massachusetts Institute of Technology, 1968. (Available from U.S. Clearinghouse Fed. Sci. Tech. Informa., 1968, AD 666554.)
18 F. V. Sturm and M. Ressel, *Z. Anal. Chem.*, 186 (1962) 63.
19 A. G. Stromberg and V. E. Gordovykh, *Russ. J. Inorg. Chem.*, 8 (1963) 1234.
20 M. Kozlovsky and A. Zebreva in I. M. Kolthoff, P. Zuman and L. Meites (Eds.), *Progress in Polarography, Vol. 3*, Wiley–Interscience, New York, 1972, pp. 157–194.
21 M. S. Shuman and G. P. Woodward Jr. in Delbert D. Hemphill (Ed.), *Trace Substances in Environmental Health, Vol. 6*, U. of Missouri, Missouri, 1972, pp. 269–277.
22 W. Kemula in I. S. Longmuir (Ed.), *Advances in Polarography, Vol. 1*, Pergamon, Oxford, 1960, p. 105.

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A CHRONOPOTENTIOMETRIC STUDY OF THE REDUCTION OF DITHIOCARBAMATE COMPLEXES OF NICKEL(II)

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Although extensive physical and chemical studies have been carried out on the behaviour of dithiocarbamates and their transitional metal complexes, little has been reported on their electrochemical behaviour, apart from some work on the polarographic determination of a number of elements[1,2].

Bond *et al.*[3] have recently studied the electrochemical reduction of a number of bis(π-cyclopentadienyl)-N,N-dialkyldithiocarbamate vanadium(IV) tetraphenylborates in acetone, using polarography, cyclic voltammetry and controlled potential electrolysis. Chant *et al.*[4] have reported results of a preliminary investigation into the redox properties of a number of dithiocarbamates of the six first-row transition metals in acetone by means of polarography and cyclic voltammetry.

In the present work, a chronopotentiometric study was carried out on the following dithiocarbamate complexes of nickel(II), in which the substituent R-group was varied widely and included straight-chain, branched-chain and ring structures:

$\mathrm{Ni(Me_2dtc)_2}$
$\mathrm{Ni(nAm_2dtc)_2}$
$\mathrm{Ni(iAm_2dtc)_2}$
$\mathrm{Ni(piper\ dtc)_2}$
$\mathrm{Ni(Ph_2dtc)_2}$
$\mathrm{Ni(H,Me\ dtc)_2}$
$\mathrm{Ni(Et_2dtc)_2}$
$\mathrm{Ni(Hex_2dtc)_2}$
$\mathrm{Ni(cycHex_2dtc)_2}$
$\mathrm{Ni(THQdtc)_2}$
$\mathrm{Ni(Bz_2dtc)_2}$
$\mathrm{Ni(h,Et\ dtc)_2}$
$\mathrm{Ni(nPr_2dtc)_2}$
$\mathrm{Ni(iPr_2dtc)_2}$
$\mathrm{Ni(morph\ dtc)_2}$
$\mathrm{Ni(H,Ph\ dtc)_2}$
$\mathrm{Ni(EtOH,H\ dtc)_2}$
$\mathrm{Ni(nBu_2dtc)_2}$
$\mathrm{Ni(iBu_2dtc)_2}$
$\mathrm{Ni(pyrrole\ dtc)_2}$
$\mathrm{Ni(Me,Ph\ dtc)_2}$
$\mathrm{Ni(H_2dtc)_2}$
$\mathrm{Ni(Et,Ph\ dtc)_2}$

Chronopotentiometry has several advantages over polarography, especially for kinetic studies and investigations on the mechanism of reduction. Further, in the work, the effect of the substituent alkyl group was investigated. As far as the authors are aware, no reports of chronopotentiometric studies on transition metal dithiocarbamates have, to date, appeared in the literature.

THEORETICAL CONSIDERATIONS

In chronopotentiometry, the period of time required to deplete the surface layer—the transition time (τ)—is related to the bulk concentration of the reducible species by the Sand equation

$$\tau^{\frac{1}{2}} = \pi^{\frac{1}{2}} nFAD^{\frac{1}{2}} C/2i$$

where C is the concentration of the electroactive species (mole dm^{-3}), i is the constant electrolysis current (in A), D is the diffusion coefficient (cm^2 s^{-1}), F is the Faraday, n the number of electrons involved in the reduction, and A is the area of the electrode (cm^2). For this equation to be valid, whether or not the electrode reaction is reversible, the electroactive species must reach the electrode surface by linear diffusion.

A feature, therefore, of the Sand equation is its use in the calculation of diffusion coefficients. In interpreting the potential–time curves obtained in chronopotentiometry Karaoglanoff[5] has shown that for a system, where both oxidized and reduced species are soluble in either solvent or electrode, the potential of the working electrode (E) is given by:

$$E = E_{\frac{1}{2}} - \frac{RT}{nF} \ln \frac{t^{\frac{1}{2}}}{\tau^{\frac{1}{2}} - t^{\frac{1}{2}}} \tag{1}$$

where $E_{\frac{1}{2}}$ is the polarographic half-wave potential and t is the electrolysis time.

For the deposition of a metal on a platinum cathode, the potential–time curve for a reversible reduction should follow the relationship

$$E = E_{\frac{1}{2}} + RT \ln(\tau^{\frac{1}{2}} - t^{\frac{1}{2}}) \tag{2}$$

When the electrode reaction does not proceed reversibly, the observed potential at any instant is greater than corresponds to eqns. (1) and (2). The mathematical treatment of potential–time curves for irreversible reactions has been developed by Delahay and Berzins[6]. If the effects of any reverse reactions are ignored, the following relationship can be obtained:

$$k_{\mathrm{f,h}} = \pi^{\frac{1}{2}} D_0^{\frac{1}{2}} / 2 f_0 (\tau^{\frac{1}{2}} - t^{\frac{1}{2}}) \tag{3}$$

where $k_{\mathrm{f,h}}$ is the rate constant for the forward electrochemical reaction, and f_0 and D_0 are the activity coefficient and diffusion coefficient of the electroactive species, respectively.

By applying the absolute rate theory, the following relationship can be obtained

$$k_{\mathrm{f,h}} = k^0_{\mathrm{f,h}} \exp\{-(\alpha n_{\mathrm{a}} F/RT)E\} \tag{4}$$

where $k^0_{\mathrm{f,h}}$ is the formal rate constant for the forward electrochemical process, measured at the potential of the normal hydrogen electrode (NHE), α is the transfer coefficient and n_{a} the number of electrons involved in the rate-determining step. Thus, it is possible to determine the parameters αn_{a} and $k^0_{\mathrm{f,h}}$ which characterize an irreversible reaction.

EXPERIMENTAL

Preparation of complexes

The alkali metal dithiocarbamates used to prepare the nickel(II) complexes were prepared by shaking together an equimolecular mixture of the appropriate secondary amine and an aqueous solution of an alkali metal hydroxide. To the mixture, an excess of carbon disulphide was added, the temperature being maintained below 10°C during this addition. The reaction mixture was then stirred vigorously and allowed to warm slowly to room temperature. On gradual evaporation to incipient dryness, the alkali-metal dithiocarbamates deposited and were recrystallized from an alcohol–ether mixture.

The nickel(II) dithiocarbamates were in general prepared by mixing an aqueous solution of nickel sulphate and an aqueous solution of the appropriate alkali-metal dithiocarbamate in a 1:2 molar ratio. The green-coloured complexes were recrystallized from chloroform. The Ni(H_2dtc)$_2$, Ni(aniline dtc)$_2$, Ni(Me aniline dtc)$_2$ and Ni(Et aniline dtc)$_2$ complexes were prepared by the method of Coucouvanis and Fackler[7] or a minor modification of it. The dibenzyl- and diphenyl-derivatives of nickel were prepared by the method of Kupchik and Calabretta[8]. The purity of each complex was checked by elemental analysis and melting-point determination. Results are shown for some of the complexes in Table I. Analyses were carried out by the Australian Microanalytical Service.

TABLE I

ELEMENTAL ANALYSIS OF THE COMPLEXES

Complex	*Found (%)*				*Calculated (%)*				*M.p. (°C)*
	C	*H*	*N*	*S*	*C*	*H*	*N*	*S*	
Ni(Me_2dtc)$_2$	24.2	4.0	9.4	—	24.1	4.0	9.4	—	~275 (dec.)
Ni(Et_2dtc)$_2$	33.9	5.7	8.0	—	33.8	5.7	7.9	—	237.8
Ni(nPr_2dtc)$_2$	41.2	6.9	6.8	—	40.9	6.9	6.8	—	134.
Ni(nBu_2dtc)$_2$	45.9	8.0	5.7	—	46.2	7.8	6.0	—	95
Ni(nAm_2dtc)$_2$	51.1	8.6	5.4	—	50.5	8.5	5.4	—	80.2
Ni(iPr_2dtc)$_2$	40.5	6.7	7.0	—	40.9	6.9	6.8	—	>300
Ni(iBu_2dtc)$_2$	46.0	7.8	6.2	—	46.2	7.8	6.0	—	178
Ni(Morph dtc)$_2$	30.3	4.1	7.6	—	31.2	4.2	7.3	—	>300
Ni(pyrrole dtc)$_2$	33.9	4.6	7.7	—	34.2	4.6	8.0	—	>300
Ni(H,Ph dtc)$_2$	39.8	3.2	7.2	28.7	42.5	3.6	7.1	32.5	>300
Ni(Me,Ph dtc)$_2$	45.3	3.9	6.7	30.0	45.4	3.8	6.6	30.3	>300
Ni(Et,Ph dtc)$_2$	47.9	4.4	6.2	28.3	47.9	4.5	6.2	28.4	276.4
Ni(Ph_2dtc)$_2$	57.2	3.8	5.1	23.1	51.0	3.7	5.1	23.4	>300
Ni(Bz_2dtc)$_2$	59.4	4.5	4.7	21.0	59.7	4.7	4.6	21.3	241.4

Solvent system

Four solvents were considered, acetonitrile, dimethylsulphoxide, dimethylformamide, and propylene carbonate (4-methyldioxolone-2). After preliminary work, it was decided to use propylene carbonate. All the complexes were soluble in this solvent and it possesses favourable properties, a high dielectric constant (64.4 at 25°C) and a wide potential range. It is also non-toxic, chemically stable, non-hygroscopic, easy to purify, and of low vapour pressure.

The propylene carbonate used (Koch-Light Puriss grade) was purified by double vacuum distillation. Under a pressure of 0.1 mm Hg the middle 60% fraction coming off between 120 and 130°C was collected and stored over a molecular sieve in a nitrogen atmosphere.

Supporting electrolyte

Analar-grade sodium perchlorate was used as supporting electrolyte. It was dried at 80°C for 48 h before use and 0.2 *M* solutions in propylene carbonate were used.

The working potential range of the solvent-support system at a mercury electrode was *ca.* +0.65 to −1.65 V *versus* S.C.E.

Reference electrode system

The Ag–Ag^+ couple is a widely used reference system in non-aqueous solvents[9]. In the present work, an Ag–AgCl reference electrode (Metrohm) was used and the potential checked daily. The Ag–AgCl electrode was made up in propylene carbonate with sodium perchlorate (0.2 *M*). All electrode potentials in propylene carbonate were measured against it.

Apparatus

For all the chronopotentiometric investigations, a Beckman Electroscan 30 was used. The cell was similar in design to that of Delahay and Mattax[10], but with some minor modifications. The lower electrode consisted of 5 cm^3 of mercury (area 1.486 cm^2) through which electrical contact was made by a platinum wire fused into the glass. The other electrode consisted of a Beckman platinum electrode.

Measurements

Nickel dithiocarbamates were made up in stock solutions of 10^{-3} *M* and the solutions tested were prepared by suitable dilution. Measurements were carried out at 29°C. All solutions were deoxygenated by nitrogen (oxygen-free).

RESULTS AND DISCUSSION

The chronopotentiometric reduction of twenty-three nickel(II) dithiocarbamate complexes, in which the alkyl group substituent consisted of a straight chain, a branched chain or a ring structure, was examined at platinum and mercury pool electrodes. Results for the reduction of all the complexes were determined. In Tables II and III representative selections are shown.

In all cases there was a single reduction step, except for Ni(diphenyldithiocarbamate), which showed two steps. Values for $i\tau^{\frac{1}{2}}$ were determined many times, and there was no evidence of a decrease in $i\tau^{\frac{1}{2}}$ with increasing current density. Such a decrease would indicate that dissociation precedes the electrochemical reaction[11]. However, the product $i\tau^{\frac{1}{2}}$ for the complexes was independent of the current density. It is concluded that either the complexes are directly reduced or that, if dissociation of the complexes before reduction does occur, it is so rapid that no kinetic effects are observed[6]. If the reductions of the complexes were irreversible processes with one rate-determining step, then the plot of log $[1-(t/\tau)^{\frac{1}{2}}]$ *vs.* E should yield a straight line whose reciprocal slope is 2.303 $RT/\alpha n_a F$ and from which αn_a may be determined. Further, from the plot of E *vs.* log $k_{f,h}$ the rate constant for the reduction and αn_a may also be determined.

Graphs were drawn for all the complexes, checking for both irreversibility and reversibility. All complexes with the exception of nickel dibenzyldithiocarbamate, $Ni(Bz_2dtc)_2$ showed irreversibility: the latter showed the behaviour expected of a reversible process.

TABLE II

CHRONOPOTENTIOMETRIC RESULTS FOR DIFFERENT COMPLEXES OF THE NICKEL-(II)-DISUBSTITUTED DITHIOCARBAMATE SYSTEM

Complex	*Current (mA)*	$\tau(s)$	$i\tau^{\frac{1}{2}}(mA\,s^{\frac{1}{2}})$	*Complex*	*Current (mA)*	$\tau(s)$	$i\tau^{\frac{1}{2}}(mA\,s^{\frac{1}{2}})$
Ni(Me_2dtc)$_2$	0.050	43.0	0.328	Ni(Morph dtc)$_2$	0.050	27.5	0.262
	0.060	30.0	0.329		0.060	19.5	0.265
	0.065	25.0	0.325		0.065	16.0	0.260
	0.075	19.0	0.327		0.080	11.0	0.265
	0.085	15.0	0.329		0.085	10.0	0.268
	0.105	9.7	0.327		0.095	8.0	0.268
	0.120	7.0	0.317		0.100	6.7	0.259
	0.140	5.2	0.319	Ni(Pyrrol dtc)$_2$	0.050	24.0	0.245
Ni(nPr_2dtc)$_2$	0.050	25.0	0.250		0.060	17.0	0.247
	0.060	18.0	0.251		0.075	11.0	0.248
	0.085	8.5	0.248		0.085	8.5	0.248
	0.100	6.5	0.254		0.100	6.0	0.245
	0.110	5.0	0.248		0.120	4.0	0.240
	0.125	4.0	0.250	Ni(Bz_2dtc)$_2$	0.080	48.0	0.554
Ni(i-Bu_2dtc)$_2$	0.020	45.0	0.134		0.090	36.5	0.544
	0.030	21.0	0.137		0.100	29.5	0.543
	0.035	15.0	0.135		0.110	25.5	0.555
	0.040	12.0	0.138		0.120	22.5	0.569
	0.050	8.0	0.141		0.130	19.0	0.567
	0.060	6.5	0.140	Ni(H.Et dtc)$_2$	0.030	21.0	0.137
					0.045	9.0	0.135
					0.055	6.5	0.140
					0.070	4.0	0.140
					0.080	3.0	0.138

TABLE III

CHRONOPOTENTIOMETRIC RESULTS FOR NICKEL DIPHENYL DITHIOCARBAMATE

Complex	*Current (mA)*	$\tau(s)$	$\tau_2(s)$	$i\tau^{\frac{1}{2}}$	$i\tau_2^{\frac{1}{2}}$
Ni(Ph_2dtc)$_2$	0.050	2.5	7.4	0.142	0.245
	0.055	3.1	9.0	0.141	0.240
	0.070	4.0	12.5	0.140	0.247
	0.080	7.0	20.5	0.145	0.248
	0.090	8.0	23.7	0.141	0.243

From the graphs, the values of αn_a were determined and in Table IV are compared with values of αn_a obtained also from the plot of E *vs.* log $f_0 k_{f,h}$. The latter plots for the isobutyl-, methylaniline-, and diphenylderivatives are shown in Fig. 1. From the results, it is clear that one electron is involved in the rate-determining step for the reduction of all the complexes, except nickel diphenyldithiocarbamate, where two electrons are involved.

It is difficult to draw conclusions from the rate constants for the different complexes, as they depend on several factors, including the concentration of the electroactive species, the presence of surface-active agents, etc.[12]. Thus, the rate con-

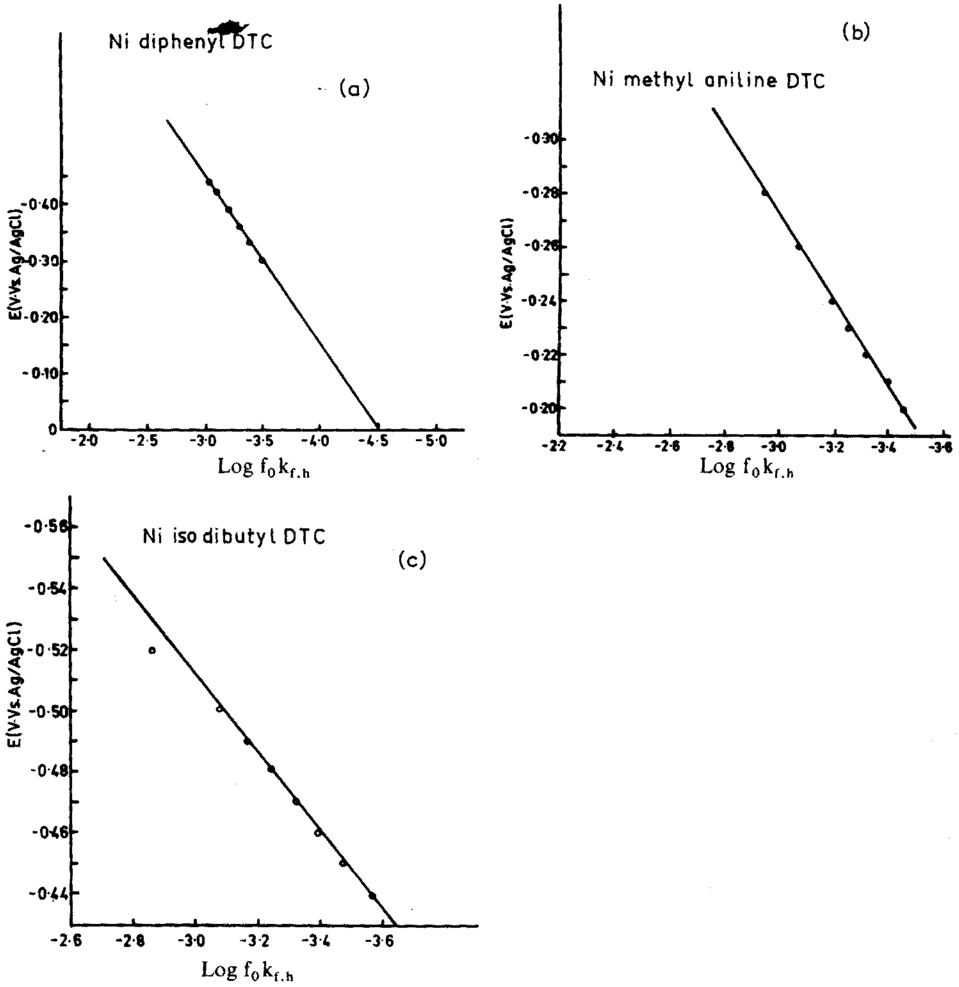

Fig. 1. E *vs.* $\log[f_0 k_{f,h}]$ plots for (a) Ni diphenyl dtc; (b) Ni methylaniline dtc; (c) Ni diisobutyl dtc.

stants determined here are relevant only for the experimental conditions described; it was assumed that the activity coefficients of the electroactive species can be equated to unity.

A comparison of the rate constants with the polarographic reduction potentials for some of the complexes is shown in Table V. The results indicate that the rate constants follow the same trend as the polarographic reduction potentials, *i.e.*, the more stable the complex towards the mercury drop, the smaller the rate constant. It is interesting to note that Chant *et al.*[4] in measuring oxidation potentials of a number of dithiocarbamate complexes, found the dibenzyl derivative to be the most difficult to oxidize and the dicyclohexyl derivative the easiest. On the basis of the rate constants reported in Table IV it could be concluded that the dicyclohexyl derivative is one of the easiest to reduce and the dibenzyl derivative one of the most difficult.

TABLE IV

VALUES OF αn_a AND log $k^0_{f,h}$ WITH THE MERCURY ELECTRODE

Complex	*αn_a (from E vs. log $[1-(t/\tau)^{\frac{1}{2}}]$)*	*αn_a (from E vs. log $f_0 k_{f,h}$)*	*log $k^0_{f,h}$*
Ni(Me$_2$dtc)$_2$	0.28	0.28	−4.00
Ni(Et$_2$dtc)$_2$	0.279	0.28	−3.75
Ni(nPr$_2$dtc)$_2$	0.41	0.45	−3.70
Ni(nBu$_2$dtc)$_2$	0.33	0.33	−3.60
Ni(nAm$_2$dtc)$_2$	0.22	0.21	−3.50
Ni(Hex$_2$dtc)$_2$	0.42	0.42	−5.70
Ni(iPr$_2$dtc)$_2$	0.18	0.20	−3.94
Ni-(iBu$_2$dtc)$_2$	0.27	0.28	−3.65
Ni-(iAm$_2$dtc)$_2$	0.23	0.28	−4.75
Ni-(cycHex$_2$dtc)$_2$	0.21	0.21	−3.50
Ni(Morph dtc)$_2$	0.16	0.17	−3.66
Ni-(Pyrrole dtc)$_2$	0.21	0.24	−4.89
Ni-(Piper dtc)$_2$	0.19	0.19	−3.54
Ni-(THQdtc)$_2$	0.24	0.26	−4.60
Ni(H,Ph dtc)$_2$	0.43	0.41	−4.25
Ni(Me,Ph dtc)$_2$	0.33	0.34	−4.09
Ni(Et,Ph dtc)$_2$	0.18	0.20	−3.88
Ni(Ph$_2$dtc)$_2$	0.78	0.78	−4.50
Ni(Ind dtc)$_2$	0.40	0.37	−3.80
Ni-(H$_2$dtc)$_2$	0.15	0.19	−3.97
Ni-(H,Me dtc)$_2$	0.36	0.32	−3.92
Ni(H,Et dtc)$_2$	0.29	0.29	−3.55
Ni(H,EtOH dtc)$_2$[a]	0.12	0.25	−4.32

[a] For Ni(H,EtOH dtc)$_2$ very poor waves were obtained.

TABLE V

COMPARISON OF E_p AND log $f_0 k_{f,h}$ VALUES FOR SOME NICKEL COMPLEXES

	E_p	*log $fk^0_{f,h}$*		E_p	*log $fk^0_{f,h}$*
Ni(Me$_2$dtc)$_2$	−1.02	−4.00	Ni(H,Et dtc)$_2$	−0.700	−3.55
Ni(Et$_2$dtc)$_2$	−0.76	−3.75	Ni(H,Ph dtc)$_2$	−0.88	−4.25
Ni(nBu$_2$dtc)$_2$	−0.55	−3.60	Ni(Me,Ph dtc)$_2$	−0.54	−4.09
Ni(H$_2$dtc)$_2$	−1.130	−3.97	Ni(Et,Ph dtc)$_2$	−0.50	−3.88
Ni(H,Me dtc)$_2$	−0.950	−3.92			

From the overall results, it is clear that the R-group substituent exerts a definite effect on the behaviour of the complex. It would appear, therefore, that during reduction an electron enters an orbital associated with the bonding orbitals. Although it has been suggested that in nickel diethyldithiocarbamate, the electron transfer process is metal based[4], the present results indicate that all the nickel dithiocarbamates do not transfer electrons by the same process, but that in proceeding from the dibenzyl derivative to the dicyclohexyl derivative there is a shift to localization of electron transfer on the dithiocarbamate ligand.

SUMMARY

A chronopotentiometric study has been carried out on 23 nickel di-substituted dithiocarbamate complexes in which the substituent R-group was varied widely and included straight chain, branched chain and ring substituents. In all cases, there was a single reduction step, except for the diphenyldithiocarbamate complex where a two step reduction was obtained. All the complexes except nickel dibenzyldithiocarbamate showed irreversibility. Values of αn_a were determined for each complex and showed that, in all cases (except nickel diphenyldithiocarbamate), one electron was involved in the rate-determining step. Rate constants ($\log f_0 k_{f,h}$) were determined for the complexes. It was found that the substituent R-group had a marked effect on the reduction-behaviour of the complex.

REFERENCES

1 T. Fujinaga and K. Yamashita, *Bull. Chem. Soc. Jap.*, 37 (1964) 989.
2 T. Fujinaga, H. A. Brodowsky, T. Nagai and K. Yamashita, *Rev. Polarogr.*, 11 (1963) 217.
3 A. M. Bond, A. T. Casey and J. R. Thackeray, *Inorg. Chem.*, 12 (1973) 887.
4 R. Chant, A. Hendrikson, R. L. Martin and N. Rohde, *Aust. J. Chem.*, 26 (1973) 2533.
5 Z. Karaoglanoff, *Z. Elektrochem.*, 12 (1906) 5.
6 P. Delahay and T. Berzins, *J. Amer. Chem. Soc.*, 75 (1953) 2486.
7 D. Coucouvanis and J. P. Fackler, Jr., *Inorg. Chem.*, 6 (1967) 11.
8 E. J. Kupchik and P. J. Calabretta, *Inorg. Chem.*, 4 (1965) 973.
9 J. N. Butler, *Advan. Electrochem. Electrochem. Eng.*, 27 (1970) 167.
10 P. Delahay and C. Mattax, *J. Amer. Chem. Soc.*, 76 (1954) 874.
11 L. Gierst and A. Juliard, *Proceedings of the 2nd Meeting of the International Committee of Electrochemical Thermodynamics and Kinetics, Tamburini, Milan, 1950*, pp. 117, 279.
12 H. A. Laitinen and W. J. Subcasky, *J. Amer. Chem. Soc.*, 80 (1958) 2623.

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POTENTIOMETRIC STUDIES ON ORGANIC COMPOUNDS CONTAINING SULPHUR WITH A SULPHIDE ION-SELECTIVE MEMBRANE ELECTRODE. DIRECT POTENTIOMETRIC TITRATION OF SOME PHYSIOLOGICALLY ACTIVE MERCAPTOPYRIMIDINES

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Recently, the possibility of direct potentiometric determination of thiourea and some thiourea derivatives with silver(I) solution has been reported[1,2]. It was of interest to extend these investigations to the group of 2-mercaptopyrimidines, which may be regarded as cyclic derivatives of thiourea; in their molecules the same active (from the analytical point of view) thiourea function is to be found. Of these compounds the most interesting ones, because of their proven pharmacological effect, are thiouracil (2-mercapto-4-hydroxypyrimidine) and its 6-alkyl-derivative (6-methyl-2-thiouracil), as well as 2,4-dithiouracil. The titrimetric analytical procedures which have been recommended so far for the determination of these compounds, suffer from the great disadvantages of being indirect, tedious and subject to interferences[3–10].

The present paper describes the results of a potentiometric investigation of the above-mentioned compounds, with a sulphide ion-selective electrode as the indicator electrode in order to establish the proper conditions for their direct titration with silver(I) solution.

EXPERIMENTAL

E.m.f. measurements were carried out with a Radelkis Precision pH-meter type OP-205 (Radelkis, Budapest). A Radelkis sulphide ion-selective electrode (Type OP-S-711) was used as indicator electrode with a saturated calomel reference electrode. The reference electrode was connected with the solution to be titrated through a 0.1 M KNO_3 agar salt bridge.

I.r. spectra were recorded with a Zeiss UR-10 instrument.

The stock solutions of 2-thiouracil, 6-methyl-2-thiouracil and 2,4-dithiouracil were prepared daily, by dissolving an appropriate amount of the corresponding analytical-grade reagent in 0.1 M sodium hydroxide. Standard solutions of silver nitrate (0.1 and 0.01 M) were used in all cases.

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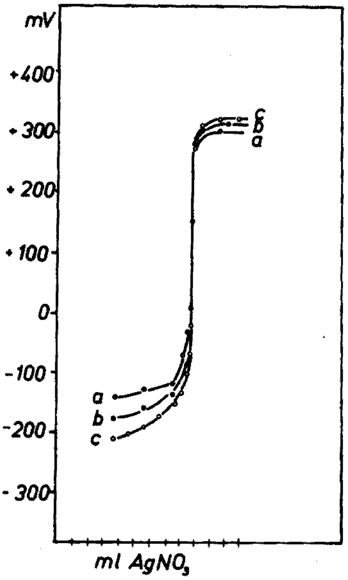
RESULTS AND DISCUSSION

By analogy with thiourea, it was reasonable to expect the formation of silver sulphide as a first step when alkaline solutions of the above-mentioned compounds were titrated with silver nitrate. Hence, preliminary experiments were first undertaken in alkaline medium (0.1 and 1.0 *M* sodium hydroxide). It was soon realised that with these compounds, silver sulphide was partly formed only after the solutions had been boiled in the presence of excess of silver nitrate for a long time. Hence, the only possible interactions under the conditions of potentiometric titrations seemed to be the formation of the sparingly soluble silver salts of the corresponding thiouracil.

The potentials exhibited by 0.1 *M* solutions of 2-thiouracil, 6-methyl-2-thiouracil and 2,4-dithiouracil, measured directly with the sulphide-selective electrode in 0.1 *M* sodium hydroxide, were −120, −80 and −470 mV *vs.* SCE respectively. This indicates the well manifested sulphide function of the enumerated compounds in this medium. But when these compounds were titrated potentiometrically with silver nitrate in 0.1 *M* sodium hydroxide, the appearance of the jumps on the titration curves was impeded by the coprecipitation of silver oxide which started before the theoretical end-points were reached. Its formation was easily identified by the change in the colour of the precipitates from white (in the case of 2-thiouracil or 6-methyl-2-thiouracil) or yellow for 2,4-dithiouracil to brown, as well as by reading the exhibited electrode potential. In order to avoid this interference of silver oxide, the solutions to be titrated were buffered with acetate buffer of pH 5.6. Under



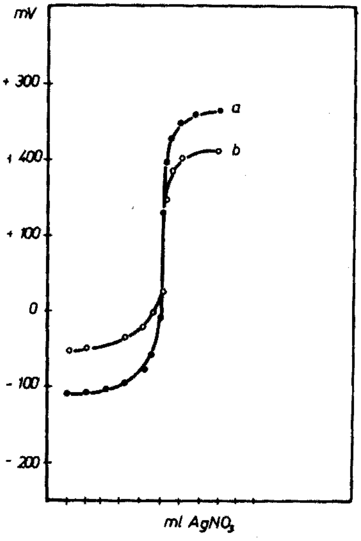


Fig. 1. Potentiometric titration curves of (a) $1.00\cdot10^{-1}$ *M*, (b) $1.25\cdot10^{-2}$ *M* and (c) $1.00\cdot10^{-3}$ *M* solutions of thiouracil in acetate buffer.

Fig. 2. Potentiometric titration curves of (a) $5\cdot10^{-2}$ *M* and (b) $5\cdot10^{-3}$ *M* solutions of 6-methyl-2-thiouracil in acetate buffer.

these conditions, only one jump occurred on the potentiometric curves for 2-thiouracil and 6-methyl-2-thiouracil, pointing to a stoichiometry of 1:1 mole of reactant to reagent. Under the same conditions, one mole of 2,4-dithiouracil reacted with two moles of silver nitrate; two jumps appeared on the titration curve. The buffered solutions exhibited less negative potentials than in 0.1 *M* sodium hydroxide medium and the precipitation reactions were not sufficiently fast in the case of 6-methyl-2-thiouracil and 2-thiouracil. Accordingly, it was necessary to examine the influence of both pH and temperature on the reaction rate. The pH range 5.6–9 was examined. Up to pH 8, no interference from the formation of silver oxide was found for a large range of concentrations of the titrant (from 10^{-1} *M* down to 10^{-4} *M*). At pH 9, the starting potentials approached the values in 0.1 *M* sodium hydroxide and the potentials changed rapidly in the course of the titration. Heating the solutions immediately before titration to 50–60°C also contributed to obtaining a sharp jump at the end-point.

In accordance with the above investigations, the following procedure was adopted for the potentiometric argentimetric determination of the three thiouracil compounds: to aliquots of the corresponding thiouracil, dissolved in 0.1 *M* sodium hydroxide, 10 ml of 0.2 *M* sodium acetate was added and the pH was then adjusted to 8 by adding dropwise 1 *M* acetic acid. The shapes of the titration curves, obtained by following the above directions, are shown in Figs. 1–3. The results of the determinations are summarized in Table I.

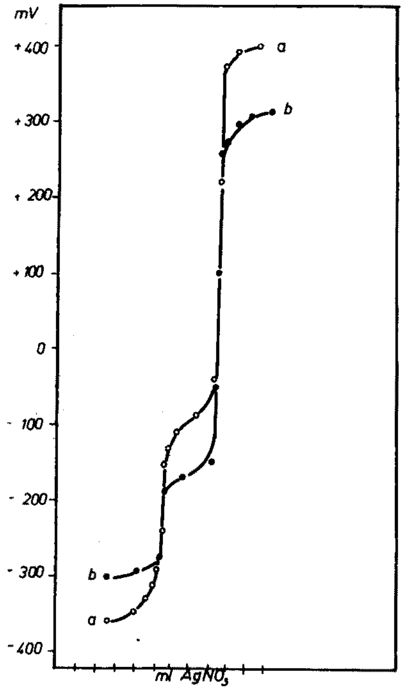


Fig. 3. Potentiometric titration curves of (a) $1.25 \cdot 10^{-2}$ *M* and (b) $1.00 \cdot 10^{-3}$ *M* solutions of 2,4-dithiouracil in acetate buffer.

TABLE I

TITRATION OF THIOURACIL COMPOUNDS

Substance titrated	*Taken (mg)*	*Found*[a] *(mg)*	*Purity (%)*
2-Thiouracil	63.8	63.8	100.0
	25.6	26.0	101.6
	12.8	12.8	100.0
	6.4	6.5	102.1
6-Methyl-2-thiouracil	28.4	28.6	100.7
	7.1	7.5	105.6
2,4-Dithiouracil	36.0	35.3	98.0
	28.8	28.5	98.9
	14.4	14.0	97.2
	7.2	7.1	98.6

[a] Mean of 3 determinations.

Identification of the products

In order to identify the products of the reactions, the precipitates obtained after the titrations were filtered, washed with distilled water and dried, and their i.r. spectra were then recorded (Figs. 4(a) and 5(a)). The i.r. spectra of the corresponding pure thiouracils (2-thiouracil and 2,4-dithiouracil) were taken for the sake of comparison (Figs. 4(b) and 5(b)).

Recently it has been shown[11,12] on the basis of theoretical considerations, that the stretching vibrations of the C=S bond for the different thiocarbonyl compounds should be found in the range 400–700 cm^{-1}. Hence, in the i.r. spectrum of 2-thiouracil, $\nu_{C=S}$ appeared at 455 cm^{-1}. For 2,4-dithiouracil, with two thio-

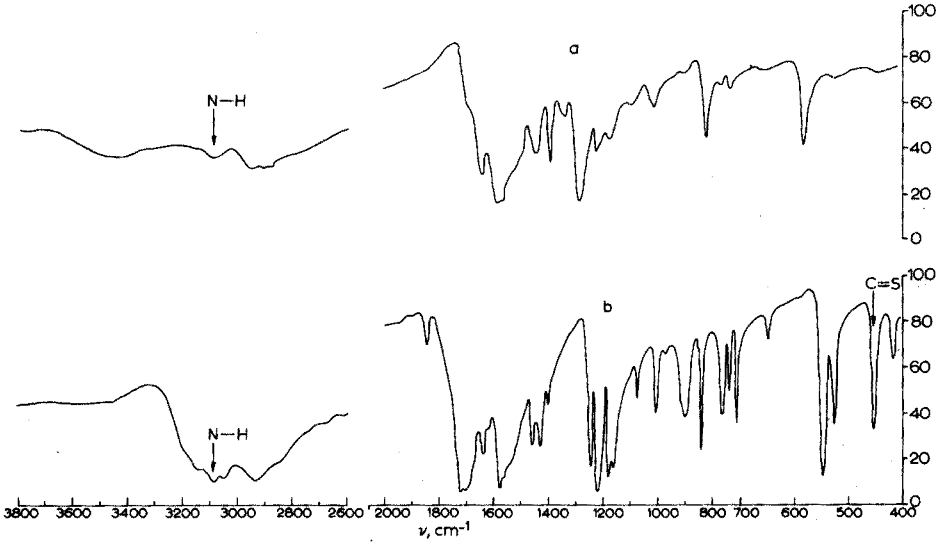


Fig. 4. Infrared spectrum of (a) silver thiouracil and (b) pure thiouracil.

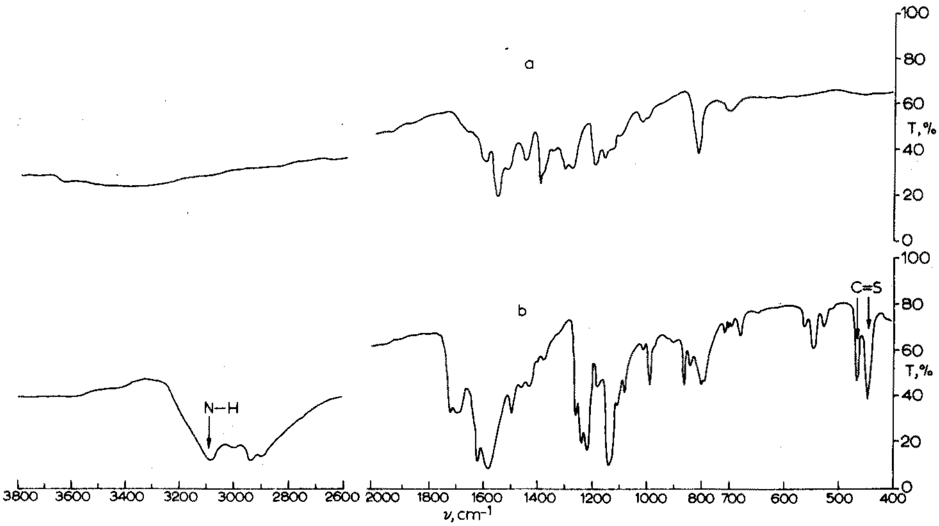
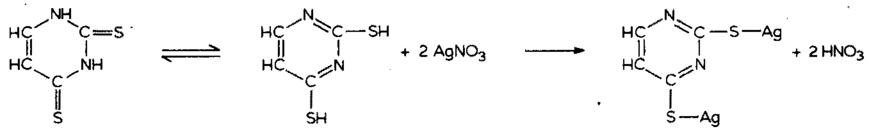


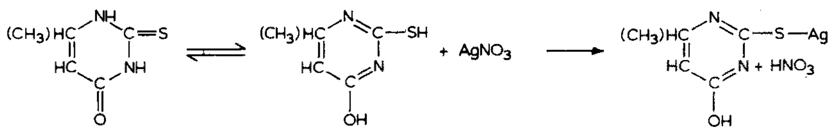
Fig. 5. Infrared spectrum of (a) silver dithiouracil and (b) pure dithiouracil.

carbonyl groups $\nu_{C=S}$ appeared at 450 and 470 cm^{-1} (Fig. 5(a)). In the i.r. spectra of the solid residues, obtained after the titration of 2-thiouracil and 2.4-dithiouracil with silver nitrate, $\nu_{C=S}$ completely disappeared. In the molecule of 2-thiouracil there is also one C=O group. It is well known that the pyrimidine derivatives exist under different tautometric forms[13]. For 2-thiouracil both keto–enol and thione–thiol tautomerism is possible. That is why quite broad bands are found in the spectrum of its silver residue in the range of 2900–3500 cm^{-1}, characteristic for the OH-group of different degrees of association. This provided good evidence that in both cases the silver ions had replaced the hydrogen atom in the –SH groups.

Both potentiometric and i.r. investigations support the following reaction mechanisms for the case of 2-thiouracil and the quite similar 6-methyl-2-thiouracil:



and the following mechanism for the titration of 2,4-dithiouracil



SUMMARY

Potentiometric titrations of 2-thiouracil, 6-methyl-2-thiouracil and 2.4-

dithiouracil with silver nitrate solutions, with a sulphide-selective indicator electrode, are described. Satisfactory direct titrations of all three compounds are possible in the range 10^{-1}–10^{-3} M at about pH 8; the titration curve of 2,4-dithiouracil shows two sharp potential breaks. The silver complexes of the thiouracil compounds are formed.

REFERENCES

1 M. K. Pápay, K. Tóth and E. Pungor, *Anal. Chim. Acta*, 56 (1971) 291.
2 M. K. Pápay, V. P. Izvekov, K. Tóth and E. Pungor, *Anal. Chim. Acta*, 69 (1974) 173.
3 *U.S. Pharmacopeia*, Mack Pub. Co. Easton, Pa., 15th Revision, 1955, p. 443.
4 *British Pharmacopeia*, Pharmaceutical Press, London, 1953, p. 349.
5 R. Middeldorf, *Arzneim. Forsch.*, 1 (1951) 311.
6 H. Wojahn, *Arch. Pharm. (Weinheim)*, 284 (1951) 243.
7 H. Wojahn and E. Wempe, *Pharm. Zentralh.*, 92 (1953) 124.
8 H. Wojahn and E. Wempe, *Arch. Pharm. (Weinheim)*, 286 (1953) 344.
9 C. F. Abbot, *J. Pharm. Pharmocol.*, 5 (1953) 53.
10 J. F. Alicino, *Microchem. J.*, 4 (1960) 551.
11 K. J. Jensen, B. M. Dahl and P. G. Nielsen, *Acta Chem. Scand.*, 25 (1971) 2029.
12 E. Ja. Shtenberg, Ju. I. Mushkina and A. I. Finkelshtein, *Opt. Spektrosk.*, 33 (1972) 1072.
13 E. Emmet Reid (Ed.), *Organic Chemistry of Bivalent Sulfur*, Chemical Publ., New York, 1966, p. 237.

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SHORT COMMUNICATION

Neutron activation analysis for uranium in fossil bones

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(Received 10th July 1974)

It has been found[1,2] that relative dating of fossil bones found in the same deposit can be accomplished by measuring the fluorine, nitrogen, manganese or uranium contents, as the contents of these elements increase with burial age of fossil bone. In this respect, it would be interesting to study the variation of uranium content in fossil bone with its age; but, in order to accumulate experimental data, a reliable method for the determination of uranium in such samples is essential. Several analytical procedures[3–6] have been developed for the determination of uranium in bones and various types of rocks. Among them, activation analysis seems most suitable because of its high sensitivity and reliability. Nozaki *et al.*[6] used ^{239}U, which is produced by the ^{238}U(n, γ)^{239}U reaction, to assay uranium in human bones, drinking water and daily diet by means of the MIBK solvent extraction for radiochemical separation and a reactivation technique for yield evaluation. The main drawbacks of the use of ^{239}U are that ^{239}U has a short half-life (23.5 min), and that it needs a tedious procedure like reactivation to evaluate the chemical yield of uranium.

Most previously published procedures based on the measurement of ^{239}Np (a decay product of ^{239}U) activity[3,7,8] either omit the determination of chemical yield or require double countings, one for ^{239}Np and the other for ^{237}Np (α-counting) which is introduced for the evaluation of chemical yield. But if chemical separation is involved, it is attractive to use the ^{239}Np isotope because of its longer half-life (2.346 day). When a Ge(Li) detector is used and ^{238}Np is available for the determination of radiochemical yield, this feature is even more attractive. In this communication, a simple method is described for the accurate determination of uranium in fossil bones.

Experimental

Samples. The sample fossil bones were obtained from East Anglia, North Africa and other areas. The surface of the fossil bone was polished and washed with distilled water to remove the soil and other impurities, and then the bone was powdered and used for the experiment.

Irradiation. Weighed bone samples of about 100 mg were placed in a plastic capsule and irradiated in the central core hole of the TRIGA type reactor at Rikkyo University for about 10 h at a neutron flux of about 10^{12} n cm^{-2} s^{-1}.

Uranium standards (U content 1.900 μg) were also irradiated in the same capsule. After irradiation, the samples were left for about 1 day to allow the activity of ^{239}Np to grow and the short-lived radioactivities to decay before chemical separation was started.

Chemical separation. Place the irradiated sample in a 200-ml beaker. Add 20 ml of concentrated nitric acid, 5 ml of concentrated perchloric acid, 4 ml of ^{237}Np carrier (about 2 μg of ^{237}Np) containing a known amount of ^{238}Np radioactivity, and 2 ml of lanthanum collector (about 5 mg of $LaCl_3$). Cover with a watch glass and dissolve on a hot plate by gentle heating. After a clear solution has been obtained, begin the chemical separation. The chemical procedure adopted in this experiment is a modification of the method of Hamaguchi *et al.*[9], which is schematically represented in Fig. 1.

Irradiated sample
  | ^{237}Np carrier (+known amount of ^{238}Np)
  | 20 ml conc. HNO_3 + 5 ml conc. $HClO_4$
  | La collector
Solution
  0.3 g NH_2OH. HCl (to reduce Np to lower oxidation states)
Centrifugation
Aqueous phase (discard) — LaF_3 fraction
  | 0.1 g H_3g H_3BO_3 + 10 ml conc. HNO_3
  | heat gently
  | 20 ml NH_4OH in glass tube
  | heat
Centrifugation
Aqueous phase (discard) — $La(OH)_3$ fraction
  | 5 ml conc. HNO_3
  | 5 ml Fe scavenger (about 5 mg $FeCl_3$)
  | 0.1 g $KBrO_3$ (to oxidize Np)
  | add Na_2CO_3 until complete precipitation of basic carbonates
Centrifugation
Basic carbonates (discard) — Aqueous phase
  | acidify with HNO_3 and boil off CO_2
  | La collector
  | add NH_4OH until complete precipitation of $La(OH)_3$
  | heat gently
Centrifugation
Aqueous phase (discard) — $La(OH)_3$ fraction
  | acidify with HNO_3
Counting
^{238}Np + ^{239}Np

Fig. 1. The scheme for chemical separation.

Counting. A Ge(Li) detector connected to a 400-channel pulse-height analyser was used for the measurements of the radioactivities of ^{238}Np and ^{239}Np. The

^{238}Np determination was made by summing the 0.986- and 1.030-MeV photopeaks, and the 0.210-, 0.228- and 0.278-MeV peaks were used for the determination of ^{238}Np. The γ-ray spectra of the final solution showed that the radiochemical purity of the neptunium was excellent.

Determination of chemical yield. The chemical yield can be obtained by comparing the activity of ^{238}Np introduced with carrier solution (initial activity of ^{238}Np) with the final ^{238}Np activity after chemical separation. But as will be shown later, it is unnecessary to determine the chemical yield for the determination of uranium content in the sample.

Results and discussion

When the same amount of ^{238}Np activity is added to both the sample and the standard solutions, the uranium content in the sample can be calculated by use of the following formula

$$\text{p.p.m. in sample} = p_9 s_8 w_s / p_8 s_9 w$$

where p_9 is the peak area of ^{239}Np in counts per unit time for the final sample solution after chemical separation; p_8, the peak area of ^{238}Np in counts per unit time for the final sample solution after chemical separation; s_9, the peak area of ^{239}Np in counts per unit time for the standard solution; s_8, the peak area of ^{238}Np in counts per unit time for the standard solution; w_s, the weight of uranium in the standard in μg; and w, the weight of the sample in g.

It is noteworthy that ^{238}Np(+ ^{237}Np) carrier solution can easily be obtained by neutron irradiation of ^{237}Np solution. As the half-lives of ^{238}Np (2.10 day) and ^{239}Np (2.346 day) are very close, corrections for the decays may be unnecessary when the activity measurements of the sample and the standard are made in a

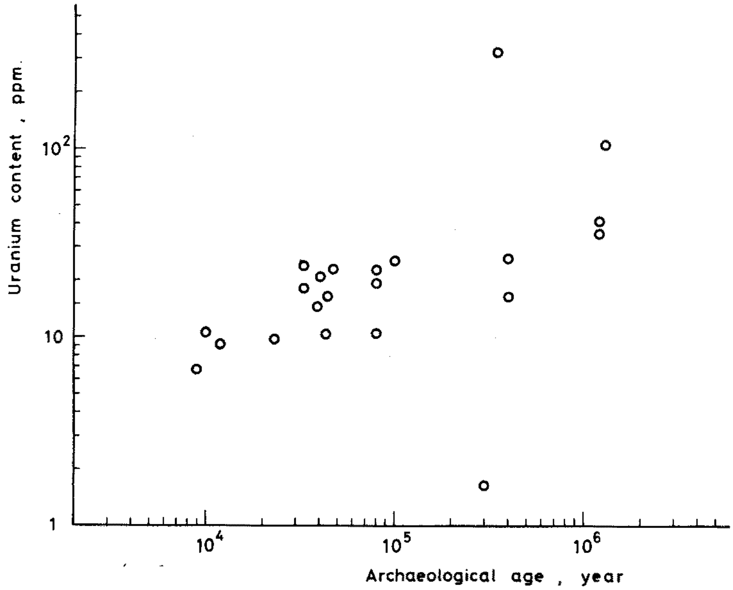

Fig. 2. Relation between uranium content and the burial age of fossil bone.

short time interval. It was found that by this method the uranium content in fossil bone at the p.p.m. level could be determined with a precision of less than 5%.

Results of the analyses done in this work are given in Fig. 2; the archaeological age determined by other methods is taken as the abscissa. The trend that the uranium content in the fossil bone increases with its age is clearly seen. It may also be seen that these fossil bones are highly enriched with uranium, as the uranium content of modern animal bone ranges from about 0.1 p.p.b. up to about 10 p.p.b.[6]. As the uranium content of fossil bone ranges from about 1 p.p.m. to about 100 p.p.m., different standards with different orders of uranium may improve the accuracy of the determination. It is obvious that the proposed analytical procedure is applicable to the determination of uranium in other matrices such as biological materials and rocks.

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REFERENCES

1 K. P. Oakley and C. R. Hoskins, *Nature (London)*, 165 (1950) 379; K. P. Oakley in D. Brothwell and E. Higgt (Eds.), *Science in Archaeology*, Thames and Hudson, 1963, pp. 24–34.
2 N. Shimoda and H. Ozaki, *Bull. Nat. Sci. Mus. Tokyo*, 10 (1967) 377.
3 J. W. Morgan and J. F. Lovering, *Anal. Chim. Acta*, 28 (1963) 405.
4 G. L. Booman and J. E. Rein in I. M. Kolthoff and J. P. Elving (Eds.), *Treatise on Analytical Chemistry, Vol. 9, part II*, Interscience, New York, 1962, pp. 138–148.
5 J. C. Cobb and J. L. Kulp, *Geochim. Cosmochim. Acta*, 24 (1961) 226.
6 T. Nozaki, M. Ichikawa, T. Sasuga and M. Inarida, *J. Radioanal. Chem.*, 6 (1970) 33.
7 D. N. Edgington, *Intern. J. Appl. Radiat. Isotop.*, 18 (1967) 11.
8 M. Picer and P. Strohal, *Anal. Chim. Acta*, 40 (1968) 131.
9 H. Hamaguchi, G. Reed and A. Turkevich, *Geochim. Cosmochim. Acta*, 12 (1957) 337.

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SHORT COMMUNICATION

Fluorescence of phenyl salicylate

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Phenyl salicylate (salol) has been employed industrially as a sunscreen, enteric coating for delayed action tablets and plasticizer, and in a variety of other pharmaceutical applications similar to those of aspirin. Its structural similarity to salicylic acid and methyl salicylate suggests that the spectroscopic properties of all three compounds should be similar. However, while these compounds fluoresce quite intensely throughout the pH region and in concentrated acid[1], phenyl salicylate exhibits a barely detectable fluorescence below pH 7 and in sulfuric acid above H_0 -6. In order to understand better the spectroscopic behavior and to determine the optimal conditions for fluorimetric determination of phenyl salicylate, the present study of the pH and solvent dependences of the electronic spectra of salol was undertaken.

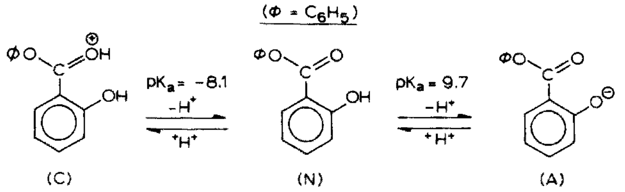
Experimental

Absorption spectra were taken on a Beckman DB-GT spectrophotometer. Fluorescence spectra were recorded on a Perkin-Elmer MPF2A fluorescence spectrophotometer whose monochromators were calibrated against the xenon line emission spectrum and whose output was corrected for instrumental response by means of a rhodamine-B quantum counter. Measurement of pH was made on an Orion Model 801 pH meter with a Beckman silver/silver chloride–glass combination electrode.

Phenyl salicylate (Merck) was purified by recrystallization from chloroform. Reagent-grade sulfuric acid, sodium hydroxide, sodium acetate, acetic acid, sodium dihydrogenphosphate and sodium monohydrogenphosphate were used to prepare solutions of known pH and Hammett acidity[2]. Spectroquality chloroform and ethanol (Matheson, Coleman and Bell, Inc.) were also employed as solvents.

Results and discussion

The long wavelength absorption and fluorescence maxima of phenyl salicylate are presented in Table I. The shifts of the long wavelength absorption maximum of the neutral molecule (N) to lower frequencies, on protonation to form the cation (C) in concentrated acid, and on dissociation to form the anion (A) in dilute base, suggest the ground state ionization sequence depicted in Scheme 1.



(Scheme 1)

TABLE I

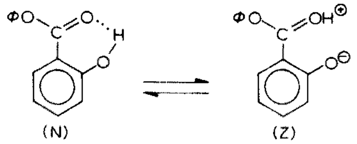
LONG WAVELENGTH ABSORPTION ($\bar{\nu}_a$) AND FLUORESCENCE ($\bar{\nu}_f$) MAXIMA OF PHENYL SALICYLATE IN VARIOUS SOLVENTS

Solvent	$\bar{\nu}_a(cm^{-1}\cdot 10^{-4})$	$\bar{\nu}_f(cm^{-1}\cdot 10^{-4})$
Sulfuric Acid (H_0 − 10.0)	3.01	2.48
Water (pH = 1.0)	3.26	~2.86 + ~2.27
Ethanol	3.22	2.94
Chloroform	3.20	2.20
Water (pH 11.0)	2.95	2.48

Upon traversing the Hammett acidity region from $H_0 - 10$ to $H_0 - 6$, the blue fluorescence of the cation (C) is quenched, the midpoint of the quenching occurring at the ground state pK_a of −8.1. From $H_0 - 6$ to pH 7, a barely discernible, broad area of fluorescence ranging from 320 nm to 500 nm, occurs. Above pH 7, the intense blue fluorescence of the anion appears (centered at pH = $pK_a = 9.7$) and rises to a maximum at pH 12.0. Above pH 13, rapid hydrolysis of the phenyl ester is apparent from the shift of the fluorescence spectrum to shorter wavelengths with time. Even at pH as low as 10, slow hydrolysis of the phenyl ester occurs. The fluorescences of the cation and anion derived from phenyl salicylate occur in the same general spectral region as the fluorescences of the corresponding species derived from salicylic acid and methyl salicylate.

Initially it was thought that the fluorescences occurring in the region $H_0 - 6$ to pH 7 might be due to impurities in the sample. However, repeated recrystallization and resublimation failed to alter the pattern of the extremely weak emission in the 320–500 nm region. Moreover, the apparent peak positions of this emission (Table I) are close to the fluorescence of the neutral molecule and zwitterion derived from methyl salicylate[1] and therefore may reasonably be attributed to fluorescence from the neutral molecule and zwitterion derived from phenyl salicylate.

In ethanol the fluorescence of phenyl salicylate is moderately intense, maximal at 340 nm (close to the maximum of *o*-methoxybenzoic acid) and tails off on the long-wavelength side, very gradually to *ca.* 500 nm. In chloroform, the fluorescence of phenyl salicylate is also moderately intense, but maximal at 455 nm, tailing off gradually on the short-wavelength side to *ca.* 320 nm. The latter emission is similar in maximum to the fluorescence of methyl salicylate in chloroform. These observations indicate that the fluorescence maximum in ethanol is due to emission from the neutral molecule (N) derived from phenyl salicylate while the fluorescence maximum in chloroform is due to emission from the zwitterion (Z) resulting from the phototautomerism of the neutral molecule in the lowest excited singlet state (Scheme 2).



(Scheme 2)

The tailing on the long wavelength side of the fluorescence of (N) in ethanol is thus attributed to a small degree of phototautomerism in that solvent while the tailing on the short wavelength side of the fluorescence of (Z) in chloroform is attributed to a high degree of phototautomerism and a small residual fluorescence from the remaining excited neutral species in that solvent.

The appearance of constant intensity fluorescence of the neutral molecule and zwitterion from $H_0 - 6$ to pH 7 is unlike that of methyl salicylate, in which the zwitterion alone fluoresces in moderately concentrated acid and both the zwitterion and neutral species fluoresce in the pH region. In the latter compound, the fluorescence of the zwitterion in concentrated acid is attributed to bimolecular phototautomerism, requiring protonation as a first step. The fluorescences of the neutral species and zwitterion in the pH region are attributed to partial intramolecular tautomerism, the concentration of protonating species being too low in the pH region to protonate the excited neutral species. Because of the failure of phenyl salicylate to demonstrate excited state protonation, as reflected by the coincidence of the inflection regions in which the absorption and fluorescence spectra change, it must be concluded that the phototautomerism of the neutral species to form the excited zwitterion is entirely intramolecular. Because this process occurs only partially, as evidenced by the occurrence of fluorescence from the neutral species, the rate constant for phototautomerism must be very near the reciprocal of the mean lifetime of the lowest excited singlet state. Since, with the instrumentation employed, fluorescences with lifetimes of 10^{-11} s^{-1} or greater can be detected and the fluorescences of the neutral species and zwitterion in water are very near the limit of detection of the fluorescence spectrometer, it may be concluded that the rate constant for intramolecular phototautomerism of the neutral species to the excited zwitterion is about 10^{11} s^{-1}. In this regard, it is rather interesting that although the quantum yields of fluorescence (and therefore the lifetimes) of the neutral species and zwitterion are much higher in ethanol and chloroform, respectively, very little phototautomerism occurs in ethanol and nearly complete phototautomerism occurs in chloroform. This suggests that in strongly hydrogen bonding solvents (*e.g.* water and ethanol), intermolecular hydrogen bonding with the solvent weakens the intramolecular hydrogen bond between the phenolic group and the carbophenoxy group and thereby decreases the rate of intramolecular phototautomerism in phenyl salicylate. Moreover, in water and sulfuric acid, the strongest hydrogen-bonding solvents studied, the intermolecular hydrogen-bonding with the solvent appears largely to quench the fluorescence of the neutral species. This may also limit the efficiency of phototautomerism of the neutral species derived from phenyl salicylate in these solvents.

In view of the fact that phenyl salicylate fluoresces most intensely in chloroform, this appears to be the solvent of choice for any fluorimetric analysis. However, in the presence of other salicylate-type drugs, most of which fluoresce at 400–450 nm, the short wavelength of fluorescence of phenyl salicylate in ethanol may be advantageous from the point of view of selectivity.

REFERENCES

1 P. J. Kovi, C. L. Miller and S. G. Schulman, *Anal. Chim. Acta*, 61 (1972) 7.
2 M. J. Jorgensen and D. R. Hartter, *J. Amer. Chem. Soc.*, 85 (1963) 878.

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SHORT COMMUNICATION

A solvent extraction–atomic fluorescence system for the determination of cadmium in complex samples

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(Received 10th July 1974)

The atomic fluorescence of cadmium was reported in one of the first papers on analytical atomic fluorescence[1], and exceptionally low detection limits have been reported[2] for this element using this technique. Despite the apparent promise of the atomic fluorescence technique for this determination, no applications have been reported for cadmium in complex samples until very recently when Rains *et al.*[3] described an atomic fluorescence procedure for the determination of cadmium in SRM-1571 (Orchard Leaves) and SRM-1577 (Bovine Liver). With both samples the sensitivity of the fluorescence technique was adequate to allow direct determination on the solution resulting from digestion of the sample with no prior separation or concentration. A hydrogen–argon–entrained air flame was used, and a large scatter correction was required. The scatter correction was achieved instrumentally by a system in which the flame was alternately irradiated with a continuum and line source. With this type of system, achievement of a proper scatter correction may be critically dependent on the method employed for balancing the two beams.

In the present report, an atomic fluorescence procedure for cadmium which avoids the scatter problem is described. The cadmium is separated from the sample matrix before measurement with an ion-association solvent-extraction technique. The applicability of the procedure for complex samples has been tested by determining cadmium in SRM-1577 (Bovine Liver) and comparing the results with previously reported values.

Experimental

Apparatus. The arrangement employed for fluorescence measurements was similar to that of other studies[4]. Instrumental requirements were as follows. The cadmium electrodeless discharge lamp operated with heating above a Type A antenna[5]. Power was supplied by a Raytheon PGM-10 2450-MHz, 100-W, microwave power supply. The monochromator was a McPherson-Heath EU-700 with a 2-mm slit width. A Hamamatsu TV R166 "solar blind" photomultiplier operated

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at 800 V, was used with a Jarrell-Ash 26-780 amplifier. An Alkemade-type burner[6] was used; flow rates were 11.5 l min^{-1} air, 7.1 l min^{-1} hydrogen, and 11.5 l min^{-1} nitrogen (sheath).

Reagents. Prepare cadmium stock solution of 1000 μg Cd ml^{-1} by dissolving 2.2820 g of $3CdSO_4 \cdot 8H_2O$ in deionized distilled water and dilute to 1 l; prepare lower concentrations by successive dilution. Prepare standards for extracted samples to contain 5% (v/v) ethylenediamine. For the extraction reagent, tricaprylmethylammonium iodide, convert the commercial chloride salt (Aliquat 336; McKerson Corp., Minneapolis) to the iodide (Aliquat 336-I) as described by McDonald and Moore[7]. Use the reagent for extractions as a 5% (v/v) solution in xylene. (Preliminary studies showed high blank values for cadmium when the solution was used without purification. Satisfactory blank levels were obtained by stripping the Aliquat 336-I solution with an equal volume of 5% ethylenediamine–water solution before use.)

Procedure. Dry bovine liver samples by lyophilization as recommended. Weigh samples of approximately 500 mg each, and digest with sulfuric acid and hydrogen peroxide as described by Gorsuch[8]. Take blanks through the same procedure.

For extraction, place a 20-ml aliquot of sample or blank in a 60-ml separatory funnel, and add 1.6 ml of 57% hydriodic acid and 4 ml of Aliquat 336-I in xylene. Shake for 1 min, and then allow the phases to separate. Discard the aqueous layer, add 4 ml of 5% ethylenediamine solution and shake for 1 min. Discard the organic phase, and use the aqueous-ethylenediamine phase for atomic fluorescence measurements.

Results and discussion

Extraction system. A preliminary investigation of the extraction efficiency with equal volumes at each stage showed a slight enhancement of the atomic fluorescence signal for extracted standards compared with unextracted standards of the same nominal concentration. This discrepancy was eliminated by preparing the unextracted standards to be approximately 5% in ethylenediamine. In the procedure finally adopted, a five-fold reduction in volume is effected in the extraction with Aliquat 336-I. A rectilinear correlation was found between the fluorescence signals for five-fold concentrated extracts of standard solutions and those for aqueous-ethylenediamine standards prepared to have a cadmium concentration five times the concentration of the standards extracted. The lowest point on the correlation curve corresponded to a concentration of 0.005 μg Cd ml^{-1} for the ethylenediamine standards (0.001 μg ml^{-1} for the initial concentration of the solution to be extracted). McDonald and Moore[7] claim that cadmium can be concentrated at least 100-fold with the Aliquat 336-I–xylene system. A brief study supported this claim for initial cadmium concentrations as low as 0.001 μg ml^{-1}.

The Aliquat 336-I extraction system has several advantages over the more commonly used chelating systems for analytical atomic spectrometry. Standards are readily prepared; chelating systems usually require that standards as well as samples be carried through the extraction procedure. Large concentration factors can be achieved; with chelating systems, the size of the concentration factor is often limited by the solubility of the organic phase in water. For example, with MIBK as the organic phase, the maximum concentration that can be achieved is about 10-fold[9]. Finally, the organic phase is easily purified before use by shaking with 5% ethylenediamine.

The principal disadvantage of the Aliquat 336-I extraction system is that one additional operation, the back-extraction step, is required. Also it is probable that there is some loss of atomization efficiency in spraying aqueous solutions rather than organic solutions, but for atomic fluorescence measurements this is compensated for by the lower flame background emission obtained with aqueous solutions, and in this work better detection limits were obtained with aqueous solutions.

Analytical curves and precision. Measurements were carried out with both separated acetylene–air and hydrogen–air flames. The lower background hydrogen flame was somewhat more convenient and provided a slightly better detection limit (approximately 0.7 ng ml^{-1}). Since the extraction step effectively avoided problems from matrix interference and scatter effects, the separated hydrogen–air flame was used for all subsequent measurements. The analytical curve exhibited the usual shape for atomic fluorescence measurements with a line source. It was linear from the lowest concentration measured (0.005 μg ml^{-1}) to nearly 10 μg ml^{-1}.

TABLE I

PRECISION FOR FIVE-FOLD CONCENTRATED EXTRACTS AND ETHYLENEDIAMINE STANDARDS

5% Ethylenediamine standards		*Concentrated extracts*	
Concentration (μg ml^{-1})	s_r[a]	*Original concentration (μg ml^{-1})*	s_r[a]
0.0050	7.9	0.0010	2.8
0.050	2.9	0.010	2.1
0.50	0.7	0.10	2.3
5.0	1.2	1.0	1.5
50.0	1.7	10.0	0

[a] Computed from six replicates.

Table I reports the precision as the percent relative standard deviation computed from six replicates at various concentration levels with and without extraction before measurement. The detection limit reported here (without an extraction step) is comparable to the best value reported[10] for atomic absorption with no prior concentration and is considerably poorer than the best reported[2] value for atomic fluorescence. The discrepancy in atomic fluorescence results may well be due to difference in the intensity of the exciting sources. A Perkin-Elmer Model 303 atomic absorption spectrophotometer was used to investigate the atomic absorption detection limits for cadmium; the lowest concentration detectable was about a factor of 10 larger than the manufacturer's claim of

0.01 μg ml^{-1}, which is, of course, about 15-fold larger than either our atomic fluorescence value or the best reported atomic absorption value. The source of the discrepancy in atomic absorption values is unknown.

TABLE II

COMPARISON OF RESULTS FOR CADMIUM IN SRM-1577 BOVINE LIVER

This study (μg g^{-1})	*Rains et al.*[3] *(μg g^{-1})*	
	A.f.s.	*A.a.s.*
Average 0.30_4[a]	0.25_3	0.26_6
s 0.023	0.024	0.020
s_r 7.6	9.8	7.6

[a] Mean of five replicates.

Bovine liver analysis. Table II summarizes the results of the determination of cadmium in SRM-1577 in this study and those of Rains *et al.*[3]. The provisional certificate for SRM-1577 reports the cadmium content as 0.27±0.04 μg g^{-1} on the basis of determination by atomic absorption spectrophotometry, isotope dilution spark source mass spectrography, and polarography. Thus the value for cadmium obtained in this study is in reasonable agreement with other reported values, and there appear to be no major obstacles to extending this extraction–atomic fluorescence method to other complex samples.

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REFERENCES

1 J. D. Winefordner and R. A. Staab, *Anal. Chem.*, 36 (1964) 165.
2 K. E. Zacha, M. P. Bratzel, J. D. Winefordner and J. M. Mansfield, *Anal. Chem.*, 40 (1968) 1733.
3 T. C. Rains, M. S. Epstein and O. Menis, *Anal. Chem.*, 46 (1974) 207.
4 W. E. Rippetoe, V. I. Muscat and T. J. Vickers, *Anal. Chem.*, 46 (1974) 796.
5 R. F. Browner, B. M. Patel, T. H. Glenn, M. E. Rietta and J. D. Winefordner, *Spectrosc. Lett.*, 5 (1972) 311.
6 J. K. Grime and T. J. Vickers, *Anal. Chem.*, 46 (1974) 1810.
7 C. W. McDonald and F. L. Moore, *Anal. Chem.*, 45 (1973) 983.
8 T. T. Gorsuch, *The Destruction of Organic Matter*, Pergamon, London, 1970.
9 W. J. Price, *Analytical Atomic Absorption Spectrometry*, Heyden, London, 1972, p. 99.
10 Varian-Techtron Applications Group, *Detection Limits for Model AA-5 Atomic Absorption Spectrophotometer*, Varian-Techtron, Walnut Creek, Calif.

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SHORT COMMUNICATION

The determination of arsenic, antimony and tin in steels by flameless atomic absorption spectrometry

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Arsenic, antimony and tin are present in steels and can cause cracking in welded sections. In this connection it was necessary to determine amounts of these elements in the range 0.002–0.1% in small steel samples. The use of flameless atomic absorption for the analysis of small samples has been reviewed by Kirkbright[1] and its application to the determinaton of antimony in metal samples after a solvent extraction stage has been described by Yanagisawa *et al.*[2]. This communication describes how flameless atomic absorption spectrometry can be used to determine arsenic, antimony and tin in small metal specimens without the need for a solvent extraction stage.

Experimental

Apparatus. A Varian Techtron AA5 atomic absorption spectrometer was used in conjunction with a Varian Techtron Model 63 carbon rod atomizer. This has a carbon furnace in the form of a cylindrical graphite tube 3 mm in diameter and 9 mm in length. A solution of the sample is injected through a small hole in the side of the tube and the atoms produced by electrically heating the furnace are viewed along the tube axis. A Hamamatsu TV Type R106 photomultiplier was used in place of the standard HTVR 213 tube and the signals produced were recorded on a Honeywell Electronik 19 recorder. Argon was used as the inert shield gas at a flow rate of $4\,\mathrm{l\,min^{-1}}$. Hollow-cathode lamps (Varian Techtron) were used as the radiation sources for arsenic, antimony and tin. The lamps were run at currents of 7,10 and 8 mA and the wavelengths used were 193.7, 217.6 and 224.6 nm, respectively. A 5-μl syringe (Varian Techtron) was used to inject the samples into the carbon tube furnace.

Deionized water was used throughout.

Calibration solutions. British Chemical Standard Steel Nos. 320–330 and No. 260/3 containing known amounts of arsenic, antimony and tin were dissolved in dilute nitric acid as described below.

Procedure. Weigh accurately 1.0 g of steel, in the form of millings or drillings, into a 250-ml borosilicate beaker and add 30 ml of dilute (A.R.) nitric acid (1+4); warm gently until dissolution is complete. Transfer the solution to a 100-ml graduated flask and make up to the mark with water. Smaller steel samples can be similarly prepared by keeping the sample weight, volume of dilute nitric acid and final solution volume in the same ratio.

Mix the sample solution well, and determine the arsenic, antimony and tin by injecting successive 5-μl volumes into the carbon furnace and comparing the signals produced with those from the similarly prepared calibration solutions.

The most suitable instrument operating conditions found for measuring these three elements are given in Table I.

TABLE I

OPTIMAL OPERATING CONDITIONS FOR DETERMINATION OF ARSENIC, ANTIMONY AND TIN

Element	*Arsenic*	*Antimony*	*Tin*
Wavelength setting (nm)	193.7	217.6	224.6
Slit width setting (μm)	200	200	200
Sample volume (μl)	5	5	5
Lamp current (mA)	7	10	8
Furnace conditions[a]			
Dry V (s)	3 (30)	3 (30)	3 (30)
Ash V (s)	4 (15)	4 (15)	4 (15)
Step atomize V (s)	6 (6)	6.5 (5)	–
Ramp atomize V (s)	—	—	7 (5)
Recorder sensitivity (mV f.s.d.)	2	20	5

[a] For each step, the voltage is given followed by the time (in brackets). In all cases, the argon flow was 66 ml s^{-1}.

Discussion and results

Argon was used as the inert support gas in all three determinations. Variations in argon flow from between 50 and 80 ml s^{-1} made no appreciable difference to the absorption signal, consequently the flow rate was set at a constant 66 ml s^{-1} (4 l min^{-1}).

Estimates of the carbon tube temperature during the final step atomize or ramp atomize stage were made with a disappearing filament (Foster Instrument Co) optical pyrometer, and indicated that a temperature of 3000 °C was achieved. This high temperature resulted in well defined absorption signals and ensured that there were no residual traces to interfere with subsequent analyses.

The effect of dissolving the steel sample in different mineral acids and the effect of various metal cations on the absorption signal were studied. Only steels that were dissolved in dilute nitric acid gave acceptable absorption signals for all three elements. No signals were obtained for arsenic and tin when dilute hydrochloric acid was used and when dilute sulphuric and perchloric acids were used the values for tin were low and not reproducible. A Gutzeit test made on the vapours evolved during the nitric acid dissolution stage gave a negative result indicating that no measurable loss of arsenic had occurred.

The effect of various cations on the absorption signal was studied by dissolving iron containing arsenic, antimony and tin in dilute nitric acid, adding the

BLE II

RCENTAGE CHANGE OF ABSORPTION SIGNAL OF ARSENIC (11.75 ng), ANTIMONY (5.75 ng) D TIN (13.5 ng) ON ADDITION OF POTENTIAL INTERFERING CATIONS

mple volume 5 μl; all samples contained 50 μg iron plus the added cation. Instrumental conditions as in Table I.)

nount of interfering ment in 5 μl sample		*Percentage interference in determination of*		
ment	*Amount (ng)*	*Arsenic*	*Antimony*	*Tin*
icon	25; 250; 2500	0, 0, 0	0, 0, 0	0, 0, 0
romium(III)	25; 250; 2500	0, 0, 0	0, 0, 0	0, 0, 0
	10,000; 15,000	−15, −20	−40, −50	−35, −65
anganese(II)	25; 250; 2500	0, 0, 0	0, 0, 0	0, 0, 0
olybdenum(VI)	25; 250; 2500	0, 0, +10	0, +10, +20	0, 0, +10
ckel(II)	25; 250; 2500	0, 0, 0	0, 0, 0	0, 0, 0
	10,000; 15,000	0, 0	0, 0	−15, −15
nadium(IV)	25; 250; 2500	0, 0, 0	0, 0, 0	0, 0, 0
tanium(IV)	25; 250; 2500	0, 0, 0	0, 0, −20	0, +10, +10
obium(V)	25; 250; 2500	0, 0, 0	0, −10, −25	0, +15, +15

cation to this solution and then injecting an aliquot into the carbon tube furnace. The results are given in Table II.

The detection limits of the method, defined as that weight of element which gave an average absorbance peak signal corresponding to twice the peak-to-peak noise of the base line, were $1 \cdot 10^{-9}$ g for arsenic, $3 \cdot 10^{-10}$ g for antimony and $8 \cdot 10^{-10}$ g for tin. In all three determinations there was curvature of the calibration curve, which limited the optimal operating range to 0.05–3 μg As ml^{-1}, 0.05–3 μg Sb ml^{-1} and 0.1–3 μg Sn ml^{-1}. Samples which resulted in solutions that were slightly more concentrated than these could still be analysed by diluting the sample solution with a high purity iron solution.

The precision of the method is such that for a mild steel containing 0.033% arsenic, 0.024% antimony and 0.027% tin, the standard deviations about the mean of 10, 12 and 12 determinations, respectively, were 0.0019% for arsenic, 0.0010% for antimony and 0.002% for tin. Similarly, a steel that contained 0.011% arsenic, 0.005% antimony and 0.009% tin gave standard deviations about the mean of 12, 12 and 11 determinations respectively which were 0.001% for arsenic, 0.0003% for antimony and 0.0009% for tin. A 5-μl injection sample was used in all determinations.

The high absolute sensitivity of the method means that these three elements can be determined in a very small steel sample such as might be obtainable from the immediate vicinity of a weld failure.

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REFERENCES

1 G. F. Kirkbright, *Analyst (London)*, 96 (1971) 609.
2 M. Yanagisawa and I. Takeuchi, *Anal. Chim. Acta*, 64 (1973) 381.

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SHORT COMMUNICATION

Colorimetric determination of sulfate in water with barium violurate

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Sulfate salts are widely distributed in nature and may be present in natural waters in concentrations up to several thousand p.p.m. Because of the cathartic action of sodium and magnesium sulfate, the recommended limit in potable waters is 250 p.p.m.

Methods currently in use include gravimetric or turbidimetric determination of precipitated barium sulfate[1]. Numerous other methods have been proposed: exchange of colored chloranilate anion from insoluble barium chloranilate by sulfate in partially non-aqueous solution[2], diazotization and coupling of benzidine from precipitated benzidinium sulfate to form an azo dye[3,4], reaction of benzidine precipitated by sulfate with phosphotungstomolybdic acid to produce a colored compound[5], ultraviolet absorption of the $[FeSO_4]^+$ complex cation[6], ultraviolet absorption of excess 4-amino-4′-chlorodiphenyl not precipitated by sulfate[7], and exchange of chromate from insoluble barium chromate by sulfate followed by spectrophotometric or titrimetric determination of the chromate anion[8–10]. Reduction of sulfate to sulfide and colorimetric determination of the sulfide has been used[11–13]. 2-Aminoperimidine has been reported to be more suitable than barium, benzidine, and 4-amino-4′-chlorodiphenyl for nephelometric determinations of sulfate ion[14].

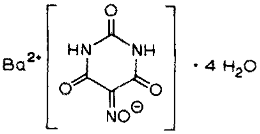
The relatively high concentrations of sulfate usually found in natural waters do not require extreme sensitivity in the method employed. Freedom of interference from other ions that may be present in high or variable concentrations is desirable, as are speed and convenience.

In the method described here, sulfate ion is determined by displacement of violurate anion from barium violurate at pH 6.0–6.2 and spectrophotometric measurement of the violurate anion at 520 nm. Anions normally present in natural waters do not interfere, and cations which could interfere by forming sulfato complexes are removed by ion exchange. The use of mixed solvents is not required.

Experimental

The compounds used were reagent grade or the highest purity commercially available. Solutions were prepared in deionized water.

Reagent. Dissolve 7.85 g (0.05 mole) of violuric acid (Fisher Scientific) in 500 ml of water containing 2.0 g (0.05 mole) of sodium hydroxide. Stir at room temperature for 15–20 min to dissolve. Add 6.11 g (0.025 mole) of barium chloride dihydrate dissolved in a minimum of water to the sodium violurate solution and stir until supernatant solution is colorless or nearly so. Collect the precipitate on a sintered glass filter and wash with water until the filtrate tests negative for barium ion with sulfate solution. Dry the precipitate under vacuum at 10–20°C. The yield of the red, monoclinic barium salt crystals, $Ba(C_4H_2O_4N_3)_2 \cdot 4\,H_2O$, I, is 99% of theoretical.



Procedure. Pass the sample solution through a small column of Amberlite IR-120 ion-exchange resin (Rohm and Haas) in the sodium form. Add 0.15 g of barium violurate reagent to 10.0 ml of sample solution, in a small erlenmeyer flask, adjusted to pH 6.0–6.2 with dilute sodium hydroxide or hydrochloric acid solution. A small glass or metal spoon designed to deliver 0.14–0.15 g is convenient, with little loss of precision observed in the results. Shake the sample plus reagent mixture for 30 min at 25 ± 0.5°C with a wrist-action shaker and then filter through Whatman No. 5 or equivalent filter paper. Measure the absorbance at 520 nm within 5 min with a Spectronic 20 spectrophotometer.

Results and discussion

When the data shown in Table I for absorbance *versus* concentration of sulfate ion is plotted graphically, the relationship is seen to be linear between about 50 p.p.m. and 900 p.p.m. Precision is good up to 700 p.p.m. For concentrations of sulfate below 50 p.p.m., standard addition of sulfate should be employed to place the measurements on the linear portion of the curve. The linear portion of the calibration curve obeys the equation

$$\text{concentration (p.p.m.)} = (\text{absorbance} \times 1370) - 23$$

TABLE I

DATA FOR CALIBRATION CURVE

Concn, SO_4^{2-} (p.p.m.)	*Absorbance at 520 nm*[a]	*Standard deviation*	*Concn. SO_4^{2-} (p.p.m.)*	*Absorbance at 520 nm*[a]	*Standard deviation*
0	0.031	0.001	500	0.338	0.009
30	0.042	0.001	600	0.460	0.005
90	0.078	0.002	700	0.525	0.008
150	0.122	0.003	800	0.600	0.018
210	0.168	0.001	900	0.675	0.006
300	0.240	0.003	1000	0.728	0.021
400	0.318	0.002			

[a] Average of five determinations.

TABLE II

STUDY OF POSSIBLE ANION INTERFERENCES

Ion	*Salt*	*Concn. (p.p.m.)*	*Absorbance*
Blank	—	—	0.031
F^-	NaF	100	0.032
Cl^-	NaCl	1000	0.039
Br^-	NaBr	1000	0.036
NO_3^-	$NaNO_3$	100	0.039
HCO_3^-	$NaHCO_3$	1000	0.032
$H_2PO_4^-$, HPO_4^{2-}	KH_2PO_4	100	0.026
CN^-	KCN	100	0.034
S^{2-}	$Na_2S \cdot 9\,H_2O$	50	0.044
OH^-	NaOH	10^{-3} *N*	0.043

TABLE III

STUDY OF POSSIBLE CATION INTERFERENCES

Ion	*Salt*	*Concn. (p.p.m.)*		*Absorbance at 520 nm*	*Absorbance after exchange*[a]
		Ion	SO_4^{2-}		
—[b]	—	0	0	0.031	—
—[b]	—	0	500	0.39	—
—[b]	—	0	900	0.67	—
Na^+	NaF	121	0	0.032	—
Na^+	NaCl	500	0	0.039	—
Na^+	NaCl	500	500	0.40	—
Na^+	NaCl	500	900	0.68	—
K^+	KCN	150	0	0.034	—
K^+	KCl	500	0	0.041	—
K^+	KCl	500	500	0.40	—
K^+	KCl	500	900	0.68	—
Mg^{2+}	$Mg(NO_3)_2 \cdot 6\,H_2O$	500	0	0.063	—
Mg^{2+}	$Mg(NO_3)_2 \cdot 6\,H_2O$	100	500	0.32	—
Mg^{2+}	$Mg(NO_3)_2 \cdot 6\,H_2O$	500	500	0.25	—
Mg^{2+}	$Mg(NO_3)_2 \cdot 6\,H_2O$	500	500	—	0.40
Ca^{2+}	$Ca(NO_3)_2 \cdot 4\,H_2O$	500	0	0.082	—
Ca^{2+}	$Ca(NO_3)_2 \cdot 4\,H_2O$	100	500	0.30	—
Ca^{2+}	$Ca(NO_3)_2 \cdot 4\,H_2O$	500	500	0.30	—
Ca^{2+}	$Ca(NO_3)_2 \cdot 4\,H_2O$	500	500	—	0.40
Al^{3+}	$Al(NO_3)_3 \cdot 9\,H_2O$	500	0	0.051	—
Al^{3+}	$Al(NO_3)_3 \cdot 9\,H_2O$	500	500	0.094	—
Al^{3+}	$Al(NO_3)_3 \cdot 9\,H_2O$	500	500	—	0.39
Mn^{2+}	$MnCl_2 \cdot 4\,H_2O$	100	0	0.041	—
Mn^{2+}	$MnCl_2 \cdot 4\,H_2O$	100	500	0.36	—
Mn^{2+}	$MnCl_2 \cdot 4\,H_2O$	100	500	—	0.40
NH_4^+	NH_4Cl	500	0	0.032	—
NH_4^+	NH_4Cl	500	500	0.32	—
NH_4^+	NH_4Cl	500	500	—	0.40
H^+	HCl	10^{-3} *N*	500	0.38	—

[a] Treatment consisted of passing sample solution through a column of IR-120 ion exhange resin in the sodium form before addition of reagent.

[b] Reference points from calibration curve data.

The quantity of reagent used need not be measured precisely. When 0.15 g of reagent is used, the blank is 0.03 when compared to water, and the limiting concentration of sulfate is about 900 p.p.m. Good precision is obtained when the temperature is controlled to ±0.5°C or less. The effect of time of reaction of reagent with sample solution indicated an optimal response at 30 min. The response of the reagent with increase in pH increases slightly with increase in pH from 4.5 to 8.5; pH 6.0–6.2 was selected as a convenient range on the most linear portion of the response *versus* pH curve. Adjustment of pH, if required, should be made with dilute sodium hydroxide or hydrochloric acid solution.

None of the common anions in the concentrations normally encountered interfere, as seen in Table II. Cations such as calcium and magnesium interfere by partially removing sulfate in weak sulfato complexes. Aluminum, as a typical small trivalent cation, interferes more strongly by forming more stable sulfato complexes. As shown in Table III, a sulfonic acid ion exchange resin in the sodium form destroys these complexes and removes the cation by exchange for sodium ion.

The absorbance at 520 nm produced by 500 p.p.m. sulfate increases linearly from 0.39 at 24°C to 0.61 at 69°C. Greater sensitivity for the method should be possible if the reaction of sample with reagent were done at a temperature higher than 25°C. Modification of the method for determinations at a higher temperature would require further study, as the blanks would be affected and a greater quantity of reagent might be necessary. The method as described minimizes the blank and responds to a wide range of sulfate concentrations.

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REFERENCES

1 *Standard Methods for the Examination of Water and Wastewater*, Am. Public Health Assoc., New York, 13th edn., 1971, pp. 330–336.
2 R. J. Bertolacini and J. E. Barney, *Anal. Chem.*, 29 (1957) 281.
3 B. S. Kahn and S. L. Leiboff, *J. Biol. Chem.*, 80 (1928) 623.
4 B. Klein, *Anal. Chem.*, 16 (1944) 536.
5 A. D. Marenzi and R. R. Banfi, *Anales farm. bioquim (Buenos Aires)*, 8 (1937) 62.
6 R. Goguel, *Anal. Chem.*, 41 (1969) 1034.
7 A. S. Jones and D. S. Letham, *Analyst (London)*, 81 (1956) 15.
8 I. Iwasaki, S. Utsumi and T. Tarutani, *J. Chem. Soc. Jap., Pure Chem. Sect.*, 74 (1953) 400.
9 K. Lang, *Biochem. Z.*, 213 (1929) 469.
10 S. Morgulis and M. G. Hemphill, *J. Biol. Chem.*, 96 (1932) 573.
11 L. Gustafsson, *Talanta*, 4 (1960) 227.
12 J. B. Davis and F. Lindstrom, *Anal. Chem.*, 44 (1972) 524.
13 G. Norwitz, *Analyst (London)*, 96 (1971) 494.
14 W. I. Stephen, *Anal. Chim. Acta*, 50 (1970) 413.

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SHORT COMMUNICATION

Photometric determination of tin in ores, rocks and alloys with pyrocatechol violet after extraction with N-benzoyl-N-phenylhydroxylamine

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Microamounts of tin in natural and industrial samples can be determined by various methods: spectral, neutron activation, spectrophotometric, polarographic, atomic absorption, etc.[1–11]. Spectrophotometric methods have the advantage of economy in apparatus and their low selectivity can be overcome by preliminary separations[12–17]. For the spectrophotometric determination of tin, phenylfluorone, dithiol and pyrocatechol violet have been widely applied[18–22]. Pyrocatechol violet offers some advantages over the other reagents. It is soluble in water and forms water-soluble tin(IV) complexes in relatively strongly acidic media, so that protective colloids are unnecessary. The molar absorptivity of the pyrocatechol violet complex of tin(IV) is higher than that of the other photometric reagents[23]. Under the conditions for tin(IV) determination, Ti(IV), Al, Ga, In, Zr, Th, Sb(III), Bi(III), Mo(VI), W(VI) and Fe(III), interfere[24], hence a prior separation of tin is essential.

A spectrophotometric method for the determination of micro amounts of tin in natural and industrial samples, after extractive separation of tin with N-benzoyl-N-phenylhydroxylamine (BPHA)[25] is described in this communication.

Experimental

Apparatus. A Spekol ZV spectrophotometer was used.

Standard solution of tin(IV) (1000 µg ml^{-1}). Dissolve 0.7384 g of $SnCl_4 \cdot 5H_2O$ (A.R. grade) in 150 ml of 10 *M* hydrochloric acid in a 250-ml measuring flask and dilute to the mark. Standardize the solution gravimetrically, by precipitation as the hydroxide and weighing as oxide. Prepare solutions containing 100 and 10 µg Sn ml^{-1} by dilution with 6 *M* hydrochloric acid.

Reagents. BPHA solution (1% w/v in 50% v/v acetic acid) and pyrocatechol violet solution (aqueous 0.04% w/v) were stored in the refrigerator.

All reagents were of analytical-reagent grade. Before use chloroform was rinsed with water and purified by distillation.

Decomposition of the samples. Tin occurs in rocks and poor tin ores mainly as cassiterite (tin dioxide); it is generally acknowledged that its decomposition is a serious analytical problem[7,26]. The most suitable decomposition method is fusion with sodium peroxide and extraction with water. This method ensures conversion of tin dioxide to water-soluble sodium stannate and its separation from iron(III), titanium(IV), zirconium(IV) and other easily hydrolysable elements. Tin is extracted from an aliquot part of the filtered aqueous extract. When the aqueous extract is adjusted to the required acidity, hydrogen peroxide is obtained and masks molybdenum, tungsten and partly vanadium. A disadvantage of this method is the possible loss of tin by partial adsorption of the hydroxide precipitate; however, spectral analysis of the precipitate has shown that if the concentration of tin in the original sample is about 0.1%, the adsorbed tin is less than 0.0001%. In analysis of alloys soluble in hydrochloric acid, the volatility of tin tetrachloride must be considered. It is known that when samples are dissolved in hydrochloric acid in the presence of another acid such as nitric, sulphuric, perchloric or hydrogen peroxide, no loss of tin occurs[27,28].

Brass was dissolved without difficulty in the conventional manner.

Solvent extraction with BPHA. Tin was separated from the interfering elements by solvent extraction from a 0.5 *M* hydrochloric acid solution with BPHA[25]. Some changes in the composition of the aqueous phase had to be taken into account, related to the decomposition of the sample.

When rock samples were analyzed, the alkaline extract was neutralized with hydrochloric acid before solvent extraction. The relatively high content of chloride made it necessary to study the effect of chloride on the extraction. When extraction was done at constant acidity (0.5 *M* HCl) in the presence of 0.5–2.0 *M* sodium chloride, extraction of 100 μg of tin was found to be 98.5–99% complete; even with 4.0 *M* sodium chloride, extraction was 98.0% complete.

For the analysis of iron-containing alloys such as brass, the behaviour of iron(III) during the extraction had to be studied. It was established that iron(III) was partially extracted but its interference was avoided by adding ascorbic acid. Tin could be determined accurately in the presence of 1.5–100-fold amounts of iron.

Photometric determination of tin. The photometric determination of tin with pyrocatechol violet was suggested by Ross and White[21]; it is applicable to 5–50 μg of tin in 25 ml. When high-grade reagent (UCb, Belgium) was used, it was found that the detection limit could be lowered down to 1 μg of tin in 25 ml. Calibration curves were plotted for 1–5 μg of tin in 25 ml, with 3-cm cells, and for 10–40 μg in 25 ml with 1-cm cells.

When the solutions were evaporated in a water bath almost to dryness, no losses of tin were found.

Procedures. For rock or ore samples, mix the dry weighed sample with a 7–8-fold amount of sodium peroxide in a sintered corundum crucible. Fuse the sample in a muffle furnace at 600–650°C to an easily flowing mass, and then extract in about 50 ml of hot water. Transfer to a 100 ml volumetric flask, cool to room temperature, dilute to the mark with water, swirl and filter the resulting solution immediately through a dry filter, collecting the filtrate in a dry beaker. Pipette 10-ml portions into 50-ml reaction vessels, and carefully add hydrochloric acid (1+1) to give pH 0.3–0.5 (indicator paper).

For brass, treat the sample with 15 ml of a mixture (2+1) of hydrochloric and nitric acids; if necessary, heat gently to attain full decomposition. Transfer the solution to a 100-ml volumetric flask and dilute to the mark. Pipette suitable aliquot parts into 50-ml vessels for extraction. If the sample is decomposed with large amounts of hydrochloric acid, adjust the solution with ammonia to pH 0.5.

Add 1 ml of 2 *M* tartaric acid, 0.01 g of ascorbic acid, and 1 ml of a 1% (w/v) solution of BPHA to the pipetted solution. Extract the tin with an equal volume of chloroform by swirling for 10 min on a shaker. Strip tin from the organic phase with 10 ml of 8 *M* hydrochloric acid by shaking for 5 min. Evaporate the back-extract in a water bath to a volume of 0.5 ml. Add 2 ml of the pyrocatechol violet solution and 5 ml of phthalate buffer, pH 2.5, to the cooled solution, and dilute to about 20 ml with distilled water. Adjust the pH to the optimal value (2.5±0.1; pH meter) with diluted (1+1) ammonia solution. Transfer the solution to a 25-ml volumetric flask and dilute to the mark with water. Measure the absorbance at 550 nm after 15 min in 1 or 3-cm cells (depending on the amount of tin), against a reagent blank. Prepare the calibration curves similarly with standard solutions taken throughout the entire procedure.

Results

Three ore samples of low tin content were analyzed, as well as a sample of greissen granite and a standard brass sample. The results obtained, compared with results obtained by other methods and in other laboratories, are shown in Table I. It is clear that the proposed method can be successfully applied to the determination of low concentrations of tin in natural and industrial raw materials.

TABLE I

ANALYSIS OF TIN-CONTAINING MATERIALS

Sample	*No. of detns.*	*Tin (%)* $\bar{x}$	*s*	s_r	*Comparative method*	*Tin (%)*
Cassiterite tin ore	5	0.130	$6 \cdot 10^{-3}$	4.6	—	—
Cassiterite tin ore	5	0.108	$3.2 \cdot 10^{-3}$	2.9	Spectral	0.110
Cassiterite tin ore	5	0.029	$1.0 \cdot 10^{-3}$	3.4	Spectral	0.027
Cassiterite tin ore	7	0.0053	$4.1 \cdot 10^{-4}$	7.7	Spectral	—
Greissen granite	6	0.191	$3.7 \cdot 10^{-3}$	1.9	x-Ray fluoresc.	0.204
					Emission spectral	0.220
					Spectro-photometr.	0.195
					Spectro-photometr.	0.190
					Spectro-photometr.	0.210
					Polaro-graphic	0.212
Brass	6	0.65	$2.24 \cdot 10^{-3}$	0.3	Standard sample	0.64

REFERENCES

1 G. F. Ivanova, *Geokhimiya*, 12 (1966) 1502.
2 Yu. G. Lavrent'ev, *Zavod. Lab.*, 35 (1969) 933.
3 W. H. Blackburn, T. B. Griswald and W. H. Dennen, *Chem. Geol.*, 7 (1971) 143.
4 H. Hamaguchi, K. Kawabuchi, N. Onuma and R. Ruroda, *Anal. Chim. Acta*, 30 (1964) 335.
5 B. M. Tejam and B. C. Haldar, *Radiochem. Radioanal. Lett.*, 13 (1973) 25.
6 J. D. Smith, *Anal. Chim. Acta*, 57 (1971) 371.
7 H. Onishi and E. B. Sandell, *Anal. Chim. Acta*, 14 (1956) 153.
8 V. A. Nazarenko and N. V. Lebedeva, *Zavod. Lab.*, 28 (1962) 268.
9 L. B. Ginzburg and E. P. Shkrobot, *Zavod. Lab.*, 23 (1957) 527.
10 A. M. Bond, T. A. O'Donell and A. B. Wangh, *Anal. Chem.*, 42 (1970) 1168.
11 B. Moldan, J. Rubeska, M. Miksovsky and M. Huka, *Anal. Chim. Acta*, 52 (1970) 91.
12 M. Farnsworth and J. Pekala, *Anal. Chem.*, 26 (1954) 735.
13 E. J. Newman and P. D. Jones, *Analyst. (London)*, 91 (1966) 406.
14 V. A. Khamizova, *Zh. Anal. Khim.*, 25 (1970) 1525.
15 C. L. Luke, *Anal. Chim. Acta*, 39 (1967) 404.
16 E. Baumgärtel and P. Gärtner, *Z. Anal. Chem.*, 208 (1965) 417.
17 E. N. Pollock and L. P. Zopatti, *Anal. Chem.*, 37 (1965) 290.
18 Z. Marczenko, *Fotometricheszoe opredelenie elementov*, MIR Publ. House, Moscow, 1971, p. 288.
19 N. V. Lebedeva and V. A. Nazarenko, *Tr. Kom. Anal. Khim., Akad. Nauk SSSR*, 11 (1960) 284.
20 A. K. Babko and N. N. Karnukova, *Zh. Anal. Khim.*, 22 (1967) 868.
21 J. W. Ross and J. C. White, *Anal. Chem.*, 33 (1961) 421.
22 H. B. Corlun, *Anal. Chem.*, 45 (1973) 534.
23 A. Ashton, A. G. Fogg and D. T. Burns, *Z. Anal. Chem.*, 264 (1973) 133.
24 V. Suk and M. Malat, *Chemist-Analyst*, 45 (1956) 30.
25 N. Jordanov, St. Mareva and M. Koeva, *Anal. Chim. Acta*, 59 (1972) 75.
26 E. Dolzhal, P. Povondra and Z. Shul'tsek, *Metodi razlozheniya gornykh porod i mineralov*, Moscow Publ. House, 1968, p. 133.
27 E. Asmus, H. J. Altman and E. Thomasz, *Z. Anal. Chem.*, 216 (1966) 3; 223 (1966) 401.
28 K. Tanaka and N. Takgi, *Anal. Chim. Acta*, 48 (1969) 357.

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SHORT COMMUNICATION

The thermal oxidation of pyrrolidine

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Thermal oxidation of most nitrogen-containing compounds causes yellow-brown substances to be formed, the depth of colour usually depending on the degree of oxidation. The product is always a complex mixture which is not susceptible to satisfactory analysis. In this study, the main product from the relatively mild thermal oxidation of pyrrolidine was identified. Subsequently, a pure sample of the main product was submitted to thermal oxidation and its main product was identified. Continuation of this step-wise process, with thin-layer chromatography as the main analytical method, enabled part of the chemical pathway by which pyrrolidine is transformed to a brown material to be elucidated. In the chain of compounds that has been identified, the last, 2-hydroxy-5-(N-2,5-dioxopyrrolidyl)-pyrrole contains a chromophore and readily undergoes polymerization to yield a brown resin. The evidence suggests that brown substances are polymeric and that they contain several different chromophores in the same molecule.

Experimental

Chromatographic plates were prepared in the standard manner with the Shandon equipment, the spreader gap being 250 μm. The slurry consisted of silica gel GF_{254} (Merck) and water (5 g+10 ml per 20 cm × 20 cm plate). After the freshly coated plates had dried (30 min), the adsorbent was activated by heating the plates at 105°C for 1 h. Chromatographic plates were stored in a desiccator until required.

Individual compounds were characterized by u.v. spectrometry (Unicam SP 500), i.r. spectrometry (Unicam SP 100) mass spectrometry and elemental microanalysis.

Oxidation of pyrrolidine. Air was bubbled through boiling pyrrolidine at 12.5 ml min^{-1} for 5 h. The resulting brown mixture was evaporated under reduced pressure to near dryness, the residue was dissolved in some water, and a sample of the solution was chromatographed on silica gel together with the reference compounds pyrrolidine, 2-pyrrolidone and succinimide, with ethanol

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as eluent. Chromatograms were viewed in u.v. radiation ($\lambda_{max}=254$ nm and 365 nm) and also after treatment with iodine vapour and with Ehrlich's reagent[1]. Figure 1 shows that the oxidized sample contains components which have R_F values identical with those of pyrrolidine, 2-pyrrolidone and succinimide, as well as five other components, two of which (components 5 and 8) were rendered visible only with Ehrlich's reagent; presumably, they are trace components. Component 6 appears to be the main product.

Analytical quantities of component 6 were obtained by preparative thin-layer chromatography with ethanol as both the eluent and the extractive solvent (Found: 56.4% C, 8.45% H, 16.35% N; calculated for 2-pyrrolidone: 56.5% C, 8.2% H, 16.5% N). The i.r. spectrum of component 6 was identical with that of 2-pyrrolidone. Hence, component 6 is 2-pyrrolidone.

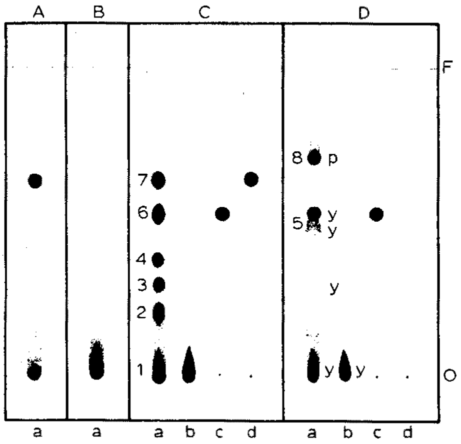


Fig. 1. Chromatogram of oxidized pyrrolidine on silica gel GF_{254}. Solvent: ethanol. Detection: (A) u.v. light ($\lambda_{max}=254$ nm); (B) u.v. light ($\lambda_{max}=365$ nm); (C) iodine vapour; (D) Ehrlich's reagent. (a) Oxidized pyrrolidine (150 μg); (b) pyrrolidine (25 μg); (c) 2-pyrrolidone (25 μg); (d) succinimide (25 μg). p = Purple; y = yellow.

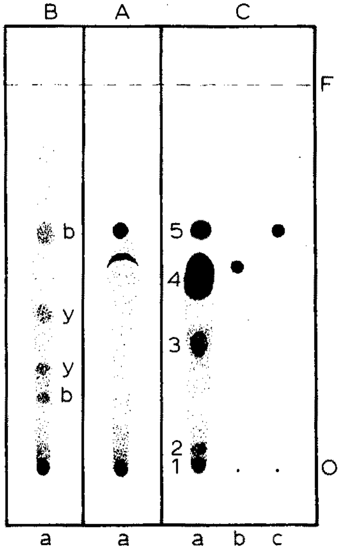


Fig. 2. Chromatogram of oxidised 2-pyrrolidone on silica gel GF_{254}. Solvent: ethanol. Detection: (A), (B), (C) as in Fig. 1. (a) Oxidized 2-pyrrolidone (200 μg); (b) 2-pyrrolidone (25 μg); (c) succinimide (25 μg). b = Blue; y = yellow.

Oxidation of 2-pyrrolidone. Air (at 12.5 ml min^{-1}) was bubbled through 2-pyrrolidone maintained at 150°C for 15 h. The resulting brown liquid was dissolved in water, and a sample of the solution, together with samples of the reference compounds 2-pyrrolidone and succinimide, were chromatographed on silica gel with ethanol as the eluent. Figure 2 shows that component 5 has an R_F value identical with that of succinimide. Analytical amounts of component 5 were obtained by preparative t.l.c. After recrystallization from acetone and sublimation under reduced pressure, a sample had m.p. = 126°C (mixed melting point with authentic succinimide, 126°C). (Found: 48.65% C, 5.0% H, 14.25% N; calculated for succinimide: 48.5% C, 5.05% H, 14.1% N). The i.r. spectrum of component 5 was identical with that of succinimide. Hence component 5 is succinimide.

Oxidation of succinimide. Succinimide was boiled under reflux for 1 h in the presence of air, the resulting dark brown solid was treated with acetone, and the extract was examined by t.l.c. The only product appeared to be a brown material. Subsequently, the solution was evaporated to dryness under reduced pressure, and the residue was recrystallized from acetone. After crystals of succinimide had been filtered off, this process was repeated to yield a mother liquor richer in oxidation products than the initial extract. A sample of this solution was chromatographed by the two-development technique with ethyl acetate as the eluent. Figure 3 shows that the mixture, although it contains many fluorescent compounds, contains essentially components 1, 2, and 3, the last component being succinimide. A small amount of compounds 1 plus 2 was obtained by preparative t.l.c. with ethyl acetate as the eluent and acetone as the extractive solvent. The crude sample (of compounds 1 plus 2) was dissolved in boiling ethyl acetate and filtered through a pre-washed plug of silica gel. After the solution had been evaporated to near dryness, the white, crystalline product was freeze-dried (24 h.).

Heat and u.v. radiation caused components 1 and 2 to isomerize (and, in the case of heat, to form brown compounds when the exposure time exceeded that described below) as is illustrated in Fig. 4. A sample (50 μg.) containing a mixture of components 1 and 2 was chromatographed by the two-development technique in two dimensions with ethyl acetate as the eluent. After the first development,

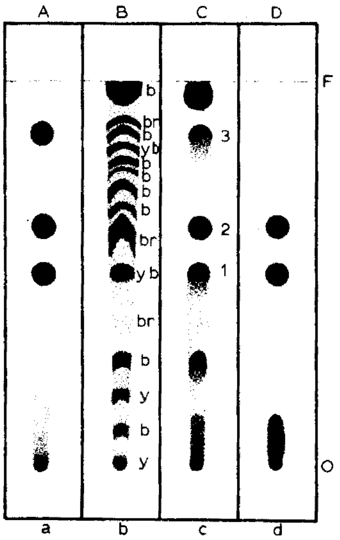


Fig. 3. Chromatogram of oxidised succinimide on silica gel GF_{254}. Solvent: ethyl acetate; two developments, each to a distance of 15 cm. Detection: (A), (B), (C) as in Fig. 1; (D) concentrated sulphuric acid. (a), (b), (c), and (d) = Oxidized succinimide (50 μg), Y = yellow; b = blue; br = brown.

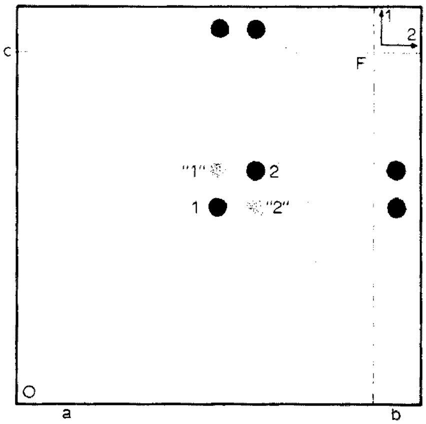


Fig. 4. Chromatogram of the oxidation products of succinimide on silica gel GF_{254}. Solvent: ethyl acetate in both directions; two developments in each direction, each to a distance of 15 cm. Spray: concentrated sulphuric acid. (a), (b), and (c) A mixture of components 1 and 2 (25 μg).

the chromatoplate was heated at 110°C for 5 min before it was developed in the second direction. In this chromatogram, unchanged compounds will lie on the diagonal OF (*i.e.* components 1 and 2) whereas compounds formed during the intermediate heating process will be situated away from the diagonal (*i.e.* components "2" and "1"). Figure 4 shows that some of component 1 has been converted to component 2, and some of component 2 to component 1 by the action of heat. Hence, components 1 and 2 are interconvertible.

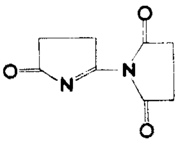
An exactly similar experiment in which the chromatoplate was exposed to u.v. radiation ($\lambda_{max}=254$ nm) for 1 h, produced a chromatogram identical with that shown in Fig. 4. Hence, u.v. energy also causes the isomerization.

On changing the pH of a solution containing components 1 and 2, with aqueous 1% hydrochloric acid or ammonia, different ultra-violet absorbing species are formed, and the conversion is reversible provided that the exposure to alkali is short; this indicates keto–enol tautomerism. (Found: 53.25% C, 4.55% H, 15.35% N, corresponding to the empirical formula $C_8H_8N_2O_3$.) The i.r. spectrum of components 1 plus 2 shows several carbonyl peaks, but yields very little other information concerning their structure. The mass spectrum of a mixture of components 1 and 2 shows a molecular ion peak at $m/e=180$. Two abundant fragments have m/e values of 96 and 84. After hydrolysis of a sample of the mixture with thoroughly degassed 6 *M* hydrochloric acid (1.5 ml.) at 110°C for 24 h in a sealed tube, t.l.c. showed that the hydrolysate consisted mainly of succinic acid together with a small amount of an oxygen-rich, unstable polybasic acid.

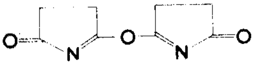
Another sample of brown solid from the oxidation of succinimide was dissolved in water and dialysed against tap-water (72 h) and distilled water (3 × 2 l; 24 h each). The resulting solution was evaporated to dryness under reduced pressure to yield a brown solid. (Found: 53.2% C, 3.55% H, 15.0% N; *cf.* components 1 and 2, 53.25% C, 4.55% H, 15.35% N.) The i.r. spectrum of the brown material was uninformative. A chromatographic investigation of this material showed that it contained neither succinimide nor components 1 and 2, and its dialytic behaviour indicates that it is polymeric.

Discussion

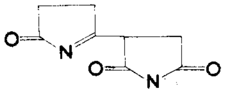
The empirical formula of components 1 and 2 (from the oxidation of succinimide) is $C_8H_8O_3N_2$, the molecular weight is 180 and they are formed from succinimide. Three possible structures are:



A

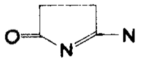


B

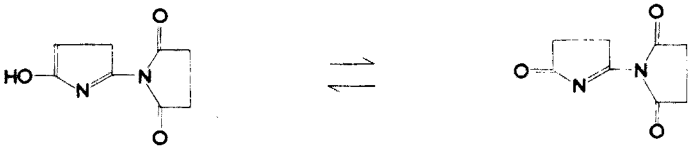


C

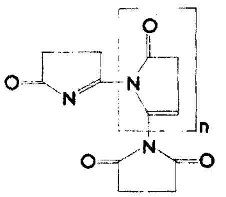
All of these can form tautomers but only structure A is supported by the mass spectrum which indicates fragments having molecular masses of 96 and 84, corresponding to:



It is concluded that components 1 and 2 are, respectively,



and the polymeric brown substances have the idealized structures:



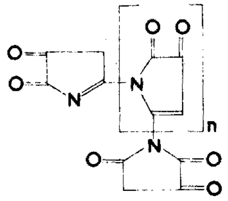


Table 1 shows the compositions of the repeating units in these oligomers. The brown product from the oxidation of succinimide is not likely to be a mixture of these two model oligomers, because the repeat units are interchangeable; in any particular molecule they may occur in any ratio.

In polymers of this type, the magnitude of an individual chromophore, *i.e.*, the wavelength at which it exhibits maximum absorption, depends on the extent to which it has been oxidized as well as on the size of the molecule. Consequently, a mixture composed of oligomers will absorb energy of many different wavelengths and will appear brown. Although these ideas have been developed from experiments based on derivatives of pyrrolidine, investigations not described here indicate that they are also applicable to the formation of brown materials from other cyclic compounds containing nitrogen, *e.g.*, piperidine and caprolactam.

Conclusion

Pyrrolidine is oxidized to brown material via 2-pyrrolidone and succinimide which undergoes dimerization, thus:

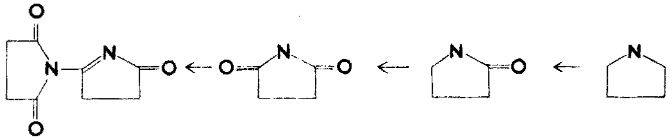


TABLE I

COMPOSITION OF BROWN MATERIAL AND VARIOUS POSTULATED MODEL COMPOUNDS

Calculated for repeat unit	*C (%)*	*H (%)*	*N (%)*	*O (%)*
$C_4H_3N_1O_1$	59.3	3.7	17.3	19.7
$C_4H_1N_1O_2$	50.5	1.1	14.7	33.7
Found	53.2	3.5	15.0	28.25

Subsequently, the dimer polymerizes to yield the brown material. The observed composition of the brown material is consistent with the composition of the polymer which would result by continuing the condensation.

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REFERENCES

1 J. G. Kirchner in E. S. Perry and A. Weissberger (Eds.), *Technique of Organic Chemistry, Vol. XII*, Interscience, New York, 1967, p. 158.

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SHORT COMMUNICATION

Important phénomène de surface observé en testant une spirale de réaction en téflon montée sur un analyseur automatique à flux continu

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(Reçu le 16 septembre 1974)

Lors des essais de mise au point de deux nouvelles méthodes d'analyse automatique en flux continu (type Auto-Analyzer, Technicon), en l'occurence le dosage du lactose par potentiométrie différentielle[1] et celui des protéines du lait par photométrie[2], la très classique spirale de réaction de verre (Technicon, 40 feet, 1,6 mm i.d.) a été remplacée, à titre d'essai, par une spirale analogue en téflon bobinée au laboratoire avec du tuyau de PTFE. Cette solution présentait en effet de notables avantages, notamment:

— un coût extrêmement modique,
— un matériau incassable, aisé à remplacer si nécessaire,
— une contamination minimale d'un échantillon à l'autre vu le caractère peu "mouillable" du matériau,
— la possibilité de choisir exactement la longueur et le diamètre intérieur du tube de téflon (temps de réaction),
— la possibilité de choisir la forme à donner à la spirale (adaptation à n'importe quel type de bain marie),
— une résistance chimique égale à celle du verre.

On peut rappeler, dans le même ordre d'idées, la proposition de remplacer les bobines de mélange de verre par des bobines de polyéthylène[3].

En dépit de nombreuses tentatives, cette nouvelle formule technologique a dû néanmoins être abandonnée pour une seule et unique raison: le régime d'écoulement du flux bullé a une trop forte tendance à pulser à la sortie d'une telle spirale de réaction, bien que l'écoulement à l'entrée de cette spirale soit relativement régulier, puisqu'imposé par la pompe péristaltique.

Description du phénomène

En observant les trains de bulles, le phénomène peut être décrit comme suit: une quelconque petite diminution du débit—donc de la vitesse—du flux entraîne une légère augmentation de la résistance, qui va diminuer un peu plus le débit, et ainsi de suite par récurrence jusqu'à l'arrêt quasi complet du flux à la sortie de la spirale. Comme cette dernière continue a être alimentée en amont par la pompe, la pression augmente progressivement (ce qui se traduit par une compression des bulles) jusqu'à une valeur critique suffisante pour débloquer le flux. Aussitôt que ce dernier se remet à couler, la résistance diminue, donc la vitesse et le débit augmentent fortement et ainsi de suite par récurrence jusqu'à la disparition presque totale de la surpression. A ce moment, la vitesse recommence à décroître et le cycle peut se répéter. A la limite, il semble qu'il n'y ait que deux types d'écoulements stables possibles, discrets: l'écoulement minimum (presque nul) et l'écoulement maximum. Le système dit à flux "continu" oscillerait constamment entre ces deux extrêmes: la moindre variation primaire de débit peut donc être amplifiée dans des proportions considérables par ce mécanisme. On conclut donc que dans une telle spirale, la vitesse n'est pas seulement fonction de la différence des pressions entre l'entrée et la sortie de la spirale, mais encore d'un coefficient de friction lui-même fonction de la vitesse.

Influences de quelques paramètres importants

Sans chercher à traiter le sujet de manière quantitative et exhaustive, on peut caractériser l'influence des principaux paramètres qui interviennent dans ce phénomène.

Segmentation. Le phénomène ne se produit pratiquement que lorsque le flux est segmenté. Si l'on remplace le flux d'air (bulles) par un flux d'eau—les autres facteurs restant inchangés—les pulsations disparaissent. Une série d'essais complémentaires a été réalisée avec une spirale de téflon du même type (6 m de long; 1,8 mm i.d.) que l'on alimente par de l'eau (sans bulles) provenant d'un réservoir maintenu successivement sous diverses pressions par de l'air comprimé. Les résultats obtenus montrent que le débit est directement proportionnel à la perte de charge, ce qui est en accord avec la loi de Poiseuille et confirme que le liquide est newtonien.

Il semble qu'il faille rechercher l'origine de ce phénomène dans une modification du système des 3 vecteurs qui symbolisent les tensions interfaciales liquide–air, air–téflon et téflon–liquide. Cette dernière joue un rôle considérable vu l'extrême hydrophobicité du téflon. Outre les deux nouveaux interfaces qu'elles engendrent (air–liquide et air–téflon), les bulles interviennent par leur compressibilité. Preuve en soit l'essai suivant: pour régulariser le débit, un "pulse chamber" (Technicon PCl, no 116–0120) a été monté entre la pompe et la spirale de téflon. Contrairement à ce qui pouvait laisser supposer une telle désignation, l'amplitude des pulsations du flux a fortement augmenté et leur fréquence a baissé.

Pour des conditions de travail données, la période du système pulsé est très constante.

Vitesse de pompage. La tendance à pulser décroît fortement lorsque la vitesse de pompage (pompe péristaltique Ismatec (CH-Zürich), modèle mp 25 G J-4) augmente. Au-delà d'une certaine vitesse critique, les pulsations ne peuvent même plus s'amorcer ou deviennent négligeables. Mais dans de telles conditions, la spirale de réaction devient toujours moins intéressante en tant que telle.

Température. Ce facteur est capital. Si le phénomène peut déjà se produire à température ambiante, il croît fortement avec la température, ce qui s'explique vraisemblablement par une diminution de la viscosité du fluide en mouvement (frottements "amortisseurs" contre les parois), peut-être aussi par une modification des tensions interfaciales.

Tension superficielle. Si l'on ajoute quelques % de détergent (Teepol de Shell) à l'un des flux, l'écoulement s'en trouve d'abord notablement amélioré (on observe alors une légère mousse à la sortie du débulleur). Pourtant, après un certain temps d'utilisation (de quelques minutes à quelques heures, selon la concentration utilisée), le phénomène peut réapparaître, même fortement amplifié. Lors d'un lavage ultérieur de la spirale sans détergent (surtout si la concentration précédemment utilisée était forte), l'écoulement peut se restabliser momentanément.

Un tel comportement semble indiquer que dans une première étape, le tensio-actif—distribué de façon homogène dans le flux—commence par améliorer le contact du flux avec le téflon. Le comportement de ce matériau tend à s'apparenter à celui du verre. Puis le détergent pourrait s'accumuler à l'interface, modifiant du tout au tout le régime d'écoulement. Le lavage provoquerait la désorption du tensio-actif qui repasserait momentanément à une concentration idoine.

A l'inverse du téflon, la spirale de verre s'est en effet avérée être un régulateur de débit, les variations de débit (que l'on peut suivre grâce aux bulles) étant nettement plus fortes au début qu'à la fin de la spirale.

Dimensions de la spirale. Bien qu'intervenant dans les pertes de charge, la longueur et la section du tube de téflon ne semblent pas jouer un rôle important. Il faut évidemment une longueur minimale pour que le processus apparaisse (quelques m), au-delà de laquelle ce dernier ne varie guère. On a obtenu des pulsations analogues avec des spirales de 3, 6, 12 et 18 m.

Etat de surface. L'état de surface (interne) du téflon intervient aussi. Afin de diminuer sa rugosité, la spirale a été chauffée pendant 10 min à 380°C, c'est à dire au-dessus de son point de fusion, puis refroidie très lentement jusqu'à température ambiante, afin de favoriser une certaine cristallisation du PTFE. Un tel traitement améliore sensiblement l'écoulement du flux bullé, sans supprimer toutefois les pulsations.

Conclusion

Il ressort de cette brève étude que le téflon (PTFE) se prête assez mal à la réalisation de spirales de réaction d'une certaine importance, vraisemblablement en raison de sa forte hydrophobicité. Le flux qui doit être continu et régulier—aux à-coups près dus à la pompe—se met à pulser à la sortie d'une telle spirale, ce qui se fait sentir depuis l'introduction de l'échantillon (rapport non constant avec le réactif) jusqu'au débullage et à la détection. Le phénomène est particulièrement sensible avec une méthode de mesure électrochimique, où les potentiels électrocinétiques ne peuvent être négligés. L'emploi de matériaux synthétiques moins hydrophobes, à résistance comparable, devrait permettre de sauvegarder les avantages de la spirale de téflon (*cf.* début) tout en limitant au maximum ses inconvénients.

L'emploi d'un tube de téflon analogue à celui de la spirale étudiée s'est avéré par contre des plus avantageux pour remplacer les connections en tygon ou PVC ("transmission tubing") lors de la construction du manifold. Ces connections sont en effet suffisamment courtes pour que les pulsations ne puissent s'y générer.

Les constatations rapportées dans cette brève communication sont confirmées par l'information suivante[4]: la maison Carlo Erba (Milan), qui avait mis sur le marché, ces dernières années, des bobines de réaction en téflon pour son analyseur automatique à flux continu, vient d'y renoncer pour revenir aux bobines de verre, les flux obtenus n'étant pas suffisamments constants.

BIBLIOGRAPHIE

1 J. Bosset, B. Blanc et E. Plattner, *Anal. Chim. Acta*, en voie de publication.
2 J. Bosset, B. Blanc et E. Plattner, *Anal. Chim. Acta*, 75 (1975) 343.
3 L. Amador, *Clin. Chem.*, 18 (2) (1972) 164.
4 Communication personnelle de la représentation suisse, la maison Brechbühler (CH-8902-Urdorf).

Analytica Chimica Acta, 75 (1975) 478–480

SHORT COMMUNICATION

Coulometric titration of hydrofluoric acid with a vitreous carbon working electrode

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(Received 23rd July 1974)

Previous work has shown that vitreous carbon is a satisfactory working electrode for the coulometric titration of acids[1] and bases[2] as demonstrated for potassium hydrogenphthalate. The present work was undertaken with the object of showing that this electrode material could be incorporated into a coulometric titration cell which was unattacked by fluoride ions and, therefore, suitable for use in such a titration. The cell was constructed of plastic materials resistant to hydrofluoric acid and required two electrodes, one of vitreous carbon and the other of silver.

Experimental

Standard hydrofluoric acid solution. Approximately 0.1 *M* hydrofluoric acid was prepared by diluting about 5 g of 40% (w/w) redistilled hydrofluoric acid to 1 l with distilled water in a screw-topped polythene bottle. This solution was standardized by titration of about 23-g weighed aliquots with standard 0.1 *M* sodium hydroxide solution in the presence of 0.05% *m*-cresol purple indicator. A 100-g portion of this stock solution was transferred to a 125-ml polythene dropping bottle fitted with an elongated nozzle. Weighed portions of the solution from 1 g to 0.1 g containing 10^{-4}–10^{-5} moles of hydrofluoric acid were added to the coulometric cell (Fig. 1). Weighings were carried out using a Torbal Model ET-1 160-g capacity balance reading to 1 mg.

Coulometric titrations. The current was supplied from a Thorn coulometric titrator (TE110), which was calibrated as described previously[3].

Pressure electrical contacts were made by screwed terminal blocks to the vitreous carbon and silver electrodes. Since silver fluoride is very soluble it is assumed that the electrode reactions were:

Vitreous carbon cathode: $H^+ + e = \frac{1}{2} H_2$ or $H_2O + e = \frac{1}{2} H_2 + OH^-$
Silver anode: $Ag + Cl^- = AgCl + e$

During electrolysis the silver electrode became coated with silver chloride but could be used for passage of charges up to 100 coulombs without the necessity of cleaning by dipping in concentrated ammonia solution.

The coulometric cell was filled with 25 ml of 1 *M* potassium chloride solution. Pure nitrogen gas was bubbled through the solution for 10 min and 2–3

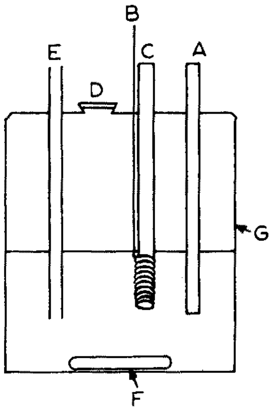

Fig. 1. Cell for coulometric titration of hydrofluoric acid. A, 3-mm diameter vitreous carbon rod; B, 28 s.w.g. silver wire formed into a coil 100-cm long; C, 3-mm diameter polythene rod; D, removable polythene stopper for addition of hydrofluoric acid; E, teflon tube for bubbling nitrogen; F, polythene-coated magnetic stirrer bar; G, 70-ml polymethylpentene beaker.

drops of 0.05% *m*-cresol purple solution were added as indicator. A current of 10.016 mA was passed through a vitreous carbon electrode with an immersed area of 1.48 cm^2, thus the current density was 6.8 mA cm^{-2}.

To determine the blank value, the current was passed until the indicator colour changed sharply from yellow to purple. The blank value was of the order of a few seconds for 2–3 drops of indicator. The weighed sample of hydrofluoric acid was then added and the electrolysis continued until the indicator again changed colour. The titration times were of the order of 1000 s for 10^{-4} moles of hydrofluoric acid.

Results and conclusions

Typical results are shown in Table I. It can be concluded that this coulometric titration is satisfactory for quantities of hydrofluoric acid in the range 1–0.2·10^{-4} mole. The loss in accuracy and in precision at the lowest value determined (10^{-5} mole) is probably due to the fact that such samples involved 1% errors in both

TABLE I

COULOMETRIC TITRATION OF HYDROFLUORIC ACID

Moles HF taken[a] *(10^{-4})*	*No. of results*	*Mean % error*	s_r
1.0	4	−0.9	0.3
0.8	6	−0.4	0.6
0.6	6	−0.9	1.0
0.4	6	−1.0	1.0
0.2	6	−1.1	1.1
0.1	6	−2.2	6.2

[a] Approximate range value taken; since each sample had a different weight, each titration result had to be calculated from the known standardized concentration.

sample weighing and in time measurement. There seems no immediate reason why the precision for both these could not be increased if required.

However, accuracy may be limited by the solubility of silver chloride, since silver chloride may dissolve in alkali metal chloride solutions to form ions such as $AgCl_2^-$. If $AgCl_2^-$ were electroactive at the working cathode, the titration of acids would no longer occur at the required 100% current efficiency. The silver anode is normally placed in a compartment separated from the titrand by a glass sinter; owing to the titrand being hydrofluoric acid, the use of such a sinter was considered undesirable here.

REFERENCES

1 V. J. Jennings, A. Dodson and G. Tedds, *Talanta*, 20 (1973) 681.
2 V. J. Jennings, A. Dodson and G. Tedds, *Talanta*, 21 (1974) 622.
3 V. J. Jennings, A. Dodson and A. M. Atkinson, *Analyst (London)*, 97 (1972) 923.

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SHORT COMMUNICATION

Vitreous carbon combination electrodes in hydrofluoric acid titrations

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(Received 14th October 1974)

The use of combination vitreous (or glassy) carbon electrodes in finding end-points of acid–base titrations has been reported previously[1]. The electrodes are prepared by electrolysis of a pair of vitreous carbon electrodes so that oxygen is produced at the anode and hydrogen at the cathode. The anode is attacked by the oxygen and a shiny surface layer is formed[2]. During acid–base titrations the potential of combination electrode is measured, and the end-point appears as a peak in the graph of potential against volume alkali added. In a recent paper, Bond *et al.*[3] have commented favourably on the inertness of vitreous carbon towards hydrofluoric acid. The possible advantages of vitreous carbon combination electrodes in hydrofluoric acid titrations are obvious since glass pH electrodes are unsuitable.

Experimental

Figure 1 is a cross-sectional diagram of a vitreous carbon combination electrode. Two pieces of vitreous carbon 10 mm long and 3 mm in diameter were sealed into a teflon holder with araldite, an epoxy resin. The surface of the electrode

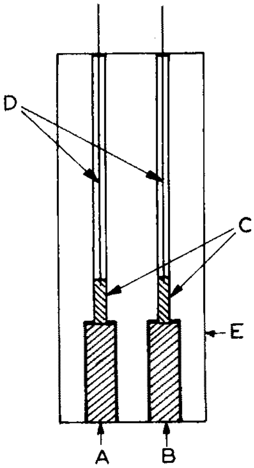


Fig. 1. Cross-sectional diagram of vitreous carbon combination electrode: A, vitreous carbon anode; B, vitreous carbon cathode; C, mercury contacts; D, copper wires; E, teflon cylinder.

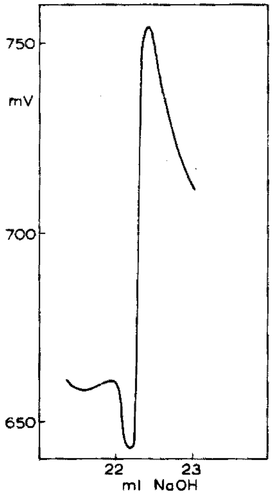
was ground with moist silicon carbide paper (Grade 240C). It was then electrolysed in a solution of either 0.5 or 1 *M* sodium sulphate solution with a current of 5 mA (current density 70 mA cm^{-2}) for times between 2 and 1000 s. Then the electrode was washed and stored in distilled water when not in use.

The titration cell was a 150-ml teflon beaker. About 23 g of 0.1 *M* hydrofluoric acid was weighed into the beaker, the combination electrode was immersed in the acid, and the potential was measured on a Corning EEL 109 general-purpose digital pH meter. Sodium hydroxide solution (0.1 *M*) was added from a 50-ml burette and the potential was read after each addition of titrant. In the vicinity of the end-point the titrant was added in 0.1-ml increments and the potential was read 1 min after each addition. The end-point was determined from the graphical plot in the usual way. This end-point was then compared with the values obtained for the same weight of 0.1 *M* hydrofluoric acid with 0.05% *m*-cresol purple solution as indicator; the colorimetric end-point was assumed to be the true value.

TABLE I

EFFECT OF CHARGE ON PEAK POTENTIAL AND POTENTIAL STEP

Charge (C)	0.1	0.5	1	5
Peak potential (mV)	796	782	718	754
Potential step height (mV)	31	35	90	112
Titration error (%)	0.5	0.4	+0.3	0.6



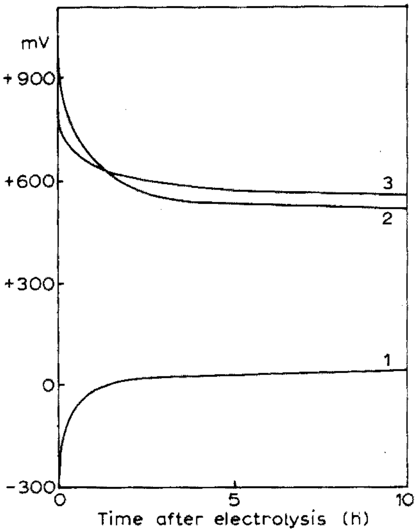


Fig. 2. Graph of potential across vitreous carbon combination electrode (electrolysis charge, 5 C) *versus* ml of 0.1 *M* sodium hydroxide added to 23.015 g of *ca.* 0.1 *M* hydrofluoric acid.

Fig. 3. Potential of vitreous carbon combination electrode *versus* time after electrolysis (electrolysis charge, 1 C). Curve 1, vitreous carbon cathode *versus* s.c.e.; curve 2, vitreous carbon combination pair; curve 3, vitreous carbon anode *versus* s.c.e.

Results and discussion

Table I shows the effect of charge on the height of the potential step. Figure 2 is a graph of a titration for which the combination electrode used had been given an electrolysis change of 5 coulombs. The end-point was taken at the estimated peak potential. Table I shows that the peak height increased from about 30 to 100 mV for a charge increase of 0.1 to 5 coulombs. The potential step height for a combination electrode decreased with time after its initial charge. For example, a combination electrode given a charge of 1 coulomb gave a 90-mV peak on the first day, but this declined to 60 mV and 50 mV by the second and sixth days respectively. This effect is partly due to the potential variation with the anode of the combination electrode, but is also due to variation of the cathode. This effect is shown in Fig. 3, where the potential–time variations of the anode and the cathode measured against a saturated calomel reference electrode are plotted.

BLE II

FECT OF REPEATED 5-C CHARGE ON THE COMBINATION ELECTRODE BEFORE EACH
RATION

ration number	1	2	3	4	5	6	7	8
k potential (mV)	754	795	830	831	839	849	842	864
ential step height (mV)	112	103	86	83	79	83	73	68
ration error (%)[a]	+0.6	+0.7	+0.3	+0.4	+0.5	+0.4	+0.5	+0.3

ean error +0.5%; or 100.5% hydrofluoric acid found with a relative standard deviation of 0.2%.

The effect of electrolysis immediately before each titration on the combination electrode is shown in Table II. Electrolysis charges of 5 coulombs were used since this charge gave the longest peak step. It may be seen from the results that peak step falls while the peak potential rises for titration after each electrolysis. However, the general shape of the 8 graphs obtained was the same as shown in Fig. 2. For example, the small dip in potential always appeared before the peak. The mean error for the combination electrode in these titrations was 0.5%, or about 0.1 ml. It was noticed that the shiny layer formed on the anode after the initial electrolysis peeled off during subsequent electrolysis, but was then replaced by a fresh shiny layer.

Some experiments were conducted on a pair of untreated vitreous carbon rods of diameter 0.3 cm with an active surface area each of 4.4 cm^2. External electrical contact was made by pressure. No measurable stable potential difference was observed. An electrolysis change of 6.3 coulombs was passed between them. They were then used for a hydrofluoric acid titration. As expected, a graph showing an end-point peak of height 64 mV and a potential of 913 mV was obtained. The electrolysis was repeated twice with similar results, though the peak height and potential both decreased by the third titration to 57 mV and 839 mV, respectively. After the fourth attempt, the peak had nearly disappeared. By then the anode was severely etched and no shiny layer was visible. After the fifth and for all three further electrolyses, S-shaped titration curves were obtained similar in

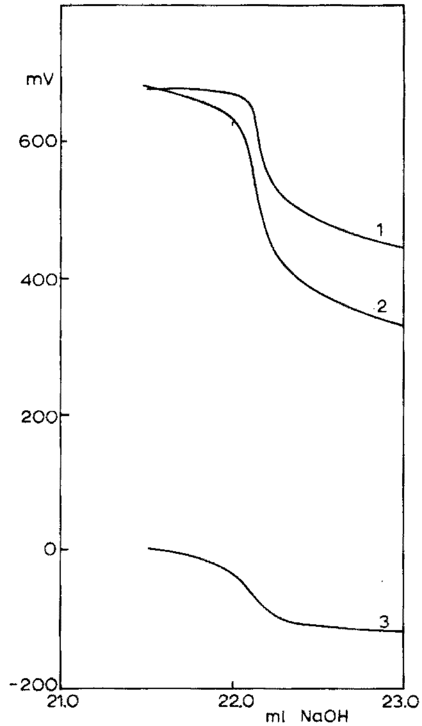


Fig. 4. Potentials of anode and cathode of vitreous carbon combination electrode *versus* ml of 0.1 *M* sodium hydroxide. About 0.1 *M* hydrofluoric acid (22.953 g) was titrated. Curve 1, vitreous carbon combination electrode; curve 2, vitreous carbon anode measured against s.c.e.; curve 3, vitreous carbon cathode measured against s.c.e.

shape to that shown in Fig. 4, curve 1. Figure 4 also shows the behaviour of both the anode and cathode against a saturated calomel electrode. It can be seen that while the cathode and anode both gave S-shaped curves, the potential change was much greater for the anode. Such S-shaped curves are expected where an indicator electrode potential is proportional to pH. Plots of the first differential of these curves showed that both maximum rates of potential change were within 0.1 ml of each other. A similar experiment was carried out with the usual small area combination electrode, which gave a peak end-point. It was found that the maximum rate of change in the anode potential came about 0.5 ml after that of the cathode. The peak is therefore due to the potential lag of the anode compared to the cathode.

While a peak potential end-point has advantages in application, S-shaped curves can be achieved, if required, by using a vitreous carbon combination electrode, which has been electrolysed with very small charges. Table III shows the results obtained for a charge of 0.01 coulomb applied before each titration. The quite close agreement in end-point potentials is significant in proving that this treatment may be used successfully for location of end-points. When a further charge of 0.06 coulomb was applied before the fifth titration, a peak end-point was obtained with a height of 24 mV and a potential of 715 mV. This latter result confirms the previous finding that a 0.1-C charge will give a peak end-point.

The thickness of the anode film formed by the charge of 0.01 coulomb may be calculated approximately as 10^{-6} cm if it is assumed that the structure of the film is graphitic oxide; although this oxide is of unknown composition, the carbon–oxygen ratio is said[4] to be greater than 2 and to contain hydroxyl groups.

TABLE III

EFFECT OF REPEATED 0.01-C CHARGE ON THE COMBINATION ELECTRODE BEFORE EACH TITRATION

Titration number	1	2	3	4
Maximum rate of potential change (mV ml^{-1})	6000	6550	7300	6250
End-point potential (mV)	533	538	550	523
Titration error (%)	0.0	0.0	+0.2	+0.3

A possible mechanism for the behaviour of the vitreous carbon combination electrode could be based on analogy with previous work in redox titrations[5]. In this redox work, the potential difference found across a pair of differently pretreated platinum electrodes was explained as being due to kinetic differences between the redox reactions occurring at each electrode surface. Similarly, in the present work, if each vitreous carbon electrode is behaving as an oxygen electrode[6], there would also be kinetic differences, since their surfaces are not identical.

REFERENCES

1 A. Dodson and V. J. Jennings, *Anal. Chim. Acta*, (1974).
2 A. Dodson and V. J. Jennings, *Nature (London)*, 240 (1972) 15.
3 A. M. Bond, T. A. O'Donnell and R. J. Taylor, *Anal. Chem.*, 46 (1974) 1063.
4 G. R. Hennig, *Prog. Inorg. Chem.*, 1 (1954) 129.
5 L. Kekedy and F. Makkay, *Talanta*, 16 (1959) 1212.
6 J. Doležal and K. Stulik, *J. Electroanal. Chem. Interfacial Electrochem.*, 17 (1968) 87.

486 *Analytica Chimica Acta*, 75 (1975) 486–489
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SHORT COMMUNICATION

Application de la polarographie à tension alternative surimposée et de la polarographie impulsionnelle à la détermination de traces de silice dans l'eau

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(Reçu le 10 Septembre 1974)

Les deux techniques usuelles pour la détermination de la silice dans les eaux sont la spectrophotométrie et la polarographie, appliquées aux complexes molybdosilicates fortement colorés. Les formes jaune et bleue (réduite) ont donné lieu à de nombreux travaux[1–4] en milieu aqueux tamponné, mais aussi en milieu organique (éthanol–éthanoïque)[5]. Les travaux de Massart[6] et Sen et Chatterjee[7] ont montré que la réduction électrochimique impliquait une variation du degré d'oxydation du molybdène qui passe de Mo(VI) à Mo(V).

L'existence de plusieurs formes α, β et γ[1,4] impose des conditions opératoires assez strictes. La forme β se transformant avec le temps en forme α; il a été montré que le rapport des concentrations en H^+ et MoO_4^{2-} favorable à la formation de molybdosilicate α était compris[1,8] entre 1,5 et 2.

Enfin l'extraction de la forme α par l'acétate d'éthyle semble meilleure que celle obtenue avec des esters d'alcools plus condensés[9].

Dans le présent travail nous nous sommes intéressés au couplage d'extraction–réduction électrochimique du complexe molybdosilicique en recherchant une amélioration du seuil de sensibilité à l'aide de la polarographie à tension alternative surimposée et de la polarographie impulsionnelle dérivée (à impulsions surimposées).

Partie experimentale

Mode operatoire. Aprés une étude des milieux éthanol–éthanoïque[10] préconisés par certains auteurs[5,7], nous avons recherché une simplification de la méthode en revenant à des mélanges hydroalcooliques ajustés à pH 1,98 par le tampon Britton–Robinson.

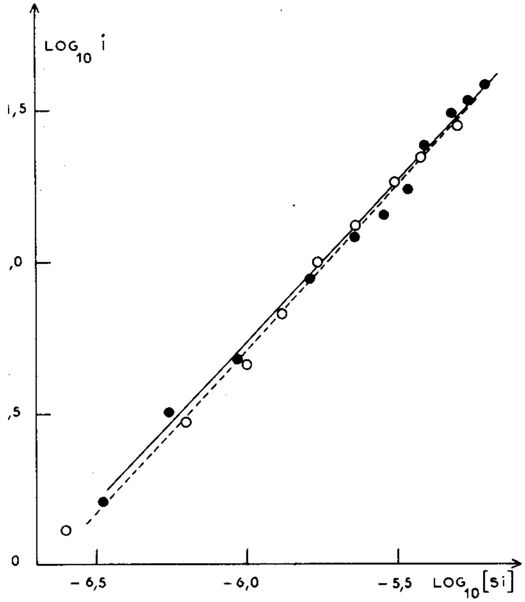
La procédure d'extraction du molybdosilicate est la suivante: à 10 ml de solution à analyser ajouter 1 ml d'acide sulfurique 0.5 *M* et 1 ml de molybdate d'ammonium à 10% dans l'eau. Agiter et laisser reposer 15 min. Ajouter alors 5 ml d'acide sulfurique 9 *M* et extraire par 10 ml d'acétate d'éthyle. Laisser décanter 2 min.

Prélever 5 ml de phase organique, ajouter 5 ml d'éthanol 0,1 *M* en LiCl et 10 ml de tampon Britton–Robinson à pH 1,98. Placer cette solution dans la cellule polarographique, dégazer pendant 15 min à l'azote et tracer les polarogrammes de −0,2 à −0,7 V/ECS.

Appareillage—reactifs. Les unités PRG 3 et PRG 4 Solea–Tacussel sont utilisées, pour la polarographie à tension alternative surimposée (p.t.a.s.) et pour la polarographie impulsionnelle dérivée (p.i.d.). Tous les réactifs sont de qualités analytique. L'eau est dionisée, puis bidistillée. Les solutions sont stockées en bouteilles de polyéthylène. Les électrodes de références sont soit au calomel, saturée (ECS) soit Ag/AgCl mais tous les potentiels seront référés par rapport à l'ECS.

Resultats et discussions

A partir d'une solution mère $1{,}64 \cdot 10^{-3}$ M en silice, obtenue par fusion alcaline nous avons établi les droites d'étalonnage (Fig. 1) et les limites de détection. Le complexe molybdosilicate donne en p.t.a.s. trois pics (Fig. 2) à −0,274, −0,384 and −0,539 V/ECS; le dernier étant moins sensible mais nettement plus favorable aux déterminations car les deux premiers se recouvrent partiellement. Le blanc présence d'ailleurs une bosse à −0,36 V/ECS assez gênante tandis qu'autour de −0,50 V/ECS le courant de base est peu élevé.



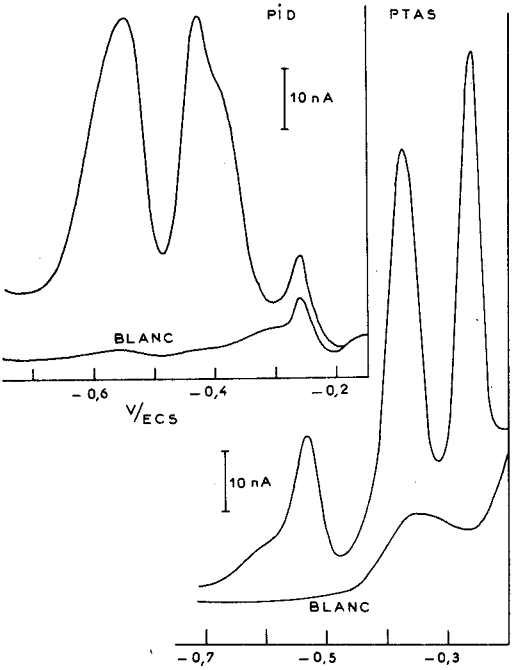


Fig. 1. Droites d'étalonnage en p.t.a.s. (●) et en p.i.d. (○) établies en fonction de la concentration en silice de la solution initiale.

Fig. 2. Polarogrammes du complexe molybdosilicate en p.t.a.s. et p.i.d. pour $[\mathrm{Si}] = 1{,}63 \cdot 10^{-5}$ M (0,98 p.p.m. de SiO_2).

Les paramètres optima adoptés sont $\Delta E = 10$ mV, $N = 60$ Hz, $t = 2$ s, déphasage nul. Les variations de ΔE et N pour améliorer la sensibilité n'ont pas été concluantes, mais par contre, un déphasage de −1 à −2 degré par rapport à la tension peut diminuer le courant de base et favoriser la détection.

En p.i.d. le polarogramme (Fig. 2), bien que différent de celui de la p.t.a.s., montre encore trois pics à −0,260; −0,430 et −0,545 V/ECS. Seul le troisième pic à −0,545 V/ECS est utilisable à des fins analytiques car proportionnel à la concentration initiale en silice. Les paramètres optima sont: $\Delta E = 40$ mV; impulsion 50 ms; échantillonage 50,70‰; durée de vie de goutte 3 s; et retard à l'impulsion, 2,80 s.

Les droites d'étalonnage ont été établies au moyen d'essais entièrement indépendants. Bien que des traces de silice soient décelables dès $2{,}5 \cdot 10^{-7}$ *M* (15 μg l^{-1}) en p.i.d., l'identification précise par les trois pics se situe vers $6 \cdot 10^{-7}$ *M* (36 μg l^{-1}).

De même en p.t.a.s. les valeurs de la limite et de l'identification sont $1{,}5 \cdot 10^{-7}$ et $1{,}6 \cdot 10^{-6}$ *M* (9,6 μg l^{-1} et 96 μg l^{-1}). La reproductibilité de la méthode a été testée par deux séries d'essais indépendants. Pour une solution initiale $1{,}64 \cdot 10^{-5}$ *M* (990 μg l^{-1}) cinq essais donnent $\bar{i} = 54{,}2$ nA avec un écart type de $s = 0{,}7$ et pour une solution initiale de $1{,}64 \cdot 10^{-6}$ *M* (99 μg l^{-1}) cinq essais donnent $\bar{i} = 5{,}0$ nA et $s = 0{,}12$.

Les interférences des ions phosphates, tungstates et de l'arsenic(III) ont été envisagées. Les ions tungstates n'ont aucune influence sur l'extraction du complexe molybdosilicate. Par contre, l'arsenic(III) et les ions phosphates interfèrent sous certaines conditions en donnant une réponse analogue à celle de la silice.

Lors de l'extraction par l'acétate d'éthyle la solution est fortement acidifiée. Avec 5 ml d'acide sulfurique 9 *M*, la normalité atteint 5,1. L'arsenic est extrait dans ces conditions mais pas les ions phosphates. Par contre en acidifiant peu

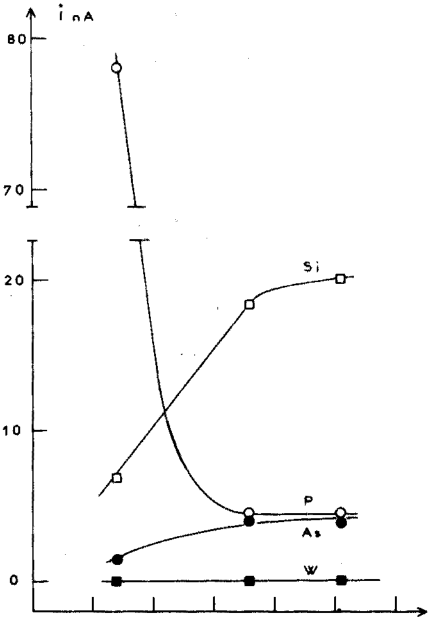


Fig. 3. Evolution des intensités du troisième pic en fonction de l'élément interférant et de la normalité en H_2SO_4 de la phase aqueuse lors de l'extraction (Si = $1{,}64 \cdot 10^{-5}$ *M*; P = $7{,}65 \cdot 10^{-5}$ *M*; As = $1{,}48 \cdot 10^{-5}$ *M*; W = $9{,}35 \cdot 10^{-6}$ *M*).

(1 ml H_2SO_4, 9 M) vers une normalité de 1,4, ceux-ci sont extraits mais As(III) l'est très peu. Le complexe molybdosilicate est un peu mieux extrait pour les fortes acidités, mais reste mesurable dans tous les cas. La Figure 3 donne un aperçu des évolutions des courants de réponse pour les solutions initiales suivantes: silice $1{,}64 \cdot 10^{-5}$ M; phosphate $7{,}65 \cdot 10^{-5}$ M; As(III) $1{,}43 \cdot 10^{-5}$ M; tungstate $9{,}35 \cdot 10^{-5}$ M.

En ramenant le courant de réponse à une solution 10^{-5} M nous pouvons estimer l'interférence de chaque élément sur la silice par l'intensité correspondante de son signal (Tableau I).

TABLEAU I

VALEURS DE L'INTENSITÉ, EN nA, DU SIGNAL DE RÉPONSE À UNE SOLUTION 10^{-5} M EN Si, As, P ET W

Elément	*Molarité en H_2SO_4 à l'extraction*		
	0,7	*1,8*	*2,55*
Si	4,2	11,2	12,2
As	0,98	2,86	2,72
P	10,2	0,59	0,59
W	0	0	0

En conclusion les deux méthodes permettent un dosage précis de la silice présente dans les eaux dans le domaine 10–100 $\mu g\ l^{-1}$. Les interférences des ions phosphates peuvent être amoindries en jouant sur les conditions d'acidité lors de l'extraction, comme pour l'arsenic(III), tandis que les ions tungstates sont sans influence.

BIBLIOGRAPHIE

1 J. D. H. Strickland, *J. Amer. Chem. Soc.*, 74 (1952) 862.
2 D. T. Chow et R. J. Robinson, *Anal. Chem.*, 25 (1953) 646.
3 H. Hahn et K. Grasshoff, *Z. Anal. Chem.*, 173 (1960) 29, 198.
4 W. Kemula et S. Rosolowski, *Chem. Anal. (Warsaw)*, 7 (1962) 915; *Rocz. Chem.*, 36 (1962) 179.
5 F. Pottkamp et F. Umland, *Z. Anal. Chem.*, 255 (1971) 367.
6 R. Massart, *Ann. Chim. (Paris)*, 4 (1969) 365, 441.
7 B. P. Sen et S. N. Chatterjee, *Anal. Chem.*, 38 (1966) 536.
8 A. Halasz et E. Pungor, *Talanta*, 18 (1971) 569.
9 D. R. Schink, *Anal. Chem.*, 37 (1965) 764.
10 K. Grasshoff et H. Hahn, *Z. Anal. Chem.*, 247 (1969) 168.

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BOOK REVIEWS

L. Sucha and S. Kotrly, *Solution Equilibria in Analytical Chemistry*, Van Nostrand–Reinhold Company, London, 1973, 372 pp., price £7.50.

This book has the aim of providing a concise and unified approach to the principles of ionic equilibria on which very many analytical methods are based. The treatment is rigorous rather than approximate. No one will deny that some knowledge of the theoretical basis of chemical reactions is of inestimable value to the analytical chemist; it is, however, quite essential for those who are concerned with the development of analytical processes. This book may fill this need.

An introductory chapter is followed by a discussion of some fundamental physical chemistry on thermodynamics and kinetics of chemical reactions. Graphical methods are given in Chapter III, while Chapters IV and V deal with protolytic equilibria. Metal complex equilibria, precipitation reactions and oxidation–reduction equilibria are covered in the next three chapters; the remaining chapters describe the theory of titration curves and end-point detection, extraction equilibria and kinetic methods of analysis.

The authors have succeeded in bringing together most of the relevant information which practising analysts would wish to possess. The various systems encountered in analytical processes are well correlated throughout the text, and worked examples and graphical solutions to various problems are liberally distributed throughout the book. This is not a book for the gentle reader: it demands considerable concentration to follow the arguments, but as an addition to the specialized literature of analytical chemistry, it must find an accepted place.

W. I. Stephen (Birmingham)

Computers in Chemical Research and Education, Proceedings of the International Conference, Ljubljana/Zagreb, July 1973. Edited by D. Hadzi and J. Zupan, Elsevier, Amsterdam, 1973, price Dfl. 150.00.

The proceedings comprise three, soft-cover volumes of manuscripts copied by off-set lithography. There are six major sections: Computer control of experiments, data aquisition and refinement (202 pp.); Handling of chemical informations (*sic*) (112 pp.); Analysis and simulation of spectra–structure determination from complex data (152 pp.); Theoretical chemistry–phase structures (325 pp.); Computer designed synthesis (58 pp.); and chemical education (223 pp.). There is also an introductory paper on computer networks, minicomputers, and chemistry by Peter Lykos (22 pp.). There is a total of fifty eight papers. The *pros* and *cons* of publishing symposia proceedings have already been discussed *ad nauseum.* These proceedings are typical of their kind. They occupy more than 6 cm of shelf space, and provide information which, if of any value, will be published again in scientific journals, and will only then be abstracted. No doubt they will form a memento of the symposium for those who attended, but they will rarely be referred to again.

A. Townshend (Birmingham)

K. W. Bagnall, *The Actinide Elements*, in P. L. Robinson (Ed.), *Topics in Inorganic and General Chemistry, Monograph 15*, Elsevier Publishing Co., Amsterdam, 1972, xl + 272 pp., price Dfl. 80.00.

The actinide elements include some of the newest and rarest elements (curium, californium, americium, etc.), seldom if ever encountered by most chemists, and thus whose chemistry is least familiar; they also include uranium and thorium, which are encountered more often. This book is doubly welcome, therefore, in that it gives a comprehensive account of the chemistry of the rare actinide elements and their compounds, and also relates this to the more familiar thorium and uranium chemistry.

The book follows a similar format to others in this series of monographs. The first chapter describes the discovery of the actinide elements. The oxidation states, and the separation and purification of these elements occupies the next two chapters. The following eight chapters deal in detail with the chemistry of the metals and their compounds. The final chapter discusses the 5f-electrons, and their influence on the magnetic and spectral properties of these elements.

The monograph is well-written, and only a few typographical errors were detected. It is recommended to all chemists with an interest in the inorganic aspects of their subject, including any analytical chemists who are, or are likely to be, concerned with analytical operations involving these elements.

A. Townshend (Birmingham)

Official, standardised and recommended methods of analysis, Edited by N. W. Hanson, The Society for Analytical Chemistry, London, 2nd edition (1973), 1974, xxiv + 897 pp., price £ 17.00.

The importance of standard methods of analysis is emphasized by the increase in size of this edition of the Analytical Methods Committee's recommendations, compared to the 1963 edition. The pattern of the book has been retained, but Part I covering standardized methods of analysis has been expanded to 500 pages with many new standard procedures. Part II, which is a bibliography of official, standardized and recommended methods of analysis which have been published throughout the world, has also required considerable expansion. The great value of this compilation is that every method given in Part I has been thoroughly checked on a collaborative basis by the Analytical Methods Committee of the Society, and can therefore be regarded as thoroughly reliable. Since many more topics are now covered, this edition should be even more valuable than the earlier edition.

F. R. Dollish, W. G. Fateley and F. F. Bentley, *Characteristic Raman Frequencies of Organic Compounds*, Wiley–Interscience, New York, 1974, xviii+443 pp., price £ 12.60.

Raman spectra can be recorded easily and routinely with modern instrumentation, and this book on interpretation of the spectra will be widely welcomed. The text provides a complete survey (with references through 1972) of the application of Raman spectroscopy to identification of organic compounds, including aliphatic, aromatic and heterocyclic compounds. Useful tables abound, and 108 Raman spectra are given in an Appendix. The subject matter is dealt with clearly and succinctly.

L. Erdey and G. Svehla, *Ascorbinometric Titrations*, Akademiai Kiado, Budapest, 1973, 183 pp., price £ 3.40.

The use of ascorbic acid as a reducing titrant was pioneered by the late Laszlo Erdey in Budapest over 25 years ago. A considerable amount of work on this reagent has subsequently been reported, and the present monograph brings this conveniently together, to provide a useful source of information on this analytical reagent.

Z. K. Jelinek, *Particle Size Analysis*, Ellis Horwood Series in Analytical Chemistry, J. Wiley, London, 1974, 178 pp., price £ 5.00.

An ever-growing interest in particle size analysis is reflected in this monograph of practical methods from a Czechoslovakian authority. The text is quite comprehensive, and apparatus, techniques and procedures are discussed for all the major methods as well as the less common ones. Data interpretation is given prominence, and the book should prove of value to those wishing to gain an appreciation of the practical implications of particle size analysis.

Process Engineering of Pyrometallurgy, Edited by M. J. Jones. Institution of Mining and Metallurgy, London, 1974, vi+105 pp., price £ 6.50.

This paperback reports the proceedings of a joint meeting of the Institution of Mining and Metallurgy with the Institution of Chemical Engineers. It contains 11 papers on diverse metallurgical topics.

Absorption Spectra in the Ultraviolet and Visible Region, Vol. XVIII, Edited by L. Lang. Akademiai Kiado, Budapest, 1974, 400 pp., price £ 7.00.

A further 400 spectra for different compounds are given in this volume, which maintains this valuable compilation.

R. M. Scott and M. Lündeen, *Thin-Layer Chromatography Abstracts, 1971–1973*, Ann Arbor Science Publishers–J. Wiley, New York, 1973, 589 pp., price £ 10.40.

The increased use of t.l.c. methods is indicated by the inclusion of some 1340 abstracts covering the period 1971 through part of 1973. The main applications are to lipids, steroids and drugs of abuse. The abstracts are organized on a chronological basis under 23 headings.

D. W. Breck, *Zeolite Molecular Sieves: Structure, Chemistry and Use*, Interscience–Wiley, New York, 1974, ix+771 pp., price £ 18.00.

This book is intended as an introduction to the subject, and as a comprehensive source of information. The whole range of mineral and synthetic zeolites is described, and detailed discussions of their structure and chemical and physical properties are included. Ion-exchange and adsorption properties are dealt with, and a chapter is included on the manufacture and properties of commercial products.

R. G. Cooks, J. H. Beynon, R. M. Caprioli and G. R. Lester, *Metastable Ions*, Elsevier, Amsterdam, 1973, x+296 pp., price Dfl. 75.00.

The mass spectrometer is concerned in both the production and the identification of metastable ions, and it is the interaction between this instrument and metastable ions that forms the basis of the present text. The book contains an outline of the basic theory of the components of a mass spectrometer, and describes the types of ions that might be formed in the instrument. After a chapter on the energy of ion beams, the properties of molecular ions and analytical applications (analysis of mixtures, isotopes and isomers, and of exact mass measurements) are described at length. A chapter on evaluation of the structure of gaseous metastable ions is also included. An appendix gives a wide-ranging discussion on the theory of mass spectra.

The book will be valuable to all chemists who have occasion to use mass spectrometry in an attempt to solve their problems. They should not be put off by some of the introductory quotations which seem to indicate that much of the interpretation is speculation.

A. Blazek, *Thermal Analysis*, Van Nostrand–Reinhold, London, 1973, 286 pp., price £ 9.00.

This monograph is intended as a practical introduction to those thermal methods of analysis in which the techniques of thermogravimetry (TG) and differential thermal analysis (DTA) are used. The physical and chemical principles, the scope and applications of the two methods, and the interpretation of data, are given thorough treatment.

As a concise review of the basic techniques of TG and DTA, this text will find general acceptance amongst those who know little of the subject and wish to gain some insight into the usefulness of these thermal methods. Practical applications are given very good coverage and this feature will commend the book to those interested in using the techniques to solve analytical problems. Thermal methods are relatively simple and direct to apply: thermal data are often unique and the methods provide unequivocal means of comparison or identification of chemical substances. If this book serves to promote these methods, it will have served a useful purpose.

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INTERNATIONAL CONFERENCE ON MODERN TRENDS IN ACTIVATION ANALYSIS

edited by **T. BRAUN**, Institute of Inorganic and Analytical Chemistry, L. Eötvös University, and **E. BUJDOSÓ**, Head of the Isotope Laboratory, Research Institute for Non-ferrous Metals, Budapest.

Reprinted from the Journal of Radioanalytical Chemistry.

1974. 934 pages. US$ 86.50/Dfl. 225.00 ISBN 0-444-99879-9

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